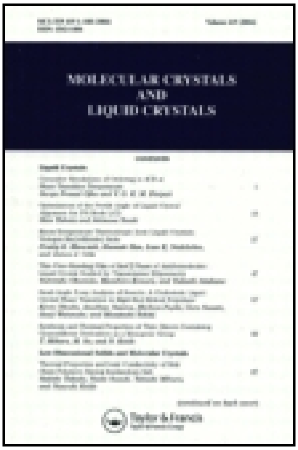

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Masumi Takeshima, K. Mizuno & Atsuo H. Matsui (1998): Instability of self-trapped excitons in the 1D system, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 314:1, 125-130

To link to this article: http://dx.doi.org/10.1080/10587259808042467

Mol. Cryst. Liq. Cryst., 1998, Vol. 314, pp. 125–130
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Instability of self-trapped excitons in the 1D system

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Instability of self-trapped excitons in aromatic microcrystallites is discussed using a one-dimensional (1D) model and the tight-binding approach. It is shown that the instability in the 1D system is the result of widening of the exciton extent as the microcrystallite size. The self-trap depth decreases as the size decreases but it is always finite. Such a behavior of excitons is very different from at in the two- and three-dimensional systems

Keywords: self-trapped excitons, microcrystallites, one-dimensional

INTRODUCTION

Recent establishment of microcrystallization technology in aromatic materials has opened a new way of studying the Frenkel exciton behavior[1] in such materials. The free exciton (FE) migration has been discussed in terms of exciton bandwidths of anthracene and pyrene bulk crystals[1,2]. Thereby it has become possible to analyze the self-trapped exciton (STE) formation [2] in that emphasis.

Many theories have been published on STE[3-5], but they are applicable exclusively to bulk crystals only.

This paper presents a theoretical study of the STE behavior in microcrystallites of aromatic materials using the tight-binding approach. The emphasis is placed on pyrene, for which STE is observed in its bulk crystals[6] but it has not been observed in microcrystallites[7]. Using a one-dimensional (1D) model the present theory can explain the disappearances of STE in microcrystallites quite satisfactorily. STE in the two-dimensional and the three-dimensional microcrystallites is, however, found[8] to become more stabilized than in bulk crystals. There are supporting experimental data[9] for such results.

THEORY

We assume that the (1) resonant transfer is the mechanism for the exciton motion and (2) the site shift energy is the cause of the energy change in the condensed state from the free molecule state. The motion of Frenkel excitons in the 1D picture is then described by the Hamiltonian[10]

$$H_0 = \sum_{j \neq j'} \left[B_{j'}^{+} B_j W(j'-j) + B_j^{+} B_j D(j'-j) \right] \qquad (1)$$

omitting an additive constant term. In Eq.(1) $B_{j'}^{+}$ and B_j are respectively the creation and annihilation operators of an exciton at the respective lattice sites j' and j , $W(j'-j)$ is the transfer matrix between the sites j' and j due to the electron-electron Coulomb interaction for the resonance transfer of the exciton energy, and $D(j'-j)$ is the intermolecular interaction between the molecules located at j' and j, i.e., the site shift energy.

We use the nearest-neighbor interaction approximation such that $W(j'-j) \equiv W$ and $D(j'-j) \equiv D$ only for $j'-j = \pm 1$ otherwise zero. We assume that microcrystallites are embedded in a solvent material whose molecular excitation energy differs from the exciton energy, ensuring that both states are not in resonance. We have applied the boundary condition $W(j'-j)=0$ when either of j or j' is located outside the microcrystallite. Although the value of $D(\pm 1)$ for the solvent material differs in general from that of the microcrystallite material, we have assumed it to be same for convenience in applying the boundary condition.

Let us consider a 1D microcrystallite with the lattice constant a and the displacement of the j th lattice by q_j from the equilibrium position. We obtain $W(j'-j)$ and $D(j'-j)$ for the displaced lattice as

$$W(j'-j) = W + W'(q_{j'} - q_j), \qquad D(j'-j) = D + D'(q_{j'} - q_j). \qquad (2)$$

Here $W' \equiv PW$ and $D' \equiv QD$ are respectively the first derivatives of W and D with respect to a. We assume that the material outside the microcrystallite forms a rigid lattice, meaning $q_{N+1}-q_N=0$ and $q_0-q_{-1}=0$, letting j run from 0 to N. These relations are found to be approximately true though not shown here.

The total Hamiltonian, which is obtained by adding the phonon term to H_0, is solved for the state vector $|\Phi\rangle$ given by

$$|\Phi\rangle = \sum_{j=0}^{N} \alpha_j B_j^{+} |\Phi_g\rangle, \qquad (3)$$

where $|\Phi_g\rangle$ is the state vector of the ground state and α_j is the amplitude. We seek the minimum of $\langle\Phi|H|\Phi\rangle$ for a trial function of α_j, chosen to be zero outside the boundary. A trial function we apply for direct materials, i.e., $W < 0$, is given as

$$\alpha_j = \alpha_{nm} \sin(\pi/(N+2)j)\exp(-\beta|j - J + 1/2|). \qquad (4)$$

In Eq.(4) $\beta > 0$, and j_0 is the center position of a microcrystallite. When $\beta = 0$, we have an FE state under deformed lattice.

Now let us consider a microcrystallite consisting of $2J$ molecules, i.e., $N=2J-1$ with $j_0=J-1/2$, and define j as a new integer from 0 to $2J-1$. The energy matrix $\langle\Phi|H|\Phi\rangle$ is then obtained in the form

$$\langle\Phi|H|\Phi\rangle = 2D + H_{ph} + B\Lambda_{exc}, \qquad (5)$$

where $B=2|W|$ is the half width of the exciton band of the bulk crystal, H_{ph} phonon term under the displaced lattice[8] (not shown here) and Λ_{exc} normalized exciton term

$$\Lambda_{exc} = 1 - \sum_{j=0}^{2J-1} \alpha_{j+1}\alpha_j - \gamma \sum_{j=0}^{2J-1} \left[(\alpha_{j+1}\alpha_j)^2 - 2\theta\alpha_{j+1}\alpha_j(\alpha_j^2 + \alpha_{j+1}^2) + (\alpha_j^2 + \alpha_{j+1}^2)^2 \right], \qquad (7)$$

where $\theta = QD/(PB)$ and $\gamma = P^2B/(2M\omega_0^2)$; $M\omega_0^2$ is the force constant in which M is the mass of the lattice molecule. We find the minimum of Λ_{exc} as a function of β. The value $B[\Lambda_{exc}(0) - \Lambda_{exc}(\beta_m)] \equiv E_{sf}$, where β_m is the value of β giving the minimum of the function $\Lambda_{exc}(\beta)$, gives the self-trap depth as far as the exciton is well localized, i.e., under $\beta_m J > 1$.

CALCULATED RESULTS

An example of the calculated results on Λ_{exc} is shown in Fig. 1. As is seen in Fig. 1, there is no barrier between the FE band edge at β=0 and the STE state at $\beta = \beta_m$. This is a characteristic feature of the 1D system. In the 2D and 3D system[8] a barrier appears under some conditions.

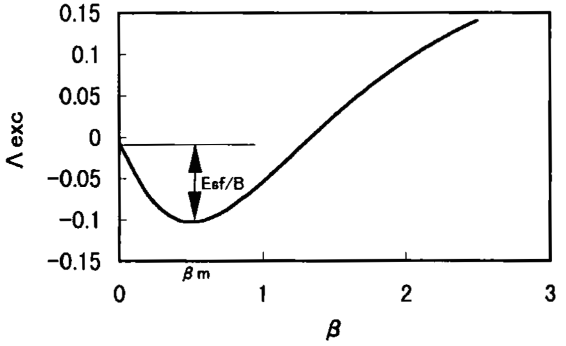

Fig. 1. Λ_{exc} versus β calculated for γ =0.1, θ =1 and 2J=200.

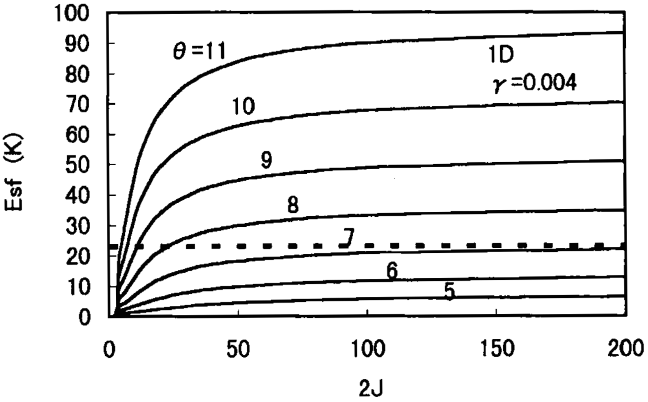

Fig. 2. E_{sf} in Kelvin as a function of 2J.

Figure 2 shows the self-trap depth E_{sf} measured in Kelvin as a function of $2J$ under $\gamma=0.004$, which is applicable to pyrene. The self-trap depth decreases with decreasing microcrystallite size. Such a behavior is a characteristic of the 1D system in contrast to the 2D and 3D systems[8] where the self-trap depth increases with decreasing size. The self-trap depth 15 cm^{-1}, which was reported [2] for the lowest ^1L_b exciton band of the bulk pyrene crystal, corresponds to 21.6K. With the theoretical curves at $2J=200$ one finds that $\theta=7.0$ explains the experimental result of 15 cm^{-1}. The curve for $\theta=7.0$ shows that E_{sf} is larger than 3.6 K even of $2J=4$. From this fact STE could be stable at a temperature as low as 2 K.

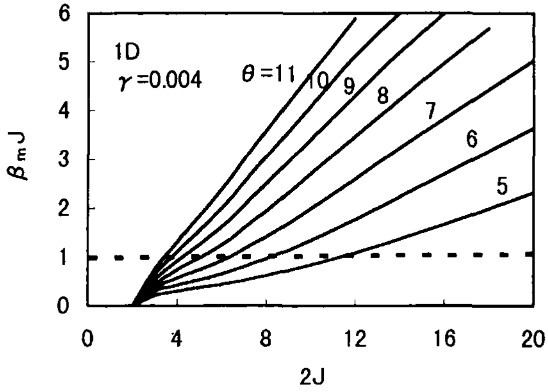

Fig. 3. $\beta_m J$ as a function of $2J$.

In order to discuss the STE extent, we show in Fig.3 $\beta_m J$ as a function of $2J$. $\beta_m J<1$ means that the exciton is extended, i.e., we have practically FE and not STE. The curve for $\theta=7.0$ shows that $\beta_m J< 1$ in the range $2J < 8$. This means that the relevant state is practically the FE state and not the STE state. $\beta_m J$ increases with increasing microcrystallite size and we have $\beta_m J >>1$ at sufficiently large sizes. Thus STE in stable at least in the bulk crystal. The theoretical result mentioned above agrees well with the experimental observation that STE is observed in the bulk crystal[6] but not in microcrystallites[7]. The decrease of $\beta_m J$ is due to the decrease of β_m and J both. It is concluded therefore that the 1D theory can explain the disappearance of STE in pyrene microcrystallites very well.

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