RESEARCH ARTICLES

J. Sci. Soc. Thailand, 9 (1983) 63-72

IMPURITY BAND IN DILUTE MIXED MOLECULAR CRYSTALS

K. WANACHOTE and I.M. TANG

a. *Department of Physics, Faculty of Sciences, King Mongkut Institute of Technology, Thonburi, Thailand.*

b. *Department of Physics, Faculty of Sciences, Mahidol University, Bangkok, Thailand.*

(Received 8 April 1983)

Abstract

The monomer self energy in dilute mixed molecular crystals is obtained by considering a set of diagrams which when summed yields a self energy expression in the form of a continued fraction. Using some theorem concerning Sturm sequences, the analytic behavior of the exciton propagator is obtained. The bandwidth of the impurity band in dilute $C_{10}D_8/C_{10}H_8$ *mixed naphthalene crystals is determined by examining the branch cut appearing in the exciton propagator.*

Introduction

Three interrelated problems face the diagram approach to the study of random disorder systems such as mixed molecular crystals and binary alloys. First of all, there is the problem of which diagrams should be considered. Next, there is the problem of what are relative weights of each diagram. The weighing of the diagrams arises from the configurational averaging of the random varibles which define the disorder in the system. Finally, there is the problem of whether the partial summation of the diagrams considered will yield expressions which have the correct analytic properties. For mixed molecular crystals[1], the physical interpretations of what the monomer states, dimer states, trimer states, etc. are, dictate which diagrams should be considered. Since the monomer states are interpreted as arising from the multiple scattering of an exciton of the host crystal by a single impurity molecule, the self energy corrections due to the monomer states would be the sum of the irreducible diagrams which have a single vertex in them. Interpretating the dimer states as arising from the multiple scattering of the exciton by two impurity molecules with the added condition that the repeated scattering by one impurity molecule is interrupted by a scattering by the other imputiry molecule, one finds that the dimer self energy is the sum of the irreducible 2-vertex diagrams. Similar interpretations of the trimer states and other higher-order states lead to the self energy corrections due to these states being the sum of the irreducible 3-vertex, 4-vertex and higher-vertex diagrams.

In the dilute limit, the solution to the second problem is to assign the same weight c (the impurity concentration) to each vertex in every diagram. In general, the configurational averaging of the random variables leads to each vertex being weighted by the cumulant function[2]. In two recent papers on mixed molecular crystals of arbitrary concentration[3], one of the present authors (IMT) used the full cumulant functions in the summations of the monomer and dimer diagrams. Leath and coworkers[4] have pointed out that the use of the full cumulant functions in the calculations of the configuration averaged self energy corrections will lead to inconsistencies since the formulation of the full cumulant functions require that the contributions of all diagrams be taken into account but the evaluations of the self energy corrections require that many diagrams be neglected. To prevent the inconsistencies from arising, Gaspard and Cyrot-Lackman[5] introduced the modified cumulant functions $p\text{-}P_n$ (c). The modified cumulant functions, which are to be used in the evaluations of the self energy corrections due to one-vertex diagrams, two vertex diagrams, ... and p-vertex diagrams, are evaluated by taking into consideration only those diagrams which contain p or less vertices. In this way, self consistency is obtained.

Nickel and Bulter[6] have shown, however, that in some cases, self consistency was achieved at the cost of the partially summed self energy expression being non analytic. In particular, the configuration averaged Green's function was found to have off-real-axis branch points on the physical sheet of the complex energy plane. Recently, Mills and Ratanavararsaksa[7] introduced the "traveling cluster approximation" which preserved both the self consistency and analyticity requirements. Their method required that the only graphs which should be summed are those which preserved the Herglotz property in the resulting propagators. The Herglots property is just the set of properties required for the propagators to have the desired analytic behavior. Odagaki and Yonezawa[8] have shown that the desired analytic properties can also be achieved by a homomorphic partitioning of the Hamiltonian which describes the disordered system. Their homomorphic cluster coherent potential approximation was recently used by Friesner and Silbey[9] to renormalize both the site energy and exciton bandwidth in an exciton-phonon interaction model system.

The purpose of this paper is to study the monomer states in *dilute* mixed molecular crystals by considering a set of diagrams which when summed yields a continued fraction representation of the exciton propagator. By refering to some theorems regarding Sturm sequences,[10] it can be established that the branch cuts of the exciton propagator appear on the real axis. Finally, we give the results of our numerical calculations of the concentrational dependence of the impurity bandwidth in dilute $C_{10}D_8/ C_{10} H_8$ mixed naphthalene crystals.

Diagram Summation

In the mixed molecular crystals such as naphthalene-d_8/naphthalene-h_8 crystals, where some of the host $C_{10} D_8$ molecules on random sites are replaced by $D_{10} H_0$ molecules, the isotopic substitution will lead to diagonal disorder. Since the excitation modes of the guest molecules are different from those of the host molecules, the excitons of the host crystal as they are moving through the crystal will experience a perturbation whenever they encounter a guest molecule. The nature of the perturbation and the disorder are easily seen if we write down the Hamiltonian for the system

$$H = \sum_j E_j^A + \text{intermolecular potentials} + \sum_i (E_i^B - E_i^A) \qquad (1)$$

where $E^{A(B)}$ is the excitation energy of the host (guest) molecule and where the summation over j is over all the sites of the lattice and the summation over i is only over those random sites which are occupied by the guest molecules. Since the intermolecular potentials are invariant under isotopic substitution, we have not separated them into potentials between host molecules, between guest molecules and those between host and guest molecules. The first two terms are just the Hamiltonian for the host crystal. The third term can be viewed as being a random perturbations which are acting on the exciton described by the first two terms.

The self energy correction will be the sum of all the irreducible diagrams which can arise from the perturbation. Since the above Hamiltonian is for a particular arrangement of the guest molecules in the host crystal, a configuration averaging has to be done in order that the results correspond to those of a real mixed crystal. The configurational averaging leads to each vertex in the diagrams being weighted by a cumulant function. Once the averaging has been done, the self energy diagrams are often rearranged as follows

$$\Sigma_{\text{self energy}} = \Sigma_{\text{monomer}} + \Sigma_{\text{dimer}} + \Sigma_{\text{trimer}} + \ldots\ldots\ldots\ldots \qquad (2)$$

where Σ_{monomer} is the correction due to the monomer state and is the sum of all 1-vertex diagrams like those shown in Figure 1a ; Σ_{dimer}, the correction due to the dimer states and is sum of all irreducible 2-vertex diagrams of the types shown in Figure 1b ; and where the higher order corrections are the sums of higher order vertex diagrams.

In the dilute limit, P_n (c) = c for all values of n no natter how the cumulant functions are calculated and so the same weight is assigned to every vertex. Hong and Kopelman[11] were able to formally sum both the monomer and dimer series represented by Figures 1a and 1b. However, not all 2-vertex diagrams were inclued in the dimer series considered by Hong and Kopelman. In their summation of the 2-vertex diagrams of the types shown in Figure 2a, they started at r = 2. This meant the 2-vertex diagrams of the types shown in Figure 2b. were left out. In fact, these diagrams (and many more) would be completely left out in the rearrangement of diagrams indicated by eqn. (2). Instead of including the 2-vertex diagrams of Figure 2b. in the dimer series, we propose that they and other higher order vertex diagrams which contain multiply scattering processes which are not interrupted by a a scattering by the initial impurity molecule, be included in the monomer series. This would, of course, be equivalent to replacing the bare propagators in the diagrams by dressed propagators.

The summation of the "dressed" monomer diagrams results in the configuration averaged monomer self energy being in the continued fraction form

$$\Sigma_{\text{monomer}} = \cfrac{c\triangle}{1 - \cfrac{\triangle}{G_O^{-1} - \cfrac{c\triangle}{1 - \cfrac{\triangle}{G_O^{-1} - \cfrac{c\triangle}{1 - \cfrac{}{\ddots}}}}}} \tag{3}$$

where $\triangle = E^B - E^A$, G_O (E) is the bare propagator (the exciton propagator for the pure $C_{10}D_8$ crystal). As was pointed out by Hong and Kopelman, the singularities lying outside the density of states band of the bare propagator are the zeros of the denominators of the self energy expression. By terminating the continued fraction at the first appearance of c in the denominator, the second appearance, the third and so on, we find that the singularities are the zeros of the following sequence of polynomials which are the denominators of the first convergent, the second convergent, etc.)

$$F_1(E) = 1 - \triangle G_O(E)$$

$$F_2(E) = (1 - \triangle G_O(E) (\ F_1(E) - c \triangle G_O(E)$$

$$F_3(E) = (1 - (1 - c) \triangle G_O(E))\ F_2(E) - c \triangle^2 G_O(E)\ F_1(E)$$

$$\vdots$$

$$F_n(E) = (1 - (1 - c) \triangle G_O(E))\ F_{n-1}(E) - c \triangle^2 G_O(E)\ F_{n-2}(E) \tag{4}$$

The first polynomial in this sequence gives the location of the singularity determined by Hong and Kopelman. The above squence of polynomials is know as a sturm sequence[10] Since every zero of the n-th polynomial in a Sturm sequence lies inbetween two of the zeros of the n+1 polynomial in the sequence, the singularities of eqn. (3) should not move off the real axis and the branch cuts which would appear as higher and higher order polynomials are considered would be on the real axis.

The continued fraction can be terminated by writing the self energy as

$$\Sigma_{\text{monomer}} = t(E) = \frac{c\,\triangle}{1 - \dfrac{\triangle}{G_O(E)^{-1} - t(E)}} \tag{5}$$

The solution for eqn. (5) is

$$t(E) = \frac{(1 - c\,(\triangle\, G_O(E) - 1}{2\,G_O(E)} \left\{ 1 - \left[1 - \frac{4\,c\,\triangle\,G_O(E)}{(\,(1-c)\,\triangle\,G_O(E) - 1\,)^2} \right]^{\frac{1}{2}} \right\}$$

The negative sign is used in order to insure the proper behavior as E goes to inifinity. As we see, the analytic expression for the self energy has a cut in the E-plane. This cut will manifest itself as an impurity side band in the exciton band spectrum of the dilute mixed molecular crystal.

Impurity Bandwidth

To be able to apply the results of the previous section to the determination of the impurity bandwidth in dilute $C_{10}D_8/C_{10}H_8$ crystals, the difference in the excitation energies of the two types of molecules and the values of the exciton propagator in the host $C_{10}D_8$ crystal at different energies must be known. For the $C_{10}D_8/C_{10}H_8$ system, the energy difference is equal to 115 cm^{-1} which is the deepest trap possible for any of the mixed naphthalene crystals. The values of the exciton propagator can be calculated using the spectral representation

$$G_O(E) = \int \frac{\rho(E')}{E' - E}\, dE' \tag{7}$$

where $\rho(E)$ is the density of states function for the excition in the pure naphthalene-d_8 crystal and which can be calculated from the dispersion relation given in ref. 11. In our

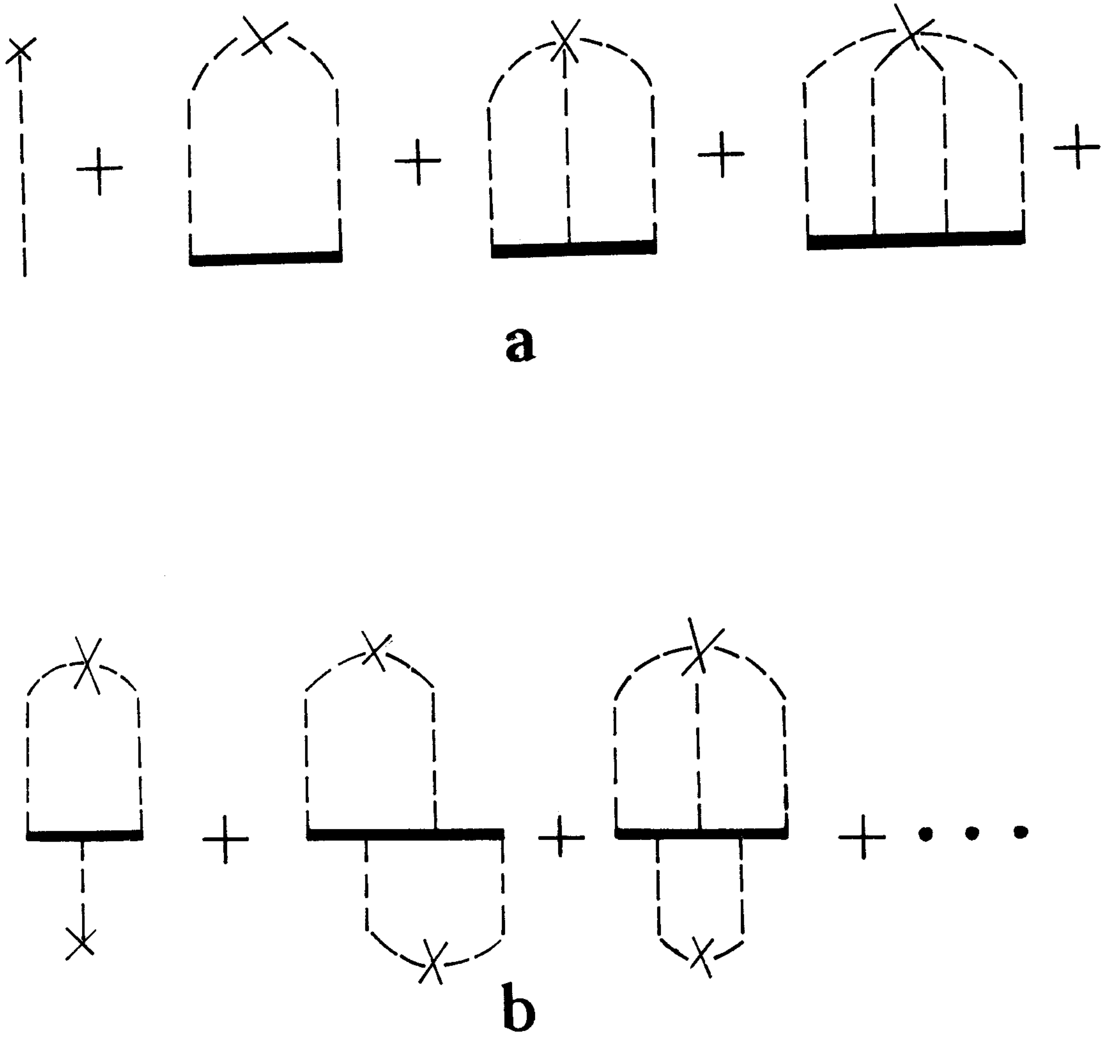

Figure 1. 1a. Diagrams in the expansion of the exciton self energy which appear in the monomer self energy series. 1b. Some of the diagrams which appear in the dimer self energy series.

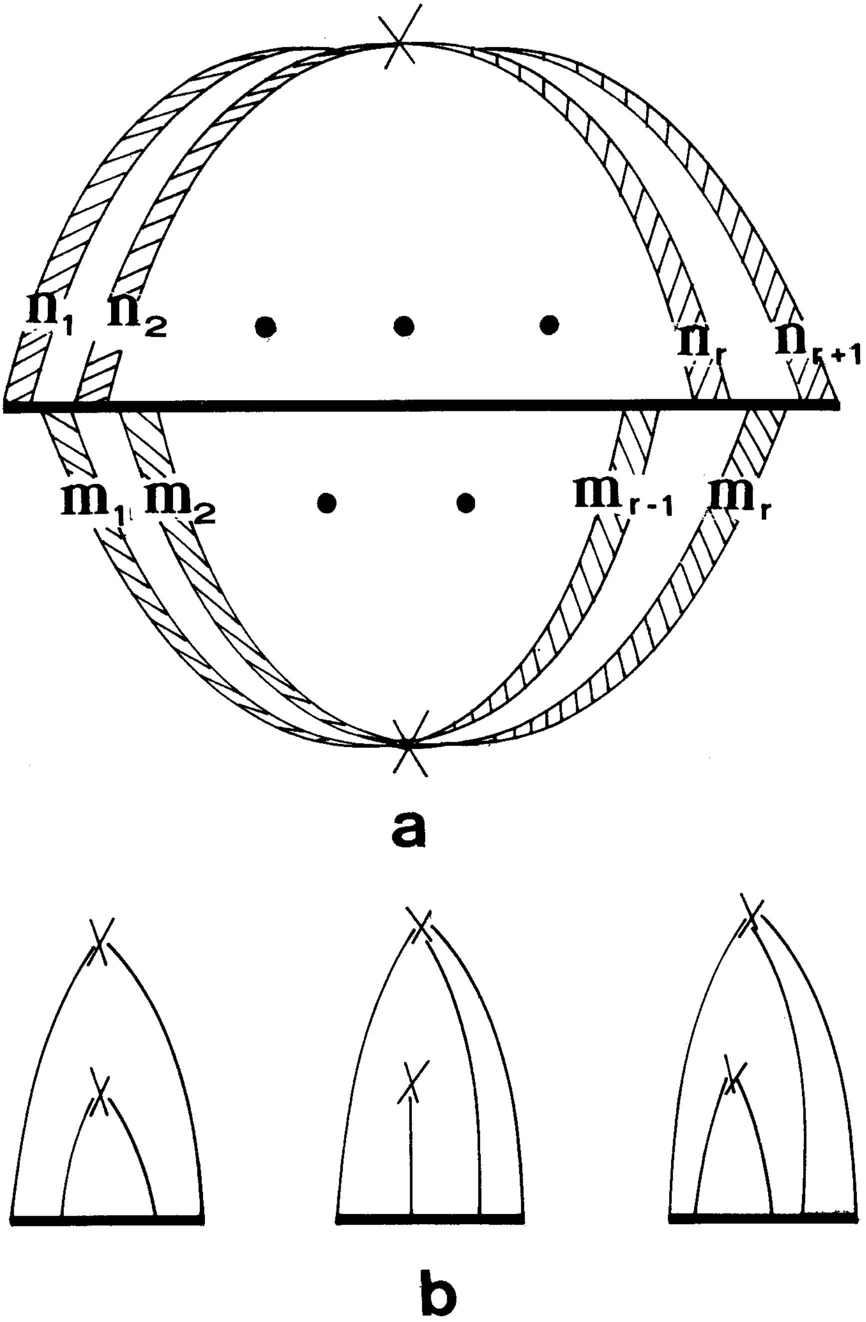

Figure 2. 2a. Some of the higher order diagrams which appear in the dimer self energy series. These diagrams are of the $S_{r,r+1}$ type treated by Hong and Kopelman in ref. 11. In these diagrams, the repeated scattering of the exciton by the first impurity molecule is interrupted by the repeated scattering by the second impurity which inturn is interrupted by scattering by the first molecule and so forth. 2b. Some of the dimer (2-vertex) diagrams which are left out is the summation of $S_{r,r+1}$ is started at $r=2$.

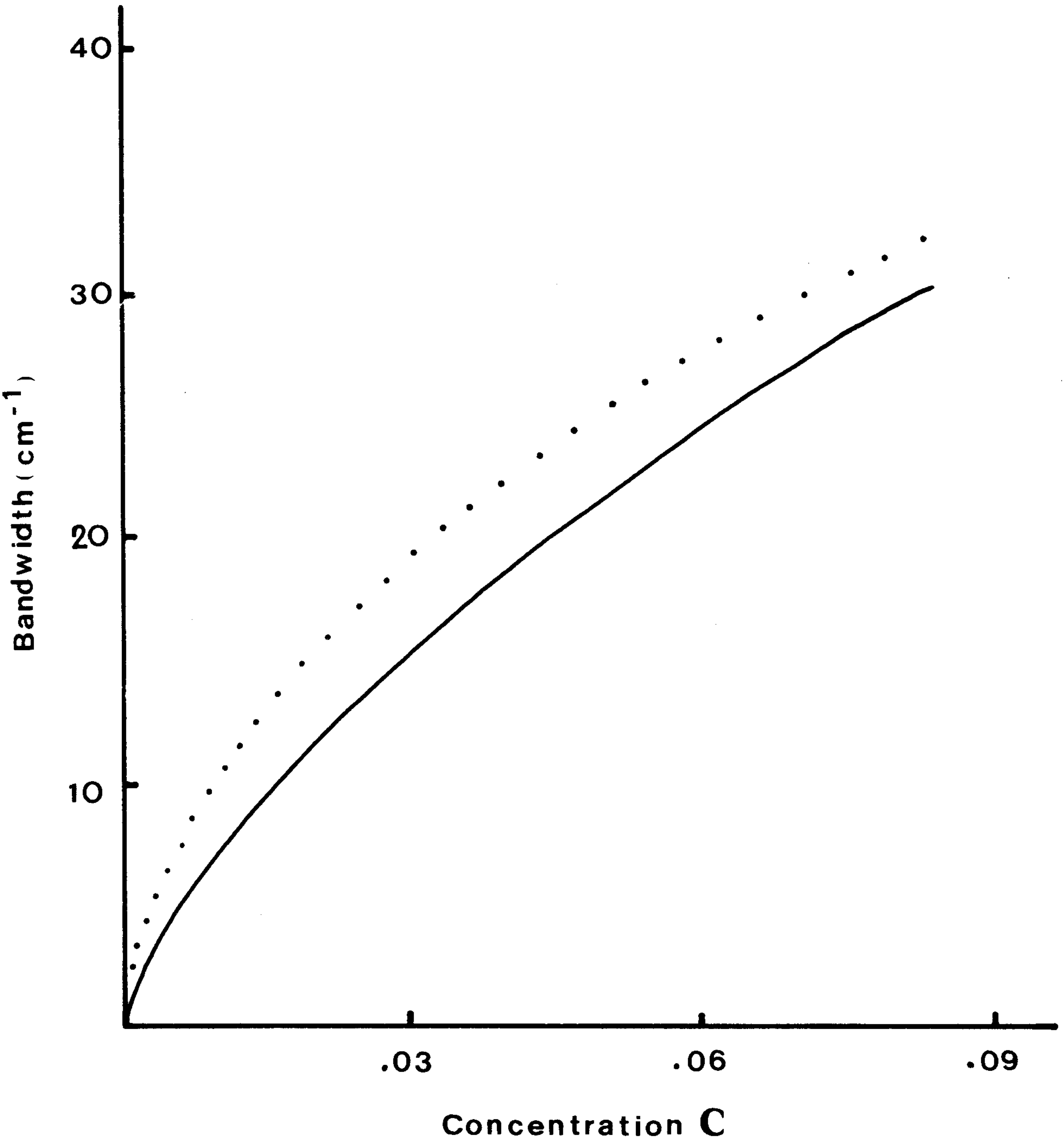

Figure 3. Concentrational dependence of the bandwidth in dilute C_{10} D_8/C_{10} H_8 mixed naphthalene crystals. (______) gives the dependence predicted by eqn. (8). (..........) gives the $(c - c^2)^{1/2}$ dependence obtained by Hoshen and Jortner in ref. 13. and by Bellows and Prasad in ref. 14.

calculation of the density of states, we have used the set of parameters values given as Set I in refs. 11 and 12.

The bandwidths for a given value of c was determined by substituting the numerical values of $\triangle$ and G_0 (E) into the square root term appearing in eqn. (6) and then look for the values of E for which

$$-1 \leqslant \frac{2(c \triangle G_O(E))^{1/2}}{(1-c) \triangle G_O(E) - 1} \geqslant +1 \tag{8}$$

The bandwidth of the impurity band would be the difference between the values of E which satisfied the upper and lower bounds. The results of these calculations are plotted in Figure 3.

The concentrational dependence of the bandwidth of the impurity band in the exciton spectrum of various isotopically mixed naphthalene crystals has been determined by Hoshen and Jortner[13] using the coherent potential approximation approach. They found that the bandwidth goes as $(c - c^2)^{1/2}$. We have plotted this dependence on Figure 3. for comparison with our results. More recently, Bellows and Prasad[14] have used the average t-matrix approximation to determine the concentrational dependence of the impurity band in the phonon spectrum of organic alloys in which the disorder is due primarily to the presence of the mass defects at the sites and not to the existance of chemical changes arising from the presence of different types of molecules in the system. They also found that the bandwidth varies essentially as $(c - c^2)^{1/2}$ for small values of c.

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บทคัดย่อ

ได้คำนวณพลังงานตัวเองของ โมโนเมอร์ ในผลึกโมเลกุลผสมอย่างเจือจาง โดยพิจารณาชุดของแผนภูมิ ซึ่งเมื่อบวกกันแล้วจะได้พลังงานดังกล่าวเป็นเศษส่วนแบบต่อเนื่อง โดยการใช้ทฤษฎีเกี่ยวกับ Sturm sequences สามารถหาพฤติกรรมของ exciton propagator ได้ สามารถกำหนดความกว้างของแถบสิ่งเจือปนในผลึก แนพธาลีนผสม $C_{10}D_8/C_{10}H_8$ ได้จากการคำนวณเช่นนี้