

Coherent one-dimensional exciton transport and impurity scattering

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A model is developed which describes the transport of coherent one-dimensional excitons in molecular crystals containing a low concentration impurity having excited state energy above that of the host crystal's exciton band. An expression is obtained for the exciton mean-square displacement and the exciton flux. The model is then employed to determine the effect of impurity scattering on an experimental observable, the time dependence of trap emission after impulse optical excitation of a one-dimensional exciton system. The resulting formula is used to calculate, without adjustable parameters, the time-dependent intensity of phosphorescent trap emission from crystals of 1,2,4,5-tetrachlorobenzene (TCB) containing the naturally occurring scattering impurity, *hd*-TCB, at 1.25°K. The results are compared to experiment and found to be in good agreement. Although the question remains open, the results are consistent with a coherent mode of triplet exciton transport in TCB and indicate the importance of naturally occurring isotopic impurity scattering in this type of system.

I. INTRODUCTION

In order to understand the nature of energy transport via Frenkel excitons¹ in real molecular solids it is not sufficient to consider an idealized perfect lattice, since unavoidable impurities in experimental samples can have a dramatic effect on exciton transport. Although impurity effects have been the subject of extensive research, most attention has been focused on two areas: (1) the low concentration limit of impurities which have excited state energies below the exciton band of the host—these give rise to “trap” states which can localize an excitation and thereby inhibit transport²; (2) the high concentration limit of impurities having excited state energies above the host exciton band in connection with the percolation problem.³ A third area which has not received as much attention is the case of high energy impurities in low concentrations. These impurities can act as exciton scattering sites hampering long range exciton migration. The low concentration impurity scattering problem is of particular importance since a real molecular crystal always contains naturally occurring isotopic impurities, no matter how chemically pure the sample. For example, a “pure” naphthalene crystal contains more than 0.1% monodeuteronaphthalene.

Hochstrasser pointed out in work on 1,4-dibromonaphthalene⁴ (DBN) that inhibition of exciton migration by impurity scattering will be particularly effective in a crystal which has finite interactions responsible for migration primarily along one crystallographic axis.^{4,5} In two- or three-dimensional systems randomly distributed impurities must be present in very large fractions to completely “cage” an exciton.⁶

In this paper a model for the effects of low concentration scattering impurities on coherent exciton migration in one-dimensional systems is presented. The mean-square displacement of an ensemble of excitons is calculated in terms of parameters which may be experimentally determined. This is in turn used to calculate the exciton flux and comparison is made to results obtained by Greer⁷ for a related problem. The relation-

ship between impurity scattering and exciton localization by low energy impurities (trapping) is then discussed. Rate equations are solved which permit the calculation of the time-dependent intensity of trap emission in a crystal with randomly distributed scattering sites and traps.

In a crystal having impurities with excited state energies significantly above the host exciton band an exciton-impurity scattering event in one dimension will result principally in reflection. Thus, an exciton can become “caged” between two impurity scatterers, inhibiting long range migration. On first inspection of this problem it would seem that the ability of such barriers to impede exciton transport would depend solely on the ratio of the barrier height S to the intermolecular interaction responsible for exciton transport β . However, it is also necessary to consider the distribution of exciton population among the band states determined by the ratio of 2β to the mean thermal energy KT , since the mean-square displacement is peaked sharply around the center of the band. For $2\beta/KT \gg 1$ the center of the band is not thermally populated and therefore exciton transport is severely reduced. On the other hand, for $2\beta/KT \approx 1$ the band center will be populated and significant transport may take place. This type of consideration can produce a temperature dependence in the mean-square displacement and in experimental observables which depend on it, such as the time-dependent intensity of trap emission following impulse optical excitation of the host exciton band. As sample temperatures are increased exciton-phonon scattering severely reduces the exciton coherence length.⁸ Thus, for the system to remain in the coherent limit and still have $2\beta/KT \approx 1$, the exciton bandwidth must be reasonably small. Temperature-dependent phenomena of this type will most likely be encountered in triplet exciton systems which have relatively small bandwidths.⁹

In a crystal containing trap sites the intensity of trap emission is in part determined by the ability of the exciton to migrate to the vicinity of the trap, which in turn is strongly influenced by the extent of impurity scattering and the dimensionality of the exciton transport. The triplet exciton bands of 1, 2, 4, 5-tetrachlorobenzene

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(TCB), known to exhibit many of the properties characteristic of one-dimensional systems,^{2(d),5} illustrate this situation. Experimental data presented below on the time dependence of TCB x-trap emission will show that impurity scattering from the naturally occurring isotopic impurity *hd*-TCB is a major factor determining the rate of exciton trapping if this system is taken to be in the one-dimensional coherent limit.

II. IMPURITY SCATTERING AND THE MEAN-SQUARE DISPLACEMENT

Consider a molecular crystal having an appreciable excited state intermolecular interaction β , only along one crystallographic axis. This situation will give rise to "one-dimensional" exciton bands with exciton transport occurring along this axis. If the crystal contains a low concentration impurity with a well-defined excited state energy level above the exciton-band energy, then exciton transport can be described as a combination of perfect crystal transport and exciton impurity scattering events. A well-defined impurity level will exist if S , the difference in energy between the impurity level and the band center, is large relative to the strength of the intermolecular interaction,^{2(a)} i.e., $S/\beta > 1$. (If $S/\beta < 1$, the impurity energy level will be amalgamated into the band.¹⁰)

In the low temperature coherent limit exciton transport is wavelike,^{1(b),8(b)} and with the condition that $S/\beta > 1$ an exciton-impurity scattering event in one dimension will result primarily in reflection with a small amplitude for transmission.

In a crystal having a mean impurity scattering frequency large relative to the exciton-phonon scattering frequency the migration of a coherent exciton wave packet centered about a state $|k\rangle$ will describe a random walk when viewed on a sufficiently long time scale in the following manner: Since the probability of reflection is large, an exciton wave packet can become caged between two impurities until it finally escapes from one end of the cage. After escaping from between impurities 1 and 2 on the 1 side, for example, it will be caught between impurities 0 and 1. When it escapes from between 0 and 1 the exciton wave packet again may leave from either end. Since the penetration probability is small, many reflections from the impurities will occur before the exciton wave packet finally tunnels out from one end of the cage. This assures equal probability of leaving a particular cage in either direction. When viewed on the appropriate time scale the exciton appears to step in random directions from one cage to another. The step size is determined by the cage size, and the step frequency is determined by the time required to tunnel out of a particular cage.

The result is that an ensemble of exciton wave packets $|k\rangle$ execute a random walk. The position distribution of wave packets is a Gaussian function characterized by a standard deviation equal to the time-dependent mean-square displacement determined by the step size l and the step frequency $n_l(k)$.

If the scattering impurities have a periodic distribu-

tion with $l - 1$ host molecules between them, after a time t the mean-square displacement from the starting position is

$$D_{t,i}^2(k) = n_l(k) t^2 a^2 \quad (1)$$

The distance d traveled in a single step is given by $d = al$, where a is the lattice constant. For a distribution of cage sizes $P(l)$ the average mean-square displacement is

$$\langle D_i^2(k) \rangle = \sum_{l=0}^{\infty} P(l) n_l(k) t^2 a^2 \quad (2)$$

$n_l(k)$, the number of steps of l molecules per unit time, is determined by the time required to escape from the cage formed by impurities separated by $l - 1$ host molecules. For a wave packet centered around the state $|k\rangle$

$$n_l(k) = V_g(k) \varphi(k) / la \quad (3)$$

In this expression the wave packet's single collision tunneling probability $\varphi(k)$ is multiplied by the exciton-impurity collision frequency $V_g(k)/al$, where $V_g(k)$ is the absolute value of the group velocity of the wave packet. For randomly distributed impurities, $P(l)$, the normalized probability of separation by l lattice sites, is the exponential distribution $\chi(1 - \chi)^l$, where χ is the mole fraction of the impurity in the crystal. Therefore, for an exciton wave packet centered around $|k\rangle$ the mean-square displacement is given by

$$\begin{aligned} \langle D_i^2(k) \rangle &= \sum_{l=0}^{\infty} P(l) \frac{V_g(k) \varphi(k)}{la} t^2 a^2 = t V_g(k) \varphi(k) \bar{d} \\ &= t V_g(k) \varphi(k) (\chi^{-1} - 1) a \quad (4) \end{aligned}$$

where \bar{d} is the mean impurity separation. Note that this displacement, unlike that in a typical diffusion problem, is dependent on \bar{d} to the first power.

The one-dimensional exciton band dispersion in the nearest neighbor approximation is given by¹¹

$$E(k) = E^0 + 2\beta \cos ka \quad (5)$$

where E^0 is the band center. An impurity molecule has excited state energy $E_0 + S$. The intermolecular interaction matrix element between an impurity and its nearest neighbors is defined to be β' . Using these, the single collision tunneling probability $\varphi(k)$ for an exciton wave packet centered about the wave vector state $|k\rangle$ can be calculated by considering the exciton to be a plane wave scattering from a potential barrier in a one-dimensional lattice. The secular equations describing an infinite one-dimensional lattice with a scattering molecule at site 0 are

$$\begin{aligned} &\vdots \\ &\vdots \\ E(k) b_{-2} &= E_0 b_{-2} - \beta b_{-1} - \beta b_{-3} \\ E(k) b_{-1} &= E_0 b_{-1} - \beta' b_0 - \beta b_{-2} \\ E(k) b_0 &= (E_0 + S) b_0 - \beta' b_{+1} - \beta' b_{-1} \\ E(k) b_{+1} &= E_0 b_{+1} - \beta b_{+2} - \beta' b_0 \\ E(k) b_{+2} &= E_0 b_{+2} - \beta b_{+3} - \beta b_{+1} \\ &\vdots \\ &\vdots \end{aligned} \quad (6)$$

where b_n is the amplitude of the spatial wavefunction at site n . For the case of the scattering of a plane wave k , the solution is assumed to have the form

$$\begin{aligned} b_n &= e^{ikna} + \alpha e^{-ikna} \quad (n < 0), \\ b_n &= \gamma e^{ikna} \quad (n > 0). \end{aligned} \quad (7)$$

This corresponds to a plane wave of unit amplitude impinging from the left and scattering at site 0 with amplitudes α and γ for reflection and transmission, respectively. By substituting Eqs. (5) and (7) into (6), satisfying continuity at the barrier site, and solving for $|\gamma|^2$, the barrier tunneling probability is obtained as

$$\varphi(k) = \frac{4\left(\frac{\beta'}{\beta}\right)^2 \sin^2 ka}{\left[S + 2\left(\frac{\beta^2 - \beta'^2}{\beta}\right) \cos ka\right]^2 + 4\left(\frac{\beta'}{\beta}\right)^2 \sin^2 ka}. \quad (8)$$

If the nearest neighbor exciton interactions coupling host molecule to host molecule and host molecule to impurity molecule are equal, i. e., $\beta' = \beta$, the Eq. (8) simplifies to

$$\varphi(k) = \frac{4\beta^2 \sin^2 ka}{S^2 + 4\beta^2 \sin^2 ka}. \quad (9)$$

Note that $\varphi(k)$ is zero at the band edges $k=0$ and $k=\pm\pi/a$, and that for the case of $\beta' = \beta$, $\varphi(k)$ is at a maximum at $k=\pm\pi/2a$, the band center.

The absolute value of the group velocity given by

$$V_g(k) = \left| \frac{1}{\hbar} \frac{\partial E(k)}{\partial k} \right| = \left| \frac{2\beta\alpha}{\hbar} \sin ka \right| \quad (10)$$

is also peaked at the center of the band. Thus, $\langle D_t^2(k) \rangle$ can be substantially greater for excitons near the band center than for those at the band edges. Substituting Eqs. (9) and (10) into (4), the mean-square displacement of a state $|k\rangle$ at time t is given by

$$\langle D_t^2(k) \rangle = \left| \frac{8a\beta^3 \sin^3 ka}{S^2 + 4\beta^2 \sin^2 ka} \frac{\bar{d}t}{\hbar} \right|. \quad (11)$$

For the problem of interest here the impurity is not amalgamated into the band and therefore $S^2 \gg 4\beta^2$. Eq. (11) reduces to

$$\langle D_t^2(k) \rangle = \left| \frac{8a\beta^3 \bar{d}t}{\hbar S^2} \sin^3 ka \right|. \quad (12)$$

The $\sin^3 ka$ dependence results in a very sharp peaking of the mean-square displacement around the state $|k\rangle = \pm\pi/2a$, the band center.

In a real crystal there is a distribution of excitons among the band wave vector states $|k\rangle$. To obtain the average mean-square displacement of an ensemble of excitons at a temperature T an ensemble average over the band states must be performed. Here we will assume that the band is in thermal equilibrium with the lattice at temperature T .^{5(b),12,2(c),2(d)} The ramifications of a nonequilibrium exciton population distribution will be discussed below in connection with the exciton trapping problem. Thus,

$$\overline{\langle D_t^2(T) \rangle} = \frac{\sum_{k=-\pi/a}^{\pi/a} \langle D_t^2(k) \rangle e^{-E(k)/KT}}{\sum_{k=-\pi/a}^{\pi/a} e^{-E(k)/KT}}. \quad (13)$$

The denominator is the partition function for a system of one-dimensional excitons with a dispersion given by Eq. (5).^{2(d)} For the case of $\beta' = \beta$ and $S^2 > 4\beta^2$ substituting Eqs. (5) and (12) into (13) yields the thermal average mean-square displacement for the ensemble

$$\overline{\langle D_t^2(T) \rangle} = \frac{\sum_{k=-\pi/a}^{\pi/a} \left| \frac{8a\beta^3 \bar{d}t}{\hbar S^2} \sin^3(ka) \right| e^{-2\beta \cos ka / KT}}{\sum_{k=-\pi/a}^{\pi/a} e^{-2\beta \cos ka / KT}}. \quad (14)$$

Since both summations are symmetrical about $k=0$, the limits of summation can be changed. For a band with a large number of states the sums can be taken to integrals. Substituting $y = 2\beta/KT$ and $\theta = ka$ yields

$$\overline{\langle D_t^2(T) \rangle} = \frac{8a\beta^3 \bar{d}t}{\hbar S^2} \frac{\int_0^\pi \sin^3 \theta e^{-y \cos \theta} d\theta}{\int_0^\pi e^{-y \cos \theta} d\theta} \quad (15)$$

or

$$\overline{\langle D_t^2(T) \rangle} = \frac{8a\beta^3 \bar{d}t}{\hbar S^2 \pi^{1/2}} \frac{I_{3/2}(y)}{I_0(y) (y/2)^{3/2}}, \quad (16)$$

where $I_{3/2}(y)$ and $I_0(y)$ are modified Bessel functions. Equation (16) gives the thermal average mean-square displacement for an ensemble of coherent excitons at time t and temperature T in a one-dimensional system with mean impurity separation \bar{d} , band-impurity energy difference S , and intermolecular interaction matrix element β . The more general result, in which β and β' are unequal, may be obtained by substituting Eqs. (8) and (10) into (4) and taking the thermal ensemble average. In this case the mean-square displacement is

$$\overline{\langle D_t^2(t) \rangle} = \frac{8a\beta \bar{d}t}{\hbar} \frac{\sum_{k=0}^{\pi/a} \frac{(\beta'/\beta)^2 \sin^3(ka) e^{-2\beta \cos ka / KT}}{\left[S + 2\left(\frac{\beta^2 - \beta'^2}{\beta}\right) \cos ka \right]^2 + 4(\beta'/\beta)^2 \sin^2 ka}}{\sum_{k=0}^{\pi/a} e^{-2\beta \cos ka / KT}} \quad (17)$$

The exciton probability distribution at time t is given by

$$P_t(n) = \frac{a}{\sigma(t)\sqrt{2\pi}} e^{-(na)^2/2\sigma^2(t)}, \quad (18)$$

where $\sigma(t) = \overline{\langle D_t^2(T) \rangle}^{1/2}$ and n is the number of lattice sites displacement from the initial position, equivalent to a distance $x = na$. Strictly speaking the probability distribution $P_t(n)$ should be calculated in increments of \bar{d} , since there is an equal time-averaged probability of finding the exciton on any lattice site in a particular cage.

The model developed above permits the calculation of the mean-square displacement of an ensemble of coherent one-dimensional excitons at thermal equilibrium at temperature T in a crystal containing a low concentration scattering impurity. Since the inclusion of scattering impurities in an otherwise perfect crystal changes the apparent mode of exciton migration from coherent

TABLE I. Median distance (lattice sites) for excitons in a one-dimensional band with bandwidth 1.25 cm^{-1} and a scattering impurity band center separation of 5 cm^{-1} .

Time (μsec)	Impurity concentration		
	0^a	$10^{-4}{}^b$	$10^{-3}{}^b$
0	0	0	0
200	1.5×10^7	2.7×10^4	8.5×10^3
400	3.0×10^7	3.8×10^4	1.2×10^4
600	4.5×10^7	4.7×10^4	1.5×10^4
800	6.0×10^7	5.4×10^4	1.7×10^4
1000	7.5×10^7	6.0×10^4	1.9×10^4

^aCalculated from the thermal average group velocity in one direction.

^bMedian random walk distance calculated from Eq. (16) and $D_{\text{med}} = 0.67 \langle D_i^2(t) \rangle^{1/2}$.

to diffusive when viewed on a time scale long relative to the impurity scattering time, a dramatic effect on the distance of migration can be expected even if the impurities are extremely dilute and chemically very similar to the host. As an example of this sort of effect the distances traveled by a coherently migrating exciton in a "perfect" crystal and in crystals having several different concentrations of scattering impurities are displayed in Table I. In this example the exciton bandwidth is taken to be 1.25 cm^{-1} , which is representative of a narrow triplet exciton band arising from weak exchange interactions. A value of 5 cm^{-1} is used for S , the difference in energy between the triplet band center and the corresponding impurity excited state. The temperature is 1.6°K . The perfect crystal coherent migration distances are calculated from the thermal average group velocity in one direction, and the median distances traveled in a crystal with scattering impurities are calculated using Eq. (16). Table I demonstrates the dramatic reduction in mobility produced by low concentration impurities even for a small value of S .

The effect of varying the exciton bandwidth is displayed in Fig. 1, where the thermal average mean-square displacement calculated from Eq. (16) is plotted versus temperature. The impurity concentration is 10^{-2} , and although the bandwidth changes the same ratio $S/\beta = 10$ is used for all curves. Thus, $\varphi(k)$, the k -dependent transmission probability, is the same for all curves. Since the mean-square displacement is sharply peaked at the center of the band [cf. Eq. (12)], narrow bands for which $4\beta < KT$ over the entire range of temperatures considered display little temperature dependence. However, in wider bands large changes in the k -state population distribution occur with changing temperature. This produces highly temperature-dependent mean-square displacements. Note that at a given temperature the system with the largest bandwidth does not necessarily have the greatest mean-square displacement, even though the ratio of S/β is kept constant. In all cases it has been assumed that the host-guest interaction ma-

trix element β' is equal to the host-host interaction β . The effect of varying β' can be calculated using Eq. (17). Application of Eq. (17) yields the result that the mean-square displacement is scaled approximately by a factor of $(\beta'/\beta)^2$. Increasing β' couples the impurity more strongly to the host molecules on either side, thus increasing the tunneling probability and therefore the mean-square displacement.

Recently, Greer⁷ examined the exciton transmission characteristics of a perfect one-dimensional molecular crystal containing a defective segment, i.e., a region with substitutional scattering impurities. In the limiting case that the defective segment contains one impurity molecule Greer's result [Ref. 7, Eq. (48)] is identical to the single collision barrier penetration probability employed in Eq. (9). In general, however, these two models treat different, though related, problems. Greer obtains recursion relations for the transmission probability of an exciton through a finite defective segment containing an arbitrary concentration of impurities. For the problem involving a random distribution of impurities in the segment he is able to obtain approximate solutions for the transmission probability valid in several limiting cases. This permits him to obtain an upper bound to the dependence of the exciton flux in the region of the crystal after the defect segment on the number of impurity molecules in the defect segment. The result that the flux falls off faster than $N^{-1/2} e^{-KN}$, where N is the number of impurity molecules in the defective region, is valid for large N in the infinite time limit.

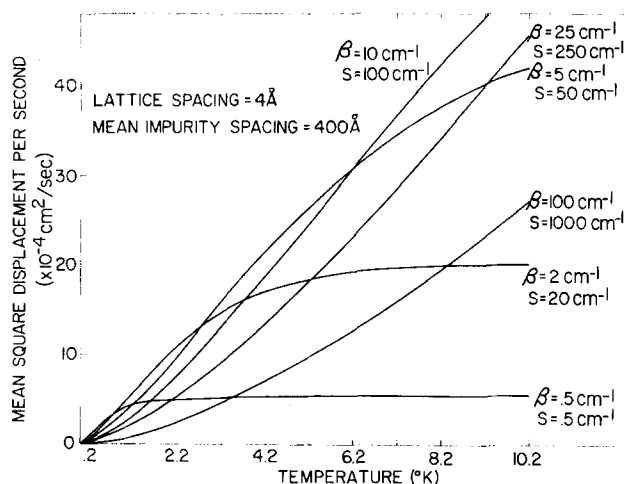


FIG. 1. The exciton mean-square displacement per second for a one-dimensional system containing scattering impurities is graphed as a function of temperature for various values of the intermolecular interaction matrix element β . The band is assumed to be in thermal equilibrium at all temperatures. The lattice spacing is 4 \AA and the mean impurity separation is 400 \AA . S is the energy difference between the center of the band and the scattering impurity. The same ratio $S/\beta = 10$ is used for all curves; thus, the k -dependent transmission probability is the same for all curves. At low temperature, where $2\beta/KT > 1$, the population is near the bottom of the band, resulting in small displacements. As the temperature is raised more mobile states are populated. When $2\beta/KT < 1$ the displacement becomes effectively temperature independent. Note that in the temperature range considered the widest bands do not necessarily have the greatest mean-square displacement.

Greer begins with an infinite ensemble of excitons on one side of the defect region, thereby enabling the flux to remain finite at very long times.

In contrast the model presented here deals with a finite ensemble of excitons migrating in the interior of a defect region, i. e., the entire crystal contains scattering impurities. The dependence of the flux F on N can be calculated using Eq. (18) as

$$F = CN e^{-BN^2}, \quad (19)$$

where C and B are parameters independent of N , but dependent on the time t . Here N is the number of scattering impurities traversed after a time t . This result is not strictly analogous to Greer's since for a finite size exciton ensemble the flux tends to zero at infinite time.

III. IMPURITY SCATTERING AND TRAPPING

It is clear from physical and theoretical considerations that the presence of scattering impurities in an otherwise perfect crystal will have a considerable effect on exciton migration when the temperature is reduced sufficiently such that exciton-phonon scattering is relatively infrequent compared to exciton-impurity scattering. However, it is not yet possible to directly measure exciton displacements in a bulk crystal. Therefore, the results obtained for the thermal average mean-square displacement in Sec. II will be applied to an experimental observable, the time-dependent intensity of emission from excitations localized on low energy impurity sites (traps) after impulse optical excitation of a crystal dilute in both scattering impurities and trapping impurities. In such optical excitation experiments the trapping impurities play the role of "sensitizers"^{3(b)} to exciton migration; after excitons encounter these sensitizers the event is recorded by emission of a photon of characteristic frequency. However, to use trapping as a probe of exciton migration the exciton-trap interaction must be well understood in order to decouple the two problems. The exciton-trap interaction has been the focus of many current theoretical investigations.^{2(e)} However, by carefully choosing experimental conditions it is possible to greatly simplify this problem. The rate at which excitons reach traps can be directly related to the rate of exciton migration in our model provided several physically reasonable conditions are met. The first is that the exciton-trap interaction is fairly short range, so that proximity of the exciton to the trapping impurity is a necessary condition for trapping. For narrow exciton bands in one dimension (e.g., the case of one-dimensional triplet excitons) the intermolecular interaction is very short ranged and the presence of scattering impurities tends to mitigate still further long range interactions. Second, we must have a reasonable knowledge of what fraction of exciton-trap encounters result in trapping. In the above model an exciton remains caged between scattering impurities for a significant period of time. During this period the time averaged exciton probability is uniformly distributed throughout the cage. An exciton which is in a cage with a trapping impurity will have a probability of trapping which is tremendously greater than that which would be predicted by considering coherently migrating excitons in the absence of scat-

tering impurities because the scattering impurities greatly extend the exciton-trap interaction time. Thus, we assume that for efficient barriers, i. e., $S/\beta > 1$, a necessary and sufficient condition for trapping is that the cage within which the exciton is localized contains at least one trap. Finally, although it will become clear below that the process of "detrapping" (i. e., thermally assisted promotion from a localized trap state to a delocalized band state) can be explicitly treated, the necessary complications can be avoided by lowering the thermal energy available to the point where $KT \ll \Delta$, where Δ is the difference in energy between the trap and band.

For an ensemble of excitons the time-dependent population of the band $E(t)$ and of the trap states $T(t)$ can be described by a kinetic scheme which explicitly considers the rate constant for decay from the band in the absence of trapping, K_E , the rate constant for decay from the trap states, K_T , and the time-dependent rate for localization per unit population, $K_L(t)$:

$$\dot{E}(t) = -[K_E + K_L(t)] E(t), \quad (20)$$

$$\dot{T}(t) = -K_T T(t) + K_L(t) E(t). \quad (21)$$

Detrapping could be included by adding a term $+K_p T(t)$ to Eq. (20) and subtracting that term from Eq. (21), where K_p is the rate constant for promotion from the localized state. A similar kinetic scheme has previously been considered¹³ which employed a time-independent localization rate constant. In that case it is assumed that all excitons have equal probability of trapping. However, in the model developed above this is not the case.

The rate of localization can be directly calculated in light of the previous discussion. As the excitons move from cage to cage an ever increasing fraction of the ensemble encounters cages with traps. The probability of encountering at least one trap in n lattice sites is

$$P(n) = 1 - (1 - f)^n, \quad (22)$$

where f is the mole fraction of traps present. The probability of excitons migrating n lattice sites in time t , $P_t(n)$, is given by Eq. (18). Thus, the total fraction of the ensemble which has trapped after time t is

$$F(t) = \sum_{n=-\infty}^{\infty} P(n) P_t(n) \\ = 1 - \sqrt{\frac{2a^2}{\pi\sigma^2(t)}} \sum_{n=0}^{\infty} (1 - f)^n e^{-(na)^2/2\sigma^2(t)}, \quad (23)$$

where the mean-square displacement $\overline{D_t^2(T)}$ contained in $\sigma(t)$ can be calculated using Eq. (16) or (17).

Note that Eq. (23) is strictly valid only in the limit that the number of steps in the random walk is large enough to treat the position distribution as a continuous function. This condition occurs in samples in which the fraction of scattering impurities is larger than the fraction of trapping impurities. Taking the sum to an integral Eq. (23) can be evaluated to yield

$$F(t) = 1 - e^{At} \operatorname{erfc}(\sqrt{At}), \quad (24)$$

where $\operatorname{erfc}(u)$ is the well-known statistical function, error function complement, and A is given by

$$A = \frac{\langle D_i^2(T) \rangle [\ln(1-f)]^2}{2t} \quad (25)$$

A is time independent since $\langle D_i^2(T) \rangle$ is linearly dependent on the time t . The rate of localization per unit population $K_L(t)$ is the time derivative of the total fraction of trapped excitons after time t ,

$$K_L(t) = \frac{\partial}{\partial t} F(t) = A \left[\frac{1}{(\pi A t)^{1/2}} - e^{A t} \operatorname{erfc}(A t)^{1/2} \right] \quad (26)$$

$K_L(t)$ is thus a *time-dependent* rate "constant" which has been calculated by explicitly considering the dynamics of exciton migration. In general, Eq. (26) is valid for any diffusive motion in one dimension in the presence of randomly distributed trapping impurities. For example, in the case of a "pure" random walk with step frequency ω and step size l the mean-square displacement is just $l^2 \omega t$, in which case A can be calculated from Eq. (25) and substituted into Eq. (26)

Figure 2 displays $K_L(t)$ versus time for three values of A . It can be seen that $K_L(t)$ is a highly time-dependent function. The integrated area under each curve is unity, which can be seen from Eq. (24), and is thus independent of the value of A . The rate of localization is $K_L(t)$ multiplied by the exciton population at time t , $E(t)$. Since $E(t)$ is a continuously decreasing function, those curves which have the most area at early time (i.e., those with the largest value of A) have the fastest trapping rate.

The expression for $K_L(t)$ can be substituted into Eqs. (21) and (22) along with the initial conditions of unit exciton population, i.e., $E(0) = 1$ and $T(0) = 0$. These conditions correspond to the case of impulse optical excitation. In general, $T(0)$ will depend on the method of

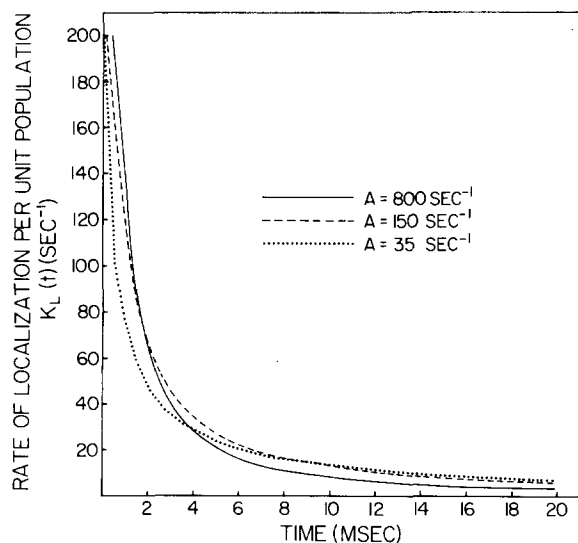


FIG. 2. The rate of localization per unit population $K_L(t)$ is plotted versus time for three values of A , a parameter which depends on the mean-square displacement and the mole fraction of trapping impurities. The figure illustrates clearly the time dependent nature of the localization function for systems in which exciton transport is macroscopically diffusive and traps are randomly distributed. This is in contrast to previous work which utilized a time independent trapping rate constant.

preparation of the excited state. If the traps are dilute, very few excitons are created in cages containing traps and setting $T(0) = 0$ introduces only a small error into the calculated excited state populations. The resulting expression obtained for the time-dependent trap population is

$$T(t) = e^{-K_T t} \left[\frac{2}{\sqrt{\pi}} \int_0^{\sqrt{A}t} du \exp\left(\frac{(K_T + K_E)u^2}{A} + e^{u^2} \operatorname{erfc}(u) - 1\right) - \int_0^{A t} dz e^z \operatorname{erfc}(z^{1/2}) \exp\left(\frac{(K_T + K_E)z}{A} + e^z \operatorname{erfc}(z^{1/2}) - 1\right) \right] \quad (27)$$

The integrals in Eq. (27) can be numerically evaluated to give the time-dependent trap population, which is proportional to the time-dependent intensity of trap emission following impulse optical excitation. This provides the necessary physical observable. Implicit in the mathematical development of Eq. (27) are two assumptions. The first is that Eq. (18) remains valid in the presence of trapping which would tend to perturb the Gaussian nature of the exciton spatial distribution. Second, in Eq. (23) it is assumed that the dominant decay path for the exciton population is via trapping. These assumptions will be discussed in detail in a subsequent publication on impurity scattering and trapping where alternative formalisms will be presented which avoid the assumptions. For the physical situations discussed below, the above assumptions result in very minor changes in the calculated curves. The parameters on which the trap intensity depends in addition to the radiative rate constant are the concentrations of scattering and trapping impurities, the temperature, the intermolecular interaction matrix element, the difference in energy between the band center and corresponding impurity energy level, and the exciton and trap rate constants for radiative plus nonradiative decay to the ground state. These parameters are amenable to independent experimental determination. Thus, low temperature time-dependent optical experiments can be used to determine the applicability of the model presented here to particular experimental system.

Equation (27) gives the intensity of trap emission as a function of time. The emission builds up in a complicated fashion determined by the functional form of $K_L(t)$ and decays with the trap lifetime $1/K_T$. To illustrate, in Fig. 3 the time-dependent trap intensity following an impulse excitation which creates unit exciton population is plotted for different values of the band-impurity energy spacings. The parameters are typical of narrow triplet exciton bands in molecular crystals; the bandwidth is 1 cm^{-1} , $K_T = K_E = 33.3 \text{ sec}^{-1}$, the concentration of scattering impurities is 10^{-3} , the concentration of traps is 5×10^{-5} , and the temperature is 1°K . As the ratio S/β increases the buildup rate slows, the total integrated intensity of trap emission decreases, and more decay takes place via exciton emission. This last phenomenon was first reported by Hochstrasser and Whiteman,¹⁴ who observed a 60-fold increase in exciton emission at 4.2°K in 1,4-dibromonaphthalene when 17% d_8 -dibromonaphthalene was added.

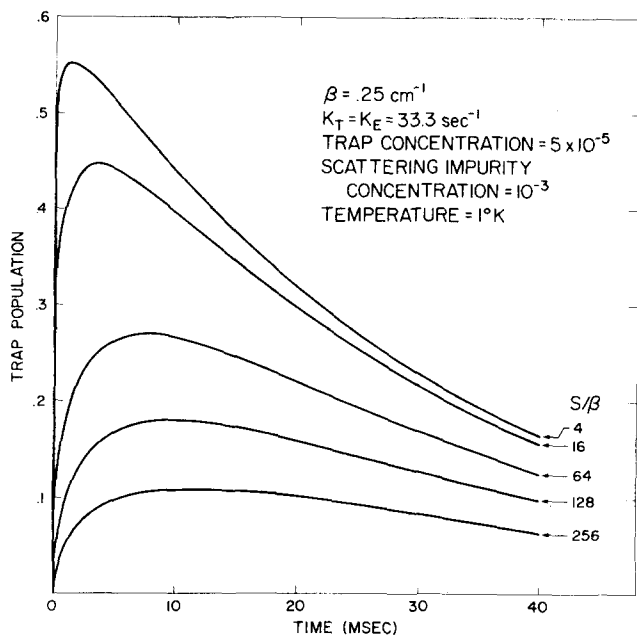


FIG. 3. Calculated trap populations as a function of time are used to illustrate the effect of increasing S , the energy difference between the scattering impurity and the band center, on the time-dependent intensity of trap emission following impulse optical excitation of the exciton band. The parameters used describe a narrow exciton band of width 1 cm^{-1} in thermal equilibrium at 1°K . Rate constants for exciton and trap decay, K_E and K_T , respectively, are 33.3 sec^{-1} and trap and scattering impurity concentrations are 5×10^{-5} and 10^{-3} , respectively. As S increases the buildup maximum is shifted to longer times and the integrated intensity of the trap emission decreases.

Figure 4 is an illustration of the effect of temperature on the trap buildup rate in a system which exhibits a large temperature dependence in the mean-square displacement throughout the temperature range of interest. Here the bandwidth is 29.6 cm^{-1} , $K_T = K_E = 313 \text{ sec}^{-1}$, the scattering impurity concentration is 10^{-3} , the difference in energy between the scattering impurity and the center of the band is 50 cm^{-1} , and the trap concentration is 5×10^{-5} . The increase in buildup rate with increasing temperature is a consequence of populating more of the highly mobile k states near the band center. As the temperature rises exciton-phonon scattering and detrapping will become increasingly important and must be taken into consideration when appropriate.

IV. APPLICATION TO 1,2,4,5-TETRACHLOROBENZENE

In this section the results obtained above will be applied to the first triplet exciton band in single crystals of 1,2,4,5-tetrachlorobenzene. A good deal of previous low temperature experimental work on this system has been interpreted in terms of a one-dimensional coherent transport model.^{2(c),2(d),5(a),13} In addition, a so-called "pure" crystal of TCB contains 0.03% monodeutero-TCB (hd -TCB). The hd -TCB's first excited triplet state lies 10.4 cm^{-1} above the center of TCB's exciton band, which is 1.4 cm^{-1} wide. Monodeutero-TCB is thus the type of scattering impurity considered in the previous sections. It has a large enough S so that its first triplet

state is not amalgamated into the band, yet it is small enough that the probability of a scattering event resulting in reflection is not unity.

A proper description of coherent transport in real crystals of TCB should include impurity scattering. If the exciton coherence length is sufficiently long, the model developed above will apply. Since the mean-square displacement is not a direct observable, the intensity of optical emission from the naturally occurring 17.3 cm^{-1} deep x-trap found in TCB can be employed as the observable. Equation (27) gives as a function of time the trap population, which is proportional to the intensity of trap phosphorescent emission after impulse optical excitation of the exciton band. The parameters necessary for the evaluation of Eq. (27) are (1) the exciton intermolecular interaction matrix element β , (2) the energy difference between the band center and the impurity state S , (3) the mole fraction of scattering impurities, (4) the mole fraction of traps, (5) the exciton lifetime, (6) the trap lifetime, and (7) the temperature.

For the TCB triplet exciton system all of these parameters are available. The exciton bandwidth 4β has been measured by two independent means.^{2(d),5(a)} These experimental results are in excellent agreement and yield a value of $\beta = 0.35 \text{ cm}^{-1}$. A reasonable value for S can be obtained by using the difference between the triplet state energies of h_2 -TCB and hd -TCB impurities in a d_2 -TCB host crystal. This number was measured spec-

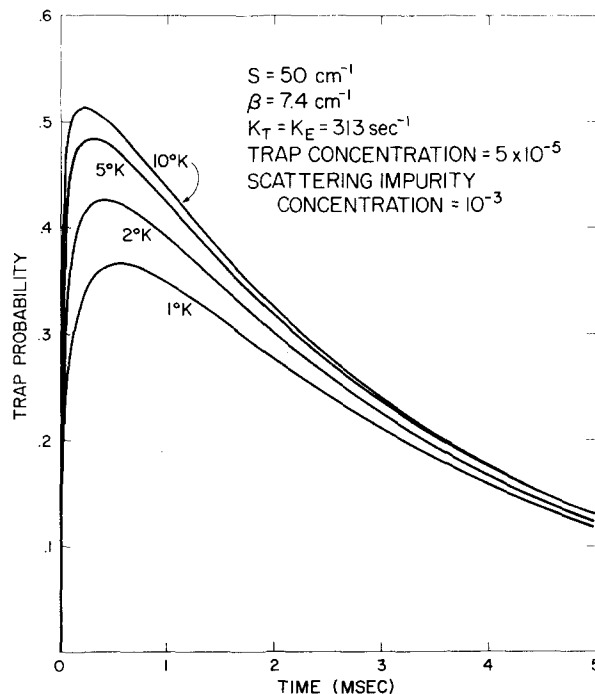


FIG. 4. The effect of temperature on the time-dependent trap population in the presence of exciton scattering impurities is illustrated for an example of a wide triplet exciton band. The impurity concentrations are the same as Fig. 2 but $\beta = 7.4 \text{ cm}^{-1}$, $S = 50 \text{ cm}^{-1}$, and the rate of decay $K_T = K_E = 313 \text{ sec}^{-1}$. As temperature is increased the population is shifted to the center of the band, resulting in a large increase in the mean-square displacement. The buildup rate increases as does the fraction of the ensemble which decays via trap emission.

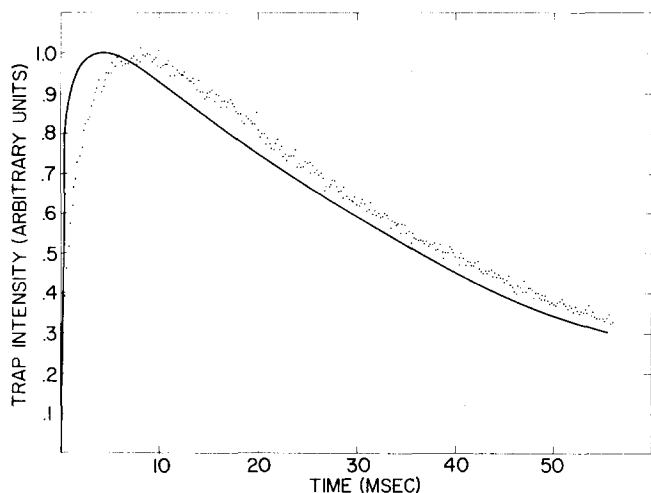


FIG. 5. The points are the experimentally determined time dependent emission from the x trap in h_2 -1,2,4,5-tetrachlorobenzene (h_2 -TCB) following impulse optical excitation. The solid line is the calculated trap intensity assuming the excitons are scattered only by the naturally occurring (0.03%) isotopic impurity hd -TCB. The calculated curve does not utilize adjustable parameters. The experimentally determined parameters used in the calculation are $\beta = 0.35 \text{ cm}^{-1}$, $S = 10.4 \text{ cm}^{-1}$, $K_T = 27 \text{ sec}^{-1}$, $K_B = 36 \text{ sec}^{-1}$, the x-trap concentration is 5×10^{-5} , and the excitons are taken to be in thermal equilibrium at the experimental temperature 1.25°K. If the dominant mode of exciton transport is coherent in the TCB system at very low temperatures, the agreement between theory and experiment demonstrates that isotopic impurity scattering has a major influence on exciton transport in the TCB system.

troscopically and has a value of 10.4 cm^{-1} . Since the scattering impurity under consideration is the naturally occurring isotopic species hd -TCB, the natural abundance of deuterium can be used to obtain an impurity mole fraction of 3×10^{-4} . Although there are three triplet sublevels, at low temperatures in the absence of spin-lattice relaxation they can be considered as separate ensembles. Only one trap sublevel is observed in emission to the origin and has a lifetime of 39 msec. (Another sublevel which is formally allowed by symmetry is not observed. Experiments performed on TCB traps in a durene host indicate that it is weakly radiative and has a lifetime of ~ 760 msec.) Experiments performed on this system have indicated^{5(c)} that spin polarization is preserved upon trapping. The lifetime of the exciton sublevel coupled to this trap level has been determined to be 28 msec. Both values are in agreement with previously reported values.^{5(b),13} An x-trap mole fraction of 5×10^{-5} was experimentally determined using the method of Ref. 2(d). The details of this determination will be discussed in a subsequent publication. The temperature employed for this calculation was 1.25°K. This is the temperature used in the experimental investigation discussed below.

Using these seven parameters and Eq. (27) of Sec. III the time-dependent intensity of x-trap emission after impulse optical excitation of the TCB triplet exciton band can be calculated with *no adjustable parameters*. The result of this calculation is the solid curve in Fig. 5. In the same figure experimental results are displayed.

In the experiment the x-trap time-dependent phosphorescent emission was recorded using a monochromator, phototube, and analog-to-digital data handling equipment. The samples were excited either directly into the triplet state with a 20 nsec duration doubled ruby laser pulse or into the first singlet state with a 3 μ sec duration filtered flash lamp pulse. In each case the results were the same. Details of sample preparation,^{2(d)} and x-trap^{5(b)} and TCB exciton¹⁵ spectra are given elsewhere. The temperature was maintained at 1.25°K by pumping on the liquid helium bath in which the TCB single crystal was immersed. This temperature is sufficiently low to assure that detrapping does not occur.¹⁶

Although the maximum intensity in the calculated curve occurs somewhat earlier than in the experimental curve, the overall agreement between experiment and theory is good. The model used in the calculation is based on a coherent mode of exciton transport. Earlier experimental results have indicated that exciton-phonon scattering times may be quite long in this system at temperatures below 3°K.^{2(d),5(a),12} The results presented here are also consistent with a long exciton-phonon scattering time. If coherent migration is in fact the dominant mode of exciton transport, then exciton-impurity scattering is clearly a major scattering mechanism in this system at very low temperatures. This can be seen by considering the trapping rate in the absence of scattering impurities. From the thermal average mean square velocity given in Table I and the known concentration of trapping impurities the mean first encounter time can be calculated and is on the order of microseconds. As discussed in Sec. III, without scattering impurities to localize excitons in the vicinity of the traps a knowledge is required of the fraction of exciton-trap encounters γ which result in trapping. To match the observed build up rate γ must be on the order of 10^{-4} , which seems quite low. If γ is between 0.1 and 1.0, which seems reasonable,^{13,17} the trap buildup time calculated in the absence of scattering would be orders of magnitude too fast. Experimental results like those displayed in Fig. 5 were previously reported and interpreted in terms of a strictly phenomenological scattering time.¹³ Using curve fitting techniques a time on the order of 10 nsec was obtained and attributed to exciton-phonon scattering. Impurity scattering was not considered. An estimate of the impurity scattering time can be obtained by dividing the thermal average group velocity by the median barrier separation. This time is also on the order of 10 nsec, and again demonstrates the exciton scattering by the naturally occurring isotopic impurity hd -TCB is a major scattering mechanism. Although the discussion here involves one-dimensional systems, it is reasonable to assume that exciton-isotopic impurity scattering is also significant in multidimensional systems. However, caging of excitons by low concentration impurities will not occur in multidimensional systems and therefore the effect on an observable such as trapping will not be as dramatic as in the one-dimensional case.

There are several factors which may contribute to the early peaking of the calculated curve in Fig. 5 besides the simple possibility that some of the values of the

parameters used in the calculation are in error. Another possibility is that there are other scattering species, either chemical impurities such as ^{13}C substituted molecules or crystal lattice defects, which cause significant scattering. The additional scattering centers would further hinder exciton transport and therefore shift the experimentally observed peak to longer time.

Another factor which may enter here and could become very important under different experimental circumstances involves the question of thermal equilibrium. The mean-square displacement is sharply peaked around the center of the band [Eq. (12)] and consequently the band center states will trap at a faster rate than states near the band edges. This can result in depletion of population from the band center if exciton-phonon scattering is not fast enough to maintain a thermal distribution of population. In this very slow exciton-phonon scattering limit exciton-phonon scattering from the band edges toward the band center can become the rate determining step in exciton trapping. Thus, the thermal equilibrium trapping rate discussed above is the fastest possible rate, for it permits the slowly trapped band edge states to be efficiently funneled through the band center. Therefore, if a system is in the very slow exciton-phonon scattering limit, the peak in the experimental results will be shifted toward long times relative to the calculated curve which assumed thermal equilibrium. In this situation raising the sample temperature, which results in increased exciton-phonon scattering, will actually enhance exciton trapping until a temperature is reached at which the phonon scattering rate begins to dominate the impurity scattering rate.

An additional factor which would affect the time dependence of the trap population and therefore the trap intensity is exciton-phonon scattering. The model presented above includes only the effects of exciton-impurity scattering. An exciton-phonon scattering time which is comparable to the exciton-impurity scattering time would still permit the above model to be used, but would result in a reduction in the trapping rate. This will shift the experimental curve toward long time relative to the calculated curve, as is the case in Fig. 5. An average exciton-phonon scattering time on the order of tens of nanoseconds would be required to account for the observed discrepancy. However, it is not possible at this time to distinguish between the various factors which could account for the early peaking of the calculated curve.

Finally, it is important to consider whether a strictly incoherent mode of exciton transport can account for the experimental data. To this end we first considered a random walk exciton on a one-dimensional lattice without scattering impurities. A value for the random walk step time for TCB can be estimated to be on the order of 5 psec.¹⁷ In this case the time-dependent trap buildup, *in the absence of scattering impurities*, is the right order of magnitude to account for the observed data. The probability of taking a step past an *hd*-TCB impurity is on the order of 0.001. This will reduce the ability of a one-dimensional random walk exciton to reach a trap. It is therefore possible to eliminate a *strictly one-di-*

mensional random walk as the mode of exciton transport in the TCB system at 1.35 °K.

Although a one-dimensional random walk is unlikely, it is important to consider the effect that small multi-dimensional intermolecular interactions could have on exciton transport in this system. Both theoretical and experimental considerations are consistent with a basically one-dimensional character for the TCB triplet exciton system. Experimental results indicate that a second intermolecular interaction is down by a factor of at least 10^4 relative to the dominant linear chain intermolecular interaction.¹⁸ However, for a random walk process even an interaction down by a factor of 10^6 could be significant in this system. This small two-dimensional intermolecular interaction would permit a random walking exciton to sample greater than an order of magnitude more lattice sites than a strictly one-dimensional random walker. The problem is complicated by the effect of the *hd*-TCB scattering impurities on what is basically a one-dimensional random walk. However, if the exciton traps on a single encounter and if the multidimensional interactions are not too small, it would be possible to account for the experimental data in Fig. 5 strictly on the basis of an incoherent (random walk) mode of exciton transport.

To try and resolve some of the questions pertaining to triplet exciton transport in TCB at very low temperatures we are currently conducting experiments on TCB samples containing known concentrations of d_2 -TCB. The d_2 -TCB acts as a scattering impurity and therefore the model for coherent one-dimensional transport and trapping developed in Sec. II and III can be employed and compared to experiments in which the concentration of the scattering impurity is varied. These experimental results and the question of the importance of multi-dimensional triplet exciton transport in TCB will be discussed in a subsequent publication.

V. CONCLUSIONS

A model has been presented which permits the calculation of the mean-square displacement of an ensemble of coherently migrating one-dimensional excitons in a crystal containing scattering impurities. The mean-square displacement as a function of the exciton wave vector k is very sharply peaked near the band center. This can result in an ensemble mean-square displacement which increases with increasing temperature if exciton-phonon scattering does not dominate impurity scattering. The model was applied to the problem of exciton trapping. An expression was obtained for the time dependent trap population after impulse optical excitation of a crystal. Since the trap population is proportional to the intensity of trap emission, this provides the necessary experimental observable. The time dependent trap population function depends on parameters which are experimentally accessible and therefore can provide a test for one-dimensional coherent exciton transport.

The trapping model was applied to triplet excitons in "pure" crystals of 1, 2, 4, 5-tetrachlorobenzene (TCB) in

which the naturally occurring isotopic impurity mono-deutero-TCB acts as a scattering impurity. Without adjustable parameters the model produced good agreement with experimental data on time dependent trap emission in the TCB system. However, it was pointed out that although TCB is basically a one-dimensional exciton transport system, incoherent exciton migration coupled with a small degree of multidimensional transport could also account for the experimental data. If transport is basically coherent, the results indicate that exciton-impurity scattering from naturally occurring isotopic impurities is an important scattering mechanism in this system at very low temperatures.

ACKNOWLEDGMENTS

This research has been supported in part by the National Science Foundation Division of Materials Research, and in part by the Research Corporation. In addition, acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

¹(a) J. Frenkel, *Phys. Rev.* **37**, 17 (1931); **37**, 1276 (1931); (b) A. S. Davydov, *Theory of Molecular Excitons* (Plenum, New York, 1971).

²(a) G. F. Koster and J. C. Slater, *Phys. Rev.* **95**, 1167 (1954); **96**, 1208 (1954); (b) V. L. Broude and E. I. Rashba, *Fiz. Tverd. Tela* **3**, 1941 (1961) [*Sov. Phys. Solid State* **3**, 1415 (1962)]; E. I. Rashba, *Fiz. Tverd. Tela* **5**, 1040 (1963) [*Sov. Phys. Solid State* **5**, 757 (1963)]; V. L. Broude and S. M. Kochubei, *Fiz. Tverd. Tela* **6**, 354 (1964) [*Sov. Phys. Solid State* **6**, 285 (1964)]; M. D. Fayer and C. B. Harris, *Chem. Phys. Lett.* **25**, 149 (1974); R. C. Powell and R. G. Kepler, *Phys. Rev. Lett.* **22**, 636 (1969); R. C. Powell, *Phys. Rev. B* **4**, 628 (1971); R. C. Powell, *J. Chem. Phys.* **58**, 920 (1973); R. E. Merrifield, *J. Chem. Phys.* **38**, 920 (1962); (c) M. D. Fayer and C. B. Harris, *Phys. Rev. B* **9**, 748 (1974); (d) D. D. Dlott and M. D. Fayer, *Chem. Phys. Lett.* **41**, 305 (1976); (e) R. M. Pearlstein, *J. Chem. Phys.* **56**, 2431 (1970); R. P. Hemenger and R. M. Pearlstein, *Chem. Phys.* **2**, 424 (1973); R. P. Hemenger, K. Lakatos-Lindenberg, and R. M. Pearlstein, *J. Chem. Phys.* **60**, 3271 (1974).

³(a) V. K. Shante and S. Kirkpatrick, *Adv. Phys.* **20**, 235 (1971); J. M. Ziman, *J. Phys. C* **1**, 1532 (1968); T. P.

Eggarter and M. H. Cohen, *Phys. Rev. Lett.* **25**, 807 (1970); **27**, 129 (1971); J. Jortner and M. H. Cohen, *J. Chem. Phys.* **55**, 5380 (1971); H. K. Hong and R. Kopelman, *Phys. Rev. Lett.* **25**, 1030 (1970); *J. Chem. Phys.* **55**, 724 (1971); R. Kopelman, E. M. Monberg, F. W. Ochs, and P. N. Prasad, *Phys. Rev. Lett.* **34**, 1506 (1975); (b) R. Kopelman, "Radiationless Processes in Molecules and Condensed Phases," in *Topics in Applied Physics*, edited by Francis K. Fong (Springer, New York, 1976), Vol. 15.

⁴R. M. Hochstrasser and J. D. Whiteman, *J. Chem. Phys.* **56**, 5945 (1972).

⁵(a) A. H. Francis and C. B. Harris, *Chem. Phys. Lett.* **9**, 181, 188 (1971); (b) A. H. Francis and C. B. Harris, *J. Chem. Phys.* **57**, 1050 (1972); (c) A. H. Francis and C. B. Harris, *J. Chem. Phys.* **55**, 3595 (1971).

⁶S. Arnold, R. R. Alfano, M. Pope, W. Yu, P. Ho, R. Selsby, J. Tharrats, and C. E. Swenberg, *J. Chem. Phys.* **64**, 5104 (1976).

⁷W. L. Greer, *J. Chem. Phys.* **60**, 744 (1974).

⁸(a) T. Holstein, *Ann. Phys. (N.Y.)* **8**, 325 (1959); **8**, 343 (1959); R. W. Munn and W. Siebrand, *J. Chem. Phys.* **52**, 47 (1970); R. W. Munn, *J. Chem. Phys.* **52**, 64 (1970); J. M. Schurr, *Mol. Phys.* **27**, 357 (1974); R. Reineker and H. Haken, *Z. Phys.* **250**, 300 (1972); H. Haken and P. Reineker, *Z. Phys.* **249**, 253 (1972); V. M. Kenkre and R. S. Knox, *Phys. Rev. B* **9**, 5279 (1974); (b) M. Grover and R. Silbey, *J. Chem. Phys.* **52**, 2099 (1970); **54**, 4843 (1971).

⁹D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953).

¹⁰J. Hoshen and J. Jortner, *J. Chem. Phys.* **56**, 933 (1972); **56**, 4138 (1972); **56**, 5550 (1972); P. Soven, *Phys. Rev.* **156**, 809 (1967); **178**, 1136 (1969); *Phys. Rev. B* **2**, 4715 (1970); H. K. Hong and G. W. Robinson, *J. Chem. Phys.* **52**, 825 (1970); **54**, 1369 (1970); H. K. Hong and R. Kopelman, *J. Chem. Phys.* **55**, 5380 (1971); D. P. Craig and M. R. Philpott, *Proc. R. Soc. (London) Ser. A* **290**, 583 (1966); **290**, 602 (1966); **293**, 213 (1966).

¹¹J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University, Cambridge, 1972).

¹²C. B. Harris and M. D. Fayer, *Phys. Rev. B* **10**, 1784 (1974).

¹³C. B. Harris, R. M. Shelby, and A. H. Zewail, *J. Chem. Phys.* **64**, 3192 (1976).

¹⁴R. M. Hochstrasser and J. D. Whiteman, *Proceedings of the International Conference on Organic Scintillators and Liquid Scintillation Counting, University of California*, edited by D. L. Horrocks and L. T. Peng (Academic, New York, 1971).

¹⁵G. A. George and G. C. Morris, *Mol. Cryst. Liq. Cryst.* **11**, 61 (1970).

¹⁶H. C. Brenner, J. C. Brock, M. D. Fayer, and C. B. Harris, *Chem. Phys. Lett.* **33**, 471 (1975).

¹⁷R. S. Knox (private communication).

¹⁸A. H. Zewail (private communication).