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Energy migration in randomly doped crystals: geometrical properties of space and kinetic laws

P. Evesque
Laboratoire d'Optique Physique, ESPCI, 10, rue Vauquelin, 75231 Paris Cedex 05, France

Résumé. — Les lois cinétiques de la migration d'énergie dans les états excités des cristaux dopés ont été calculées en utilisant un modèle de percolation. Le cas où la densité d'excitations est régie par un processus d'annihilation a été particulièrement étudié. Dans ce cas, nous avons trouvé que le nombre $I$ de fusions par unité de temps décroît avec le temps en suivant les lois : $I \sim t^{-\alpha}$ (où $\alpha = 1 - \frac{d}{2}$) aux temps courts, $I \sim t^{-\beta}$ (où $\beta = 1 + \frac{d}{2}$) aux temps plus longs et $I \sim t^{-2}$ aux temps très longs. $d$ est l'exposant spectral d'Alexander et d'Orbach, et $\varepsilon$ est relié aux exposants critiques de la percolation par $\varepsilon = \beta/(\beta + \gamma)$. Les cas où cette théorie peut être appliquée aux problèmes des cristaux dopés avec des forces à courte portée sont ensuite discutés. Un nouveau résultat expérimental obtenu sur un cristal de naphtalène $D_8$ dopé avec du naphtalène $H_8$ est produit et est en bon accord avec la théorie.

Abstract. — The kinetics of energy migration in the excited states of doped crystals are calculated using a percolation model. Special care has been taken in the case where an annihilation process controls the density $n$ of excitations at time $t$. In this case the number $I$ of fusions per unit of time follows the laws : $I \sim t^{-\alpha}$ (with $\alpha = 1 - \frac{d}{2}$) at short times, $I \sim t^{-\beta}$ (with $\beta = 1 + \frac{d}{2}$) at longer times, $I \sim t^{-2}$ at very long times. $d$ is the spectral dimension of Alexander and Orbach, and $\varepsilon$ is related to the other classical percolation exponents through $\varepsilon = \beta/(\beta + \gamma)$. The applicability of this theory to randomly doped crystals with short-range interactions is then discussed. A new experimental result which has been obtained in a naphthalene $D_8$ crystal doped with naphthalene $H_8$ is produced and is in good agreement with the theory.

1. Introduction.

The problem of energy migration in the excited states of doped crystals has been extensively studied during the past few years. This field was first stimulated by the work of Dexter [1] who predicted that, when a crystal is doped with two kinds of impurities A and B at large concentrations, one can observe a transfer of the excitation from an excited A impurity to a B type. The A impurity has been called the donor, or the trap, and the B, the acceptor, or the supertrap. This trapping phenomenon has been found to be very dependent on the nature of the interaction (dipole-dipole, dipole-quadrupole).

This pioneering work has been extended by Inokuti et al. [2], who derived the time dependence for the low-energy migration case. The decay laws they determined were generally of the kind :

$$I \sim \exp(-t^\gamma)$$

(1)

where $\alpha$ is an exponent which depends on the nature of the interaction ($\alpha = 1/2$ for dipole-dipole, ...). The major aim of this paper is to demonstrate that an anomalous behaviour can also be generated by a long-range migration. It will be due, in this case, to some special geometrical properties of the diffusion : if energy migration exists between donors and if these donors are randomly distributed, one should expect that the number of paths connecting two donors far away from each other will be strongly reduced compared to that expected in a classical three-dimensional case. This problem looks very much like a percolation one.

For instance, we report in figure 1, a simulation of a 2-D crystal doped with one impurity at a concentration of 8%. The donors have been connected together by taking into account only the shortest possible jumps which will allow the migration. One can see in this picture that the way to go from one part of this crystal to another one is much more 1-dimensional than two-dimensional. This randomness reduces the effective dimensionality for energy migration.

The approximation by which this figure is generated involves a cut-off in the distribution of the transfer...
rates. The validity of this approximation will depend obviously on the nature of the interactions: the more it will be short-range, the more accurate this approximation will be.

In the first section, we shall recall the solution of the diffusion problem in a pure one-dimensional case: this will lead us to introduce a spectral dimension which governs the number of sites \( N(t) \) that an excitation has visited at time \( t \). Then in the second part, this solution will be extended to spaces of higher dimensionality and the kinetic laws of a supertrapping process of two-exciton fusion will be calculated. The idea of the compact exploration [3] will be introduced. This means that for a space of sufficiently low dimensionality, an excitation returns to its starting point sufficiently often that it knows exactly the details of the total volume it has previously explored. However, in so far as figure 1 really describes the problem, we should also expect some influence of finite clusters on the kinetics. These clusters can be taken into account by using a percolation model which will be solved in the third section. In part four, we discuss the influence of jumps longer than those shown in figure 1. Because of these jumps, the system will turn back into a two-dimensional one, and this cancels the effects of percolation and leads to a cross-over behaviour. Finally, we shall present an experimental result which demonstrates the existence of such a compact exploration.


This problem has been solved by Alexander et al. [4] for different distributions \( p(W) \) of the transfer rate \( W \). If there is a cut-off in this distribution \( p(W) \), (this implies none of the \( W \) smaller than \( W_0 \)), they have found that, for sufficiently long times, the time dependence of the migration is identical to the 1-D one for a unique value of \( W \). The mean value of the number of visited sites \( N(t) \) at time \( t \) is:

\[
N(t) \sim t^{1/2}
\]

(2)

However, if this cut-off does not exist and if the density \( p(W) \) varies as \( W^\alpha(0 < \alpha < 1) \) when \( W \) goes to zero, the same authors have found that the number of visited sites is given by:

\[
N(t) \sim t^V
\]

with

\[
V = (1 - \alpha)/(2 - \alpha).
\]

(3)

Equation 3 shows that under these circumstances, the \( V \) exponent may be different from and smaller than 1/2. In the following 2 \( V \) will be called the spectral exponent of a disordered one-dimensional system.

In this paper, we propose to generalize this result. We shall consider the problem of energy migration between the donors of figure 1 as a diffusion problem in a space which reflects the geometry of the paths. This space will be no longer strictly one- or two-dimensional as shown by this picture, but will be of a fractal dimensionality \( \tilde{d} \). Such a fractal space is mapped on an Euclidian space of dimensionality \( d \).

In any volume \( l^d \) of length \( l \) of this Euclidian space, there are \( N_0 \sim l^d \) sites. However only \( N \) of these sites pertain to the fractal space. The variation of \( N \) with \( l \) (\( N \sim l^d \)) leads to the definition of the fractal dimensionality \( \tilde{d} \) of the fractal space.

However as proved in [5] and [6] this dimensionality \( \tilde{d} \) does not describe the time dependence of the number of visited sites, and we must introduce a spectral exponent \( \tilde{d} \) which will govern this dependence:

\[
N(t) \sim t^{\tilde{d}/2}
\]

If there were no disorder in the transfer rates between adjacent sites, this spectral exponent would be strictly \( \tilde{d} \) as defined in reference 6; however if some « strong » disorder exists, these two exponents should be different and related to each other, as in the 1-D case, by:

\[
\tilde{d} = 2 V \tilde{d}.
\]

(4)
As long as \( \bar{d} < 2 \), the number of visited sites at time \( t \) will be much smaller than the number of jumps which is proportional to the time. Therefore we expect that the kinetics of supertrapping or fusion processes will be changed.

3. Kinetic laws in fractal \( \bar{d} \) systems.

De Gennes [3] has studied the time dependence of chemical reactions for spaces with \( \bar{d} < 2 \). In such spaces, the particle which migrates returns very often to its starting point and the exploration of the space becomes a compact one. If \( N(t) \) is the number of sites visited by this particle at time \( t \), the differential equation which governs chemical reaction between two molecules \( A \) and \( B \) at concentrations \( n_A \) and \( n_B \) is (Eq. III.21 of ref. 3):

\[
- \frac{dn_A}{dt} = - \frac{dn_B}{dt} = kn_A n_B
\]

with

\[
k = k_0 N(t)/t.
\]

These equations can also be viewed as describing a supertrapping process in doped crystals. In this case \( n_A \) will stand for the concentration of excited donors and \( n_B \) for the concentration of unexcited acceptors. In a similar way, assuming \( A \) and \( B \) to be identical molecules or particles will lead to \( n_A = n_B \) and equation 5 will describe the fusion of two excitations. As argued in the first section, \( N(t) \) should be:

\[
N(t) \sim t^{(\bar{d}/2)} \quad \text{with} \quad \bar{d} < 2.
\]

Thus the solution of (5) leads in the case \( n_B \gg n_A \) to a supertrapping process given by:

\[
n_A = n_{A_0} \exp(-2k_0 n_{B_0} t^{(\bar{d}/2)}/\bar{d})
\]

where \( n_{A_0}(n_{B_0}) \) stands for the initial concentrations in \( A(B) \).

On the other hand, if we look at the fusion of two excitations, one will find (\( n_A = n_B \)):

\[
(n_A)^{-1} = n_{A_0}^{-1} + 2k_0 t^{(\bar{d}/2)/\bar{d}}.
\]

In some cases, we can look directly at the number \( I \) of fusions per unit time. This one is given by

\[
- \frac{dn_A}{(2 \ dt)}.
\]

Thus one should get for \( I \):

\[
I = k_0 t^{(\bar{d}/2)-1}(n_{A_0}^{-1} + 2k_0 t^{(\bar{d}/2)/\bar{d}})^{-2}.
\]

The limiting cases of equations 7, 8 and 9 can be demonstrated also by using the concept of a compact exploration introduced by de Gennes [2]. Equation 7 has been established by him in reference 7 and only equations 8 and 9 have been deduced physically here. The basic idea of this calculation is to average over the different initial positions the time for which the fusion will occur.

For a jump time \( \bar{C} \) between adjacent sites, the number \( N(t) \) of sites visited at time \( t \) by a particle will be given by (6). Thus, in so far as \( \bar{d} \) is smaller than 2, the time \( \bar{C} \) spent on each site of this volume will be much larger than \( \bar{C} \) since:

\[
\bar{C} = t/N(t) \sim t^{-1/2} \bar{C}^{(\bar{d}/2)}. \quad (10)
\]

We can then assume that if 2 particles were localized on two volumes such that they intersect at time \( t \), these two particles have fused together and they are then annihilated at time \( t \). Assuming an initial random distribution of particles, and looking only at short times, the integral of the number \( I \) of fusion processes per unit time, will be equal to one half of the probability of finding two particles in a volume of \( N(t) \) sites

\[
\int_0^t I \ dt = n_{A_0}^2 N(t)/2.
\]

Then substitution of (6) in (11) will lead to the number \( I \) of fusion per unit time for small time \( (n_{A_0} N < 1) \):

\[
I \sim \frac{dn_{A_0}^2}{(n_{A_0} N)^2}.
\]

For sufficiently long times, this decay law is no longer valid: if \( n_{A_0} N \) is larger than one, the system turns out to be roughly homogeneous because it is then made up of a series of contiguous volumes, each one containing \( N \) sites; consequently, each volume contains either 1 or 0 particles depending on whether the number of the particles initially located in it was odd or even.

Thus the total density of particles \( n_A \) at a sufficiently long time \( t \) will be given by:

\[
n = 1/(2N) \sim t^{-\bar{d}/2}, \quad \text{for} \quad n_{A_0} N > 1.
\]

As the variation of this density arises only from the fusion process, one expects the fusion probability per unit time \( I \) to be:

\[
I = - \frac{dn/2}{dt} \sim t^{-1+2/\bar{d}}, \quad \text{for} \quad n_{A_0} > 1.
\]

Equations 12 and 14 are the limiting cases of equation 9 respectively for short and long times; equation 13 is equivalent to equation 8.

The above demonstration shows that the compact exploration concept leads to exact results. It will be used in the next sections where the calculation has to be generalized in order to take into account the finite clusters of figure 1.

4. Diffusion in a percolation case.

As it has been previously shown [8], the infinite cluster of a percolation problem at threshold is a fractal with a dimension \( d \). However the migration on such a fractal is governed by a spectral dimension \( \bar{d} \) different from \( d \) [5, 6]. As demonstrated by Alexander et al. [5], \( \bar{d} \) is smaller than 2 and should be about 4/3 in any percolation case without disorder in the jump rates; the number \( N(t) \) of visited sites in this compact diffusion case is then given by (6).

As pointed out by de Gennes [7], these laws have to
be modified in order to take into account finite clusters and the real structure of the infinite one. Following references 7, we can look at the system as if it were made up of clusters with \( s \) sites plus an infinite cluster. At a concentration below the percolation threshold \( c_0 \), the infinite cluster does not exist and the finite ones are unlikely to be larger than a certain value \( S^* \) which depends on the concentration. Above the threshold, a site has a probability \( P_\infty \) to belong to the infinite cluster and a probability \( P_s \) to belong to an \( s \) cluster: the finite clusters cannot be larger than a certain value \( S^* \) and they have a fractal behaviour governed by \( \tilde{d} \) and \( \tilde{d} \). The infinite cluster has the same fractal behaviour as long as the length scale considered is smaller than \( (S^*)^{1/\tilde{d}} \). For length larger than this, this infinite cluster has a normal Euclidean dimension.

The probability of finding an excitation on a \( s \) cluster will be approximated by the classical scaling law as in reference 6:

\[
P_s = s^{-(1+\varepsilon)} \quad \text{for} \quad s < S^* \\
P_s = 0 \quad \text{for} \quad s > S^* \\
P_\infty \quad \text{for the infinite cluster. (15)}
\]

We can express \( P_s, \tilde{d}, \tilde{d}, \varepsilon \) and \( S^* \), as functions of the classical exponents \( (\beta, \gamma, \nu) \) of a classical \( d \) dimensional percolation system and of its correlation length \( \xi \) and concentration \( c \):

\[
P_\infty = (c-c_0)^\beta \\
\tilde{d} = d - \beta/\nu \\
\tilde{d} = (d\nu - \beta)(2\nu + \tilde{d} - \beta) \sim 4/3 \\
\varepsilon = \beta(\beta + \gamma) \\
\xi = (S^*)^{1/\tilde{d}} = (c-c_0)^{-\varepsilon}.
\]

4.1 The infinite cluster. As the total initial density of excitations is \( n_{\infty} \), the initial density of excitations in the infinite cluster is:

\[
n_\infty = n_{\infty} P_\infty.
\]

At short times this cluster is fractal with a spectral exponent \( \tilde{d} = 4/3 \). The concentration of excitations at time \( t \) is thus given by equation 8 and the number \( I \) of fusions per unit time is given in (9). For times such that \( N(t) > S^* \) the infinite cluster has a spectral exponent of 2 which modifies (8) and (9). This leads us to summarize the kinetic laws as follows:

4.2 The contribution of finite clusters. At sufficiently long times \( (N(t) > S^*) \) the exploration on such clusters is finished and they will keep only 0 or one excitation, depending on the initial even or odd number of excitations.

We shall first calculate the final concentration of excitations in the finite clusters. Labelling \( x_s \) the number of clusters of size \( s \), the initial density of excitations \( P_s \) on these clusters is \( P_s = n_{\infty} P_s \) and the density of excitations lying initially in one \( s \) cluster is \( n_{\infty} s \). Because of (15) one gets for \( x_s \):

\[
x_s \sim s^{-(2+\varepsilon)}.
\]

As a matter of fact, the real value of \( P_s \) is:

\[
P_s = s^{-((1+\varepsilon)} f((c-c_0) s^\varepsilon)\text{where} f(z)\text{is a characteristic function of the percolation problem. By approximating} f(z)\text{to a gate function, one obtains equation 15. This approximation should be accurate as shown in figure 11 of reference 8 and as far as one is not interested in very small clusters. The }\beta, \gamma \text{and } \nu \text{notations are those of reference 8. }\tilde{d}\text{stands for the critical exponent for the conductivity.}
\]

The problem of a supertrapping process has been extensively treated by de Gennes 7 and it will be limited here to the case of the annihilation of two excitations.

According to the compact exploration concept it will be assumed that no more annihilation will occur in cluster of size \( s < N(t) \). Thus as \( t \) increases, \( N(t) \) increases and the number of clusters which participate to annihilation decreases. A summation over all clusters, is then needed in order to investigate the time dependence. We shall first look at the infinite cluster and afterwards we shall determine the contribution due to finite clusters.

\[
\begin{align*}
n_{\infty} N(t) &< 1 \quad \frac{N(t)}{d} = 4/3 \\
n_{\infty} N(t) &> 1 \quad \frac{N(t)}{d} = 2
\end{align*}
\]

We shall assume that if the initial value \( n_{\infty} \) is smaller than \( 1/2 \), the \( s \) cluster will never contribute to annihilation; on the contrary if \( n_{\infty} > 1/2 \), this cluster will contribute and its final density will be \( 1/2 \) on the average. Thus labelling \( x_0 = n_{\infty} \), the final concentration of excitations on the finite clusters will be given approximately by:

\[
n = (1/2) \sum_{s > x_0} x_s + \sum_{s > a} n_{\infty} s x_s
\]

where \( \alpha \) is the minimum size of finite clusters for
which (18) is valid. Taking then into account \( s_0 = n_{\alpha_0}^{-1} \) and (18), one obtains after summation:

\[
n \sim n_{\alpha_0} \alpha^{-\epsilon}.
\]  

(20)

At first sight this result could seem rather strange: since the reaction which governs the final density of excitations is the fusion of two excitations, one would expect a non-linear behaviour of \( n(\infty) \) as a function of the initial density \( n_{\alpha_0} \); on the contrary, equation 20 indicates a linear behaviour. This feature arises from the large number of small clusters. In such clusters the probability of finding two excitations at the origin of time is small enough that we can neglect the fusion process. Because of (15) and (18), these small clusters are in a number much larger than the largest clusters and the initial probability of finding an excitation in a small cluster is larger than that of finding this excitation in a large cluster; the final and the initial density of excitation will then mostly arise from the small cluster contribution which will hide the large clusters ones.

Thus in order to detect the fusion effects, it should be more appropriate to look only at the behaviour of large clusters. This can be achieved if the excitation created by the fusion of two excitations stands at a different energy and luminesces with a lifetime shorter than the time needed for the fusion. In this case one can directly measure the number \( I \) of fusions per unit of time by measuring the bi-excitation luminescence.

In the following parts of this section, we shall limit the calculation to the variation of the excitation number at a given time, on the finite clusters, and to the number \( I \) of fusions at the same time.

At a long enough time \( t \) \((N(t) > S^*)\), the exploration of finite clusters is completely achieved and this leads to:

\[
n = \text{const.} \quad \text{for} \quad N(t) > S^*.
\]  

(21)

\[
I = 0
\]  

For shorter times and if \( n_{\alpha_0} S^* > 1 \), there are two different regimes:

i) The first one will correspond to times such that \( n_{\alpha_0} N(t) > 1 \). In this case the fusion processes will only happen in \( s \) clusters such that \( s > N(t) \), the other clusters having been entirely explored. As before, we will assume a compact exploration which leads to consider these largest clusters as made up by joined volumes \( N(i) \) in which 0 or 1 excitation only lays. The excitation concentration in such an \( s \) cluster is \( s/2 N(i) \). Since the number of \( s \) clusters is \( x_s \), the total number \( n' \) of excitations in these large clusters is:

\[
n' = (1/2) \sum_{s>N(t)} s x_s N(t).
\]  

(22)

Owing to (18) this equation becomes after summation:

\[
n' = N(t)^{-(1+\epsilon)/2} - S^{*\epsilon} N(t)/2.
\]  

(23)

The number of fusions per unit of time is proportional to the time derivative of \( n' \). As \( N(t) \) is proportional to \( t^{d/2} \), this differentiation leads to:

\[
I \sim t^{-1-\epsilon(d+\epsilon)/2} \quad \text{for} \quad N(t) > 1
\]  

and \( N(t) < S^* \).

(24)

ii) For very short times \( n_{\alpha_0} N(t) < 1 \), the clusters will be populated randomly; for any \( s \) cluster such that \( s > N(t) \), the probability that a fusion will occur between \( t \) and \( t + dt \) will be given by the difference between the probability of finding two excitations in the volume \( N(t + dt) \), and that of finding them in the volume \( N(t) \). On the contrary, the probability of a fusion process in an \( s \) cluster for which \( s < N(t) \) is 0. The total fusion probability will be given by:

\[
I = \sum_{s > N(t) + dt} s N(t + dt) n_{\alpha_0}^s - \sum_{s > N(t)} s N(t) n_{\alpha_0}^s.
\]  

(25)

As \( s x_s \) is the probability \( P_s \) that a site pertains to an \( s \) cluster, \( s x_s \) is given by equation 15. After summation of equation 25, one gets:

\[
I = \{ \frac{(N(t + dt)^{1-\epsilon} - N(t)^{1-\epsilon})}{N(t + dt) - N(t)} \} n_{\alpha_0}^s.
\]  

(26)

As \( N(t) \sim V_0 t^{d/2} \), one finally gets after differentiating of (26):

\[
I = n_{\alpha_0}^2 \left\{ V_0^{1-\epsilon} t^{(1-\epsilon)/2-1} - V_0 t^{d/2-1} S^{*\epsilon} \right\}.
\]  

(27)

As long as \( N(t) \) is much smaller than \( S^* \) this equation 27 can be approximated by:

\[
I = n_{\alpha_0}^2 V_0^{1-\epsilon} t^{(1-\epsilon)/2-1}.
\]  

(28)

Let us now summarize the contribution of finite clusters:

\[
N(t) \sim t^{\tilde{d}/2}
\]  

\[
I \sim n_{\alpha_0} N(t) \{ (N(t)^{-\epsilon} - S^{*\epsilon}) / \tilde{t} \} \quad \text{for} \quad n_{\alpha_0} N(t) < 1
\]  

(29a)

\[
N(t) \sim t^{d/2}
\]  

\[
I \sim (N(t)^{-\epsilon} - S^{*\epsilon}) / 2 \tilde{t} N(t) \sim t^{-1-\epsilon(d+\epsilon)/2} \quad \text{for} \quad n_{\alpha_0} N(t) > 1
\]  

(29b)

\[
\tilde{d} = 4/3; \quad \epsilon = \beta/(\beta + \gamma)
\]  

(29c)

\[
I = 0 \quad \text{for} \quad N(t) > S^*.
\]  

(29d)

\[
N(t) > S^*.
\]  

(29e)
For a percolation problem the exponents $\beta$ and $\gamma$ are known. Using the value of reference 7, one obtains for a two-dimensional system for instance:

$$\epsilon = 0.055,$$

and for a three-dimensional one, $\epsilon = 0.21$.

The kinetic laws which are expected for a percolation problem have been established (Eqs. 17 and 29). It is important to generalize these results to more difficult cases such as that shown in figure 1; here the transfers can occur not only between adjacent sites but also for longer jumps. This situation will be studied in the next section.

5. Generalization and limitations of the percolation model.

The generalization of the percolation model to the problem of diffusion in randomly diluted systems will not only depend on the applicability of the scaling laws far away from the percolation threshold but also on the nature of the interaction which allows the migration. In the case of long-range interactions, such as dipole-dipole ones, the transfer rates vary smoothly with distance. As the time goes on, new jumps become possible and the geometrical properties of the paths will change continuously with time. This could invalidate the applicability of the percolation model.

On the contrary, if the interactions are short-range as in the superexchange case, the transfer rates will strongly depend on the length $l$ of the jumps. At each length $l$ will correspond a transfer rate $W_l$. Assuming a cut-off $W_{l_0}$ in the transfer rates will then lead to considering the system as made up of clusters the size of which will be smaller than $S^*$. ($S^*$ is a function of the concentration of impurities and of $l_0$). If the time $T_{l_0}$ required to explore a $S^*$ cluster is smaller than the first jump rate $W_{l_1}$, which has been neglected, (29) must describe the cluster exploration. After a time equal to $T_{l_0}$ the exploration will be finished and no more fusion process will be expected. However, this exploration starts again after the time $1/W_{l_1}$ because new connections have to be considered. As these new connections pertain to a percolation problem in a space, the dimensionality of which is equal to the first one, the scaling laws of both problems should be equal and the migration should obey to equivalent laws. The only difference between them will come from the difference in the jump times. However such an expansion will lead us to consider the system as above the percolation threshold for long enough times. At these times, the system is no more a fractal one but turns back into a homogeneous one for which the kinetic laws will be the classical ones. A cross-over between the fractal kinetic laws and the classical ones is then expected for times long enough to consider the system as a percolation one.

A peculiar behaviour should be also expected when the cluster size considered in this expansion is such that the time needed to explore this cluster is longer than the first jump time neglected $W_{l_1}^{-1}$. In such a case, these longer jumps have to be taken into account, changing the dynamical properties of the paths. However, as long as $W_{l_1}/W_{l_1}^*$ is large, this feature is only expected for large clusters and should then only happen towards the percolation threshold. Moreover, in so far as this time is such that some connections are still forbidden, the system will look like a percolation one below the percolation threshold and it must follow scaling laws with critical exponents. These critical exponents will be the classical static ones, but the dynamic $d$ spectral dimension will be changed, because of the change in the transfer rate distribution as it has been demonstrated in reference 4 and recalled in the first section of this paper (Eq. 4).

6. Experimental test for the kinetic laws.

In order to prove the existence of this behaviour we have investigated the time dependence of the fusion of two triplet excitations in crystals of perdeuterated naphthalene doped with perhydrogenated naphthalene at a concentration of $10\%$ and at low temperature ($T < 4\,\text{K}$).

This system doped with betamethylnaphthalene has been extensively studied by Kopelman and co-workers [9] who measured the ratio of the triplet luminescence intensity of betamethylnaphthalene and naphthalene as a function of the two molecular concentrations. They fitted their static experimental results with a percolation model.

Thus it should be expected in this system that the kinetic laws of a triplet excitation would be ruled by a compact exploration and should lead to a triplet-triplet fusion probability which displays a time dependence as predicted in (29) under some specific conditions:

i) The migration between naphthalene D$_8$ states has to be neglected; we then need to study the sample at a temperature sufficiently low to prevent the excitation from jumping from a naphthalene H$_4$ to a naphthalene D$_8$. This condition was realized at temperatures lower than 4.2 K.

ii) The spontaneous decay time ($\tau$) of the triplet state must not be the leading process. This requires the study of the emission at short times ($t < \tau \sim 1\,\text{s}$) with a high density of excitations. The experimental time scale was then 0.2 s; we used a pulsed dye laser of pulse duration 15 ns, and of repetition rate 5 Hz. In order to get a high density of excitations, we excited the sample through the triplet-state upper Davydoff component of the host. As the temperature was low enough, the excitations were at once trapped by the naphthalene H$_4$.

iii) In order to get directly the number $I$ of fusions per unit of time, the luminescence life-time of the...
singlet state which is created by the fusion must be much shorter than the time required for the fusion. As the fusion process is limited by the migration time, in this experiment, the decay time of the singlet state ($\tau \sim 100$ ns) will never be a pertinent parameter for the studied time scale and singlet state luminescence intensity $I_s$ at time $t$ will reflect exactly the time dependence of the fusion probability:

$$I \sim I_s.$$ (31)

We report in figure 2a and 2b, this singlet luminescence intensity as a function of time in linear and log log coordinates respectively.

![Image of figure 2a and 2b](image)

Fig. 2. — Time dependence of the singlet luminescence of naphthalene $H_8$ in a crystal of naphthalene $D_8$ doped at 10%. This luminescence is created by the fusion of two triplet excitations. a) linear scale, b) log log scale.

The log log plot of this figure demonstrates unambiguously that for short times, the time dependence of the fusion probability follows: $I = t^{-\alpha}$ with $\alpha = 0.4 \pm 0.03$. At longer times, this law fails in complete agreement with equations 29b and 29c or 17 which predict such a crossover behaviour. Moreover the comparison of equation 28 and the experimental result leads to evaluate $\alpha$ to be:

$$\alpha = -\tilde{d}(1 - \varepsilon)/2 + 1.$$ (32)

As the interactions between triplet states of naphthalene connect only the molecules in a same plane, the percolation model which has to be considered is a two-dimensional one. This leads us to evaluate $\varepsilon$ as 0.055 (Eq. 29). Assuming then $\tilde{d}$ to be 4/3 leads to the theoretical value of:

$$\alpha_{th} = 0.37.$$ (33)

Experimental and theoretical results are thus in relatively good agreement because of the experimental uncertainty. Moreover, we should expect a slight difference between the theoretical $\tilde{d}$ exponent and the one for the real problem of doped crystals: a strict cut-off of the jump probability with distance will no longer be realistic in this case. It will diminish the theoretical exponent $\tilde{d}$ as it has been demonstrated in the first part of this paper.

This result which is in complete disagreement with the theoretical predictions for small migration [2] is thus an unambiguous proof of the validity of the percolation model [9] for the energy migration in doped organic crystals, and definitely demonstrates the incoherence of the excitation motion at such low concentrations of traps.

7. Conclusions.

As long as the interactions which generate the energy migration in doped crystals are of a long range type, the jump times between neighbouring impurities will vary smoothly with distance. This leads us to associate this problem with a space dimensionality larger than 2 when the migration occurs and the kinetics of the supertrapping process is only controlled by the interaction type and the mean jump time [10].

On the contrary, the assumptions which ruled our calculations were to operate a cut-off in the jump time distribution between the impurities. This allowed us to map out the migration as in figure 1 and to reduce the problem to a dynamic percolation one. Such an approximation leads to consider the clusters as lying on a space with a fractal dimension $d$. However as this dimension $d$ is defined through a number of sites per unit volume, it does not describe the geometrical properties of the paths. These ones are ruled by the spectral exponent $\tilde{d}$ introduced by Alexander and Orbach [5] which is approximately 4/3.

Extending then to this case the work of de Gennes on the chemical reactions in fractal spaces, and using his compact exploration assumption, the kinetic equations have been solved and the characteristic time dependences of the supertrapping process and of the fusion of two excitations have been found for the infinite cluster case. Moreover, in order to take account of the small clusters, we used a scaling law approach to solve the entire problem of the fusion reaction in a percolation network. It has been demonstrated that a cross-over between fractal kinetic laws and classical ones should be expected for impurity concentrations large enough and at times sufficiently long.

This theory should be applied when the interactions...
are of short-range type. It has been demonstrated that the fusion of two triplet excitations of naphthalene $D_8$ crystals doped with 10 % of naphthalene $H_8$ is controlled by this fractal behaviour at low temperature.

The special case of organic molecules triplet states is peculiarly well adapted to study such a fractal behaviour; this is mostly due to the large difference between the nearest neighbours jump time ($\sim 10^{-11}$ s) and the luminescence lifetime ($\sim 1$ s), a difference which allows us to study the energy migration dynamics on a large length scale even when the exploration is a compact one. However, this fractal anomalous behaviour can much more easily be studied through the fusion of two triplet excitations than from the direct triplet-state luminescence in presence of supertraps: as it has been demonstrated from the percolation case, below the percolation threshold, the smallest clusters are in much larger concentration than the largest clusters and the supertrapping process will only change a small part of the total triplet luminescence. On the contrary, the fusion of two triplet excitations can only occur in the largest clusters and the study of the singlet luminescence created by these fusions will only reflect the dynamics of the migration.

Following a similar procedure, as far as an up conversion process is expected, it would be better to study it than the direct luminescence, in order to detect the anomalous dimensionality of the energy migration.

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References