Electronic energy transfer in impurity bands of mixed organic solids

Joseph Klafter and Joshua Jortner

Department of Chemistry, Tel-Aviv University, Tel Aviv, Israel
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In this paper we consider some implications of the Anderson transition (AT) for the termination of electronic energy transfer (EET) in an impurity band of a low-temperature, isotopically mixed organic solid. The critical impurity concentration $\overline{C}$ for the occurrence of the AT was found to be compatible with the experimental data for triplet EET. The mechanism of EET in extended states was described in terms of a strong scattering, random phase model, which leads to a minimum diffusion coefficient $D_m \simeq 10^{-4} - 10^{-5}$ cm^2 sec^{-1}. Energy transfer from the impurity band to an energy sink (ETFIBTES) from extended states was described in terms of diffusion-controlled kinetics, providing a proper interpretation for the onset of EET in singlet impurity bands, which corresponds to a kinetic threshold, and the critical concentration for EET in triplet impurity bands, which marks the AT. Finally, we considered ETFIBTES from localized states, when the localization length is comparable to the spacing between the energy sinks, proposing a novel method for the determination of the localization length in disordered organic solids.

I. INTRODUCTION

The problem of electronic energy transfer (EET) in an impurity band of isotopically mixed organic solids[1-4] is of considerable current interest. Recent experimental studies of triplet EET in the isotopic impurity band of benzene,[1] naphthalene,[2,3] and phenazine[4] imply the existence of a "critical" concentration $\overline{C}$ of the isotopic impurity below which EET in the impurity band is abruptly switched off. Two distinct models have been advanced to account for this phenomenon:

(a) *The dynamic percolation picture.* Kopelman *et al.*[2] have argued that the states in the impurity band are extended, the EET being determined by superexchange interactions. Energy transfer is limited by the finite lifetime τ of the electronic excitation, so that for $\tau \to \infty$ $\overline{C} \to 0$. This is essentially a kinetic model.

(b) *The Anderson transition.* The present authors have proposed[5] that the critical concentration for triplet EET is a manifestation of the Anderson transition (AT) from extended to localized electronic states,[6] due to the effects of diagonal disorder, which originates from inhomogeneous broadening W of the diagonal site-excitation energies. Recent spectroscopic studies[4,7] of dilute isotopic impurity states provide strong evidence for substantial inhomogeneous broadening, $W \sim 0.1-4$ cm^{-1} within the monomer band. On the other hand, off-diagonal disorder which prevails in any substitutionally disordered binary crystal does not lead to localization.[8,9] We have recently studied[10] the simultaneous effects of diagonal disorder, originating from inhomogeneous broadening and of off-diagonal disorder, arising from the static fluctuations of the interimpurity exchange integrals, which originate from the random distribution of the impurities. We have demonstrated that for reasonable values of W, implied by the available spectroscopic data,[4,7] the effect of diagonal disorder dominates, resulting in an AT.

It is still an open question whether the critical concentration for triplet EET in an isotopic impurity band originates from kinetic effects, as implied by Kopelman and colleagues,[2] or is a manifestation of the AT.

The possible identification of an AT in an impurity band is of considerable interest as it will render the utilization of low-temperature mixed organic solids as useful model systems for the study of the general problem-of localization in disordered materials. In this paper we explore the experimental consequences of the Anderson transition (AT), providing a set of predictions which can be confronted with experiment. We shall consider the AT in an impurity band where the effects of diagonal disorder dominate, so that the role of the energetic spread of the exchange integrals can be disregarded. Accordingly, we shall confine ourselves to a superlattice approximation for the distribution of the impurities. We shall address ourselves to the evaluation of the critical impurity concentration $\overline{C}$ for excitation localization in a system where the exciton band structure is dominated by two-dimensional (2-D) interactions, as is appropriate for triplet excitations in naphthalene and in phenazine. The AT for the appearance of extended states in the middle of the band will be determined by using the upper-limit approximations of Anderson[6] and of Abou-Chacra *et al.*[11] The resulting estimates of $\overline{C}$ are compatible with recent experimental data for triplet EET. Next, we shall explore the features of EET in the vicinity of $\overline{C}$. For impurity concentrations C above the AT, i.e., for $C > \overline{C}$, we account for EET within the extended states by introducing the notion of a minimum diffusion coefficient (MDC), which is evaluated within the framework of the random phase model. The kinetic implications for triplet exciton trapping by energy sinks, such as supertraps or impurity dimers, at $C > \overline{C}$ are elucidated and some new experiments are proposed to determine the MDC. We were also able to advance simple kinetic arguments to provide a proper interpretation of the dramatic difference between the features of EET of triplet excitations and of singlet excitations, which differ by 8 orders of magnitude in their lifetimes. Finally, we consider the interesting problem of EET from localized states at $C < \overline{C}$ to energy sinks. In this context we introduce the concept of the localization length for the excitation in the impurity band at $C < \overline{C}$ and explore the onset of reactivity, $\tilde{C}$, where the energy sink is sensitized. This analysis establishes the relation

between the reactivity threshold $\bar{C}$ and the critical concentration $\overline{C}$, providing a new experimental method for the determination of the localization length in an impurity band.

II. ANDERSON TRANSITION IN THE IMPURITY BAND

The width of the impurity band in an isotopically mixed solid is dominated by superexchange interactions.[1,2] The transfer integral J between a pair of impurity molecules separated by n host molecules is given by[1,2]

$$J = \beta(\beta/\Delta)^n , \tag{1}$$

where β is the near neighbor exchange integral which is invariant to isotopic substitution, and Δ is the energy separation between the trap state and the host exciton band. Equation (1) can be recast in the form

$$J = \beta \exp\{-\ln(\Delta/\beta)[(r/d) - 1]\} . \tag{2}$$

d is the lattice constant and r is a continuous variable introduced when one adopts a quasicontinuum approximation to describe interactions within the impurity band. We note in passing (see Appendix A) that the direct exchange contribution has the same functional form as Eq. (2). In view of the randomness in the intermolecular distances, J is defined by a probability distribution function $P(J)$ which, for a 2-D system, is given by[10]

$$P(J) = (2\pi C/J) \left[\frac{\ln(\Delta/J)}{\ln^2(\Delta/\beta)} \right] \exp \left\{ -\pi C \left[\frac{\ln^2(\Delta/J)}{\ln^2(\Delta/\beta)} \right] \right\} . \tag{3}$$

Confining our model to the superlattice approximation, we characterize the intermolecular interactions by the average value $\langle J \rangle$, which is calculated from the first moment of $P(J)$:

$$\langle J \rangle = \int dJ \, J P(J) . \tag{4}$$

A straightforward calculation leads to the result

$$\langle J \rangle = [2\pi\beta C/\ln^2(\Delta/\beta)] \exp(-\pi C) \tag{5}$$

for a 2-D band structure. The Hamiltonian of the superlattice is now given in the form

$$H = \sum_n \epsilon_n a_n^* a_n + \langle J \rangle \sum_{n<m} a_n^* a_m , \tag{6}$$

where $a_n^*(a_n)$ are the creation (annihilation) operators of the excitation on site n. The site-excitation energies ϵ_n are random variables being characterized by the Anderson rectangular probability distribution function[6]

$$P(\epsilon_n) = \begin{cases} W^{-1}; & -W/2 \leq \epsilon_n \leq W/2 \\ 0 & ; \quad \text{otherwise} . \end{cases} \tag{7}$$

W is the inhomogeneous broadening which is assumed to be constant over the low impurity concentration range $C \leq 0.1$. There are no experimental values of $W(C)$ available for isotopically mixed organic crystals. In ruby, W increases with increasing concentration. Diagonal disorder results in an AT from extended to localized states in the center of the impurity band. This transition occurs when the transfer integral $\langle J \rangle$ takes the numerical value $\langle J \rangle = \langle J \rangle_c$ and when the critical value of the exchange integral is
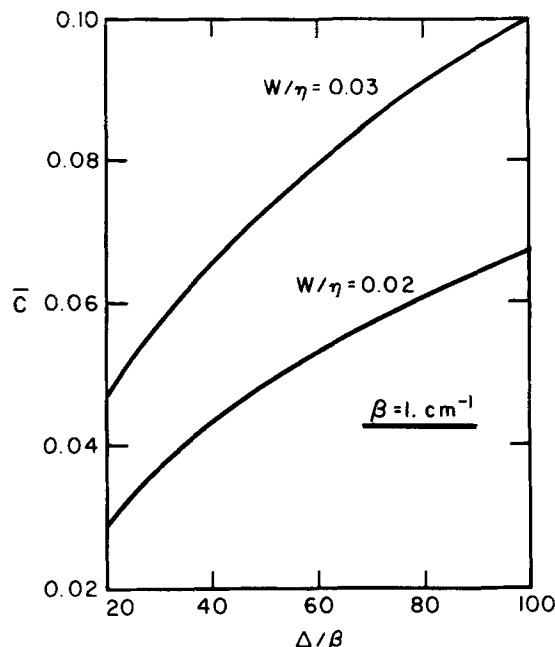

FIG. 1. The critical concentration $\overline{C}$ for the Anderson transition in a triplet impurity band where the impurity–impurity interactions are dominated by the superexchange contribution.

$$\langle J \rangle_c = W/\eta . \tag{8}$$

η is a numerical constant which varies in the range $\eta = 6-28$.[12] Luckily, the general analysis of the experimental results is not drastically affected by this uncertainty in the numerical value of η, as the inhomogeneous broadening $W(\sim 0.1-4 \text{ cm}^{-1})$[4,7] will be just scaled by the same numerical factor. The critical value $\langle J \rangle_c$, Eq. (8), together with Eq. (5), define a critical concentration $\overline{C}$ for the AT which is obtained from the equation

$$\overline{C} \exp(-\pi\overline{C}) = (W/2\pi\eta\beta) \ln^2(\Delta/\beta) . \tag{9}$$

As we are interested in the low concentration range $C < 0.1$, a reasonable estimate for $\overline{C}$ is

$$\overline{C} = [(W/\eta)/(2\pi\beta)] \ln^2(\Delta/\beta) . \tag{9'}$$

This estimate of $\overline{C}$ given by Eq. (9'), which rests on an appropriate averaging procedure, is more reliable than that originally given by us.[5] In Fig. 1 we present the results of model calculations of $\overline{C}$ for localization of triplet states in an isotopic impurity band which is determined by 2-D interactions. The values of $W/\eta \sim 0.02$ used in these estimates imply that $W \sim 0.1-0.6 \text{ cm}^{-1}$, which is in accord with the available spectroscopic data.[4,7] The resulting estimates of $\overline{C}$ are compatible with the available experimental data for triplet EET in the isotopic impurity bands of naphthalene.[2] However, this agreement, although reassuring, does not provide conclusive evidence for the validity of the AT picture, and we proceed to a discussion of some kinetic experiments.

III. MINIMUM DIFFUSION COEFFICIENT

The critical concentration $\overline{C}$ marks the transition from the region of localized states to the range where extended states prevail. At $C > \overline{C}$, EET is exhibited via

the extended states and we assume that the temperature is sufficiently low so that thermally activated transport between impurities for $C < \overline{C}$ is negligible. On the other hand, it is generally agreed that for $C \gtrsim \overline{C}$ EET in extended states can be adequately described in terms of a diffusive strong scattering motion of the electronic excitation. Thus, exciton dynamics in the impurity band are described in terms of the macroscopic diffusion coefficient,

$$D = 0 \qquad C < \overline{C},$$
$$D = D_m \qquad C = \overline{C},$$
$$D = D(C) \qquad C > \overline{C}, \tag{10}$$

where D_m is the minimum diffusion coefficient (MDC). Utilizing the random-phase model of Mott,[13] Cohen,[14] Hindley,[15] and Friedman,[16] together with Mott's assumption[13] that hopping occurs between nearest neighbors, we obtain the following expression for the diffusion coefficient at $C > \overline{C}$:

$$D = (z\langle R \rangle^2 / 4\hbar)(\langle J \rangle^2 / W), \tag{11}$$

where $\langle R \rangle = \Gamma(\tfrac{3}{2})(\pi C)^{-1/2}d$ is the average impurity–impurity spacing and z represents an average coordination number. We note in passing that the relation $D \propto W^{-1}$ was also derived by Haken[17] in the study of exciton hopping assisted by thermal fluctuations, while in the present case we are concerned with excitation scattering due to static diagonal disorder.

To obtain an explicit expression for the MDC we set $C = \overline{C}$, $\langle J \rangle = \langle J \rangle_c$, which is given by Eq. (8), and $z \simeq 4$ resulting in

$$D_m = \langle R \rangle_{\overline{C}}^2 W / \hbar \eta^2. \tag{12}$$

For the 2-D system we set $\langle R \rangle_{\overline{C}} \simeq (\pi \overline{C})^{-1/2}d$, so that

$$D_m = d^2 W / \pi \hbar \eta^2 \overline{C}. \tag{13}$$

Finally, utilizing Eq. (9'), we can recast the MDC in the form

$$D_m = 2d^2\beta / \hbar \eta \ln^2(\Delta / \beta). \tag{14}$$

It is important to note that for the 2-D system the MDC is independent of the inhomogeneous broadening W. This conclusion modifies our preliminary previous results.[5]

To obtain an order of magnitude estimate of the MDC we take $d = 10$ Å, $\beta = 1$ cm^{-1}, $\Delta / \beta = 40$–100, and $\eta = 10$, which results in the reasonable value $D_m \simeq 10^{-4}$–10^{-5} cm^2 sec^{-1}. This numerical estimate is invariant in respect to our original estimate[5] of D_m. To conclude this discussion of the MDC, we would like to point out that Eqs. (11) and (14) for D_m were derived in analogy to Mott's minimum metallic conductivity.[13] This derivation assumes hopping to nearest-neighbor sites. However, in view of the statistical considerations invoked by Thouless,[18] hopping may occur predominantly to further sites. The theory for the MDC presented herein should be considered as a first-order approximation which results in proper order of magnitude estimates. While D_m is not expected to change drastically when hopping to further sites is introduced, the concentration dependence of $D(C)$, Eq. (10), for $C > \overline{C}$ cannot be de-

rived in a reliable manner, and this problem deserves further study.

IV. DIFFUSION-CONTROLLED KINETICS IN EXTENDED STATES AT $C > \overline{C}$

In the experiments conducted up to date the impurity bands were populated either by direct optical excitation or via nonradiative relaxation from the host exciton band. The impurity bands are rather narrow, their bandwidth being $B \sim 10^{-1}$–10^{-3} cm^{-1}, so that $kT \gg B$ in the low-temperature region. Thus, we assert that all the states in the narrow impurity band are equally thermally populated and the existence of extended states in the center of the impurity band is sufficient to ensure EET in extended states, which at $C \gtrsim \overline{C}$ is characterized by the MDC. The occurrence of EET was experimentally interrogated by monitoring the emission from a low-concentration energy sink, i.e., a chemical supertrap[1,2] or an impurity dimer. At impurity concentration $C > \overline{C}$ it is legitimate to consider a kinetic model for the competition between trapping of the excitation in the impurity band by the energy sink and the unimolecular radiative and nonradiative decay of the impurity excited state. The efficiency of trapping of the excitation is determined by monitoring the emission for the energy sink. The relative yield f for energy trapping by the energy sink is

$$f(C) = k_T / (k_T + \tau^{-1}); \quad C \geq \overline{C}, \tag{15}$$

where τ is the lifetime of the excitation in the impurity band and k_T represents the rate of excitation trapping by the energy sink, which for a 2-D system is assumed to be a diffusion-controlled process,[19]

$$k_T = 2\pi D(C) N_S \delta_S,$$
$$\delta_S = \{\ln[(R/2)/(D(C)\tau)^{1/2}] + 0.577\}^{-1}, \tag{16}$$

$R \sim \langle R \rangle$ being the reaction radius, and N_S is the number density per unit area of the energy sinks.

From Eqs. (15) and (16) we conclude that the Anderson transition within an impurity band is amenable to experimental observation provided that: (A) $f(C = \overline{C}) \approx 1$, i.e., $k_T \tau \gg 1$ at $C = \overline{C}$. This condition is satisfied for electronic excitations characterized by long lifetimes. On the other hand, when (B) $f(C = \overline{C}) \ll 1$, i.e., $k_T \tau \ll 1$ at $C = \overline{C}$, the competition between excitation trapping and decay will be exhibited at $C > \overline{C}$. Such a state of affairs will be realized by excitations characterized by short lifetimes. Two distinct physical situations can now be distinguished:

(A) *Critical Threshold for EET.* $k_T \tau \gg 1$ at $C = \overline{C}$. A critical behavior will be experimentally observed. The critical concentration $\overline{C}$ is independent of the excitation lifetime and of the supertrap concentration over a broad concentration region as long as $k_T \gg \tau^{-1}$.

(B) *Kinetic Threshold for EET.* $k_T \tau \ll 1$ at $C = \overline{C}$. The excitation trapping by the energy sink at $C \gtrsim \overline{C}$ is not efficient so that a critical behavior at $C = \overline{C}$ will not be experimentally detected. Instead, a gradual increase of f will be observed for $C > \overline{C}$ and a kinetic behavior of f will be exhibited. The concentration dependence of f

will now be determined by both the excitation lifetime and by the supertrap concentration. As we expect that $D(C)$ increases with increasing C above the AT, then in this case f will reach the value of near unity at some impurity concentration $C_k (> \overline{C})$, where C_k is the kinetic concentration threshold.

Without alluding to any numerical calculations we note that triplet excitations in benzene and naphthalene are characterized by long lifetimes $\tau \simeq 1$ sec and thus will correspond to case (A), while singlet impurity excitations, which are of short lifetimes $\tau \simeq 10^{-7}$ sec, are adequately described by case (B). These simple considerations provide an adequate interpretation for the dramatic order-of-magnitude difference experimentally recorded between the high concentration onset ($C \sim 0.3$ for singlet benzene and $C \sim 0.5$ for singlet naphthalene) for singlet EET and the low concentration onset ($C \sim 0.03$ for triplet benzene and $C \sim 0.09$ for triplet naphthalene) in isotopic impurity bands. Long-lived triplet impurity excitations correspond to case (A) exhibiting the critical concentration for EET, while the singlet impurity excitations correspond to case (B), and their concentration onsets for EET mark a kinetic threshold. As expected, the critical concentration $\overline{C}$ is lower than the kinetic threshold C_k.

The experimental data recorded up to date involve the use of an energy sink for monitoring EET in a low-temperature impurity band. Experimental studies of the mutual annihilation of excitons in impurity bands of mixed molecular crystals will provide essentially a direct measurement of the excitation diffusion coefficient D and will constitute a powerful method for the study of the abrupt jump in D marking the AT and for experimental determination of the MDC. The pioneering studies of Sternlicht et al.[20] on triplet–triplet annihilation in mixed C_6H_6/C_6D_6 demonstrate a concentration dependence of the annihilation rate as well as a reduction in the phosphorescence at $C = 0.02$. These results were obtained at high temperature (4.2 °K), where phonon assisted hopping may be the dominating EET process. Further low-temperature studies in this area will be of considerable value.

V. ENERGY TRAPPING FROM LOCALIZED STATES AT $C < \overline{C}$

The Anderson transition (AT) marks a critical concentration $\overline{C}$ below which the macroscopic diffusion coefficient for the electronic excitation does vanish. However, all experiments conducted up to date utilized energy sinks (supertraps or impurity dimers) at a finite concentration $C_S (C_S \ll C)$ to monitor the EET process within the monomer impurity band. Efficient energy trapping by the energy sinks will occur not only from extended states ($C > \overline{C}$), but also from localized states just below the AT ($C \lesssim \overline{C}$) when the spatial extent of the localized states in the impurity band is comparable to the average separation $\langle R_S \rangle$ between the energy sinks. The spatial extent of the localized states is determined by the localization length.[21,22] Thus, the onset of reactivity for energy transfer from the impurity band to the supertrap will occur when

$$\mathcal{L} \simeq \langle R_S \rangle. \tag{17}$$

The localization length $\mathcal{L}$ depends on the average exchange integral $\langle J \rangle$, Eq. (5), which in turn is determined by the impurity concentration C. Thus the onset of reactivity will occur at an impurity concentration $\tilde{C}$. As the localization length diverges at $C = \overline{C}$ it is apparent that $\overline{C} \geq \tilde{C}$. In general, $\tilde{C}$ depends on the supertrap concentration C_S. We shall now proceed to investigate the dependence of $\tilde{C}$ on C_S. This problem is of considerable interest because of two reasons. First, it provides a well-defined experimental method for determination of critical concentration $\overline{C}$ as the upper limit of $\tilde{C}$ in a system where the trapping by the energy sink is efficient (case (A) of Sec. IV). Second, such studies will provide a novel experimental approach to the direct determination of the localization length in a disordered material.

Consider first the electronic states in the vicinity of the AT. It is generally agreed that below the AT the excitation is described by localized wave functions which are characterized by exponential spatial decay, while above the AT the states are extended[13];

$$\psi(r) = \begin{cases} \sum_n A_n \Phi_n(r - r_n) \exp(-\mathcal{L}_r^{-1}); & C < \overline{C} \\ \sum_n A_n \Phi_n(r - r_n); & C > \overline{C}, \end{cases} \tag{18}$$

where $\{\Phi_n\}$ are molecular wave functions on the sites $\{n\}$, and the amplitudes A_n are random with respect to their phases and amplitudes. Anderson,[21] Lukes,[22] Abram et al.,[23] and Aharony et al.[24] studied the energy dependence of the spatial extent of the localized states in the vicinity of the mobility edge. For the understanding of energy transfer from the impurity band to the supertrap we shall require the dependence of the localization length $\mathcal{L}(E, C)$ on the impurity concentration C at the center $E = 0$ of the impurity band. The hidden assumptions underlying this analysis are: (i) The lifetime of the excitation τ is long relative to the cross relaxation time τ_R from localized to extended states at $C \sim \overline{C}$ within the impurity band; (ii) The trapping time τ_t of the electronic excitation by the supertrap is short relative to or comparable to τ_R. Under these circumstances the $E = 0$ extended states in the center of the band at $C \sim \overline{C}$ are continuously fed by cross relaxation in the inhomogeneously broadened band and are subsequently effectively depleted by trapping to energy sinks. We shall thus determine the impurity concentration threshold for reactivity $\tilde{C}$ for sensitization of the energy sinks by the condition

$$\mathcal{L}(E = 0, \tilde{C}) = \langle R_S \rangle, \tag{19}$$

where $\langle R_S \rangle$ denotes the average separation between the energy sinks. According to Lukes,[22] the localization length for a 2-D impurity band within the framework of the superlattice approximation is given by

$$\mathcal{L}(E, C) = \langle R \rangle \left\{ \left(\tfrac{2}{3}\right) \ln \left[\frac{W \exp(E/W)}{2e\langle J \rangle K^{1/2}} \right] \right\}^{-3/4}, \tag{20}$$

where $\langle R \rangle \cong (\pi C)^{-1/2} d$ is the mean spacing between the impurities which form the impurity band, and K is the
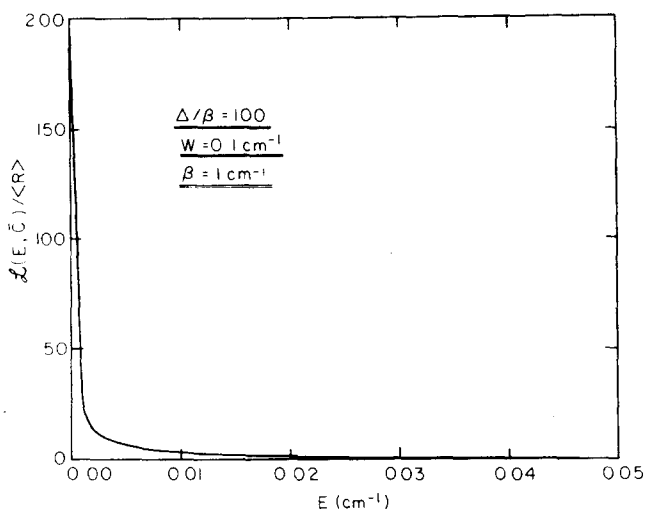
FIG. 2. The energy dependence of the localization length in the 2-D isotopic impurity band at $C = \bar{C}$.

lattice connectivity $(K \cong z - 1)$. The dependence of $\mathcal{L}$ on the impurity concentration C stems from the C dependence of the average exchange integral $\langle J \rangle$, Eq. (5). The critical concentration for the AT is obtained at $E = 0$ for the relation

$$\langle J \rangle_c = W/2eK^{1/2} , \tag{21}$$

where now $\eta = 2eK^{1/2}$. Figure 2 presents the energy dependence of $\mathcal{L}(E, \bar{C})$ demonstrating the divergence of $\mathcal{L}$ in the center of the band. We are interested in the concentration dependence of $\mathcal{L}$ at $E = 0$, which is given by

$$\mathcal{L}(E = 0, C) = \langle R \rangle \{(\tfrac{2}{3}) \ln(W/2e\langle J \rangle K^{1/2})\}^{-3/4} , \tag{22}$$

which, with the help of Eq. (21), takes the form

$$\mathcal{L}(E = 0, C) = \langle R \rangle [(\tfrac{2}{3}) \ln(\langle J \rangle_c/\langle J \rangle)]^{-3/4} . \tag{23}$$

Utilizing Eq. (5) for $\langle J \rangle$ and $\langle J \rangle_c$ we get
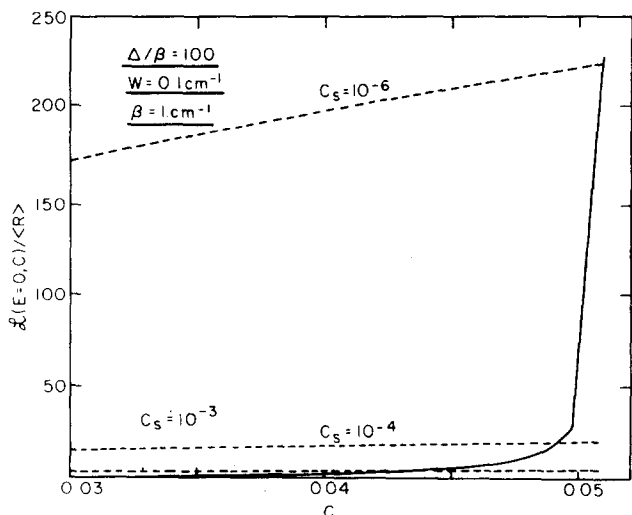

FIG. 3. The concentration dependence of the localization length in the 2-D isotopic impurity band in the center of the band $E = 0$. Solid line portrays $\mathcal{L}(E = 0, C)/\langle R \rangle$. The dashed lines represent $\langle R_S \rangle/\langle R \rangle$ for several values of the supertrap concentrations C_S.
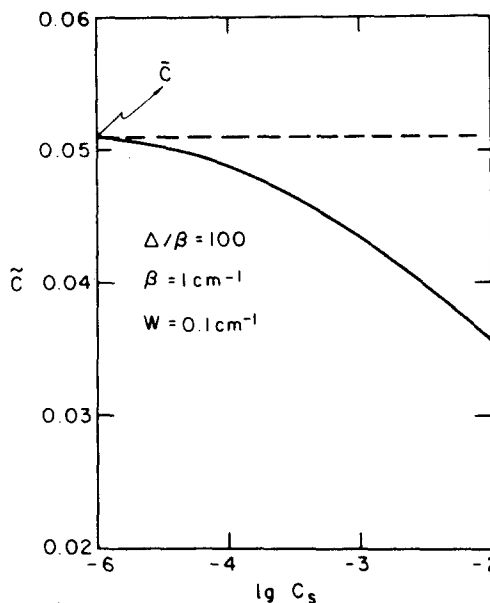

FIG. 4. The impurity concentration threshold $\tilde{C}$ for sensitization of the energy sinks and its dependence of the concentration C_S of the energy sinks. For low values of C_S, $\tilde{C}$ converges to the critical concentration $\bar{C}$.

$$\mathcal{L}(E = 0, C) = \langle R \rangle$$
$$\times ((\tfrac{2}{3}) \ln\{\exp[-\pi(\bar{C} - C)](\bar{C}/C)\})^{-3/4} . \tag{24}$$

In the vicinity of $C \sim \bar{C}$ the localization length obeys a power law. Using the expansion $\ln(1 + x)$, where $x = (\bar{C} - C)/C \ll 1$, we express Eq. (24) in the form

$$\mathcal{L}(E = 0, \bar{C})/\langle R \rangle = g(\bar{C})(\bar{C} - C)^{-3/4} ,$$

$$g(\bar{C}) = (\tfrac{2}{3})^{-3/4}(1 - \pi\bar{C})^{-3/4}\bar{C}^{3/4} , \tag{25}$$

which is the required power law.

Figure 3 exhibits the dependence of $\mathcal{L}(E = 0, C)/\langle R \rangle$, calculated from Eq. (22) on the impurity concentration C. Note that $\mathcal{L}/\langle R \rangle$ diverges at $C = \bar{C}$, which marks the AT. The onset of reactivity is obtained according to Eq. (19) from the intersection of $\mathcal{L}/\langle R \rangle$ with the curves $\langle R_S \rangle/\langle R \rangle = [C/C_S]^{1/2}$ which were calculated for several concentrations of the supertrap and is also included in Fig. 3. The resulting values of $\tilde{C}$ (Fig. 4) for very low values of the energy sink $C_S \leq 10^{-4}$ practically coincide with the critical concentration $\bar{C}$ and the onset of energy trapping by the supertrap is practically independent of C_S over a large concentration range. For higher values of C_S the value of $\tilde{C}$ is somewhat lowered relative to $\bar{C}$. It should be noted that the weak dependence of $\tilde{C}$ on the supertrap concentration at moderately low values of $C_S (\ll C)$ predicted by our model is drastically different from the strong dependence of the threshold for EET on C_S, which emerges from Kopelman's kinetic model.[2] According to our model only for high concentrations of the supertrap $C_S \sim C$ the onset of reactivity $\tilde{C}$ will be drastically reduced so that the AT will be eroded. In the study of triplet EET in 1, 4, 5, 8 $C_{10}D_4H_4$ in $C_{10}D_8$ host, Kopelman et al.[2] reported a threshold of $C \sim 10^{-3}$ for the onset of EET to supertraps, which is considerably lower than the critical concentration observed for

a variety of other similarly mixed crystals. In this system (where $\Delta = 27$ cm^{-1}) the concentration of super-traps is considerably higher than in other systems studied by these workers, so that $C_S \sim C$, raising the distinct possibility that the onset C for reactivity is now exceedingly low.

From the point of view of general methodology, the most interesting conclusion emerging from the present analysis is that the localization length at the center of an impurity band in a low-temperature mixed molecular solid can be experimentally determined by conducting EET studies at various concentrations of the supertrap.

APPENDIX A: DIRECT EXCHANGE IN MIXED ORGANIC CRYSTALS

In this paper we have utilized the approach of Nieman et al.,[25] assuming that the impurity band is dominated by superexchange interactions. However, the qualitative results are independent of the nature of the exponential interaction, being direct exchange or superexchange. When direct exchange is the leading interaction, then

$$J_{ex} = \beta \exp\{-\xi[(r/d) - 1]\}. \tag{A1}$$

$P(J)$ given by Eq. (3) is, of course, a statistical result, being again independent of the form of J. Calculating the mean value of Eq. (A1) with respect to Eq. (3), we obtain[10]

$$\langle J_{ex}\rangle = (2\pi\beta C/\xi^2)\exp(-\pi C). \tag{A2}$$

The ratio between $\langle J\rangle$ corresponding to superexchange, Eqs. (5) and (A2), is then

$$\langle J\rangle/\langle J_{ex}\rangle = \xi^2/\ln^2(\Delta/\beta). \tag{A3}$$

ξ can be deduced from theoretical calculations on the pressure dependence of the crystal parameters and of the intermolecular exchange integrals[26] which result in $(\xi/d) \simeq 2.3 \times 10^8$ cm^{-1} and $\xi \simeq 14$. Thus $\langle J\rangle/\langle J\rangle_{ex} \gg 1$. All the formalism presented in this work considering super-exchange interactions is valid also for direct exchange. We just have to replace the "tunneling factor" $\ln(\Delta/\beta)$ by the exponential parameter ξ. In the case of direct

exchange interaction one should expect no dependence of $\overline{C}$ on the depth of the substituted isotopic impurity.

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