Effects of off-diagonal disorder on localization of electronic excitations in mixed molecular solids

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In this paper we explore the effects of off-diagonal disorder on electronic energy transfer (EET) in an impurity band of an isotopically-mixed, organic solid at low temperatures. We have considered the localization of an elementary excitation in a system characterized by both diagonal disorder, originating from inhomogeneous broadening W of the site-excitation energies, and of off-diagonal disorder arising from the energetic spread σ of the transfer integrals. We have utilized an exact expression for the self-energy of a disordered system where both the site-excitation energies and the transfer integrals are characterized by a Lorentzian distribution, together with the localization function method of Liciardello and Economou to establish the localization condition in the center of the impurity band. Model calculations were performed for a Bethe lattice and for the Hubbard density of states, demonstrating the enhancement of delocalization due to off-diagonal disorder, whereupon the Anderson transition (AT) will be exhibited at higher values of W than in the original Anderson model (OAM), when $\sigma = 0$. For large values of the ratio $W/\sigma \gtrsim 12$ the effects of off-diagonal disorder are negligible. Numerical calculations of σ were performed for a random distribution of impurities, while W was roughly estimated for recent spectroscopic measurements. These data, together with the results of the model calculations for a Bethe lattice, established the existence of the critical impurity concentration $\bar{C}$ for EET in the impurity band. Off-diagonal disorder results in the lowering of $\bar{C}$ relative to the OAM; however, the effect of diagonal disorder is dominant in determining the termination of EET in the impurity band.

I. INTRODUCTORY COMMENTS

Recent experimental studies of electronic energy transfer (EET) in low temperature, isotopically-mixed, organic crystals of naphthalene,[1] benzene,[2] and phenazine[3] point towards the existence of a critical concentration of the isotopic impurity below which EET in the impurity band is switched off. Two distinct models have been introduced to account for the nature of the electronic states and of EET in isotopic impurity bands. Kopelman and colleagues[1] have introduced the notion of "exciton percolation" (EP), which rests on the assumption that the only source of disorder in a binary, isotopically-mixed crystal is due to substitutional disorder. In the absence of a diagonal disorder the electronic states in the center of the monomer impurity band are always delocalized.[4] EET in the impurity band at low temperatures proceeds via extended states, the spatial range of EET being limited by the finite lifetime of the electronic excitation. Kopelman's picture[1] constitutes a kinetic model which does not describe a critical behavior. We have proposed[5] that a critical concentration, $\bar{C}$, for triplet EET is a manifestation of an Anderson transition (AT)[6] within the isotopic impurity band. In our picture,[5] diagonal disorder of the site-excitation energies in the impurity band results in an abrupt change in the eigenstates in the impurity band from extended states at $C > \bar{C}$ to localized states at $C < \bar{C}$. EET is then essentially dominated by diagonal disorder, which originates from inhomogeneous broadening of the site-excitation energies.

The dichotomy between Kopelman's EP model[1] and the Klafter–Jortner AT model[5] involves the central issue regarding the magnitude of inhomogeneous broadening and its effect on the dynamics of EET in an isotopic impurity band. The dispute concerning the magnitude of the spread of diagonal site-excitation energies has to be settled experimentally. Strong experimental support to our original proposal[5] that diagonal disorder of site-excitation energies in dilute isotopic impurity bands is appreciable (i.e., ~0.1–5 cm^{-1}),[3] stems from recent spectroscopic studies. Smith *et al.*[3] have reported inhomogeneous broadening of ~4 cm^{-1} for triplet isotopic impurity states of phenazine in phenazine-d_4 at 1.3 K, while a study of the triplet excitation spectrum of 2% naphthalene in naphthalene-d_8 at 2 K reveals an inhomogeneous broadening of ~0.1 cm^{-1} for the monomer band.[7]

On the basis of extensive theoretical studies of the Anderson localization problem[4,8,9] and its application to EET,[5,10] we can assert that provided the inhomogeneous broadening in isotopic impurity bands in organic crystals is sufficiently large (relative to the impurity band width) an AT will be exhibited. In what follows we shall adopt our original approach, which asserts that diagonal disorder prevails in isotopically-mixed crystals. However, one should note that the AT model for EET is oversimplified as it considers only the effects of diagonal disorder in the impurity band. All previous studies of localization of electronic excitations in impurity bands of ionic[10] and organic solids[5] rest on the original Anderson model (OAM), where the site-excitation energies are taken as random variables, while the transfer integrals are assumed to be invariant to effects of disorder. In an impurity band three types of disorder are encountered: (1) Binary disorder in the alloy, (2) off-diagonal disorder due to the distribution of the transfer integrals, and (3) diagonal disorder of the site-excitation energies. Substitutional disorder must involve binary and off-diagonal disorder, while the effects of diagonal disorder depend on the magnitude of the inhomogeneous broadening. Thouless,[4] Abou-Chacra *et al.*[8,9] and Heinrichs,[11] have demonstrated that in an impurity band characterized only by the disorder effects (1) and (2) no AT is exhibited and that the states in the monomer band will always be extended. Herscovici,[12] and Economou and Antoniou[13]

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have recently shown that when only off-diagonal disorder prevails no Anderson localization will occur, while in a system characterized by both diagonal disorder and off-diagonal disorder the latter may lead to delocalization of states, which are localized within the framework of the OAM. These results were recently confirmed by numerical studies by Weaire *et al.*[14] As off-diagonal disorder always prevails in an impurity band, we are now faced with the interesting question: How do the inherent static fluctuations of the transfer integrals affect the electronic states and the features of EET in an isotopic impurity band?

In this paper we address ourselves to the problem of an electronic excitation in an impurity band in a molecular crystal, which is characterized by both inhomogeneous broadening, W, and by static fluctuations in the transfer integrals. While W is estimated on the basis of the sparse experimental data available for isotopic impurity bands,[3,7] the probability distribution of the transfer integrals, as well as the mean value and the dispersion of these transfer integrals, are evaluated for a random distribution of impurities. The problem of localization of an elementary excitation in a disordered system characterized by both diagonal and off-diagonal disorder was studied by utilization of the John–Schreiber model,[15] where both the site-excitation energies and the transfer integrals are characterized by Lorentzian distribution functions. This model results in exact expressions for the configurationally-averaged Green's function. Subsequently, the Economou–Antoniou localization criterion,[13] i.e., the $L(E)$ method, was applied to determine the condition for localization in the middle of the impurity band. Numerical calculations were conducted for two model lattice Green's functions, the Bethe lattice (Cayley tree) model, and the Hubbard model.[13] We shall be concerned only with localization in the middle of the impurity band as we assert that, even in the low temperature regime we are concerned with here, all the states in the narrow band have equal thermal population probabilities, whereupon an AT in the middle of the band is sufficient to insure EET via extended states at $C \geq \bar{C}$. In order to utilize the theoretical predictions of the model, which rest on Lorentzian distributions, to extract information concerning the characteristics of real physical systems, we have adopted a "scaling law" $\delta\Gamma_c = W_c$, to compare the critical inhomogeneous width W_c of the Anderson rectangular distribution calculated by the exact method suggested by Abou-Chacra *et al.*[8,9] for a Bethe lattice, with the Anderson critical Lorentzian parameter Γ_c calculated by the $L(E)$ method. The results of the present study will elucidate the effects of off-diagonal disorder EET in mixed organic solids. This problem is of considerable current interest, as organic solids provide a class of attractively simple materials for the study of the problem of localization of elementary excitations in disordered systems.

II. THE IMPURITY BAND

The electronic states in the impurity band of an isotopically-mixed crystal will be characterized by the impurity–impurity superexchange interaction[1,5]

$$J = \beta(\beta/\Delta)^n , \qquad \text{(II. 1)}$$

where β is the nearest-neighbor exchange integral, Δ represents the energy separation of the impurity state from the lowest exciton band center, while n corresponds to the number of host molecules separating the two impurities. Equation (II. 1) is valid in the limit $(\beta/\Delta) \ll 1$, which is of interest to us. This form of superexchange integral concurs with the results of the recent analysis of Thouless,[4] of Abou-Chacra *et al.*,[8,9] and of Heinrichs,[11] that (in the absence of diagonal disorder) the binary disorder, together with off-diagonal disorder, do not result in Anderson localization within the impurity band. In a dilute mixed crystal there will always exist a narrow but finite "strip" of extended states which correspond to the monomer excitations. Furthermore, the effective impurity–impurity couplings derived by Thouless[4] is identical with the superexchange interaction, Eq. (II. 1).

The electronic excitations in the impurity band will be characterized by the tight binding Hamiltonian

$$H = \sum_n \epsilon_n a_n^{+} a_n + J \sum_{n<m} a_n^{+} a_m , \qquad \text{(II. 2)}$$

where $a_n(a_n^{+})$ represent the excitation annihilation creation operator on the impurity site n. ϵ_n are the site-excitation energies, while J represents the nearest-neighbor excitation transfer integrals. As we are concerned with a system characterized by short range impurity–impurity coupling, Eq. (II. 1), it is sufficient to consider only the nearest-neighbor transfer integrals. Both the site-excitation energies and the transfer integrals are characterized by a statistical distribution as appropriate for a substitutionally and structurally disordered material. The site-excitation energies exhibit an energetic spread due to the inhomogeneous broadening, while the transfer integrals are specified in terms of a distribution which originates from the random substitution of the impurities on the lattice sites.

We shall consider the impurity band in a mixed organic solid where the band structure is two dimensional (2-D). This physical situation prevails for the lowest triplet excitation in naphthalene[1] and in phenazine,[3] where the triplet band structure is dominated by 2-D interactions. The probability distribution function $P(\epsilon_n)$ for ϵ_n will firstly be taken as a rectangular distribution

$$\begin{aligned} P(\epsilon_n) &= \frac{1}{W} \; ; \quad -\frac{W}{2} \leq \epsilon_n \leq \frac{W}{2} \\ &= 0 \; ; \quad \text{otherwise} \end{aligned} \qquad \text{(II. 3)}$$

as originally suggested by Anderson.[1] The energy spread W will be taken from experimental estimates of the inhomogeneous broadening[3,7] and will be chosen in the range $W = 0.1$–$4\ \text{cm}^{-1}$. It is important to note that at low impurity concentrations $(C < 0.1)$ we shall assume that W is concentration independent. The probability distribution function $P(J)$ for J is evaluated in Appendix A for a random distribution of impurities. This calculation was performed within the framework of the quasicontinuum approximation, where the interaction (II. 1) is replaced by an exponential interaction. We have shown (see Appendix A) that for a 2-D system at low $(C \ll 1)$ impurity concentrations

$$P(J) = (2\pi C/J)\,[\ln(\Delta/J)/\ln^2(\Delta/B)] \times \exp[-\pi C\,\ln^2(\Delta/J)/\ln^2(\Delta/\beta)]\,. \qquad (\mathrm{II.}\,4)$$

It can easily be demonstrated that $P(J)\to 0$ when $J\to 0$.

We can now characterize the impurity band by the first and second moments. As we show in Appendix A, for low impurity concentrations

$$\langle J\rangle = \int dJ J P(J) = \frac{2\pi\beta C}{\ln^2(\Delta/\beta)}\exp(-\pi C) \qquad (\mathrm{II.}\,5\mathrm{a})$$

$$\langle J^2\rangle = \int dJ J^2 P(J) = \frac{\pi\beta^2 C}{2\ln^2(\Delta/\beta)}\exp(-\pi C)\ ; \qquad (\mathrm{II.}\,5\mathrm{b})$$

The average impurity–impurity coupling which is determined by superexchange interactions is given by $\langle J\rangle$, Eq. (II. 5a). The dispersion, σ, of these interaction terms is

$$\sigma = [\langle J^2\rangle - \langle J\rangle^2]^{1/2} = \langle J\rangle\{[\ln^2(\Delta/\beta)/8\pi C]\exp(\pi C) - 1\}^{1/2}\,. \qquad (\mathrm{II.}\,6)$$

The energetics of the impurity band is characterized by the inhomogeneous broadening W, Eq. (II. 3), by $\langle J\rangle$, Eq. (II. 5a), and by σ, Eq. (II. 6). Figures 1 and 2 portray the concentration dependence of $W/\langle J\rangle$ and of $\sigma/\langle J\rangle$ for the typical energy parameters $\beta = 1$ cm^{-1}, $W = 1$ cm^{-1}, and for several values of Δ/β. It is evident from Fig. 1 that for $W = 1$ cm^{-1}, we get $W/\langle J\rangle \gg \sigma/\langle J\rangle$. Bearing in mind that the inhomogeneous broadening serves as a linear scaling parameter in Fig. 1, we can assert that for $W > 0.1$ cm^{-1} or so, $W/\langle J\rangle > \sigma/\langle J\rangle$. Without alluding to any quantitative calculations, we can argue at this stage that for $W \geq 0.1$ cm^{-1}, which constitutes a reasonable experimental[3,7] lower limit for W, the effects of diagonal disorder will dominate the effects of the off-diagonal disorder. Under these circumstances, we expect only minor modifications of the AT, which will be determined essentially by the effects of diagonal disorder.

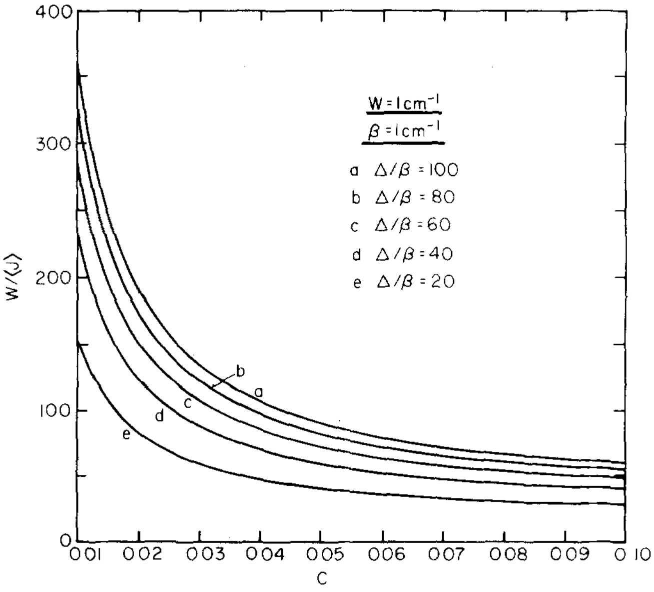

FIG. 1. The concentration dependence of W, the inhomogeneous broadening, normalized by $\langle J\rangle$, for various values of Δ/β. $W = 1$ cm^{-1} and $\beta = 1$ cm^{-1}.

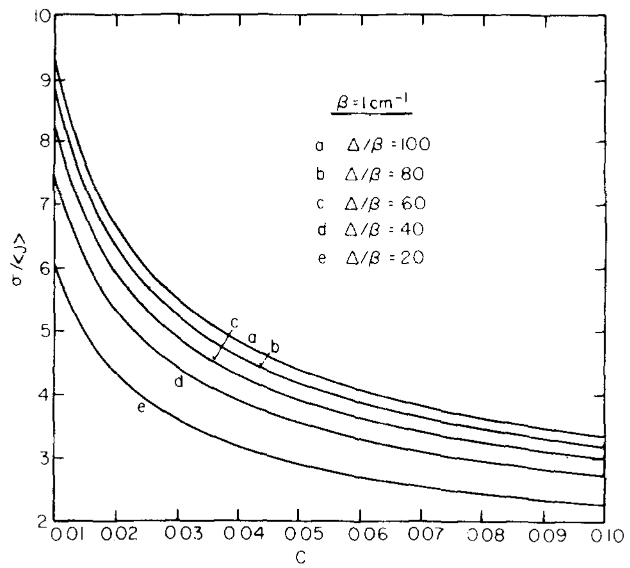

FIG. 2. The concentration dependence of $\sigma/\langle J\rangle$, the standard deviation normalized by $\langle J\rangle$, for various values of Δ/β.

In order to provide a rough estimate of the critical impurity concentration $\bar{C}$ at which the AT occurs, we shall disregard entirely for the moment the effects of off-diagonal disorder and consider a "superlattice" of impurities where the distribution of the transfer integrals is

$$P(J) = \delta(J - \langle J\rangle)\ , \qquad (\mathrm{II.}\,7)$$

while the site-excitation energies are characterized by Eq. (II. 3). Anderson's localization theory for diagonal disorder is now directly applicable and the AT will occur when[4,16]

$$\langle J\rangle = W/\gamma\ , \qquad (\mathrm{II.}\,8)$$

where $\gamma \cong 2\alpha z$; z is an (average) coordination number and α is a numerical constant which, according to different theoretical estimates,[16] is in the range $\alpha = 1$–2.7. From Eqs. (II. 5a) and (II. 8), we assert that the critical concentration for AT in an impurity "superlattice," where only diagonal disorder prevails, is roughly given by

$$\bar{C} \cong (W/2\pi\beta\gamma)\ln^2(\Delta/\beta)\ , \qquad (\mathrm{II.}\,9)$$

where the exponent term $\exp(-\pi C)$ in Eq. (II. 5a) has been neglected, as is appropriate for low concentrations. Equation (II. 9) provides a reasonable first-order approximation for $\bar{C}$. This result differs from our previous expression for $\bar{C}$,[5] where we have considered essentially an impurity "superlattice" characterized by the average impurity–impurity separation. The result of the present treatment should be preferred as the configurational average has been performed in a self-consistent manner. The following characteristics of the critical concentration should be noted:

(1) $\bar{C}$ is proportional to the inhomogeneous broadening W.

(2) $\bar{C}$ exhibits an inverse linear dependence of the nearest-neighbor host–host interaction β.

(3) $\bar{C}$ reveals only a weak logarithmic dependence on the energy mismatch Δ.

Finally, it is worthwhile to point out that the present superlattice approximation for the impurity band, which disregards off-diagonal disorder, is almost equivalent to the upper limit approximation in the self-consistent theory of Abou-Chacra *et al.*[8,9] This problem is discussed in Appendix B.

Up to this point, we have avoided the central issue pertaining to the effects of off-diagonal disorder on localization in the impurity band. Although the preceding qualitative analysis of the numerical results of Fig. 1 and 2 indicates that for "reasonable" values of W (≥ 0.1 cm^{-1}) the effects of off-diagonal disorder are of minor importance, it is interesting to provide an analysis of these effects and in what follows we shall address ourselves to a soluble model system which incorporates both the effects of diagonal and of off-diagonal disorder.

III. AN EFFECTIVE HAMILTONIAN FOR LORENTZIAN DISTRIBUTION FUNCTIONS

The solution of the localization problem for a disordered system described by the Hamiltonian (II. 2) with the probability distribution functions given by Eqs. (II. 3) and (II. 4) is a formidable task. In what follows, we shall utilize the solution for localization in a model system where the distribution functions for the diagonal and the off-diagonal terms are Lorentzians. This soluble model, suggested by John and Schreiber,[15] incorporates all the essential physical ingredients of the localization of an electronic excitation in an impurity band.

The distribution function for the transfer integrals is taken in the Lorentzian form

$$P(J)=\frac{V/\pi}{(J-\langle J\rangle)^2+V^2}\ , \tag{III. 1}$$

where V represents the width of this probability distribution. The site-excitation energies are taken to be related to the transfer integrals via

$$\epsilon_n=a\sum_m (J_{mn}-\langle J\rangle)\ ; \quad a\geq 1\ , \tag{III. 2}$$

where the scaling factor a is positive and exceeds unity, and the sum is taken over all nearest neighbors. Relation (III. 2) makes it possible to derive an exact solution for the averaged Green's function.[15] It follows from Eq. (III. 2) and from some general probability laws for a function of a random variable,[17] that the probability distribution function for the variables ϵ_n, Eq. (III. 2), is given by a Lorentzian

$$P(\epsilon_n)=\frac{\Gamma/\pi}{\epsilon_n^2+\Gamma^2}\ , \tag{III. 3}$$

which is characterized by the width

$$\Gamma=azV\ ; \quad a\geq 1\ , \tag{III. 4}$$

where z is the coordination number. The parameter az represents the ratio between the spread of the diagonal and of the off-diagonal terms.

The correlation (III. 2), with $a\geq 1$, between the width of the distribution of the diagonal site-excitation energies and the spread of the transfer integrals implies that $\Gamma > V$, i.e., the spread of the ϵ_n terms due to diagonal disorder exceeds the spread of the J terms originating from off-diagonal disorder. In view of the available experimental results and the analysis of Sec. II, we assert that this is a reasonable starting point for the theoretical study of impurity bands in isotopically-mixed, organic solids.

Following the analysis of John and Schreiber,[15] one can now define an effective Hamiltonian for the system characterized by the distribution functions (III. 2)–(III. 4).

$$\mathrm{Heff}=\Sigma_0\sum_n a_n^{+}a_n+(\langle J\rangle+\Sigma_1)\sum_{n<m} a_n^{+}a_m\ , \tag{III. 5}$$

where the (exact) self-energy is given by

$$\Sigma_0=-iazV \tag{III. 6a}$$

$$\Sigma_1=-iV \tag{III. 6b}$$

being expressed in terms of the diagonal component $\sum_0$ and the off-diagonal component $\sum_1$. It is important to emphasize that the form of $\sum_0$ and $\sum_1$ is independent of the lattice Green's function, and in Sec. IV we shall utilize several lattice Green's functions with the effective Hamiltonian (III. 5).

One should note that the exact result (III. 6) for the self-energy in the model system characterized by the Lorentzian distribution functions (III. 2)–(III. 4) differs from the self-energy derived by Antoniou and Economou, which rests on the coherent potential approximation (CPA).[13] The CPA self-energy contains only a contribution to the diagonal energy term

$$\overline{\sum_0}=-i(\Gamma+V) \tag{III. 7a}$$

$$\overline{\sum_1}=0\ . \tag{III. 7b}$$

We have shown elsewhere[18] that the "exact" self-energy (III. 6) and the CPA self-energy (III. 7) result in different features of the exciton density of states function in a structurally-disordered crystal. In what follows we shall utilize these self-energies to explore the problem of localization in a model system subjected to both diagonal and off-diagonal disorder.

IV. THE LOCALIZATION FUNCTION

Economou and Antoniou[13] have recently advanced a criterion for the localization of an elementary excitation in a disordered material where diagonal and off-diagonal disorder prevails. The Economou–Antoniou localization criterion rests on the Liciardello and Economou theory of localization[16] and is briefly reviewed in Appendix C. The localization function $L(E)$ defined by the relation[16]

$$L(E)=K\tilde{J}\,\left|\,G_{n_i}^{n_{i+1}}(E-\Sigma_0;J+\Sigma_1)\right| \tag{IV. 1}$$

states characterized by $L(E)<1$ are localized, while states corresponding to $L(E)>1$ are extended. The AT occurs at

$$L(E)=1\ . \tag{IV. 2}$$

Here K is the connectivity of the lattice, while $\tilde{J}=\exp(\langle \ln |J|\rangle)$, where $\langle\ \rangle$ denotes the average over the probability distribution function for J. $G_{n_l}^{n_l-1}$ is the logarithmic average of the n_lth site Green's function with the n_{l-1}th site excluded, which is given by[19]

$$G_{n_l}^{n_l-1}=G_{n_l}-\frac{G_{n_l,n_{l-1}}G_{n_{l-1},n_l}}{G_{n_l}}\ , \tag{IV. 3}$$

where G_{n_l} and $G_{n_{l-1},n_l}(G_{n_l,n_{l-1}})$ are the diagonal and the off-diagonal matrix elements of the lattice Green's function, respectively. The arguments of these Green's functions are the same as in Eq. (IV. 1).

We shall now utilize the self-energy (III. 6) to study the localization function in the middle of the impurity band, i.e., at $E=0$, as the existence of extended states in the center of the narrow impurity band is sufficient to insure the propagation of the electronic excitation.[5] In what follows we shall consider explicitly two model systems, the Bethe lattice and the Hubbard model.[13]

First, we consider Green's functions for a Bethe lattice. This is a useful model, as an approximate correspondence between a Bethe lattice can be established by identifying the connectivity K for the Bethe lattice with $(z-1)$ in the real lattice. The logarithmic average of the Green's function (IV. 3) for the Bethe lattice with the self-energy (III. 6) takes the form[13]

$$G_{n_l}^{n_l-1}=\{(E-\Sigma_0)-[(E-\Sigma_0)^2 - 4K(\langle J\rangle+\Sigma_1)^2]^{1/2}\}/2K(\langle J\rangle+\Sigma_1)^2\ . \tag{IV. 4}$$

$\tilde{J}$ is calculated for a Lorentzian distribution as being

$$\tilde{J}=(V^2+\langle J\rangle^2)^{1/2}\ . \tag{IV. 5}$$

Utilizing Eqs. (IV. 1), (IV. 4), and (III. 6) the localization function for the Bethe lattice is

$$L(E=0)=\frac{1}{2}\left(1+\frac{V^2}{\langle J\rangle^2}\right)^{1/2} \times\left|\frac{\dfrac{-\Sigma_0}{\langle J\rangle}-\left[\left(\dfrac{\Sigma_0}{\langle J\rangle}\right)^2-4K\left(1+\dfrac{\Sigma_1}{\langle J\rangle}\right)^2\right]^{1/2}}{\left(1+\dfrac{\Sigma_1}{\langle J\rangle}\right)^2}\right|. \tag{IV. 6}$$

The CPA result for the self-energy derived by Antoniou and Economou,[13] Eq. (III. 7), results in

$$L_{\mathrm{AE}}(E=0)=\frac{1}{2}\left(1+\frac{V^2}{\langle J\rangle^2}\right)^{1/2} \times\left|\frac{-\bar{\Sigma}_0}{\langle J\rangle}-\left[\left(\frac{\bar{\Sigma}_0}{\langle J\rangle}\right)^2-4K\right]^{1/2}\right|\ . \tag{IV. 7}$$

The ordinary Anderson localization condition under the influence of diagonal disorder is obtained by setting $V=0$ and $\Sigma_1=0$ in Eq. (IV. 6), or by taking $V=0$ and $\bar{\Sigma}_0=-i\Gamma$ in Eq. (IV. 7). Equation (IV. 2), together with either (IV. 6) or (IV. 7), then yields for the localization condition

$$\tfrac{1}{2}\left|i\Gamma/\langle J\rangle-i[(\Gamma/\langle J\rangle)^2+4K]^{1/2}\right|=1\ ,$$

which results in $\Gamma/\langle J\rangle=K-1$. A cursory examination of the localization functions (IV. 6) and (IV. 7), which incorporate the effects of off-diagonal disorder, reveals the tendency of the off-diagonal static fluctuations in the transfer integrals to delocalize the excitation. The AT in a system subjected to both diagonal disorder (Γ) and off-diagonal disorder (V) will be exhibited at a higher value of Γ than that corresponding to the limit of diagonal disorder ($V=0$). While in the Antoniou–Economou localization condition, Eq. (IV. 7), this effect of off-diagonal disorder arises only from the contribution of the $\tilde{J}$ term, Eq. (IV. 5), the exact result, Eq. (IV. 6), for $L(E)$ implies that off-diagonal disorder affects both $\tilde{J}$ and $G_{n_l}^{n_l-1}$. The exact self-energy, Eq. (III. 6), has now two components, the diagonal term Σ_0 and the off-diagonal term Σ_1. Σ_1 defines an effective transfer integral $(\langle J\rangle+\Sigma_1)$ in the effective Hamiltonian, Eq. (III. 5), which is larger than $\langle J\rangle$. This contribution of Σ_1 to the effective transfer integral results in an important modification of the condition for the AT, resulting in an enhancement of delocalization. Thus, when off-diagonal disorder coexists with diagonal disorder, the spread Γ of the diagonal site-excitation energies exceeds the value implied by the Antoniou–Economou CPA self-energy.

Model calculations were performed for the localization functions at the center of the band for various values of Γ and V. In Figs. 3(a) and 3(b), we display $L(E=0)$ and $L_{\mathrm{AE}}(E=0)$ vs $V/\langle J\rangle$ for several values of $a\equiv\Gamma/zV$. These calculations were performed for a Bethe lattice with $K=3$, which provides an approximation for a 2-D system. In Figs. 4(a) and 4(b) the localization functions are portrayed for a Bethe lattice with $K=5$, which mimics three dimensional systems. These numerical results clearly demonstrate the enhancement of delocalization by off-diagonal disorder. The AT obtained both from $L(E=0)$ and for $L_{\mathrm{AE}}(E=0)$ for finite V occurs at a higher value of Γ than for the OAM with $V=0$. Furthermore, the localization condition for the AT obtained from $L(E=0)$ is exhibited (Fig. 5) at higher values of Γ than, as expected, the result obtained from the CPA type $L_{\mathrm{AE}}(E=0)$. A rather drastic effect of V on the off-diagonal self-energy, and consequently on the localization conditions, is revealed in Fig. 4(a) where no AT is obtained in the 3-D, $K=5$ case for $1\le a\le 1.4$. To provide a quantitative measure of the effects of off-diagonal disorder we portray in Fig. 5 the critical value $(\Gamma/\langle J\rangle)_c$ of the spread of the diagonal terms versus the parameter $a=\Gamma/zV$, which represents the ratio of the diagonal fluctuations to the off-diagonal fluctuations. For moderate values of a, i.e., $1\le a\le 3$ $(\Gamma/\langle J\rangle)_c$ exceeds the value obtained from the OAM which incorporates only diagonal disorder. For large values of a, $a\ge 3$, the effects of off-diagonal disorder become negligible.

Next, we turn to model calculations based on the Hubbard lattice Green's functions[13]

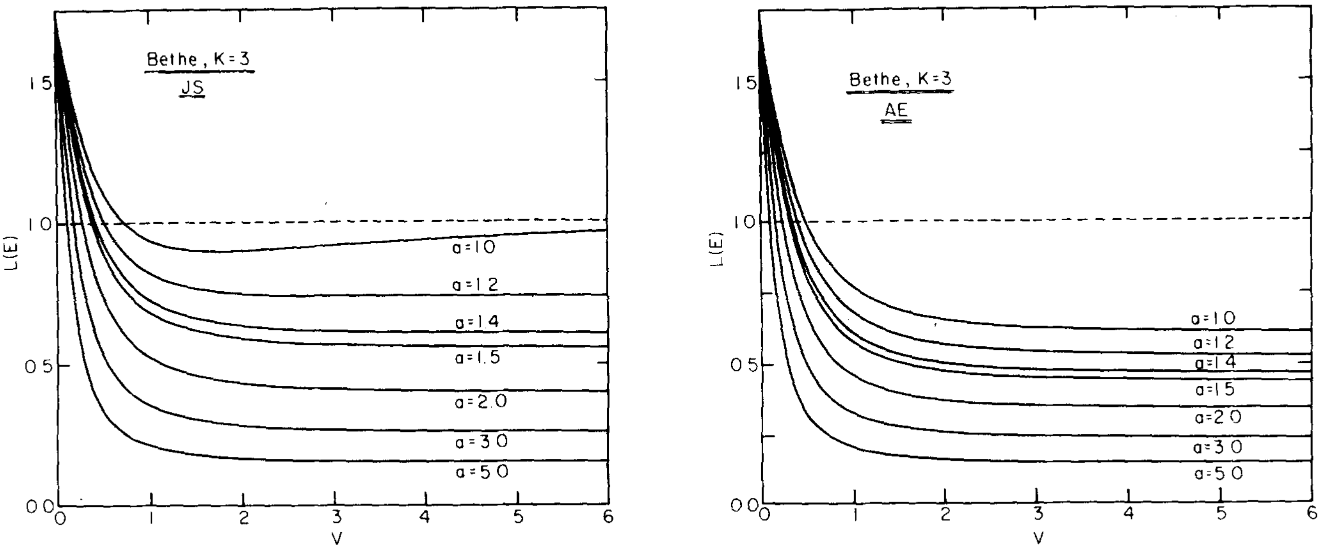

FIG. 3. (a) The localization function $L(E=0)$ in the center of the band $E=0$, calculated for various values of the parameters V and a, utilizing the exact self-energy and the Bethe lattice Green's function with $K=3$; (b) The localization function $L_{AE}(E=0)$ for various values of V and a, calculated using the CPA self-energy for the Bethe lattice $K=3$.

$$G_{n_i}=2\{E-\Sigma_0-[(E-\Sigma_0)^2 - z^2(\langle J\rangle+\Sigma_1)^2]^{1/2}\}/z^2(\langle J\rangle+\Sigma_1)^2 \qquad \text{(IV.8)}$$

and

$$G_{n_i,n_{i-1}}=[(E-\Sigma_0)G_{n_i}-1]/z(\langle J\rangle+\Sigma_1). \qquad \text{(IV.9)}$$

Utilizing Eqs. (IV.1), (IV.3), and (IV.5), together with Eqs. (IV.8) and (IV.9), we obtained the localization function in the Hubbard model. In Fig. 6 we present this localization function for $z=6$, taking $K=4.68$ which corresponds to a simple cubic lattice. As is evident from Fig. 5, the behavior of $(\Gamma/\langle J\rangle)$ is very similar to that found for a 3-D Bethe lattice. This result demonstrates that the AT in a system characterized by both diagonal and off-diagonal disorder depends on the dimensionality, but is not sensitive to the details of the Green's function. This conclusion is reassuring as it will enable us to apply the results of our model calculations for a semiquantitative discussion of the features of localization in an impurity band for real material.

The model calculations presented herein are based on Lorentzian distributions for the diagonal site-excitation energies and for the transfer integrals. From the technical point of view it was convenient to express our results (see, for example, Fig. 5) in terms of the parameter $a=\Gamma/zV$, Eq. (III.4), which provides a mea-

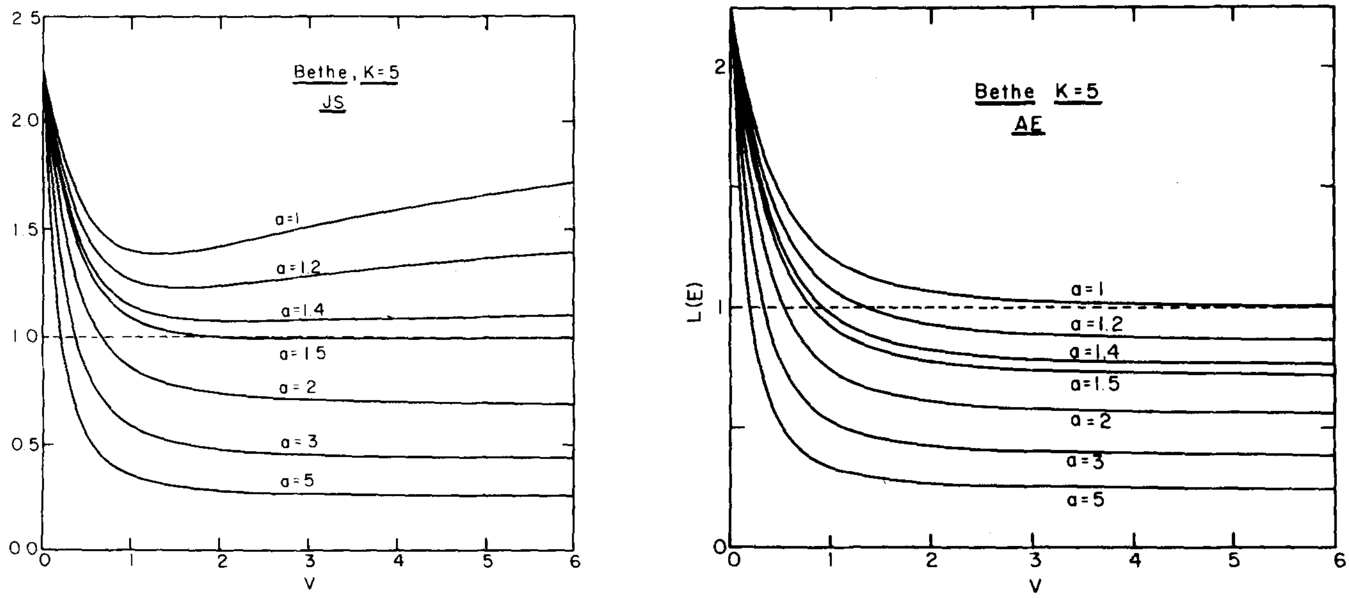

FIG. 4. Localization functions $L(E=0)$. (a) For a Bethe lattice $K=5$, using the exact self-energy; (b) For a Bethe lattice $K=5$, using the CPA self-energy.

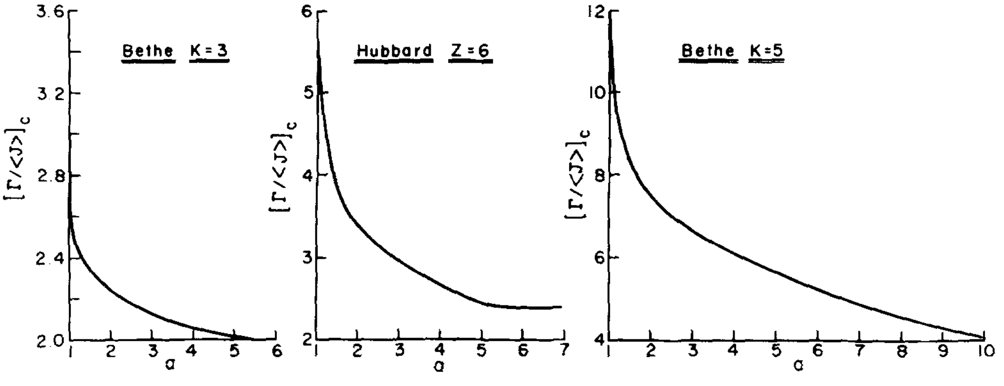

FIG. 5. The critical value $(\Gamma/\langle J\rangle)_c$ as a function of the parameter $a = \Gamma/zV$, which is a measure of ratio between diagonal and off-diagonal fluctuations. (a) Bethe lattice with $K=3$; (b) Hubbard density of states; (c) Bethe lattice with $K=5$. In Figs. (5a) and (5b) for large values of $a>3$ the curve coincides with the results of the OAM where $(\Gamma/\langle J\rangle)_c \simeq 2$.

sure of the ratio of the diagonal and the off-diagonal static fluctuations. In order to apply the results of the model calculations to the problems of EET in an impurity band of a mixed organic solid, we define a corresponding parameter a_I for the impurity band

$$a_I = W/z\sigma \ . \qquad \text{(IV. 10)}$$

The inhomogeneous broadening, W, characterizes in real life a Gaussian distribution, which will be replaced by a rectangular distribution of the diagonal site-excitation energies. The dispersion σ of the transfer integrals was obtained (see Fig. 2) in Sec. II. We recall that Figs. 1 and 2 revealed that both $W/\langle J\rangle$ and $\sigma/\langle J\rangle$ decrease with increasing of the impurity concentration C. In view of the general conclusion regarding the enhancement of delocalization by off-diagonal disorder, we can then assert that for a finite value of $\sigma/\langle J\rangle$ the AT in the impurity band will be exhibited at a lower impurity concentration (i.e., at a higher value of $W/\langle J\rangle$) than expected in the OAM, when the effects of off-diagonal disorder are disregarded. This central conclusion does hold provided that the inhomogeneous broadening is concentration independent.

In order to utilize the model calculation to provide a semiquantitative estimate of the effects of off-diagonal disorder on localization in an impurity band one has to establish the relations between the parameters W and Γ, which characterize diagonal disorder, and between σ and V which specify off-diagonal disorder. This was accomplished by invoking the following assumptions:

(a) The same scaling factor, δ, applies for both the diagonal spread and for the width of the off-diagonal distributions, i.e., we set $W = \delta\Gamma$ and $\sigma = \delta V$.

(b) The ratio of the diagonal to the off-diagonal static fluctuations is invariant to the nature of the distribution, namely, whether it is Lorentzian or short ranged, so that we set $a = a_I$, where a is given by Eq. (III. 4), while a_I is defined by Eq. (IV. 10).

(c) To determine the scaling factor δ we utilize the data for the critical values of $(W/\langle J\rangle)_c$ calculated by Abou-Chacra *et al.*[8,9] for a rectangular distribution of diagonal site-excitation energies in the absence of off-diagonal disorder, together with our data for a Lorentzian distribution in the limit $a>3$, which corresponds to the OAM. For a Bethe lattice with $K=3$, Abou-Chacra *et al.*[8,9] obtained $(W/\langle J\rangle)_c \approx 36$, while we have obtained (see Fig. 5) for the same system $(\Gamma/\langle J\rangle)_c = 2$. Thus, the scaling factor is $\delta = 18$. From now on we shall focus attention on EET in a 2-D impurity band, which is assumed to be faithfully represented by a $K=3$ Bethe lattice.

To explore the features of the parameter a_I, Eq. (IV. 10), we display in Fig. 7 the concentration dependence of a_I for a fixed value of Δ/β and for several values of W, taking $z=4$ as an average coordination number for a 2-D system. It is important to note that for the low concentration range of impurities, i.e., $C<0.1$, which is of interest to us, $a_I > 1$, thus satisfying the basic validity condition $a \gtrsim 1$ of the model.[15] We are now in a position to derive an estimate for the critical impurity concentration $\bar{C}$ at which the AT occurs in the impurity band. From the data of Fig. 5 for a $K=3$ Bethe lattice, and from the results of Fig. 7 for a 2-D impurity band, we have constructed the concentration dependence of $\delta(\Gamma/\langle J\rangle)_c$, where $\delta=18$ is the scaling factor. Thus $\delta(\Gamma/\langle J\rangle)_c$ corresponds to the "critical" value of the spread of diagonal fluctuations required to accomplish localization in the impurity band. In Fig. 8 we present the concentration dependence of $\delta(\Gamma/\langle J\rangle)_c$

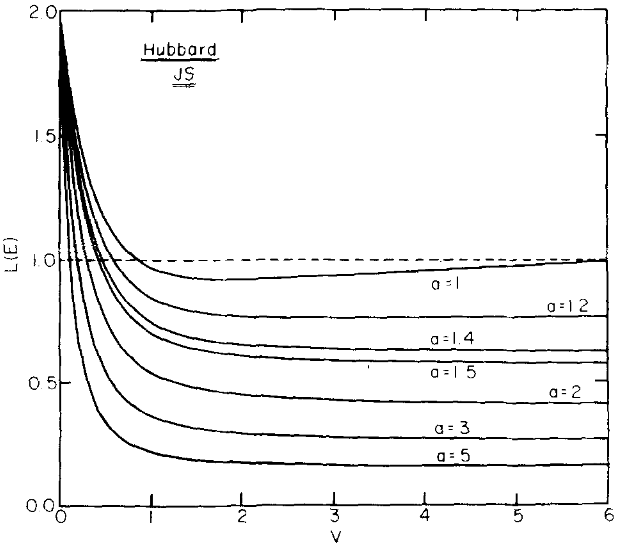

FIG. 6. The localization function $L(E)=0$ in the center of the band for various values of the parameter a. The calculation was performed for a Hubbard lattice with $z=6$, assuming that $K=4.68$ and using the exact self-energy.

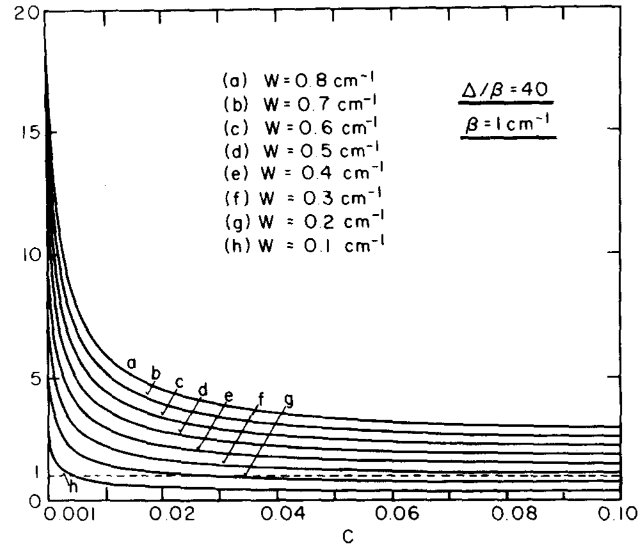

FIG. 7. The concentration dependence of the parameter $a_I = W/z\sigma$ for an impurity band for various values of W. $\Delta/\beta = 40$ and $\beta = 1$ cm^{-1}.

which is identified with $(W/\langle J\rangle)_c$. It is evident that $(W/\langle J\rangle)_c$ exhibits a linear concentration dependence, while in the OAM with $\sigma = 0$ (for $V = 0$) we have $(W/\langle J\rangle)_c \cong 36$ for all impurity concentrations. In Fig. 8 we have also plotted the concentration dependence of $W/\langle J\rangle$. The intersection between the $W/\langle J\rangle$ (for a fixed W) and the $(W/\langle J\rangle)_c$ curves in Fig. 8 results in the critical concentration $\bar{C}$ at a given value of W. It is apparent from Fig. 8 that $\bar{C}$ for the impurity band, where both diagonal and off-diagonal prevail, is lower than the critical concentration for the OAM with diagonal disorder only. In Fig. 9 we exhibit the dependence of the critical concentration $\bar{C}$ on W both for an impurity band model with finite $W/\langle J\rangle$, as well as for the OAM with $\sigma = 0$. These results clearly demonstrate the reduction of $\bar{C}$ due to off-diagonal disorder. The same qualitative feature regarding the reduction of $\bar{C}$ relative to the OAM originates also from an analysis (see Appendix D) based on the Antoniou–Economou CPA self-energy.[13]

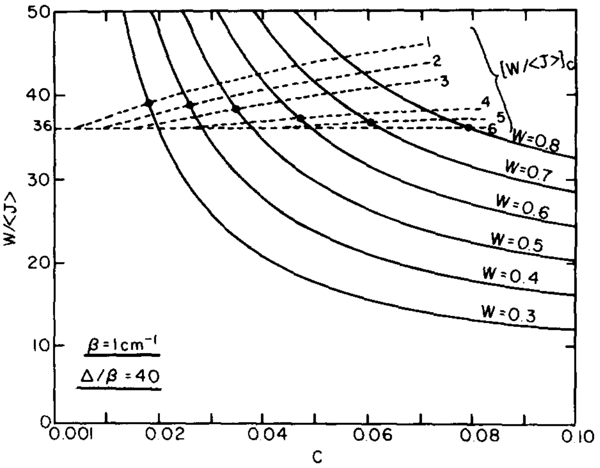

FIG. 8. The shift of the critical concentration $\bar{C}$ to lower values due to the effect of off-diagonal fluctuations. The concentration dependence of $W\langle J\rangle$ vs C for various values of W(cm^{-1}) is represented by the solid curves. The dashed curves represent the concentration dependence of $(W/\langle J\rangle)_c$ (see text) for the following values of W: (a) 0.3 cm^{-1}; (2) 0.4 cm^{-1}; (3) 0.5 cm^{-1}; (4) 0.6 cm^{-1}; (5) 0.7 cm^{-1}; and (6) 0.8 cm^{-1}. The intersection indicated by a black dot corresponds to the critical concentration $\bar{C}$ for a given value of W.

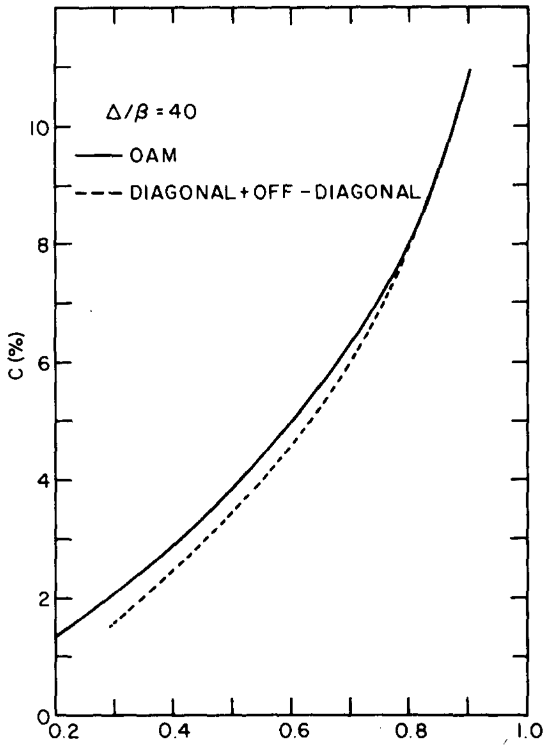

FIG. 9. The dependence of the critical concentration $\bar{C}$ on the magnitude of the inhomogeneous broadening W for the OAM, and when both diagonal and off-diagonal disorder prevail.

V. CONCLUDING REMARKS

From the foregoing results several conclusions emerge:

(1) From the point of view of general methodology the enhancement of delocalization due to off-diagonal disorder results in the lowering of the critical impurity concentration.

(2) From the practical point of view our model calculations indicate that the reduction of $\bar{C}$ due to the contribution of $\sigma/\langle J\rangle$ is not drastic. For example, for $\Delta/\beta = 40$ cm^{-1} and for reasonable values of $W = 0.2$–1 cm^{-1}, $\bar{C}$ is reduced by less than 50% due to the effects of off-diagonal disorder (Fig. 8), while at higher values of Δ/β the reduction of $\bar{C}$ is even smaller. We thus conclude that for sufficiently high values of the inhomogeneous broadening $W \gtrsim 0.2$ cm^{-1}, which seem to be supported by the available recent experimental data for isotopic impurities,[3,7] localization of electronic excitations in mixed crystals originates essentially from the effects of diagonal disorder. Under these circumstances, the OAM, Eqs. (II.7) and (II.8) provides a reasonable approximation for localization and consequent retardation of EET in impurity bands in mixed organic solids.

(3) It is unlikely that off-diagonal disorder completely erodes the localization of an electronic excitation in an impurity band. Our model calculations clearly demonstrate that off-diagonal disorder can destroy the AT, as is evident for the $K=5$ Bethe lattice [see Fig. 4(a)]. However, as long as W is finite $a\to\infty$ when $C\to 0$ and a critical concentration for EET will always be exhibited.

Finally, it will be useful to spell out the basic assumptions inherent in the present treatment of localization in an impurity band. First, it is assumed that inhomogeneous broadening in a dilute isotopic impurity band can be well defined in terms of a random distribution of site-excitation energies. We have discussed the available experimental evidence supporting this conjecture. Second, it is assumed that W is concentration independent. No experimental evidence is yet available regarding this point. For Ruby the experimental data of Koo *et al.*[20] indicate that W increases monotonously with increasing C ($W=0.4$ cm^{-1} at $C=9\times10^{-4}$, $W=0.7$ cm^{-1} at $C=1.4\times10^{-3}$, and $W=1.3$ cm^{-1} at $C=2.3\times10^{-3}$). When $W(C)$ increases with increasing C the details of the treatment should be modified but the general conclusions will be unmodified. As a matter of fact, under these circumstances, one expects to encounter even higher values of a than those obtained when W is independent of C, whereupon the effects of off-diagonal disorder will be even of less importance. Third, we have obtained an exact expression for the self-energy when $a=\Gamma/zV\gtrsim 1$. This condition seems to describe well the situation in an isotopic impurity band where $W>\sigma$. Obviously, when W becomes small $a<1$, the exact self-energy is unavailable, and one should utilize the CPA result (Appendix D) which is applicable for all values of a. Fourth, our treatment rests on localization theories for Lorentzian distributions. To make contact with realistic distributions of the diagonal and of the off-diagonal terms we have introduced our rough scaling arguments, which lack rigorous justification. Fifth, we have applied the localization theory for a Bethe lattice rather than for a real 2-D (and 3-D) system. This is not too bad, in view of the results obtained for a Hubbard lattice, which are similar to those for a $K=5$ Bethe lattice. However, in view of assumptions four and five our results are limited to a semiquantitative description of EET in an impurity band and we shall refrain, at this stage, from detailed comparison between theory and experiment. Sixth, the model calculations rest on the John–Schreiber model, which involves essentially an ordered superlattice, where both diagonal and off-diagonal disorder prevails. This is the origin for the appearance of the loosely defined coordination number z in our theoretical localization conditions. This is a somewhat oversimplified approach to handle localization in an impurity band.

In spite of this self-criticism, which calls for further work, we were able to elucidate the gross features of structural diagonal disorder and of substitutional off-diagonal disorder on EET in an impurity band in mixed organic solids. Our main operational conclusion is that the combination of the available spectroscopic data for W,[3,8] together with the results of the present theoretical analysis, strongly point towards the possibility that the enhancement of delocalization in the impurity band is not severe and that diagonal disorder plays the crucial role in localization of electronic excitations at termination of EET. In subsequent work,[21] we shall explore the confrontation between theory and experiment in this interesting field.

APPENDIX A: THE PROBABILITY DISTRIBUTION FUNCTION OF THE TRANSFER INTEGRALS

Consider a two-dimensional system with an impurity molecule on a given site taken as the origin. The probability to have one nearest neighbor at a distance r is given by

$$P(r)=2\pi Nr\exp(-\pi Nr^2) \tag{A1}$$

for a 2-D system. N is the impurity number density per unit area. To provide an explicit expression for the probability distribution function of the superexchange interaction and its concentration dependence, we start from the interaction between a pair of impurity molecules separated by n host molecules

$$J=\beta(\beta/\Delta)^n\ . \tag{A2}$$

In the quasicontinuum approximation

$$J/\beta=\exp(-\eta)\ , \tag{A3}$$

where

$$\eta=n\ln(\Delta/\beta)\ ;\qquad n=r/d-1 \tag{A4}$$

and d is the lattice constant.

The probability distribution of the transfer integral J is given by

$$P(J)=P(r)\Big/\left|\frac{dJ}{dr}\right|\ . \tag{A5}$$

According to Eqs. (A3) and (A4)

$$J=\Delta\exp(-\alpha r)\ , \tag{A6}$$

where

$$\alpha=\frac{\ln(\Delta/\beta)}{d} \tag{A7}$$

and

$$r=\frac{\ln(\Delta/J)}{\alpha}\ . \tag{A8}$$

From Eqs. (A5) and (A6) we obtain

$$P(J)=\frac{2\pi C}{J}\ \frac{\ln(\Delta/J)}{\ln^2(\Delta/\beta)}\exp\left(-\pi C\ \frac{\ln^2(\Delta/J)}{\ln^2(\Delta/\beta)}\right)\ , \tag{A9}$$

where C is the impurity concentration

$$C=Nd^2\ . \tag{A10}$$

The jth moment of $P(J)$ is

$$M_j=\int J^j\,P(J)\,dJ\ . \tag{A11}$$

We now calculate the first moment $M_1\equiv\langle J\rangle$ using the transformation (A8)

$$\langle J\rangle = 2\pi N\beta \int_d^\infty \left(\frac{\beta}{\Delta}\right)^{r/d-1} r\exp(-\pi N r^2)\,dr \tag{A12}$$

$$= 2\pi N\beta \int_0^\infty (r'+d)\exp[-\alpha r' - \pi N(r'+d)^2]\,dr' \ , \tag{A13}$$

where α is defined in terms of Eq. (A7). Then integral (A13) can be shown to be

$$\langle J\rangle = 2\pi N\beta\exp(-\pi C)\left\{\frac{1}{2\pi N} - \frac{\alpha}{4\pi N}\sqrt{\frac{1}{N}}\exp(y^2)(1-\Phi(y))\right\} , \tag{A14}$$

where

$$y = \frac{\ln(\Delta/\beta) + 2\pi C}{2\sqrt{\pi C}} \tag{A15}$$

and $\Phi(y)$ is the error function with argument (A15). The numerical calculations of $\langle J\rangle$ reported in this work are based on Eq. (A14). To obtain an approximate relation for $\langle J\rangle$ we note that for low values of $C(<0.1)$ and for high values of $\Delta/\beta = 40-100$, we ignore $2\pi C$ in comparison with $\ln(\Delta/\beta)$ in Eq. (A15). Using the relation[22]

$$\sqrt{\pi}\, z\exp(z^2)\,\mathrm{erfc}z \sim 1 + \sum_{m=1}^{\infty} (-1)^m \frac{1\cdot 3\cdots(2m-1)}{(2z^2)^m} \tag{A16}$$

we obtain the useful transparent approximation

$$\langle J\rangle \simeq \frac{2\pi\beta c}{\ln^2(\Delta/\beta)}\exp(-\pi C). \tag{A17}$$

For the second moment $M_2 \equiv \langle J^2\rangle$ we find

$$\langle J^2\rangle = 2\pi N\beta^2 \int_d^\infty \left(\frac{\beta}{\Delta}\right)^{2(r/d-1)} r\exp(-\pi N r^2)\,dr \ . \tag{A18}$$

Utilizing the same procedure adopted to derive the approximate relation (A17), we find

$$\langle J^2\rangle \simeq \frac{\pi c\beta^2}{2\ln^2(\Delta/\beta)}\exp(-\pi C) \tag{A19}$$

and

$$\sigma \simeq \langle J\rangle\left[\frac{\ln^2(\Delta/\beta)}{8\pi c}\exp(\pi C) - 1\right]^{1/2} . \tag{A20}$$

APPENDIX B: THE EQUIVALENCE BETWEEN THE "SUPERLATTICE" APPROACH AND THE UPPER LIMIT APPROXIMATION

While in the present work we handle the localization of an exciton in an impurity band by the $L(E)$ method[13,14] (see Appendix C), there is a different approach to the problem suggested by Abou-Chacra *et al.*[8,9] This alternative approach is based on a self-consistent approximation and is exact for an infinite Bethe lattice. It was demonstrated by Abou-Chacra *et al.*[8,9] that the results of the self-consistent theory for diagonal disorder are close to those of the original Anderson work.[6] The method is based on the study of the self-energy equation

$$S_i = \sum_j \frac{|J_{ij}|^2}{E - \epsilon_j - S_j} \ , \tag{B1}$$

where only the nearest-neighbor interaction J_{ij} is considered. J and ϵ_n are characterized by the distribution functions $P_{0d}(J)$ and $P_d(\epsilon_i)$, respectively. The self-consistency is introduced by finding the probability distribution of S_j which satisfies Eq. (B1). Localization is defined by the requirement that $\mathrm{Im}S_i$ tends to zero as the imaginary part of E tends to zero. Within the framework of the framework of the self-consistent theory, this results in a homogeneous integral equation.

The upper limit approximation was introduced by Anderson[6] by ignoring the real part of S_i. Antoniou and Economou[13] worked out the upper limit in the self-consistent method obtaining

$$K\int dx\int dJ P_d(E_c - x)P_{0d}(J)\left|\frac{J}{x}\right| = 1 \ , \tag{B2}$$

where K is the connectivity, E_c is the mobility edge, i.e., $E_c = 0$ at the AT, and $P_d(E_c - x)$ is the diagonal probability distribution with the argument $E_c - x$. Integrating (B2) over J and assuming that the integration over x depends only on $\langle J\rangle$, one obtains

$$K\langle J\rangle \int dx P_d(E_c - x)|x|^{-1}dx = 1 \ . \tag{B3}$$

This is the self-consistent condition for the occurrence of the AT under diagonal disorder, but with the constant exchange integral J being replaced by the average value $\langle J\rangle$. We argue that in impurity bands of mixed organic crystals diagonal fluctuations overwhelm the fluctuations of the exchange integral, thus Eq. (B2) provides a good approximation for the localization condition. One should notice that K in Eq. (B2) replaces z in a positionally-ordered system. However, K itself represents some effective connectivity of the impurity band.

APPENDIX C

In this Appendix we review the localization theory based on the $L(E)$ method,[13,14] which considerably differs from the self-consistent method of Abou-Charca *et al.*[8,9] and which was discussed in Appendix B. Localization of an excitation is defined, according to Anderson, in the following way. Consider an excitation on site 0 at time $t=0$; P_{00} is the time averaged probability of finding the excitation on the same site 0 at $t=\infty$, then $P_{00}\neq 0$ implies the existence of a localized state. Economou and Cohen[13] showed that P_{00} can be expressed as

$$P_{00} = \lim_{\eta\to 0^+}\left(\frac{\eta}{\pi}\right)\int_{-\infty}^{\infty} dE G_0(E+i\eta)G_0(E-i\eta) \ , \tag{C1}$$

where $G_0(E)$ is the diagonal Green's function in configuration space. Localization is then directly related to $G_0(E)$. Introducing the self-energy $S_0(E)$ for site 0, one obtains

$$G_0(E) = (E - \epsilon_0 - S_0)^{-1} \tag{C2}$$

ϵ_0 being the excitation energy on site 0. P_{00} can now be rewritten as

$$P_{00} = \lim_{\eta\to 0^+}\left(\frac{\eta}{\pi}\right)\int_{-\infty}^{\infty} \times dE\,\mathrm{Im}G_0(E+i\eta)/\{2i\eta - [S_0(E+i\eta) - S_0(E-i\eta)]\} \ . \tag{C3}$$

Equation (C3) demonstrates that the existence of localized states depends on $S_0(E)$ or, more precisely, on the existence of the probability distribution for the self-energy. In order to study $S_0(E)$, Anderson[6] and others[15,16] used the renormalized perturbation series

$$S_0(E) = \sum_{n\neq 0} J_{0n}(E-\epsilon_n - S_n^0)^{-1} J_{n0}$$
$$+ \sum_{\substack{n\neq 0 \\ n'\neq n,0}} J_{0n}(E-\epsilon_{n'} - S_n^{0;n})^{-1}$$
$$J_{n'n}(E-\epsilon_n - S_n^0)^{-1} J_{n0} + \cdots \,, \qquad \text{(C4)}$$

where S_n^0 is the self-energy of site n when site 0 has been removed ($\epsilon_0 \to \infty$). Equation (C4) is now rewritten as a continued fraction using (C4) to get S_n^0, $S_{n'}^{0;n}$, etc., and reinserting them in (C4).

$$S_0(E) = \sum_{n\neq 0} J_{0n}\Big(E - \epsilon_n - {\sum}' J_{nl}$$
$$\times (E-\epsilon_l - \cdots)^{-1} J_{ln} + \cdots\Big)^{-1} J_{n0} \,. \qquad \text{(C5)}$$

Equation (B1) is the first step in this continued fraction expansion. We now define

$$S_0^{(M)}(E) = \sum \prod_{i=1}^{M} \left(\frac{J_{i-1,i}}{e_i}\right) J_{0M} \,, \qquad \text{(C6)}$$

where $e_i = E - \epsilon_i - S_i^{0,n_i\cdots n_{i-1}}$ and the sum extends over all possible terms of order M. Each term may be represented in a diagrammatic way by a self-energy polygon. The contribution of term j to $S_0^{(M)}(E)$ is

$$T_j^{(M)} = \prod_{i=1}^{M}\left(\frac{J_{i-1,i}}{e_i}\right) \,. \qquad \text{(C7)}$$

Defining $x_j^{(M)}$ as

$$x_n^{(M)} = \ln |T_j^{(M)}| \qquad \text{(C8)}$$

one obtains

$$x_j^{(M)} = \sum_{i=1}^{M} (\ln |J_{i-1,i}| - \ln |e_i|) \qquad \text{(C9)}$$

and taking the configurational average, we obtain

$$\langle x_j^{(M)} \rangle = M \ln \frac{\tilde{J}}{\tilde{e}} \,, \qquad \text{(C10)}$$

where $\langle\ \rangle$ denotes configurational averaging

$$N \ln \tilde{J} = \sum_{i=1}^{N} \langle \ln |J_{i-1,i}| \rangle \qquad \text{(C11a)}$$

$$N \ln \tilde{e} = \sum_{i=1}^{N} \langle \ln |e_i| \rangle \,. \qquad \text{(C11b)}$$

Economou and Cohen[19] showed that a localization function $L(E)$ can be defined, such that $|S_0^{(M)}(E)|$ is sharply distributed around $L^M(E)$

$$L(E) = \lim_{M\to\infty} \left(\tilde{J}^{M+1} {\sum}' \tilde{G}_{n_1}\tilde{G}_{n_2}^{0n_1} - \cdots G_{n_N}^{0n_1\cdots n_{M-1}}\right)^{1/M} \,. \qquad \text{(C12)}$$

$\sum'$ indicates summation over all indices $n_1, n_2, \ldots, n_M$ with the restrictions corresponding to all self-avoiding paths of order M starting from and ending at site 0. $\tilde{G}_{n_i}^{0n_1\cdots n_2\cdots n_m}$ is defined from the relation

$$\ln \tilde{G}_{n_i}^{0n_1\cdots n_{i-1}} = \left\langle \ln \left| \frac{1}{E - \epsilon_{n_i} - S_{n_i}^{0n_1\cdots n_{i-1}}} \right| \right\rangle \,, \qquad \text{(C13)}$$

where $S_{n_i}^{0n_1\cdots n_{i-1}}$ is again the self-energy at site n_i with the sites $0n_1, \cdots n_{i-1}$ excluded. Thus if $L(E)<1$ the renormalized perturbation series converges and the corresponding states are localized. The condition $L(E)=1$ defines the mobility edges, while the AT occurs when $L(E=0)=1$. However, $L(E)$ in Eq. (C12) is too complicated for real calculations. Liciardello and Economou[16] introduced an additional approximation

$$G_{n_i}^{0n_1\cdots n_{i-1}} \approx G_{n_i}^{n_{i-1}} \qquad \text{(C14)}$$

and the expression for $L(E)$ is

$$L(E) = K\tilde{J}\,|\tilde{G}_{n_i}^{n_{i-1}}| \,. \qquad \text{(C15)}$$

Equation (IV. 3) of the present paper, derived by Economou and Cohen[16] was utilized for the calculations of $L(E)$.

APPENDIX D

In the present paper we adopted the approach of Liciardello and Economou,[16] as modified by Antoniou and Economou,[13] to the problem of exciton localization, utilizing the exact self-energy of John and Schrieber.[15] In what follows we show that the same general qualitative behavior, due to off-diagonal disorder, is obtained utilizing CPA self-energy of Antoniou and Economou. The Antoniou–Economou scheme is applicable both for a neat disordered system and for an impurity band.

Within the framework of the theory of Antoniou and Economou[13] the system is characterized by the uncorrelated parameters Γ and V. In order to compare the results of this Appendix with the model proposed in Secs. III and IV, we define Γ in the same manner $\Gamma = azV$. However, a is now not restricted by the condition $a \geq 1$. Figure D1 exhibits the localization function $L_{\mathrm{AE}}(E=0)$ obtained from Eqs. (III. 7) and (IV. 7), vs $V/\langle J\rangle$ for several values of a in the range $a<1$. These results demonstrate that for a certain range of values of a and of V, $L_{\mathrm{AE}}(E=0)\geq 1$, whereupon no localization occurs. This complete delocalization is approached at low values of a, i. e., $a \leq 0.5$. In the case of an impurity band the inhomogeneous width W is taken to be independent of C, and V is identified with $\sigma(C)$. $L_{\mathrm{AE}}(E=0)$ is

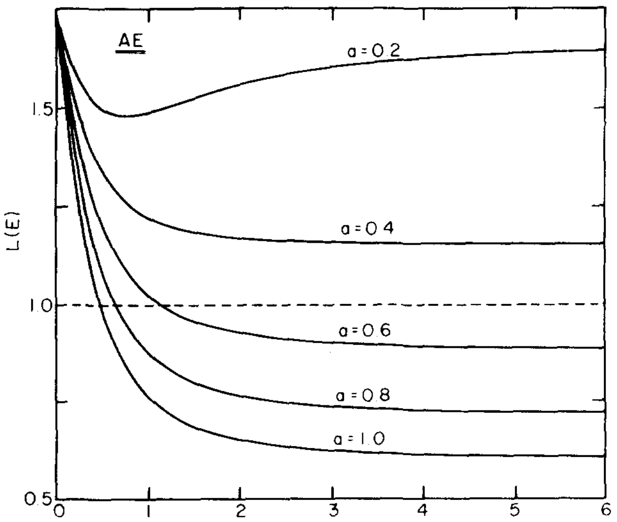

FIG. D1. The localization function $L_{\mathrm{AE}}(E=0)$ calculated for $a \leq 1$ within the framework of the CPA self-energy for a Bethe lattice with $K=3$.

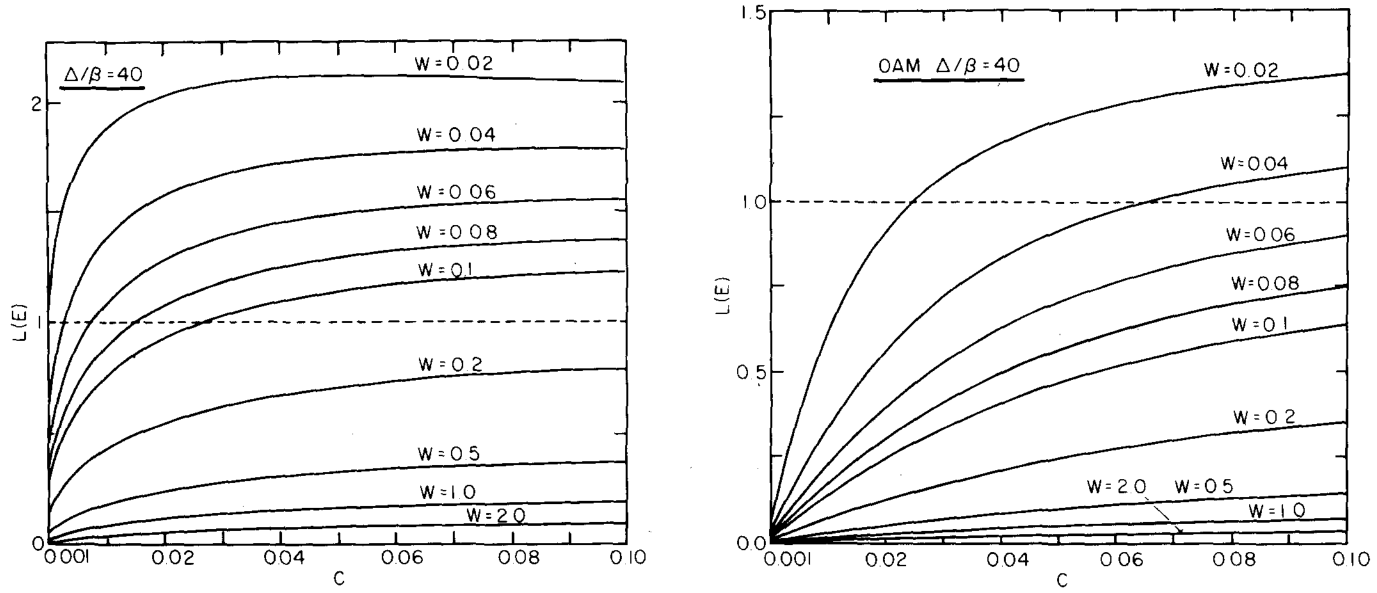

FIG. D2. (a) The localization function $L_{AE}(E=0)$ for $W/\langle J\rangle$ and $\sigma/\langle J\rangle$, calculated using the CPA self-energy; (b) $L_{AE}(E)=0$ with only diagonal disorder $W/\langle J\rangle$. Calculations were performed using the Liciardello–Economou localization criterion. $\Delta/\beta=40$.

then a function of the impurity concentration, the critical concentration $\bar{C}$ being defined by the equation

$$L_{AE}(E=0,\bar{C})=1 \ . \tag{D1}$$

Figure D2 shows $L_{AE}(E=0)$ as a function of concentration for various values of W, both for OAM with $\sigma=0$ and for the simultaneous effect of W on $\sigma(C)$. Here again, $\bar{C}$ is reduced under the effect of the off-diagonal disorder. $\bar{C}$ is found to be in the range $\bar{C}\lesssim 0.1$ for values of W which are smaller than in the model discussed in Sec. IV as no scaling procedure was adopted herein. It should be noted that even when $a<1$ an AT will always occur in the impurity band, although it may be exhibited at very low concentrations. This central feature originates from the fact that $a\to\infty$ as C approaches zero.

Finally, we would like to point out that unlike our model, which essentially considers the impurity band in terms of a superlattice with an effective concentration independent coordination number, the Antoniou–Economou model[13] is independent of z.

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