Energy Transport and Percolation on Fractal Structures with Energy Disorder

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Chemically mixed molecular crystals show, similarly to isotopically mixed crystals, percolation phenomena for triplet-excitation energy transport. However, because of strong guest-host interaction, energy disorder in the form of induced energy funnels masks the fractal nature of the percolating guest clusters. The assumption of a spectral dimension of $d_s=\frac{4}{3}$ for percolation at the critical concentration needs in the present case the introduction of an additional waiting-time distribution for a random-walk process.

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Disordered media often show dispersive kinetics, i.e., the relaxation cannot be expressed in terms of discrete decay rates.[1,2] However, the detailed description of the dynamics will critically depend on the material and the microscopic relaxation processes. One of the widely used concepts is that of random walks on lattices with randomly distributed trapping centers.[3,4] In this context the question arises whether it is possible to unravel a fractal nature of the investigated objects.[5] Examples of such fractal objects are polymers,[6] percolating clusters at criticality,[7,8] and porous glasses.[9] Percolating clusters have already been intensively studied in substitutional disordered molecular crystals[10] and thus offer a chance to test fractal concepts in detail.

Reaction kinetics studied by triplet-triplet annihilation in isotopically mixed crystals of naphthalene—which are substitutionally disordered molecular crystals—revealed at the critical concentration for percolation a spectral dimension $d_s=1.3$,[11] which is very close to the expected spectral dimension of $d_s=\frac{4}{3}$ for percolating clusters at criticality.[7] Other media like membranes and filter papers showed different spectral dimensions.[9] The question has been raised whether in these cases geometric disorder is masked by energy disorder, which will also show up in fractal-like kinetics.[12,13] This is already expected if we assume waiting-time distributions for random-walk processes.[14] Theoretical calculations have been made to combine geometric and energetic fractal effects[15-17] following the subordination principle.[18] To our knowledge experimental attempts to unravel these two contributions have not yet been reported. However, this would be of central importance in order to determine the (geometric) fractal nature of more complicated systems.

For this reason we used modified substitutionally disordered molecular crystals. To proceed we prepared chemically mixed molecular crystals of *p*-dichlorobenzene (DCB) in *p*-dibromobenzene (DBB) over a wide range of concentrations.[19] By combination of phosphorescence spectroscopy and optically detected magnetic resonance we were able to identify the statistical formation of guest aggregates such as dimers and trimers.[20] Contrary to isotopically mixed crystals these statistically formed guest aggregates are due to crystal-field effects considerably lower in energy (more than 15 cm^{-1}) than DCB monomers. Thus they serve as energy sinks at temperatures as low as 4.2 K, which is comparable to the role which doped supertraps play in isotopically mixed crystals.[10] Additionally, for this system we already reported the formation of energy funnels in the excited triplet state, which are formed by lowering DBB host molecules next to DCB guest molecules energetically 27 cm^{-1} above the DCB triplet state at 27857 cm^{-1}.[20-22] This effect of energy-funnel formation is not observed in isotopically mixed crystals. A qualitative description of the DCB-DBB system is given in Fig. 1, which shows a

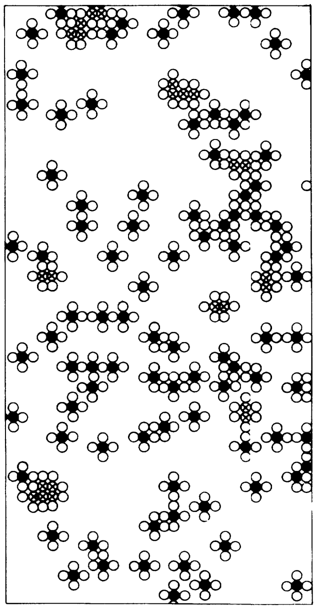

FIG. 1. Part of the statistical distribution of 6% DCB guest molecules (filled circles) on a 120×120 square lattice. Four distorted DBB molecules are indicated (empty circles) for each DCB monomer. Nearest-neighbored DCB molecules form aggregates (circles with crosses). The formation of overlapping energy funnels is clearly evident.

calculated distribution of 6% guest molecules in a crystalographic plane when we assume a statistical distribution of DCB.

The overall picture is very much the same as in isotopically mixed crystals such as naphthalene,[10] but is different with respect to the formation of energy funnels, which results at high guest concentrations in the formation of clusters of overlapping funnels. Energy transport among the dominant DCB monomers will be more effective between monomers than between monomers and aggregates because of relative concentration ratios. Additionally, transport within a cluster will be faster than between the individual clusters as it is in isotopically mixed crystals. Excitation energy will be trapped after sequential steps within the monomer manifold by the statistically formed guest aggregates. This is reflected by the observation that when we selectively excite DCB monomers by pulsed singlet-triplet laser excitation, the phosphorescence decay is faster than expected from the average DCB triplet lifetime of 16 ms.[23] Moreover, depending on DCB concentration, the decay is strongly nonexponential.[23,24] This is not surprising as cluster sizes and individual transfer routes between donors (DCB monomers) themselves and donors and acceptors (DCB aggregates) will reflect the substitutional disorder depicted in Fig. 1.

We have already shown[24] that the decay can be empirically described by a Kohlrausch-type[25] stretched-exponential behavior at short times and a monoexponential decay at long times via the equation

$$I_{\text{phos}} = I_{ET}\exp[-(t/\tau)^{\beta} - t/\tau_1] + I_0\exp(-t/\tau_0), \quad (1)$$

with $0 < \beta < 1$ and the triplet lifetime $\tau_1 \approx \tau_0$. To rule out the possibility of parallel one-step transport processes between statistically distributed donors and acceptors as has been described by Inokuti and Hirayama,[26] we tried to fit our results with a logarithmic-exponential form, which was quite less satisfying than the stretched-exponential behavior. This confirms the sequential character of the energy transport as one would already expect from a comparison with transport phenomena in isotopically mixed crystals.[10]

From Fig. 2 it can be seen that both fit parameters β and $\alpha = I_{ET}/(I_{ET}+I_0)$ strongly depend on DCB concentration, where β changes from $\beta \approx 1$ at low concentration to $\beta = 0.28 \pm 0.05$ at high concentration. In additional experiments with steady-state mercury-lamp excitation, we determined the ratio R of integrated acceptor—i.e., DCB aggregate—phosphorescence intensity I_{ag} to total phosphorescence intensity I_{tot} including donor (DCB monomer) intensity. This procedure is exactly the same as in isotopically mixed crystals, where supertraps have been artificially added.[10] The result is also shown in Fig. 2 as a function of DCB concentration. At 0.045 mol/mol a sudden increase of the intensity ratio is observed as is characteristic for dynamic percolation of clusters.[10] The critical concentration for percolation is therefore $c_p = 4.5\%$, which is slightly below values reported for isotropically mixed crystals.[10]

When we compare the chemically mixed DCB/DBB crystal with isotopically mixed systems, two remarks have to be made. Firstly, because of strong guest-host interactions, DCB aggregates are considerably lowered in energy, which causes them to act as supertraps. However, this implies that the acceptor concentration itself is increasing on doping concentration, which will continuously shift the critical concentration c_p to lower concentrations. This will result in a systematic error to c_p of about 1%.[27] Secondly, in the present case, nearest-neighbor jumps between DCB monomers do not occur in the sequential hopping transport because nearest neighbors act as supertraps. This is a particular case which has not previously been considered in the theory of percolation. However, if we replace a DCB monomer by its energy funnel, we can easily see from Fig. 1 that, nonetheless, nearest-neighbor jumps occur between these (percolating) energy funnels.

For percolating clusters at criticality, the survival probability $\phi(t)$ of donor molecules (in our case excited monomers) is for short times, with the triplet lifetime τ_1 taken into account,[16,28]

$$\phi(t) \sim \exp(-cBt^{d_s/2} - t/\tau_1), \quad (2)$$

with the corresponding spectral dimension $d_s = \frac{4}{3}$.[7] However, identifying $\beta = 0.35$ with $d_s/2$ at $c_p = 4.5\%$, we would get $d_s = 0.7$, which is in strong contradiction with results already obtained for percolating clusters in isotopically mixed crystals.[11] We believe that this deviation is due to a superimposed waiting-time distribution affecting the random-walk process. Such a waiting-time distribution might either result from additional energy disorder or a distribution over different jump distances. We believe that the latter possibility is unlikely because the relation $d_s = \frac{4}{3}$ is universal for percolating clusters and therefore also holds when next-nearest-neighbor jumps and longer-distance jumps are included. This has

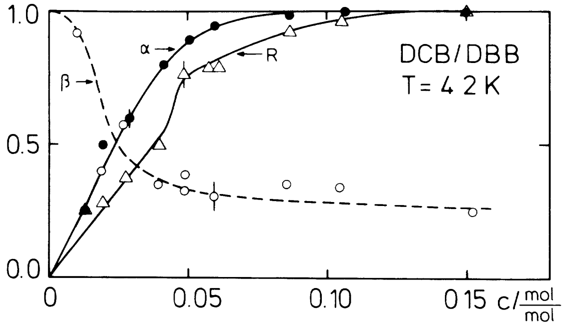

FIG. 2. Stretched exponent β, $\alpha = I_{ET}/(I_{ET}+I_0)$, and intensity ratio $R = I_{\text{ag}}/I_{\text{tot}}$ as functions of DCB concentration. Curves serve only as guidelines.

been demonstrated for isotopically mixed crystals[11] which, because dynamic percolation applies, also involve a distribution over different jump distances. Additionaly, above $c_p = 4.5\%$ β becomes nearly independent of concentration (Fig. 2) although the distribution over jump distances will change in favor of short-distance jumps. To test the remaining possibility of energy disorder we have performed a temperature-dependent analysis of the DCB monomer phosphorescence decay for a crystal with a concentration at about c_p. Some experimental results are given in Fig. 3. They clearly show that β and α are functions of temperature at least above 4.2 K. This suggests the presence of energy disorder.

Several models have been proposed to describe the influence of energy disorder on energy-transport processes.[29,30] Despite the different nature of these models, they have in common that the stretched exponential β should approach zero at temperatures close to zero. This is, however, not the case for the DCB-DBB system. We have found[27] that β is constant below 4.2 K, but that at temperatures higher than 15 K, energy transport becomes diffusive ($\beta = 1$). This is not surprising because thermally activated excitation transfer to the host exciton band has to be taken into account. On the other hand, a temperature-independent β at low temperatures proves that β cannot be described only by energetic disorder but that the presence of additional geometric disorder in the form of percolating clusters is not negligible.

The energy disorder reflected by the high-temperature behavior is, however, a trivial one which masks a possible energy disorder affecting the transport on the percolating clusters itself. More information may be obtained by inspection of the details of the transport among DCB donor molecules. When we describe triplet energy transport by a superexchange mechanism[31] it becomes obvious from inspection of Fig. 1 that basically two kinds of energies will model the exchange rates even at the lowest temperature. With respect to energy transport, those DCB molecules embedded in areas of overlapping energy funnels are only sensitive to the energy separation (tunneling potential) from the DBB molecules within the funnel ($\Delta E = 27\ \mathrm{cm}^{-1}$), whereas transport among "isolated" induced funnels mainly depends on the separation from the DBB exciton band ($\Delta E = 53\ \mathrm{cm}^{-1}$).[22,24] This fact induces additionally to the geometric disorder an energetic disorder. Unfortunately, however, this energy disorder is connected with the same energy separations as the trivial one, which causes the transition from dispersive to diffusive transport at high temperatures. An independent determination of the energy disorder becomes experimentally very difficult. This would not be the case if the DBB exciton band were much further apart from the energy funnels. Nevertheless, we believe that the established model of the induced energy funnels strongly suggests the presence of both energetic and geometric disorder.

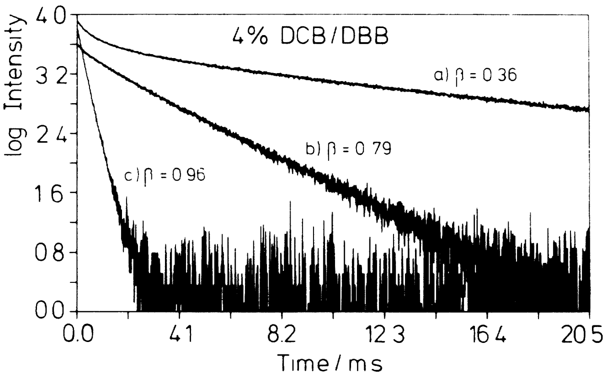

FIG. 3. Monomer phosphorescence intensity of DCB monomers after selective singlet-triplet laser excitation at different temperatures: (a) 4.2 K, (b) 12 K, and (c) 20 K. β has been obtained for a crystal with 5% DCB by a fit with Eq. (1).

It has been shown that for not too long times the kinetics of the trapping problem follows the subordination principle, which implies that both kinds of disorder can be combined multiplicatively.[15] Energy disorder can be taken into account via the assumption of a waiting-time distribution. For disordered media, a waiting-time distribution has been described by $\psi(t) \sim t^{-\gamma-1}$ with $0 < \gamma < 1$,[14] which will give in our case a survival probability of

$$\phi(t) \sim \exp(-c_p A t^{\gamma d_s/2} - t/\tau_1). \tag{3}$$

With $d_s = \frac{4}{3}$ for $c = c_p$,[7,11] we obtain from the experimentally determined $\beta = 0.35$ the waiting-time parameter $\gamma = 0.53 \pm 0.1$. As has been shown by Blumen, Klafter, and Zumofen,[32] it should be possible in the case of trapping, which applies in the present experiments, to deconvolute the product $\beta = \gamma d_s/2$; for at long times the decay should cross over from a Kohlrausch-type to an algebraic behavior. However, in our case this long-time region is masked by the finite triplet lifetime of the donor.

With the observation of dynamic percolation via static optical spectroscopy (Fig. 2) we could nevertheless show that for percolating clusters it is, in principle, possible to discriminate between energetic disorder and the fractal nature of the underlying lattice. Energy disorder has not been reported for isotopically mixed crystals,[11] which is probably due to the absence of induced energy funnels.

A final remark concerns the dependence of β on concentrations above and below c_p. As expected, above c_p β in Fig. 2 is hardly sensitive to c.[11] Additionally, α approaches 1, from which we conclude that the kinetics can be uniquely described by an equation similar to Eq. (3). However, below c_p we interpret the discontinuity in the decay as expressed by the superposition of two decay functions in Eq. (1) to a crossover from a fractal to a classical behavior: The system is only fractal over a given length scale,[28] thereby changing its spectral dimension.

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