Exciton Percolation: Isotopic-Mixed $^1B_{2u}$ Naphthalene*

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We propose a percolation model for an *exciton* insulator-to-conductor transition. Experimentally, we investigate (at 2°K) the first singlet exciton in a binary organic alloy of naphthalene-perdeuteronaphthalene. A third component, 10^{-3}-mole-fraction betamethylnaphthalene, serves as exciton-flow monitor, and the integrated relative fluorescence is derived. The $^1B_{2u}$ Frenkel-exciton data are bound by the theoretical site-percolation curves for square and simple-cubic lattices.

The classical concept of percolation[1] has been utilized for the conduction of electrons in disordered solids,[2] dense gases,[3] and solutions.[4] A model involving exciton percolation, accounting for the critical concentration at which the density-of-states function as well as the optical absorption changes from discrete to quasicontinuous, was discussed and applied to naphthalene,[5] where a random-lattice calculation was performed based on the semiempirical exciton dispersion of the pure crystal.[6] Here we propose a dynamic method of measuring *exciton percolation,* including the critical concentration for the onset of *exciton conduction* (energy transport), in an isotopic-mixed crystal (organic alloy), and present an experimental study on the lowest singlet exciton of naphthalene. This study demonstrates percolation for the exciton flow and relates the *energy* transport to the exciton delocalization in the mixed crystal, thus, in turn, to the pairwise exciton interactions and dispersion relation in the pure crystal. The naphthalene system was chosen for both theoretical reasons, i.e., its short-range exciton interactions, and experimental ones, i.e., the notorious betamethylnaphthalene (BMN) supertrap which we use here as our exciton-flow monitor.

Highly purified[7], isotopically mixed single crystals[7] of naphthalene ($C_{10}H_8$-$C_{10}D_8$), doped with about 1-mole-% BMN (only about a tenth of this dissolving homogeneously, as determined by mass spectra, gas chromatography, and absorption spectra at 2 and 77°K), were excited with 2400–2900-Å radiation at about 1.8°K, by an appropriately filtered xenon lamp.[7] The emission was monitored at 0.5 cm^{-1} resolution by a double-grating spectrometer with digital photon counting and simultaneous calibration.[7]

For each concentration noted in Fig. 1 we plotted the ratio of the $C_{10}H_8$ (trap) 0-510 (vibronic) integrated fluorescence to the 0-0 BMN (supertrap) fluorescence, including phonon sidebands. The detailed spectra and the computer data processing and integration procedures[7] will be pre-

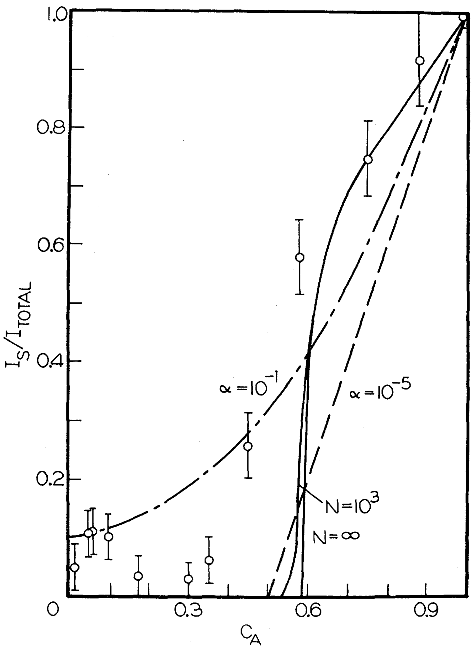

FIG. 1. Exciton transfer in $C_{10}H_8$-$C_{10}D_8$ mixed crystals. The $C_{10}H_8$ concentration is C_A, I_S is the supertrap intensity, while $I_{total} = I_S + I_A$, I_A being the $C_{10}H_8$ (510) intensity. The large error bars on the experimental points are mainly due to the difficulty of consistent doping with BMN (its actual concentration varying from point to point up to an order of magnitude). The *square-lattice* theoretical curves (solid) for the site percolation probability, $P^s(C_A)$, are taken from Ref. 8 for infinite clusters while for the quasi-infinite clusters (size of 10^3) we computed it ourselves in collaboration with Dr. J. Hoshen. Note, however, that we used the definition of $P(C)$ consistent with Ref. 9. The σ/σ_0 conductivity curves (dashed) were derived from Ref. 9 (for bond percolation, $\alpha = 10^{-5}$ and $\alpha = 0.1$).

sented elsewhere. The higher-energy $C_{10}D_8$ states are completely quenched by the trap and/or supertrap. We note that no absolute-intensity measurements are involved. While the BMN mole fraction (C_S) is always about 10^{-3}, that of the $C_{10}H_8$ (C_A) varies from about 0.01 to 0.999. The rest of the bulk crystal (C_B) is made up by the filler $C_{10}D_8$ (excepting the $C_A = 0.999$ case).

From the relative intensity plot (Fig. 1) of $I_S/I_{\rm total}$ versus C_A one can see that effectively isolated traps (where $C_A/C_B \cong 0.01$) are about as "efficient" as effectively isolated supertraps ($C_S \cong 10^{-1}C_A$), as long as both are feeding mainly on the $C_{10}D_8$ host excitons. As the $C_{10}H_8$ concentration increases, the supertrap increasingly feeds on the trap ($C_{10}H_8$) excitons (we assume that the $C_{10}H_8$ has trapped out the $C_{10}D_8$ excitons in a negligibly short time). As long as the $C_{10}H_8$ molecules are effectively isolated or form small clusters (or conglomerates[5]), this latter feeding is relatively inefficient. The creation of *quasi-infinite* (see below) clusters (or conglomerates), i.e., *effective percolation,* drastically changes the primary role of $C_{10}H_8$, from a trap for $C_{10}D_8$ to a feeder for BMN. We thus determine the condition for an effective *free flow* of $^1B_{2u}$ excitons (within their lifetime of about[10] 10^{-7} sec) *in the $C_{10}H_8$ quasilattice:* $C_A = 0.5 \pm 0.1$. The minimum *size* of the *quasi-infinite* cluster (or conglomerate), defined by the smallest aggregate with a high probability of containing a supertrap, is determined by the concentration of the supertrap and is, therefore, about 10^3 to 10^4 sites in our present experiment. However, the *effective-percolation* concentration, i.e., the concentration of $C_{10}H_8$ which assures a high probability for such a *quasi-infinite* cluster, is close[8] to that of the true percolation (infinite-cluster formation) concentration (see Fig. 1).

Naphthalene has[11] a monoclinic crystal structure ($C_{2h}{}^5$). However, with the assumption of nearest-neighbor interactions (only) one gets a two-dimensional lattice, topologically equivalent to that of the *square lattice.* The latter (again implying nearest-neighbor interactions) has a critical *site*-percolation concentration[1] of about 0.590 (for infinite clusters). Note that adding an out-of-plane interaction results in a topology equivalent to simple cubic.

While the formulation of a quantum-mechanical exciton percolation model, including tunneling effects, is in progress, at this stage we make some comparisons with classical transport models.[9, 12] The conductivity σ has been given in the zeroth approximation[9] as

$$\sigma = \sigma_0 P(C), \tag{1}$$

where $P(C)$ is the percolation probability,[9] i.e., the fraction of *total* volume occupied by the conducting (infinite) clusters of component A, and σ_0 is the bulk conductivity of this conducting volume, or, more rigorously,[9] by

$$\sigma = \mu(C)P(C), \tag{2}$$

where the effective mobility (or fudging factor) $\mu(C)$ may or may not vanish at C_c, the critical concentration below which $P(C)$ vanishes. We notice that while in Kirkpatrick's model calculations[9] $\mu(C)$ may vanish at even *higher* values of C than $P(C)$, this happens for a *three-dimensional* cubic network with binary disorder but *not* for a *two-dimensional* square net of conductances, where *both* the bond percolation probability $P^b(C)$ and σ/σ_0 vanish at $C = 0.5$. We notice a similar behavior in the work of Last and Thouless[12] on the electrical conductivity of a square sheet of graphite, the difference being that their quoted[8] theoretical $P^s(C)$ value is for the *site-percolation* probability, i.e., $C_c = 0.59 \pm 0.01$. Their experimental onset of σ/σ_0 is close to that, i.e., $C = 0.60$ [notice that our[9] $P(C)$ is their[8] $CP(C)$].

For Frenkel-exciton diffusion we have no *a priori reason* to believe that $\mu(C)$ vanishes at C_c or that it is as steep a function of C as the electronic conductivity. Equation (1) may therefore be as good a first approximation as Eq. (2). Figure 1 includes curves representing both Eqs. (1) and (2), where the latter is based on Kirkpatrick's *bond-percolation* model[9] with a best-fit ratio $\alpha = \sigma_B/\sigma_A = 0.1$ (compare with Kirkpatrick's calculation[9] where the $\alpha = 0$ and $\alpha = 10^{-5}$ effective-medium curves coincide). As we point out below, the exciton propagation (diffusion) inside each cluster is fast enough (and the supertrapping mechanism efficient enough) that in this experiment the presence of a single supertrap adjacent to (or inside) the cluster is sufficient to catch any cluster exciton and have it contribute to the current, $I_s/I_{\rm total}$, graphed in our Fig. 1. In this *limit* the above current (actually σ/σ_0) is proportional to the number of A sites included in infinite (or quasi-infinite, see below) clusters, and therefore by $P^s(C_A)$, i.e., Eq. (1). We notice (Fig. 1) that the curve of $P^s(C)$ for the *square lattice* (compare Fig. 2) accounts well for our data for $C \gtrsim C_c$. Evidently this curve represents a theoretical upper limit in concentration. A *lower bound* is harder to define, but the *simple-cubic*

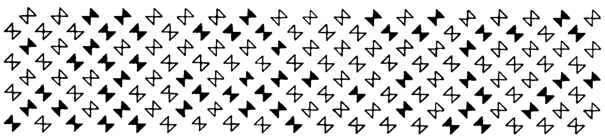

FIG. 2. A binary random square lattice, based on a Monte Carlo calculation, with 40% black and 60% white "butterflies." Note that this particular domain has an actual ratio of 36.8:63.2. We thank O. M. Kopelman and L. J. Kopelman for producing this representation.

$P^s(C_A)$ is appropriate. We also notice that our experimental curve includes a base line (analogous to the dark current in photoelectric measurements) which is due to supertrap emission originating either from its direct optical excitation or by direct trapping from A miniclusters in the B lattice, i.e., by by-passing the extended A clusters entirely and therefore *not* involving any A exciton transfer. This situation *mimicks* the the tail of Kirkpatrick's[9] curve for $\alpha \approx 0.1$.

Well below percolation, the guest clusters are effectively isolated,[13] and act primarily as traps. On the other hand, at the onset of percolation the *quasi-infinite* guest clusters act as exciton channels, leading to the supertrap. Here the nature of the exciton propagation, i.e., mobility, becomes important, in principle. Thus the lifetime of the excitation and the trapping efficiency of the supertrap could also play an important role. However, we notice here that even for the *least efficient exciton propagation,* i.e., one-dimensional random walk, given[10] a lifetime of 10^{-7} sec, a trapping efficiency[14] of 1 (BMN relative to $C_{10}H_8$), a pairwise nearest-neighbor interaction[6] of 18 cm^{-1}, and a supertrap concentration of 10^{-3}, any linear cluster section of size 10^3 will give the exciton a probability of about 0.5 for visiting a supertrap, i.e., emission from the supertrap. Any cross linking of one-dimensional chains increases this probability. The emission result at $C_A \geqslant C_c$ is, therefore, quite satisfactory as we do not expect the diffusion rate, in this experiment, to significantly hinder supertrapping. A more complete discussion is reserved for a later publication, where we shall also describe additional experiments with small enough supertrap concentrations so as to allow us to study the contributions and nature of the exciton mode of propagation, i.e., mobility. However, for the experiments presented here, our picture makes plausible the following: In the region of $C_c < C < 1$ the exciton conduction, as measured by the supertrap emission (corrected for the base line), should not be diffusion limited and thus should follow closely the simple Eq. (1) (for the correct topology). Our data (Fig. 1) indeed bear this out: We are not aware of any other physical data coming so close to this simple mathematical limit of site percolation. This, in our view, more than justifies the concept of exciton percolation in these substitutionally disordered, binary, isotopic-mixed organic crystals. The problem is reduced to one of topology, which depends in turn on both crystal structure and pairwise interactions.

Further studies are underway so as to determine the longer-range exciton interactions and transport both for this singlet exciton system, where their importance is secondary,[13] and for the lowest triplet exciton where they are of major concern, because of the much longer lifetime.[15] Finally we would point out that the exciton transfer mechanism in photosynthetic systems appears to be analogous to the one described above. The active centers (i.e., $P700$) are analogous to the BMN supertrap, the primary pigment (i.e., chlorophyl a) to the exciton-conducting $C_{10}H_8$, and the secondary pigments (i.e., chlorophyl b) to the light-absorbing filler, $C_{10}D_8$. We note that in both the naphthalene system discussed above and the well-studied photosystems,[16] effective exciton transfer occurs at $C_A/C_B > 1$.

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Effects of Quantum States on the Photocurrent in a "Superlattice"*

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Photocurrent measurements in GaAs-GaAlAs superlattices grown by molecular-beam epitaxy enable us to observe simultaneously quantum states and associated anomalous conductance. The spectrum in the photocurrent shows a series of peaks of photon energies corresponding to transitions between quantum states in the valence and conduction bands. As a function of applied voltage, the photocurrent exhibits pronounced negative differential conductance when the potential-energy difference between two adjacent wells of the superlattice exceeds the bandwidth of the quantum states.

In this Letter, we report the results of photocurrent measurements in a one-dimensional periodic structure referred to as a semiconductor "superlattice." By examining both the spectral response and the applied-voltage dependence of the photocurrent, we have not only identified quantum states, but also observed their effects in causing a negative differential conductance. Thus, our investigation gives a better exposition of the interrelationship between such quantum states and anomalous transport properties in a superlattice.

It was previously demonstrated that the electron transport properties in well-defined double barriers[1] and periodic structures[2] were largely governed by quantum states created in these structures. Furthermore, optical-reflectivity measurements[3] for a GaAs-AlAs superlattice indicated a shift due to the lowest quantum state of about 0.1 eV from the absorption edge of GaAs, and absorption spectra[4] for isolated potential wells showed a series of salient peaks corresponding to bound states and associated excitons. The development of the technique of molecular-beam epitaxy in growing extremely smooth and thin layers of GaAs and $Ga_{1-x}Al_xAs$ has made it possible to observe such quantum states in layered structures.

Superlattice structures of three different configurations have been used in the present experiments: 100 periods of 35-Å-GaAs–35-Å-$Ga_{0.8}Al_{0.2}As$; 80 periods of 50-Å-GaAs–50-Å-$Ga_{0.78}Al_{0.22}As$; and 50 periods of 110-Å-GaAs–110-Å-$Ga_{0.55}Al_{0.45}As$, as labeled by *A*, *B*, and *C*, respectively, in Fig. 1. The total thickness in all cases is of the order of 1 μm which is comparable to the absorption length for the photons involved. The structures were prepared on *n*-