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Exciton diffusion at finite frequency: Luminescence observables for anisotropic percolating solids

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A study is made of the luminescence intensities associated with exciton diffusion and trapping on a three-dimensional anisotropic percolating lattice. The calculation is based upon a relationship that exists between the frequency dependent diffusion tensor at frequencies comparable to the inverse excitation lifetime, and luminescence observables such as the host and trap luminescence intensities for conditions of constant illumination. The present approach allows the study of crossover behavior in percolative systems that are of intermediate transport dimensionality $2 < d_t < 3$. Our results suggest that curvature seen in luminescence observables near the transition need not always be a direct reflection of the critical indices associated with classical isotropic percolation. We have identified three possible sources of deviation from the classical behavior: (1) the radiative time scale of the luminescence measurements, (2) the functional dependence of the luminescence yields on the diffusion tensor, and (3) the demands of dimensional crossover in the critical region arising from the anisotropy of the medium.

I. INTRODUCTION

Excitons possess no charge, and so their transport properties cannot be probed through conductance measurements. Instead, more indirect means are required to obtain information regarding the transport properties of interest. Several techniques for doing this have been devised.¹⁻⁴ Among the most common are those which rely upon the interaction of the mobile excitation with some other species, such as impurity atoms or molecules,^{1,2} which have been doped into the solid to irreversibly trap or quench the excitation. The observed mutual annihilation of exciton pairs can be used for the same purpose.² In either case, the result is a change in the normal exciton population that is detected in the luminescence decay of the excitation back to its ground state.

Clearly, the quality of information that can be obtained from such indirect techniques depends upon our understanding of the relationship that exists between experimentally accessible quantities (such as luminescence intensities) and physical quantities of interest (such as exciton transport coefficients). The purpose of the present paper is to explore and discuss this relationship for a model system relevant to sensitized luminescence experiments on substitutionally disordered molecular solids.² Specifically, we calculate luminescence intensities associated with exciton transport and trapping in an anisotropic percolating solid in which a fraction $q = 1 - p$ of the nearest-neighbor jump rates have been randomly removed (i.e., set equal to zero). Vanishingly small jump rates between excitation sites in real solids can occur, it is believed, due to the presence of energy barriers associated with impurity molecules of higher excitation energy. Correspondingly, in the present model the quantity q is to be at least approximately associated with the fraction of such energetically inaccessible molecules in the solid.

The present analysis differs in a number of important respects from several others^{2,5,6} that have been developed to

address transport in multicomponent molecular crystals; first, we employ a well-defined transport model (nearest-neighbor bond percolation) whose transport properties are well understood. This helps to separate the uncertainties associated with the treatment of transport with those associated with the calculation of luminescence observables. The second difference is the careful and self-consistent way in which transport anisotropy is handled in the present analysis. A high level of anisotropy is a common feature of many of the molecular solids upon which exciton trapping and annihilation measurements have been performed. Thus, one of the central aims of the present study is to clarify, by the use of an analytical and numerically tractable theory, when it is appropriate to interpret a highly anisotropic disordered solid in terms of an isotropic solid of lower dimensionality. While it is trivial to accommodate anisotropy into standard theories of transport for ordered (i.e., translationally invariant) solids, it is more difficult to do this for disordered systems. The difficulty arises from the fact that the macroscopic anisotropy in the latter case is no longer simply related to that of the pure crystal—or even to that of the microscopic hopping-rate distribution functions which characterize the solid. By way of example, consider the fact that the diffusion tensor for an anisotropic random walk becomes (critically) isotropic at the percolation threshold for any finite amount of microscopic anisotropy.^{7,8} The present paper explores the consequences of this behavior for luminescence observables in exciton trapping experiments. The treatment given here is based upon an earlier theory⁸ developed specifically to describe excitation transport in strongly anisotropic, disordered materials.

The paper proceeds as follows. In the next section a master equation is introduced to describe the evolution of exciton probabilities in a disordered anisotropic medium with dilute randomly placed traps. A program for solving these equations is then outlined. The steady-state luminescence intensities can, within a certain well-defined approximation,

be written as functionals of the frequency-dependent diffusion tensor associated with transport in the disordered solid. Numerical solutions to self-consistent equations for the transport properties are then evaluated and used to examine the behavior of luminescence observables as a function of disorder, lattice anisotropy, and excitation lifetime.

II. THE MODEL

In keeping with the essential physics of the problem we are led to consider an anisotropic variation of the classical bond-percolation model in which connected bonds along different axes of a three-dimensional cubic lattice are associated with jump rates W_s that are allowed to depend upon the crystal axis $s = 1, 2, 3$ (which are also referred to as x, y , and z). Disconnected bonds (associated with zero jump rates) are assumed to occur isotropically with probability $q = 1 - p$ for each axis, as in normal bond percolation.⁹ The creation, migration, and capture of excitons in the solid is then assumed to obey a master equation for the probability

$$\begin{aligned} \frac{d}{dt} P_n + P_n/\tau_r - S(t) \\ = \sum_{s=1}^3 W_n^s (P_{n-s} - P_n) + W_{n+s}^s (P_{n+s} - P_n) \\ - \sum_{\{r\}} (P_n/\tau_c) \delta_{n,r} \end{aligned} \quad (1)$$

of finding the diffusing excitation at site $\mathbf{n} = (n_1, n_2, n_3)$ of the lattice at time t . In Eq. (1), \mathbf{s} represents a unit vector pointing along the positive s -coordinate axis from the n th site to its neighbor along that direction, and W_n^s is the hopping rate (either zero or W_s) from site \mathbf{n} to its neighbor at $\mathbf{n} - \mathbf{s}$. We assume a cubic lattice for simplicity, and, in keeping with the model described above, the hopping rates W_n^s are assumed to be independent random variables governed by an anisotropic probability distribution function of the form

$$\rho(W_n^s) = p\delta(W_n^s - W_s) + (1-p)\delta(W_n^s). \quad (2)$$

The intrinsic anisotropy of the molecular solid is characterized by the set of microscopic anisotropy ratios $\xi_{s,s'} = W_s/W_{s'}$, which are equal to one for an isotropic system.¹⁰ In what follows, we consider a quasi-two-dimensional solid which is isotropic in the x - y plane, so that $W_x = W_y = W$. Hops out of the plane are described by a different hopping rate $W_z = \zeta W$, ($\zeta < 1$) which is assumed to be smaller in magnitude than that associated with hops in the x - y plane. The second term on the left-hand side of Eq. (1) describes the radiative decay of excitons back to the ground state with lifetime τ_r . This process is assumed to be intrinsic to the excitation and independent of disorder. The spatially uniform source term $S(t)$ describes the creation of excitations through illumination. In the steady-state experiments considered here it is independent of time. The last term on the right-hand side of the Eq. (1) describes the trapping process. Excitons are assumed to be captured to trap states associated with a certain number N_t of trap molecules that are randomly distributed throughout the solid. Capture occurs by decay of probability with rate $k_c = 1/\tau_c$ from host lattice sites which are in the immediate vicinity of a trap.

(For simplicity we assume one such host site per trap.) The sum in Eq. (1) is therefore understood to run over the set $\{\mathbf{r}'\}$ of host sites from which excitation can decay to the traps. The total number of traps, N_t , is assumed to be small compared to N , the total number of host lattice sites, so that the fractional trap concentration $x = N_t/N$ is much less than 1. The goal of the calculation is an expression for the quantum yield for capture, Y , by which we mean the fraction of excitation which migrates to and gets captured by a trap before having decayed radiatively back to the ground state. In terms of steady-state observables of the luminescence experiments, Y is equal to the fraction of total luminescence emitted at wavelengths corresponding to the trap excitation energy. Denoting the trap luminescence intensity by I_t and that of the host lattice by I_h , one obtains the relationship¹¹

$$Y = I_t/(I_t + I_h). \quad (3)$$

Perhaps the key feature associated with the observed luminescence yield in mixed molecular crystals consisting of three energetically distinct species is an observed critical increase in the yield as a function of the concentration of active (energetically accessible) sites in the crystal. In the percolation picture advanced by Kopelman and co-workers² this increase is identified with the increased mobility of excitons at the transport threshold, which is itself associated with the existence of a percolating path of connected sites in the solid. For low values of p very few connected sites exist and few excitons are able to travel to the neighborhood of a trap to get captured. As a result, the luminescence yield is very small. Well above the percolation threshold exciton mobility is high, many excitons get trapped, and so nearly all of the luminescence emerges from the trap manifold. Hence the luminescence yield, Eq. (3), is, in this limit, very close to unity.

Because the luminescence observables signal events occurring in different parts of the solid, they necessarily reflect average properties of the disordered system. Hence any realistic calculation of Y requires an ensemble average over the disorder. In what follows it is implicitly assumed that this can be done in two steps. In the first step, discussed in Sec. II A, the average over transport disorder is performed. The result is a *translationally invariant* but frequency-dependent set of equations describing transport of excitation in an effective medium that characterizes the disordered system⁸ (Said another way, the averaged system is assumed to obey a translationally invariant generalized master equation.^{12(a)}) It is this latter system upon which effects of trapping are considered, and upon which the remaining average over the ensemble of trap configuration is performed. This latter step is addressed in Sec. II B.

A. Transport in the disordered solid

The transport properties of the solid are determined by the averaged solutions in Eq. (1) with the source and decay terms excluded. Disordered transport equations of this type have been extensively studied for isotropic systems.¹² Recently the transport part of Eq. (1), with anisotropy included, has been studied as well.⁸ In particular, in Ref. 8 an exact expansion for the frequency diffusion tensor was obtained

from consideration of the equations of motion for the probability currents that flow between nearest-neighbor sites. From the expansion obtained in that work, a self-consistent theory¹³ was constructed in which the macroscopic properties of the system were completely described by a self-consistent diffusion tensor with Laplace transformed components $D_s(z)$. The components of the diffusion tensor are related to the components of the (dimensionless) mean-square displacement $\langle R_s^2(t) \rangle = \sum_n P_n(\mathbf{n}\cdot\mathbf{s})^2$ through the relation⁸

$$D_s(z) = z \int_0^\infty dt e^{-zt} \frac{d}{dt} \langle R_s^2(t) \rangle. \quad (4)$$

In Eq. (4), z is the Laplace or "frequency" variable conjugate to time. In what follows, we assume that the averaged transport of excitons in the disordered lattice described by Eq. (1) is adequately described by the anisotropic extension of effective-medium theory introduced in Ref. 8. Thus we express the conditional probabilities or Green's functions $G_{\mathbf{n},0}(t) = \langle P_{\mathbf{n},0}(t) \rangle$, describing the probability for an exciton to be at site \mathbf{n} if it was initially at the origin (all decay processes excluded), in terms of the Fourier integrals of their Laplace transform⁸:

$$g_{\mathbf{n},\mathbf{m}}(z) \equiv \int_0^\infty dt e^{-zt} G_{\mathbf{n},\mathbf{m}}(t) \\ = (2\pi)^{-3} \int \frac{\exp[i\mathbf{k}\cdot(\mathbf{m}-\mathbf{n})]}{z + \sum_{s'} 2D_{s'}(z)(1 - \cos \mathbf{k}\cdot\mathbf{s}')} d\mathbf{k}. \quad (5)$$

In Eq. (5) the \mathbf{k} integral is over the first Brillouin zone of the reciprocal lattice. The theory of Ref. 8 gives the following expression:

$$D_s(z) = W_s(d_s p - 1)/(d_s - 1) \quad (6)$$

for the diffusion tensor associated with an anisotropic system described by the distribution function of Eq. (2). The direction and frequency dependent quantities $d_s(z)$ appearing in Eq. (6) are defined self-consistently through that equation and through the following integrals:

$$1/d_s(z) \\ = (2\pi)^{-3} \int \frac{2D_s(z)(1 - \cos \mathbf{k}\cdot\mathbf{s})}{z + \sum_{s'} 2D_{s'}(z)(1 - \cos \mathbf{k}\cdot\mathbf{s}')} d\mathbf{k}. \quad (7)$$

In Ref. 8, where details of the derivation leading to Eqs. (6) and (7) can be found, the quantities $d_s(z)$ are referred to as effective dimensionalities because in the isotropic limit they reduce (at zero frequency) to the Euclidian dimension. Even for a (finitely) anisotropic system they reduce at the percolation threshold to the Euclidian dimension of the underlying connected lattice and thus lead to a vanishing of the diffusion tensor at the effective medium critical point $p_c = 1/d$. For the present, it is important to note only that Eqs. (6) and (7) form a set of closed equations to be solved for $D_s(z)$ and $d_s(z)$. Moreover, a very simple relationship exists between the self-propagator $g_{00}(z)$ (the probability for the excitation to be on the site at which it started) and the quantities $d_s(z)$. In particular it follows from Eqs. (5) and (7) that

$$z g_{00}(z) = 1 - \sum_s 1/d_s. \quad (8)$$

We will make direct use of this relationship in the analysis which follows.

B. Luminescence observables

Upon averaging over the disorder in the hopping rates, a translationally invariant effective-medium obeying Eqs. (4)–(8) results. The traps, source, and radiative terms may now be reintroduced into the equations and the latter solved to obtain an expression for the yield Y to low order in the concentration of traps. Survival probabilities and luminescence observables associated with a random distribution of trapping centers in an otherwise translationally invariant medium have been studied previously. For our purposes it will suffice to consider an evaluation of Y that is to relatively low order in x , the concentration of traps. It should be added that such a low order calculation would be insufficient for time-dependent quantities such as the survival probability $n(t) = \sum_n P_n(t)$. Terms of higher order in x have been shown to dominate the behavior of this latter quantity at long times.¹⁴ Fortunately, this is unimportant for either the yield or the steady-state luminescence intensity because they are primarily determined by dynamical behavior at relatively short and intermediate times $t \lesssim \tau$, before the survival probability has reached its final asymptotic behavior.¹⁴ In other words, for sufficiently small x , the quantum yield and other steady-state trapping observables are accurately described by the low density expansion, whereas time-dependent quantities are not.

To first order in x , the quantum yield may be expressed in terms of the solution to the exactly solvable problem of a single trap^{15,16} embedded in the effective medium. Various low order improvements to the first order theory have also been obtained by a number of workers. These include the average T -matrix approximation studied by Huber and Ghosh,¹⁷ and a similar but not identical approach used by Kenkre and Parris.¹⁸ Both approaches reduce to the first order theory in the limit of small x . The approach of Kenkre and Parris has the added advantage that it recovers the exact high concentration limit, $x \rightarrow 1$, and therefore offers a reasonable interpolation for any concentration of traps. In what follows we will make use of the analysis and final expressions of Ref. 18 to study the luminescence yield. The result is an expression for the quantum yield which depends upon the Laplace transform of the self-propagator $g_{00}(z)$ at a value of its argument equal to the radiative decay frequency $\mathbf{k}_r = 1/\tau_r$ of the excitation. Specifically, one obtains¹⁸

$$Y = x\tau_r / \{ \tau_c + x\tau_r + (1-x)\tau_m \}. \quad (9)$$

Equation (9) involves the effective motion parameter τ_m , which has units of time, defined through the relation¹⁹

$$\tau_m = g_{00}(1/\tau_r). \quad (10)$$

In the present context $g_{00}(z)$ is the configurationally averaged propagator described in Eq. (5) with $\mathbf{n} = \mathbf{m} = 0$, which has been reexpressed in Eq. (8). It, and therefore the yield, is an explicit functional of the frequency-dependent diffusion tensor $D_s(z)$ which is an output of the self-consistent Eqs. (6) and (7).

We should note that it is implicitly assumed in the pres-

ent analysis that the transport properties of the lattice are the most important factor influencing the total rate for excitation trapping, and thus in determining the change in luminescence when trapping impurities are added. This is not guaranteed. Indeed, as pointed out elsewhere,^{18,20} there is always the possibility that the rate limiting step for trapping will be that associated with the capture process itself. This can occur if the rate at which excitation moves through solid is substantially greater than the rate at which capture occurs, i.e., if $\tau_m \ll \tau_c$. This limit has been observed²¹ in some pure systems, where the luminescence intensities have been shown to reflect only the capture rate k_c . In a system such as the one considered here, where the degree of disorder may be varied, one can effect changes in the rate of transport by the inclusion of energetically inaccessible impurities (broken bonds) and thereby slow the exciton down to insure that the motion limited regime is achieved. Once this is done the luminescence intensities will provide a direct probe of transport properties. In the present analysis we focus on the motion limited regime wherein $\tau_m \gg \tau_c$.

III. DISCUSSION

Combining the different results from Sec. II gives us a means for explicitly calculating the yield. First, for a given set of transport parameters $\{W, \zeta, p, \text{ and } z = 1/\tau_r\}$ we numerically solve the self-consistent Eqs. (6) and (7) to obtain the components of the diffusion tensor $D_s(z)$. Once these are obtained they can be used either in Eq. (5), or in Eqs. (7) and (8) to obtain the motion parameter $\tau_m = g_{00}[z; \{D_s(z)\}]$. The motion time can finally be used with a given set of trapping parameters $\{x, \tau_c\}$ in Eq. (9) to evaluate the yield and to study its behavior as a function of the different parameters.

In Figs. 1–4 we have followed this procedure to calculate the yield as a function of the concentration of connected bonds p , for different values of the microscopic anisotropy ζ and exciton lifetime τ_r (measured in units of the hopping

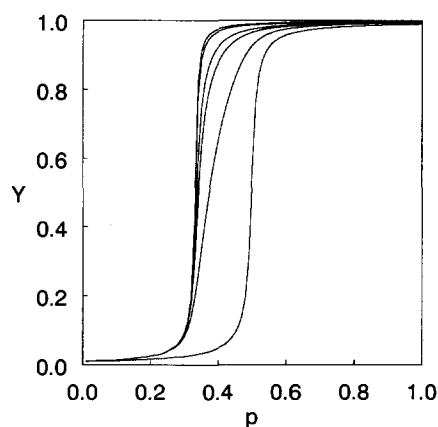


FIG. 1. Luminescence yield Y as a function of the concentration of connected bonds p , for different values of the microscopic anisotropy ratio $\zeta = W_z/W_x$. For this set of curves the radiative lifetime of the excitation was set equal to 10^4 times the hopping rate in the x - y plane, i.e., $W_x\tau_r = 10^4$. The six curves in the figure correspond, from top to bottom, to values of $\zeta = 1, 0.5, 0.1, 0.05, 0.01$, and 0 , respectively.

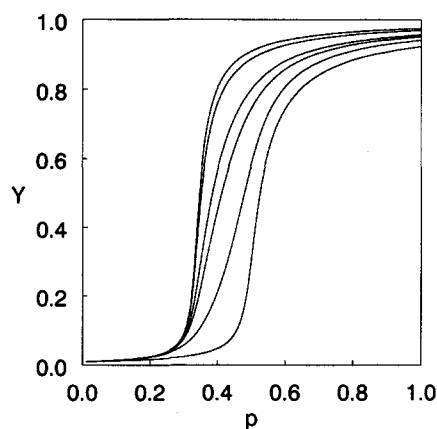


FIG. 2. Luminescence yield Y as a function of the concentration of connected bonds p , for different values of the microscopic anisotropy ratio $\zeta = W_z/W_x$. For this set of curves the radiative lifetime of the excitation was set equal to 10^3 times the hopping rate in the x - y plane, i.e., $W_x\tau_r = 10^3$. The six curves in the figure correspond, from top to bottom, to values of $\zeta = 1, 0.5, 0.1, 0.05, 0.01$, and 0 , respectively.

time $1/W$). A short description of the actual procedure used is given in the Appendix. In each of these figures we have taken the trap concentration $x = 0.01$, and the capture time $\tau_c = 0$. Figures 1–4 correspond, respectively, to exciton lifetimes which are $10^4, 10^3, 10^2$, and 10 times the mean time $1/W$ between hops in the x - y plane. In each figure the microscopic anisotropy $\zeta = W_z/W_x = W_z/W$ is varied from $\zeta = 1$ (the isotropic three-dimensional limit) to $\zeta = 0$ (the isotropic two-dimensional limit). Specifically, the six curves in each figure correspond to anisotropy ratios $\zeta = 1, 0.5, 0.1, 0.05, 0.01$, and 0 , with higher values of ζ corresponding to higher yields for a given value of p in each figure.

The critical rise in luminescence with increasing p seen in the first two figures is familiar from measurements on mixed molecular crystals reported in the literature. In each

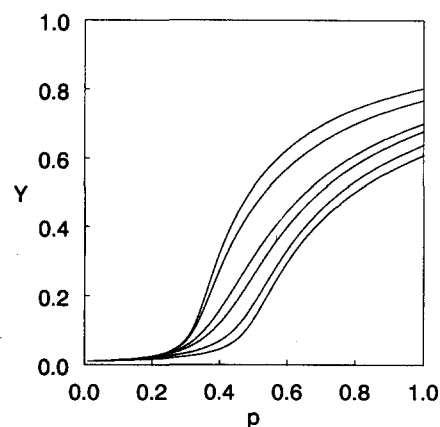


FIG. 3. Luminescence yield Y as a function of the concentration of connected bonds p , for different values of the microscopic anisotropy ratio $\zeta = W_z/W_x$. For this set of curves the radiative lifetime of the excitation was set equal to 10^2 times the hopping rate in the x - y plane, i.e., $W_x\tau_r = 10^2$. The six curves in the figure correspond, from top to bottom, to values of $\zeta = 1, 0.5, 0.1, 0.05, 0.01$, and 0 , respectively.

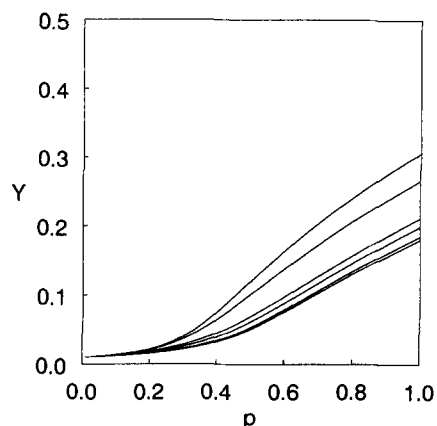


FIG. 4. Luminescence yield Y as a function of the concentration of connected bonds p , for different values of the microscopic anisotropy ratio $\zeta = W_z/W_x$. For this set of curves the radiative lifetime of the excitation was set equal to ten times the hopping rate in the x - y plane, i.e., $W_x\tau_r = 10$. The six curves in the figure correspond, from top to bottom, to values of $\zeta = 1, 0.5, 0.1, 0.05, 0.01$, and 0 , respectively.

curve a more or less abrupt rise begins at the transport threshold associated with the effective medium critical point, which is at $p = 1/3$ for the three-dimensional curves ($\zeta > 0$) and at $p = 1/2$ for the two-dimensional curves ($\zeta = 0$). Note that the critical nature of the transition becomes increasingly less pronounced as the lifetime of the excitation approaches that of the hopping time. Indeed, in Fig. 4, where the excitation makes an average of ten hops in the x - y plane before decaying radiatively back to the ground state, the yield is substantially reduced (note the change of scale). It is also interesting to note that in this figure the most anisotropic three-dimensional curve ($\zeta = 0.01$) is barely distinguishable from the two-dimensional one. This is not unexpected, since with this level of anisotropy only one exciton in ten makes a hop out of the plane within its lifetime. The difference between these curves grows dramatically as the exciton becomes longer lived and the probability for hops out of the plane increases.

This does point out an important point, however, namely that the percolation transition, as such, is strictly a zero-frequency transition. By this we mean that the diffusion tensor vanishes at the transition point only at infinite times, or equivalently only at zero values of the Laplace variable z . The observable of interest is intimately dependent upon the fact that excitons have a lifetime; it is therefore sensitive to the transport (roughly) for times up to the lifetime of the excitation. This manifests itself in the fact that the expressions we have used involve nonzero values of the Laplace variable. Thus, the critical nature of the (strict) percolation transition is washed out by the finite time scale involved. Using percolation concepts, we can say that the exciton is unable to tell whether it is part of a truly percolating structure, because it never lives long enough to find out. Only infinitely long-lived excitations display the true zero-frequency behavior, but such excitations have no luminescence. Thus, the actual situation involves a trade-off between long lifetime (desirable for its information on the transition) and intensity (which favors a shorter lifetime).

In view of these remarks, it is perhaps not entirely unexpected that the explicit curvature seen in the yield as it approaches the transition point is, in the present model, almost entirely unassociated with the critical behavior of the actual zero-frequency transport threshold. In actual fact, it arises from three separate sources: (1) the finite time scale of the experiment; (2) the functional dependence of the yield on the motion time τ_m (and thus on the diffusion tensor); and (3) the demands of dimensional crossover associated with the anisotropy of the solid. The first source we have discussed; the second depends to a certain extent upon the low order form Eq. (9) that we have used for the quantum yield, but is generally expected to persist to all orders in x . That these two sources of curvature are significant can be inferred from the fact that, in the effective medium theory that we have used, the zero-frequency diffusion tensor vanishes *linearly* at the percolation threshold.⁸ Thus in the isotropic curves ($\zeta = 1$ and $\zeta = 0$) all observed curvature arises from these two (noncritical) sources. The fact that the exact critical behavior of the diffusion tensor is not reproduced by effective medium theory does not, we believe, invalidate the suggestion that additional curvature is introduced into the yields from these other sources.

The last source of curvature which we have identified deserves some comment. The effect we refer to can be seen most easily in Figs. 1 and 2, where the curves associated with anisotropy ratio $\zeta = 0.01$ behave above $p = 1/2$ very much like the two-dimensional curves, but cross over in the region between $p = 1/3$ and $p = 1/2$ to the behavior exhibited by the isotropic three-dimensional curve. The demands associated with this dimensional crossover introduce curvature that is still very much apparent in the neighborhood of the critical region. It can be generally inferred from Figs. 1 and 2 that the general signature of anisotropy in a percolation transition as probed by the quantum yield is a broadening of the transition region, which for sufficiently long-lived excitation is very sharp in the isotropic two- and three-dimensional case, but becomes progressively wider as the level of anisotropy increases.

IV. CONCLUSIONS

We have presented an approach for calculating luminescence yields for anisotropic disordered systems, and have illustrated the approach for the specific case of an anisotropic bond-percolating lattice. Due to the nearest-neighbor restriction, the present model is of primary relevance to triplet excitations which have short-ranged transfer rates, and may not give a good indication of the behavior to be expected from longer-ranged singlet excitations. Nonetheless, the general features of the predicted yields are in very good qualitative agreement with observed behavior, and should provide additional insight into the meaning of results that have been obtained from measurements on substitutionally disordered mixed molecular crystals. The current calculations suggest that caution should be applied in the interpretation of critical behavior seen in the luminescence yields, since curvature in the critical region need not be a direct measurement of the critical indices associated with classical percolation. It is hoped that this work will complement pre-

viously obtained exact results on the one-dimensional analog to this problem.²²

APPENDIX

The actual numerical procedure used to calculate the results displayed in Figs. 1–4 was facilitated by the quasi-two-dimensional nature of the system considered. Thus the transport properties are specified by only four input parameters $\{z, W, \zeta, p\}$. For a system with additional anisotropy in the x - y plane we would require an additional parameter (ei-

ther W_y or ζ_y) and additional equations to solve. The analysis was further simplified by introducing the macroscopic anisotropy of the system, defined as

$$\eta = D_z(z)/D(z) \quad (\text{A1})$$

in which $D(z) = D_x(z) = D_y(z)$. Starting from the self-consistent Eqs. (6) and (7) we observe that for fixed z , the effective dimensionalities can be expressed as functions of η and D alone. For convenience we write $R_z(z) = 1/d_z(z)$ and $R(z) = 1/d_x(z) = 1/d_y(z)$, so that

$$R = (2\pi)^{-3} \int \frac{(1 - \cos k_x)}{z/2D + (1 - \cos k_x) + (1 - \cos k_y) + \eta(1 - \cos k_z)} d\mathbf{k}, \quad (\text{A2})$$

$$R_z = (2\pi)^{-3} \int \frac{\eta(1 - \cos k_z)}{z/2D + (1 - \cos k_x) + (1 - \cos k_y) + \eta(1 - \cos k_z)} d\mathbf{k}. \quad (\text{A3})$$

These are readily integrated numerically. Consequently, D can be considered a function of η obeying the equation which follows from Eq. (6),

$$D(z, p, \eta) - W(R - p)/(1 - R) = 0 \quad (\text{A4})$$

with $R = R(z, D, \eta)$ as above. For any value of η this equation can be numerically solved to give $D(\eta)$. It remains to determine η . This can be done by finding that value of η which obeys the equation obtained by substituting Eq. (6)

into Eq. (A1), i.e., the root of

$$\eta = \frac{W\zeta\{p - R_z[z, D(\eta), \eta]\}\{1 - R[z, D(\eta), \eta]\}}{\{1 - R_z[z, D(\eta), \eta]\}\{p - R[z, D(\eta), \eta]\}}. \quad (\text{A5})$$

This determines η for given input parameters z , W , ζ , and p . With η fixed we can then go back and calculate D according to Eq. (A4). Finally the self-propagator $g_{00}(z)$ can be calculated by numerical integration from the following expression:

$$g_{00}(z) = (2\pi)^{-3} \int \frac{d\mathbf{k}}{z + 2D\{(1 - \cos k_x) + (1 - \cos k_y) + \eta(1 - \cos k_z)\}}. \quad (\text{A6})$$

¹H. C. Wolf, in *Advances in Atomic and Molecular Physics*, edited by D. R. Bates and I. Estermann (Academic, New York, 1976), Vol. 3; R. C. Powell and Z. G. Soos, *J. Lumin.* **11**, 1 (1975).

²A. H. Francis and R. Kopelman, in *Excitation Dynamics in Molecular Solids*, Vol. 49 in *Topics in Applied Physics*, edited by W. M. Yen and P. M. Selzer (Springer, Berlin, 1981); R. Kopelman, in *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems*, Vol. 4 of *Modern Problems in Condensed Matter Sciences*, edited by V. M. Agranovich and R. M. Hochstrasser (North-Holland, Amsterdam, 1983); R. Kopelman, *J. Stat. Phys.* **42**, 185 (1986).

³A. J. Van Strien, J. F. C. van Kooten, and J. Schmidt, *Chem. Phys. Lett.* **76**, 7 (1980); V. Ern and M. Schott, in *Localization and Delocalization in Quantum Chemistry*, edited by O. Chalvet (Reidel, Dordrecht, 1976).

⁴T. S. Rose, R. Righini, and M. D. Fayer, *Chem. Phys. Lett.* **106**, 13 (1984).

⁵R. F. Loring and M. D. Fayer, *Chem. Phys.* **70**, 139 (1982); R. F. Loring, H. C. Anderson, and M. D. Fayer, *ibid.* **85**, 149 (1984).

⁶A. Blumen and R. Silbey, *J. Chem. Phys.* **70**, 3707 (1979).

⁷B. I. Shklovski, *Phys. Status Solidi B* **85**, K111 (1978); A. K. Sarychev and A. P. Vonogorodoff, *J. Phys. C* **12**, L681 (1979); **16**, L1073 (1979); L. N. Smith and C. J. Lobb, *Phys. Rev. B* **20**, 3653 (1979).

⁸P. E. Parris, *Phys. Rev. B* **36**, 5437 (1987); *J. Lumin.* **38**, 67 (1987).

⁹The bond model described here is chosen for tractability. It is hoped that results obtained for this model will (due to universality) be qualitatively relevant to site-disordered percolation as well.

¹⁰These are generally different than the macroscopic anisotropy ratio $\eta_{s,s}(z) = D_s(z)/D_s(z)$.

¹¹In writing Eq. (3) we have assumed for simplicity that the lifetimes and quantum efficiencies of host and trap states are equal (i.e., we have ig-

nored any decay channels not explicitly included in the model). In general I_h should be preceded by a factor taking into account the quantum efficiency of the host states in the absence of the traps.

¹²(a) J. Klafter and R. Silbey, *Phys. Rev. Lett.* **44**, 55 (1980); (b) T. Odagaki and M. Lax, *ibid.* **45**, 847 (1980); *Phys. Rev. B* **25**, 2301, 2307 (1982); I. Webman, *Phys. Rev. Lett.* **47**, 1496 (1981).

¹³For work based upon a similar approach see K. Kundu, P. E. Parris, and P. Phillips, *Phys. Rev. B* **35**, 3468 (1987); P. E. Parris, P. Phillips, and K. Kundu, *Physica A* **151**, 144 (1988).

¹⁴S. Havlin, B. Trus, G. H. Weiss, and D. J. Ben-Avraham, *J. Phys. A* **18**, L247, 1985; J. Klafter, G. Zumofen, and A. Blumen, *J. Phys. (Paris) Lett.* **45**, L49 (1984); G. Zumofen and A. Blumen, *Chem. Phys. Lett.* **88**, 63 (1982); M. D. Donsker and S. R. S. Varadhan, *Commun. Pure Appl. Meth.* **28**, 525 (1975); P. Grassberger and I. Procaccia, *J. Chem. Phys.* **77**, 6281 (1982).

¹⁵V. M. Kenkre and Y. M. Wong, *Phys. Rev. B* **23**, 3748 (1981).

¹⁶R. J. Elliot, J. A. Krumhansl, and P. L. Leath, *Rev. Mod. Phys.* **46**, 465 (1974).

¹⁷D. L. Huber, *Phys. Rev. B* **20**, 2307 (1979); K. K. Ghosh and D. L. Huber, *ibid.* **23**, 4441 (1981).

¹⁸V. M. Kenkre and P. E. Parris, *Phys. Rev. B* **27**, 3221 (1983).

¹⁹V. M. Kenkre, in *Exciton Dynamics in Molecular Crystals and Aggregates*, edited by G. Hoehler (Springer, Berlin, 1982).

²⁰V. M. Kenkre and P. E. Parris, *J. Lumin.* **31/32**, 612 (1984); V. M. Kenkre, P. E. Parris, and D. Schmid, *Phys. Rev. B* **32**, 4046 (1985).

²¹J. R. G. Thorne, R. G. Denning, T. J. Barker, and D. I. Grimley, *J. Phys. (Paris) C* **7**, 125 (1985).

²²P. E. Parris, *Phys. Lett. A* **114**, 250 (1986).