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Effect of Disorder on the Trapping of Frenkel Excitons in Three-Dimensional Systems

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A numerical study is made of the effect of disorder on the trapping of Frenkel excitons in three-dimensional systems at $T=0$ K. A Gaussian distribution of optical transition frequencies is assumed. The disorder enhances the decay of a $\mathbf{k}=0$ exciton created by pulsed optical excitation, but reduces the overall exciton trapping rate. An interpretation of the results in terms of increased exciton scattering and reduced exciton mobility is outlined.

KEY WORDS: Frenkel excitons; three-dimensional systems.

1. INTRODUCTION

In two previous papers[1,2] we have reported the results of numerical studies of the trapping of Frenkel excitons at $T=0$ K. In ref. 1, we considered the case of a one-dimensional array, whereas three-dimensional systems were treated in ref. 2. In both instances, it was assumed that the array of optically active centers had translational invariance so that the only disorder in the problem was that associated with the random distribution of traps. In this paper, we explore the effect of a Gaussian distribution of optical transition frequencies on the random trapping process in a simple cubic system.

The Hamiltonian characterizing the trapping takes the form[2]

$$\mathscr{H}=\sum_j v_j a_j^+ a_j + \sum_{(j,k)}{}' u(a_j^+ a_k + a_k^+ a_j) - i\sum_j \Gamma_j a_j^+ a_j \tag{1}$$

where a_j and a_j^+ are exciton annihilation and creation operators in the site representation. Also, v_j is the optical transition frequency associated with

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the jth site and u is an interaction parameter. The prime on the second summation signifies that the interaction is limited to nearest-neighbor pairs. The third term in (1) induces the trapping. We use the same model as in refs. 1 and 2, i.e., the trapping rate for the jth site is $\Gamma = 1$ (0) if site j does (does not) have a trap associated with it. The distribution of traps is postulated to be random. Unlike refs. 1 and 2, where v_j is taken to be constant, we assume v_j is characterized by a Gaussian distribution $P(v)$:

$$P(v) = \frac{1}{(2\pi\sigma^2)^{1/2}} e^{-(v-\bar{v})^2/2\sigma^2} \tag{2}$$

with mean $\bar{v}$ and variance σ^2. In what follows, we will study simple cubic arrays. We take $u = -1$, so that in the absence of disorder the exciton bandwidth is equal to 12, and the optically active ($\mathbf{k} = 0$) exciton mode lies at the bottom of the band.

As discussed in refs. 1 and 2, the trapping of a $\mathbf{k} = 0$ exciton created by pulsed optical excitation is characterized by a set of correlation functions of the form

$$G_j(t) = N^{-1/2} \sum_k \langle 0 | a_j(t) a_k^+ | 0 \rangle \tag{3}$$

where $|0\rangle$ denotes the exciton vacuum, and N is the number of centers. The G_j obey the equations of motion

$$i \frac{d}{dt} G_j(t) = \sum_j w_{jk} G_k(t) \tag{4}$$

with initial condition $G_j(0) = N^{-1/2}$. The matrix w_{jk} has the form

$$w_{jj} = v_j - i\Gamma_j \tag{5a}$$

$$w_{jk} = u, \qquad j, k \text{ nearest neighbors} \tag{5b}$$

$$w_{jk} = 0, \qquad j, k \text{ not nearest neighbors} \tag{5c}$$

Two funtions are calculated from the set of G_j:

$$P(t) = \left| \sum_j G_j(t) \right|^2 \Big/ N \tag{6}$$

and

$$Q(t) = \sum_j |G_j(t)|^2 \tag{7}$$

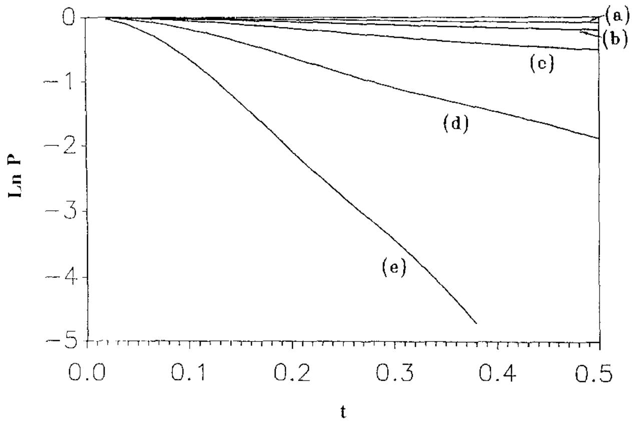

Fig. 1. Plot of ln $P(t)$ vs. t, for $\Gamma = 1$, trap concentration 0.1; (a) $\sigma = 0$, (b) $\sigma = 1$, (c) $\sigma = 2$, (d) $\sigma = 4$, (e) $\sigma = 8$. $12 \times 12 \times 12$ array.

As shown in refs. 1 and 2, $P(t)$ is the probability of finding an exciton in the $\mathbf{k} = 0$ state at time t, whereas $Q(t)$ is the probability of there being an exciton in *any* mode at time t. In general, $P(t) \leqslant Q(t)$, since both scattering and trapping processes deplete the $\mathbf{k} = 0$ mode, while only the latter affect $Q(t)$. In the absence of traps, $Q(t) = 1$, independent of the v_j, whereas $P(t) \leqslant 1$; only when there are no traps, and there is full translational symmetry, does $P(t) = Q(t) = 1$. On the other hand, if every center has a trap associated with it, and all the v_j are the same, then $P(t) = Q(t) = \exp(-2\Gamma t)$.

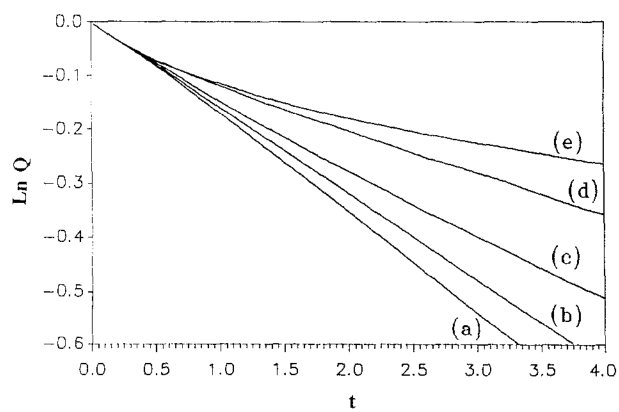

Fig. 2. Plot of ln $Q(t)$ vs. t, for $\Gamma = 1$, trap concentration 0.1; (a) $\sigma = 0$, (b) $\sigma = 1$, (c) $\sigma = 2$, (d) $\sigma = 4$, (e) $\sigma = 8$. $12 \times 12 \times 12$ array.

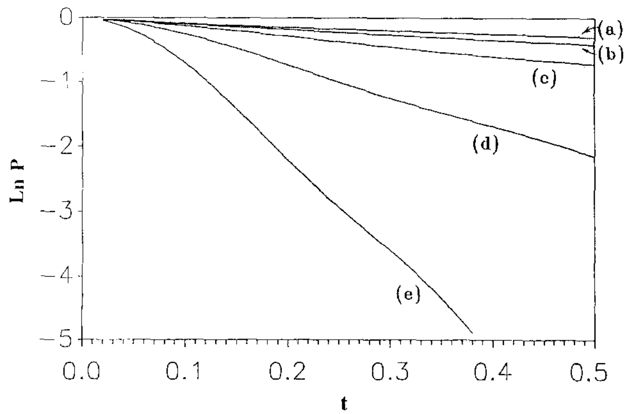

Fig. 3. Same as Fig. 1, except $\Gamma = 6$.

2. NUMERICAL CALCULATIONS

In order to study the effects of the randomness in the optical transition frequencies on the exciton trapping, we have calculated $P(t)$ and $Q(t)$ assuming a Gaussian distribution of frequencies with $\sigma = 0$, 1, 2, 4, and 8 (the results are independent of the mean frequency $\bar{v}$). The concentration of traps was 0.1, i.e., 10% of the sites had traps associated with them. Our results for $P(t)$ and $Q(t)$ for the case $\Gamma = 1$ are shown in Figs. 1 and 2, respectively. Figures 3 and 4 show the corresponding results for $\Gamma = 6$. All curves were calculated for $12 \times 12 \times 12$ arrays with periodic boundary conditions. The data shown are from a single configuration of traps and transition frequencies. Other configurations gave rise to similar data. We discuss these results below.

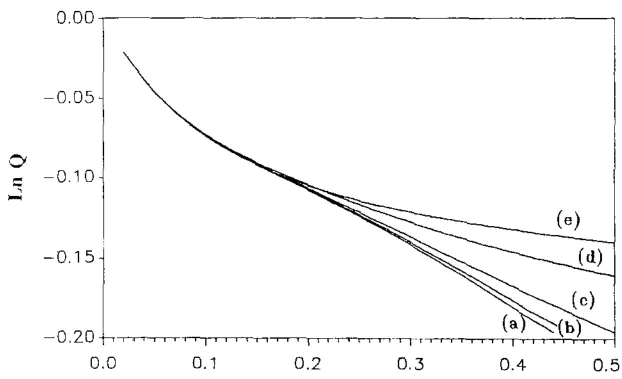

Fig. 4. Same as Fig. 2, except $\Gamma = 6$. Note change in scale relative to Fig. 2.

3. DISCUSSION

The most significant result to emerge from the calculations was the difference in behavior between $P(t)$ and $Q(t)$ that appears with increasing σ. Not surprisingly, the effect of disorder in the transition frequencies is to enhance the rate at which excitons are removed from the $\mathbf{k}=0$ mode. This is reflected in Figs. 1 and 3 in the decrease in $P(t)$ with increasing σ. The behavior of $Q(t)$ is just the opposite. $Q(t)$ increases with increasing σ. Disorder in the transition frequencies *reduces* the trapping rate, while it *enhances* the rate of depletion of the $\mathbf{k}=0$ mode.

The decrease in $P(t)$ with increasing σ is associated with the exciton scattering induced by the random variation of the transition frequencies. As shown in ref. 2, $P(t)$ decays even in the absence of traps when $\sigma \neq 0$. The contrasting behavior of $Q(t)$ can be thought of as arising from a reduction in exciton mobility due to the increased disorder. As a consequence, it takes longer for the excitons to reach the traps, so that the effective trapping rate is reduced.

The results presented here have important implications for the interpretation of exciton trapping data in real materials, especially ones where the exciton absorption line is inhomogeneously broadened due to microscopic strains. Because of the reduced mobility, care must be exercised in comparing trapping rates with the corresponding rates in "ideal" systems with minimal disorder.

REFERENCES

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