Exciton percolation I. Migration dynamics*

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The exciton transfer, via migration and trapping, in binary and ternary mixed crystals is formulated in terms of percolation theory and the cluster structure for binary randomly mixed crystals. An important limiting case (exciton supertransfer) is derived for long exciton lifetime, relative to jumping and trapping time. The exciton supertransfer case is solved analytically (in terms of the functions derived by J. Hoshen and R. Kopelman, Phys. Rev. B [in press]) and the solutions involve neither physical parameters nor physical constants. Other limiting cases are derived, as well as an algorithm for the general energy transfer case.

This algorithm relates the migration and trapping in binary and ternary systems with the trapping-free migration in binary systems. The algorithm involves the use of empirical information, i.e., the parameters describing the exciton dynamics in a pure crystal. The various formulations are valid for concentrations both above and below the critical ("percolation") concentration, with due emphasis on small, medium, and large cluster contributions. Sample calculations are given (for the square lattice with site percolation).

I. INTRODUCTION

The concept of percolation (see also our earlier paper) has been useful in certain fields of mathematics and physics. In the latter, recent interest has focused on electrical properties of disordered conductors. We have found the concept of exciton percolation a very useful one in the context of energy states and energy migration involving Frenkel excitons in disordered molecular alloys and aggregates.

Exciton percolation, or more precisely, dynamic exciton percolation, is the migration of excitons in disordered condensed phases. It is based on the presence of an exciton conducting quasilattice A. Simultaneously there exists an exciton insulating quasilattice B. Any such quasilattice may be connected or disjoint. The connectivity is operationally defined according to the exciton transfer parameters. Efficient exciton migration is achieved when the A quasilattice is effectively connected. This does not necessarily mean that the B quasilattice is effectively disjoint. The simplest case of exciton percolation occurs in a binary (two component) lattice with random substitutional disorder (especially when the B quasilattice is energetically inaccessible to the A exciton).

Preliminary accounts of exciton percolation experiments carried out in this laboratory have been given, as well as their possible relation with the primary process of photosynthesis. The present paper is the first one in a series of reports designed to define and develop the concept of exciton percolation. We also show the applicability of this concept to the interpretation of existing experimental results, and to the design of new ones intended to shed more light on the problems of exciton migration and coherence in both neat and mixed molecular alloys and aggregates.

Traditionally, condensed state theories start with simplified models involving one-dimensional chains with nearest neighbor interactions. Unfortunately, in one-dimensional systems, the concept of percolation becomes trivial and essentially meaningless. There is a basic analogy here with some other "critical phenomena" such as certain phase transitions. This makes exact analytical solutions very difficult and suggests that from the beginning one should attempt to use a method making use of the availability of modern computer facilities, while at the same time using, as far as possible, analytical solutions and interpolations so as to reduce to an absolute minimum the "computer simulation" game.

An algorithm, both for the general case and for some special limits, is given below, followed by some graphical illustrations based on sample computations. A more detailed treatment of incoherent and semicoherent exciton migration follows in a separate paper.

II. THEORY

Operationally, one measures the exciton flow (migration) with the help of microsensors, fixed or moving, distributed (often at random) throughout the bulk of the alloy (or pure substance). These "sensors" may be a defect site (physical or chemical), a doped-in impurity site, another exciton, a domain boundary, etc. We discuss here a randomly distributed sensor with a given concentration (equilibrium or steady state). The exciton flow rate (transport or migration) monitored by these sensors is therefore proportional to the number of distinct lattice sites visited by the exciton, within its lifetime. We notice that only conducting sites (including "sensors") are visited, and not insulating sites (except in the case of tunneling or by thermal promotion, i.e., modification of the exciton into a more energetic one). We also notice that at the sensor the particular exciton may become annihilated, with a probability as large as unity, while at other conducting sites this probability is usually quite low. (Annihilation of an exciton means its modification into a lower—or higher—energy exciton, a photon, a multiphonon, etc.)

Let the sensor concentration (mole fraction) be \( C_s \). We also need to define \( C'_s \), which is the effective sensor concentration

\[
C'_s = C^\gamma_s,
\]

where \( \gamma \) is the sensors registering (trapping) efficiency. We define the conducting site concentration \( C_t \) of a sensor site \( s \)

\[
C_t = C_t + C_s
\]

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Usually, the sensor sites are a small minority:

\[ C_t \gg C_s. \]  

(3)

The concentration (mole fraction) of the insulating (ballast or host) material \( h \) is obviously

\[ C_h = 1 - C_t. \]  

(4)

With a total number \( N \) of lattice sites, the number of guest sites is

\[ G = NC_e. \]  

(5)

and that of the sensors is

\[ Z = N C_s. \]  

(6)

The number of ways of distributing \( Z \) sensors among \( G \) guest sites is

\[ C_G^Z = \frac{G(G-1)(G-2)\ldots(G-Z+1)}{Z!}. \]  

(7)

The number of ways of distributing \( Z \) sensors among \( G - m \) guest sites is:

\[ C_G^{Z-m} = \frac{(G-m)(G-m-1)\ldots(G-m-Z+1)}{Z!}. \]  

(8)

We are obviously focusing our attention on a particular set of \( m \) guest sites. From the above two equations it is obvious that the probability \( P_m^* \) of not having any of the \( Z \) sensors included in a set of \( m \) sites is

\[ P_m^* = \frac{C_G^{Z-m}}{C_G^Z} = \frac{(1-m/G)[1-m/(G-1)]\ldots[1-m/(G-Z+1)]}{Z!}. \]  

If the fraction of sensors is very small (if not one can use Stirling's approximation) one gets

\[ P_m^* = (1-m/G)^Z, \quad \text{iff} \quad Z \ll G. \]  

(10)

Finally, the probability \( P_m \) for having at least one sensor included in the set of \( m \) sites is

\[ P_m = 1 - P_m^*, \]  

(11)

and thus

\[ P_m = 1 - (1-m/G)^Z, \quad \text{iff} \quad Z \ll G. \]  

(12)

Note that if the above set is small (compared to the ratio of \( C_G/C_s = G/Z \)) one gets, with the help of the binomial expansion

\[ P_m = Zm/G, \quad \text{iff} \quad 1 \ll m \ll G/Z. \]  

(13)

One practical aspect of the above results pertains to the probability of having one of the \( Z \) sensors included in a cluster of \( m \) sites, irrespective of the way one defines such a cluster (see, i.e., Hong and Kopelman\(^a\)). Furthermore, having an exciton confined to an \( m \) cluster, its probability \( F_m \) of registering at any sensor is

\[ 0 \ll F_m \ll P_m. \]  

(14)

Actually, \( F_m \) expresses the cluster's exciton transfer. In the limit of efficient exciton transport, as well as high registration efficiency (the supertransfer case, see below), one gets

\[ F_m = P_m, \quad \text{iff} \quad \text{supertransfer}. \]  

(15)

In the limit of high registration efficiency (\( \gamma \ll 1 \)), Eq. (15) is always justified for very small clusters \((m-1)\). We notice that the exciton transfer efficiency depends both on the exciton transport efficiency within the conducting cluster and the sensor registration efficiency. The transport efficiency, in its turn, is a function of both the propagation rate and the excitation lifetime. In very small clusters \((m-1)\) the propagation is essentially instantaneous. Provided that the registration time is also much shorter than the excitation lifetime, Eq. (15) will always hold.

The probability of confining an exciton onto an \( m \) cluster, provided it cannot "leak out", is the probability of having it enter the cluster. Assuming that the guest-exciton creation is simply proportional to the number of guest molecules, the probability of any guest exciton being created in the given \( m \) cluster is \( m/G \). If the total number of \( m \) clusters ("\( m \) frequency") is \( m^*_m \) then the probability \( P_m \) of creating the exciton in any \( m \) cluster is

\[ P_m = \frac{m^*_m}{m^*}/G. \]  

(16)

Note that

\[ \sum_m P_m = \sum_m \frac{m^*_m}{m^*} = 1. \]  

(17)

Finally, the probability \( B_m \) of any guest exciton being created and registered inside any \( m \) cluster is

\[ B_m = \frac{P_m}{F_m}, \]  

(18)

or

\[ B_m = \frac{P_m}{m^*_m}/m/G. \]  

(19)

The total probability of a guest exciton registering on a sensor is therefore

\[ P = \sum_m B_m = \sum_m \frac{P_m}{F_m}, \]  

(20)

or

\[ P = \sum_m \frac{P_m}{m^*_m}/m/G. \]  

(21)

We note that the cluster frequency \( m^*_m \) and the cluster registration probability \( F_m \) have to be solved as a function of \( C_s \), for the given topology of exciton interactions (and the other factors relevant to exciton transfer and therefore affecting \( F_m \)).

Limit of low guest concentration

Well below the site percolation concentration \( C_s^* \), \( m^*_m \rightarrow 0 \) for large \( m \) and so Eq. (15) will hold for the guest "miniclusters", provided that the transfer efficiency is large enough so as to result in a transfer time small compared with the exciton lifetime. We can then rewrite Eqs. (20) and (21) as

\[ P = \sum_m F_m P_m = \sum_m F_m m^*_m/m/G, \quad \text{iff miniclusters, } \gamma \gg 0. \]  

(22)

Under these conditions, Eq. (13) is also likely to hold, giving thus

\[ P = Z \sum_m (m/G)^Z = ZG^{-1} J_{AV}, \quad \text{iff} \ C_s \ll C_s^*, \ m \ll G/Z, \ \gamma \gg 0. \]  

(23)

or alternatively,
\[ B_m = Z \Delta_m (m/C)^2 = (i_m m^2 G)(Z/G), \quad \text{iff } C_e \ll C_e^* \quad m \ll G/Z, \quad \gamma \gg 0. \] (24)

Notice that we have defined [see Ref. 1] above an "average cluster size" as

\[ I_{AV} = \left( \sum \frac{m}{m} \right) \quad \text{iff } C_e \ll C_e^* \quad m \ll G/Z, \quad \gamma \gg 0. \] (23a)

Limit of high guest concentration

Sufficiently above the site percolation concentration \( C_e^* \) (for the given topology), i.e., \( C_e > C_e^* = C_e^* + 5 \) \( (\delta = 0.05) \), most of the guest sites belong to the "infinite cluster." Simultaneously, all the other clusters are very small \( (\text{miniclusters}) \). We can substitute Eq. (15) into Eq. (22), giving

\[ P = \sum \frac{m}{m} F_{m} + \sum \frac{m}{m} F_{m} \quad \text{iff } C_e \gg C_e^* \quad \gamma \gg 0, \] (25)

Noticing \( \text{that } i_m = 1 \), and using the definition \( P = \frac{m}{m} / G \),

\[ P = \frac{m}{m} / G, \] (26)

one gets (remembering Eq. 16)

\[ P = \sum \frac{m}{m} F_{m} + \sum \frac{m}{m} F_{m} \quad \text{iff } C_e \gg C_e^* \quad \gamma \gg 0, \] (27)

or utilizing Eq. (13) for the miniclusters,

\[ P = \sum \frac{m}{m} F_{m} + \sum \frac{m}{m} F_{m} \quad \text{iff } C_e \gg C_e^* \quad \gamma \gg 0. \] (28)

Remembering Eq. (24), the second term in Eq. (28) is small, giving

\[ P = \frac{m}{m} / \quad \text{iff } C_e \gg C_e^* \quad \gamma \gg 0. \] (29)

However, at the limit where \( C_e \ll C_e^* \),

\[ P = \frac{m}{m} / \quad \text{iff } C_e \ll C_e^* \quad \gamma = 1. \] (30)

Eq. (29) gives

\[ P = \frac{m}{m} / \quad \text{iff } C_e \ll C_e^* \ll C_e^* - 1. \] (31)

Below we shall deal with the evaluation of \( \frac{m}{m} \). Once this quantity is available one has solved not only Eq. (31), but also Eq. (29), as \( \frac{m}{m} \) is often available in the literature \( ^3 \) or can easily be evaluated. \( ^4 \) This also leads to the evaluation of Eqs. (25), (27), and (28), provided that the cluster frequency distribution \( (\text{the set } i_m) \) is available. \( ^5 \) The latter, as mentioned above, is only a function of topology \( (\text{for a given } C_e^*) \).

Intermediate guest concentration

This is essentially the \( C_e \) region close to the percolation concentration

\[ C_e = C_e^*. \] (32)

Well below the percolation concentration, Eq. (22) is a good approximation to the exact expression [Eqs. (20) and (21)]. For intermediate low \( C_e \), Eqs. (23) and (24) are not recommended. One should substitute Eq. (12), rather than Eq. (13), into Eq. (22). Thus Eq. (22) is replaced by

\[ p_m = \sum \frac{m}{m} + \sum \frac{m}{m} \quad \text{iff } C_e \ll C_e^* \quad \gamma \gg 0, \] (33)

which should now be considered as a good approximation to Eq. (21), having now defined \( C_e = C_e^* - \delta (\delta = 0.05) \).

An expression "symmetric" to Eq. (33) can be used above the percolation concentration, based on Eq. (27), but now including lower concentrations (compared to Eq. 28)

\[ P = \sum \frac{m}{m} + \sum \frac{m}{m} \quad \text{iff } C_e > C_e^* \quad \gamma \gg 0, \] (34)

which should again be considered as only an approximation to Eq. (21). Here again \( m' \) designates the maxicluster.

We can both remove the "discontinuity" at \( C_e \ll C_e^* \), and improve on the validity of Eqs. (33) and (34) by realizing that there is a range of \( m \) for which Eq. (15) does not hold, only Eq. (14). We now designate this whole range as \( m'' \) including, above percolation, the maxicluster. We now get

\[ P = \sum \frac{m}{m} + \sum \frac{m}{m} + \sum \frac{m}{m} \quad \text{iff } C_e > C_e^* \quad \gamma \gg 0, \] (35)

where \( \gamma'' \) is a summation excluding the whole set \( m'' \). This expression can now be written as

\[ P = \sum \frac{m}{m} + \sum \frac{m}{m} + \sum \frac{m}{m} \quad \text{iff } C_e > C_e^* \quad \gamma \gg 0, \quad \text{where} \quad m'' \] (36)

where \( m'' \) again designates the maxicluster, if it exists, i.e., if \( C_e > C_e^* \). Again, further manipulation gives

\[ P = \sum \frac{m}{m} + \sum \frac{m}{m} + \sum \frac{m}{m} \quad \text{iff } C_e > C_e^* \quad \gamma \gg 0. \] (37)

The evaluation of \( \frac{m}{m} \) will be described together with that of \( \frac{m}{m} \). In opportune cases both the sets \( m'' \) and the values of \( i_m'' \) will be small. . . . We note that the breakdown of Eq. (15) for the sets \( m'' \) depends not only on \( C_e \) and the topology, but also on \( C_e^* \) and on the intimate details of the exciton transfer mechanism and parameters.

Evaluation of \( \frac{m}{m} \)

The probability \( \frac{m}{m} \) of an exciton (confined to a given \( m \) cluster) registering on any sensor obviously depends on many factors: \( C_e \), \( C_e^* \), \( \gamma \), the interaction topology, the size of \( m \), the shape of the \( m \) cluster, the exciton interactions, lifetime, and transport mode (coherence length, scattering behavior) etc. One way of deriving \( \frac{m}{m} \) is by computer simulation, specifying all the above parameters and conditions, and averaging over crystal configurations (random lattice), cluster shapes, point of origin, sensor distribution, mode of propagation, lifetime, etc. Such "games" can be conducted, but a significant saving in effort and money is achieved with the help of the following algorithm, which gives \( \frac{m}{m} \) as an analytical expression of the sensor concentration \( C_e \), with only one quantity in this expression to be de-
rived from computer simulations that do NOT specify sensor concentrations and registration efficiencies.

Our algorithm is based on the very general derivation of Eqs. (9) to (12). For simplicity we assume first a perfect sensor registration efficiency ($\gamma = 1$). For arbitrary exciton transport efficiency, Eq. (14) holds. We define $n_m$ to be the average number of distinct sites visited, within its lifetime, by an exciton confined to a given $m$ cluster with the condition of $\gamma = 0$ (or $Z = 0 = C_g$). Obviously, one has

$$n_m \leq m.$$  \hspace{1cm} (38)

The probability $F_n$ of this set of $n_m$ sites including at least one sensor is [analogously to Eq. (12) and its derivation]

$$F_n = 1 - (1 - n_m / G)^z,$$  \hspace{1cm} iff $Z \ll G$,  \hspace{1cm} (39)

where the restriction can also be written as

$$Z / G \ll 1.$$  \hspace{1cm} (40)

Now, if we let $\gamma = 1$ this means that the above exciton probability to register on a sensor is

$$\bar{F}_n = F_n, \text{ iff } \gamma = 1.$$  \hspace{1cm} (41)

We note that the above equation holds irrespective of Eqs. (39) and (40). However, utilizing these equations one gets our algorithm

$$\bar{F}_n = 1 - (1 - n_m / G)^z,$$  \hspace{1cm} iff $Z \ll G, \gamma = 1,$  \hspace{1cm} (42)

We note that $n_m$ has to be derived for the given $C_g$, interaction topology, $m$ cluster (size and shape), the exciton interaction parameters, its lifetime and its mode of propagation and scattering. In addition $n_m$ also has to be averaged over cluster shape and composition as well as the exciton origin, propagation, and lifetime.

For the case of $\gamma \neq 1$, two methods of correction suggest themselves. One is to substitute $Z$ in Eq. (42) with

$$Z' = Z/NC_g.$$  \hspace{1cm} (43)

A better alternative, especially for low $\gamma$, is to substitute $n_m$ for $n_m'$ in the maxicluster, where $n_m'$ is the average number of distinct sites visited at least $\gamma^{-1}$ times by the confined exciton (with the condition $Z = 0$ and $\gamma = 1$ rounded to an integer).

The supertransfer limit

In the limit of efficient transfer (supertransfer case), we can write

$$n_m = m, \text{ iff supertransfer},$$  \hspace{1cm} (38a)

for all $m$. This implies a combination of long exciton lifetime and/or large exciton interactions and/or efficient trapping. In this case Eq. (15) is valid. Actually, if one has a large enough sensor concentration (but not too large) and $\gamma 
eq 1$, one always gets Eq. (15) to be valid, i.e., supertransfer, even without Eq. (38), as long as $n_m \gg G/Z$. This gives, similar to Eq. (33), but for all $C_g$ [using Eqs. (12), (15), and (20)],

$$P = \sum_{m}^n F_m P_m = \sum_{m}^P [1 - (1 - m / G)^z],$$  \hspace{1cm} iff $Z \ll G$ and supertransfer,  \hspace{1cm} (33a)

which reduces to [(see Eqs. (16) and (26)]

$$F_n = F_m P_m + \sum_{m'} [1 - (1 - m / G)^z] P_m m / G,$$  \hspace{1cm} iff $C_g \gg C_g$ and supertransfer,  \hspace{1cm} (34a)

We notice that, using Eq. (12),

$$F_n = 1 - (1 - P_m)^z,$$  \hspace{1cm} iff $Z \ll G$ and supertransfer,  \hspace{1cm} (12a)

and even

$$F_n = 1 \text{ iff } 1 \ll Z \ll G, C_g \gg C_g \text{ and supertransfer}.$$  \hspace{1cm} (12b)

Thus Eq. (34a) turns into

$$P = F_m P_m + \sum_{m'} [1 - (1 - m / G)^z] P_m m / G,$$  \hspace{1cm} iff $1 \ll Z \ll G,$  \hspace{1cm} (34b)

$$C_g \gg C_g \gg C_g$$  \hspace{1cm} and supertransfer.

We thus get, similar to Eq. (29),

$$P = P_m + \sum_{m'} [1 - (1 - m / G)^z] P_m P_m m / G,$$  \hspace{1cm} iff $C_g \gg C_g \gg C_g$, and supertransfer,  \hspace{1cm} (29a)

giving, in the limit of Eq. (30), the trivial answer

$$P = 1, \text{ iff } C_g \gg C_g \gg C_g$$  \hspace{1cm} and supertransfer.  \hspace{1cm} (31a)

We can also rewrite Eq. (34b) for regions of small miniclusters, i.e., for both the ranges $C_g \ll C_g$ and $C_g \gg C_g$ utilizing Eq. (13), similar to its use in Eq. (23) and Eq. (28),

$$P = P_m + (Z / G^2) \sum_{m'} [1 - (1 - m / G)^z] P_m m / G,$$  \hspace{1cm} iff $1 \ll Z \ll G$, supertransfer

and $C_g \ll C_g$ or $C_g \gg C_g$.  \hspace{1cm} (34c)

Alternatively,

$$P \approx P_m + \sum_{m'} [1 - (1 - m / G)^z] P_m m / G,$$  \hspace{1cm} conditions as above,  \hspace{1cm} (34c')

where $I_{av}$ is the "reduced average cluster size" (see Ref. 1):

$$I_{av} = G^{-1} \sum_{m'} [1 - (1 - m / G)^z] P_m m / G.$$  \hspace{1cm} (34e)

Note that the region covered by Eq. (34b) but not by Eq. (34c) is that of $C_g$ closer to $C_g$ (whether smaller or larger). Eq. (34c) is still more rigorous than Eq. (29a) and can also be used below the percolation concentration (where $P_m = 0$), as an approximation to Eq. (33).

Large sample limit

Rewriting Eq. (39), utilizing Eqs. (5) and (6),

$$F_n = 1 - (1 - n_m / NC_g)^{NC_g},$$  \hspace{1cm} (44)

or

$$F_n = 1 - \left(1 - \frac{n_m}{NC_g} \right)^{NC_g n_m C_g / C_g},$$  \hspace{1cm} (45)

For very large $N$, i.e., a large crystal,

$$F_n = 1 - \exp(-C_g n_m / C_g), \text{ iff } NC_g / n_m \to \infty.$$  \hspace{1cm} (46)

Furthermore, if

$$C_g / C_g = G / Z \gg n_m,$$  \hspace{1cm} (47)

We notice that the conditional relation of Eq. (48) gives
\[ Z \ll G, \]  
which was crucial to our original derivation of Eq. (10).
This consistency check indicates that Eqs. (46) and (48) can be utilized under the appropriate conditions. We notice the close analogy between Eq. (48) and Eq. (13). However, while we utilized Eq. (13) mainly for the case of small \( m \) clusters, Eq. (48) is most appropriate for use, via Eq. (41), for the case of large (and very large) clusters with inefficient exciton transport, the latter resulting from small exciton interactions and/or short exciton lifetimes and/or an unfavorable cluster topology. We notice that Eq. (46) holds if the dimension of the crystal sample is large compared to the sampling radius of the exciton, while Eq. (48) holds if the average distance to a sensor is also large compared to this exciton radius. The above statements have to be modified appropriately for \( \gamma \neq 1 \), either according to the spirit of Eq. (43) or the alternative proposed in the discussion following it.

### III. EXAMPLES OF RESULTS

Figure 1 gives the supertransfer limit for the probability \( P \) of exciton transfer and registration at the sensor, with sensor concentrations of \( C_s \) in the range \( 8 \times 10^{-3} \) to \( 2 \times 10^{-4} \), as a function of \( C_g \). \( P \) is calculated from Eq. (34b) and its equivalent expression,
\[ P = \left[ 1 - (1 - m/G)^2 \right] L_m/G, \quad \text{iff} \quad 1 \ll Z \ll G, \]  
\text{supertransfer and} \quad C_s < C_s^0. \]  

Figure 2 is a computer simulation of the exciton transfer in the following way: The computer generates the previously described three-component random lattice and the criterion used is essentially that of the previous figure. The question we are asking is whether or not the guest cluster is linked with a sensor. In the limit of supertransfer the end result should be equivalent to that of Fig. 1. The discrepancies arising will be discussed in a subsequent paper, and we'll also compare theory with experiment. As mentioned above, further applications of the algorithm are given separately.

Figure 3 gives some sample calculations according to Eqs. (18) and (42). The values of \( n_m \) were calculated for each guest concentration \( C_g \) using a 500x500 square lattice with cyclic boundary conditions and a random walk program, with 200 000 steps, performed for the
maxicluster (only). Assuming the registration efficiency to be $\gamma = 1$, the probability ($P = B_n$) of any guest exciton being created and registered inside the maxicluster is given for a series of sensor concentrations $C_n$.

IV. DISCUSSION

We note that, while the above examples have been for the oversimplified "classical" case of nearest neighbor interactions, our general formalism [Eq. (42)] is valid for a general kind of physical interactions, including long-range quantum mechanical tunneling. This will be elaborated on in a subsequent paper. It is also applicable for the kind of exchange and superexchange interactions found to exist between impurity sites in inorganic crystals, such as Ruby, as long as one can retain the concept of tight binding, i.e., Frenkel excitons. The following is a brief rationale.

Generally, our model implies that the nature of the excitation (i.e., energy) is practically independent of the size of the cluster. In addition, it implies that the excitation is essentially confined to the guest cluster. In this respect it is a classical particle picture and not one of quantum mechanical wave packets. However, our model allows the presence of the "host" to influence the nature of the bonds connecting such sites into a cluster. Thus, physically, the host influences the effective connectivity of the guest quasilattice. For instance, a physical picture in which the excitation has a small amplitude on the host sites translates into a "classical" mathematical model of guest "bonds" crisscrossing the host quasilattice. This is analogous to molecular theory, where "stick and ball" (or spring and ball) models go a long way towards the characterization of molecular symmetry, topology and dynamics (even though the treatment of electronic excitations, in contrast to vibrational ones, usually involves an approximate quantum mechanical solution).

For the case where the nature of the excitation would critically depend on the cluster size, as for large radius excitons (Wannier-Mott or charge-transfer), our model has to be dealt with very carefully. The same is true for the case of an excitation which is significantly shared between guest and host, or oscillates rapidly between being a guest excitation and being a host excitation (i.e., thermal activation and deactivation). In the latter case a possible avenue of mathematical modeling may involve the replacement of the cluster concept by that of the conglomerate. However in any of the above cases, once a correct description, whether classical or quantum mechanical, is available and amenable to giving for the binary system the information required to get effective values of $n_\text{e}$, then the mere knowledge of an effective $\gamma$ (or $\tilde{n}_\text{e}$) will give the complete description of the ternary system, with the use of Eq. (42) or its equivalents for $\tilde{n}_\text{e}$, modified by Eq. (43), as well as an augmented Eq. (36). The augmentation of Eq. (36) involves the replacement of $P_n$ [given by Eq. (16)] with $P_n$ depending on the physics of the small cluster exciton. Future papers in this series will deal specifically with problems of increasing complexity, in conjunction with experimental studies designed to test the validity of our simplifications.

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See, for instance, J. Koo, L. R. Walter, and G. Geschwind, Phys. Rev. Lett. 35, 1669 (1975). However, in this particular experimental situation we wonder to what extent the thermal activation and deactivation require explicit recognition.