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Publication Date

1977-03-01

Submitted to Journal of Chemical
Physics

LBL-5793
Preprint c.1

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March 1977

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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ENERGY TRANSFER IN ONE DIMENSIONAL SUBSTITUTIONALLY DISORDERED SYSTEMS.

I. THE EFFECTS OF COHERENCE, TUNNELING AND THERMAL PROMOTION.

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ABSTRACT

A theory for energy transfer in substitutionally disordered solids is presented that includes the effects of coherent and incoherent migration of the wavepacket, the statistical distribution of fluctuations in the potential energy surface the wavepacket encounters, and tunneling. Explicit expressions for the "diffusion" coefficient in these limits and the energy-partitioning ratios in binary systems are derived. It is also shown that an activation energy dependent upon the composition of the binary system can emerge from such a treatment and is an indication that energy transfer between localized states is facilitated by concurrent tunneling and thermal promotion.

I. INTRODUCTION

Energy transfer in many solid state and biophysical systems is characterized by substitutional or structural disorder induced by chemical and ionic impurities, irregular bond conformation, or disordered site distribution. In multi-dimensional systems such as amorphous semiconductors, the concepts of amalgamation and percolation theory[1] have been applied with moderate success in explaining the behavior of electrical conduction. Although the percolation concept may be applied to problems where the solid can be considered two- or three dimensional[2] it is not applicable to one-dimensional systems, which may be of great importance in intra-molecular energy transfer in large biomolecules as well as the class of one-dimensional organic conductors. In addition, one-dimensional systems[3] are exemplified by electronic energy or Frenkel exciton migration[4] in molecular crystals. These crystals serve as effective model systems in which to investigate the effects of substitutional disorder since isotopic substitution provides a method of introducing well-characterized small perturbations into the periodic potential without disturbing the crystal structure.

In an unperturbed crystal, the localized degenerate excited states of the molecule interact to form delocalized band states. Exciton mobility within these bands is determined by the magnitude and dimensionality of the interactions, the strength of coupling with lattice phonons, and the lifetime of the excited state. Modes of exciton migration range from the propagation of coherent exciton wavepackets[5] over many molecular sites to short-range diffusive "hopping" between adjacent molecules.[6] Isotopic substitution can reduce the delocalized bands to localized regions, making exciton mobility additionally dependent on the isotopic shift and the concentration of the substituent. As the mole fraction of a low energy isotopic trap is increased, one expects the potential surface along which the exciton travels to change from a delocalized host band interrupted by localized trap states to extended trap states interrupted by narrow barriers comprising the remaining host molecules. In such cases, the exciton mobility will be limited by the rate of transfer through or around the barrier sites. It is clear that percolation theory cannot be applied to substitutionally disordered systems when the intermolecular interaction responsible for energy transfer is principally between molecules related by translational symmetry along one axis of the crystal and vanishingly small along the others[7]. In these cases, at least three distinct modes of transfer are available: (i) the exciton may tunnel through the higher energy host molecules[8]; (ii) it may be thermally promoted by a phonon to the host band states and make its way to another trap state at a rate dictated by its mobility in a pure band[9]; (iii) finally, if the bandwidth is large enough to mask a much smaller isotopic shift, this analysis is inappropriate and exciton migration will approach an unperturbed-crystal-type behavior termed amalgamation[1,10].

In this first part of this paper, we present a theory that accounts for both the coherent nature of the wavepacket and the statistical distribution of fluctuations in the potential energy surface the wavepacket encounters. It is based on tunneling thru simple barriers whose heights are determined by differences in the zero point energy between isotopic substituents. The development proceeds from a simple but well defined model system in which only one distribution of the potential energy surface is available to the wavepacket. The effects of coherence are included in the model system and compared to the diffusive "random walk" limit. Expressions for "effective" diffusion coefficients in both limits are derived and compared to the uncorrelated migration model.

II. ENERGY TRANSFER IN DISORDERED SYSTEMS WITH A PERIODIC DISTRIBUTION IN THE PERTURBED POTENTIAL.

For our discussion, a simple disordered system may be defined by a series of identical barriers in the crystal potential field as shown in Fig. 1. The barriers are formed by molecules of the higher energy isotopic species and the distribution of barriers is such that one barrier of unit molecular dimensions occur every S_1 lattice sites. The intermolecular spacing is taken as $\underset{\sim}{a}$ and the barrier spacing is given by $S_1\underset{\sim}{a}$. Passage of a migrating exciton through a barrier may take place either by direct tunneling or by thermal promotion, but if all the barriers are identical, the exact nature of the process can be left unspecified and passage through the barrier is described by a constant transmission coefficient T. In a complex disordered system, differences in barrier heights and widths make the nature of the barrier transmission process critical to the exciton dynamics.

Within the interval between two barriers, the mode of exciton motion may be treated in two limits, the random walk "hopping" of a localized excitation or the coherent propagation of an exciton wavepacket over a distance equal to $S_1\underset{\sim}{a}$. The random walk "hopping" frequency between adjacent molecules is defined as ν_r, and is determined by the intermolecular interaction, β , according to

$$\nu_r = 4\beta/h \tag{1}$$

The coherent exciton, on the other hand is characterized by a wave vector k and a group velocity $V_g(k)$ which determine an intermolecular transfer frequency between adjacent molecules defined as ν_c. In the coherent limit, the group velocity is given by

$$V_g(k) = \frac{1}{\hbar}\ (\partial E(k)/\partial k) \tag{2}$$

and hence the transfer frequency as a function of wave vector is given simply as

$$\nu_c(k) = V_g(k)/\underset{\sim}{a} \tag{3}$$

For a Boltzmann distribution in the band, $V_g(k)$ should properly be thermally averaged[11] over the k states in the extended band in the interval $S_1\underset{\sim}{a}$. In such case, the average group velocity $V_g(T)$ is given by

$$\langle V_g(T)\rangle = \sum_k \frac{1}{\hbar}\,\frac{\partial E(k)}{\partial k}\,e^{-E(k)/kT} \Big/ \sum_k e^{(E(k)/kT)} \tag{4}$$

where the sum over k extends over the S_1 sites in the interval $S_1\underset{\sim}{a}$. Equation (4) rapidly converges for $S_1 > 20$ to a Bessel function form as

$$\langle V_g(T)\rangle = \frac{2\beta a}{\hbar}\left(\frac{2kT}{\pi\beta}\right)^{1/2}\left[I_{1/2}(Z)/I_0(Z)\right] \tag{5a}$$

where

$$Z = 2\beta/kT \tag{5b}$$

$$I_0(Z) = (1/\pi)\int_0^{\pi} Z\cos\Theta \tag{5c}$$

$$I_{1/2}(Z) = \left(\frac{1}{2}Z/\pi\right)^{1/2}\int_0^{\pi} e^{\pm Z\cos\Theta}\,\sin\Theta\;d\Theta \tag{5d}$$

This is because of this fact there is little difference between the maximum value of $V_g(k)$ when k is discrete as in Eq. (4) or continuous as in Eq. (5). In both, the maximum occurs in the center of the bands at $|k| = \frac{\pi}{2a}$ and has a value for large S_1 of:

$$V_g^{max} = \frac{1}{\hbar}\left[\frac{\partial}{\partial k}\left(E_o + 2\beta \cos ka\right)\right]_{|k| = \pi/2a} \cong \frac{2\beta a}{h} \qquad (6)$$

A. Exciton Diffusion: General Considerations.

Long range exciton diffusion in the crystal depends on transfer between extended band states separated by intervening barriers. A critical parameter is the average time spent in an extended trap state between two barriers each a single site in width. This is equivalent to the effective tunnelling time through a barrier and for a single barrier is defined as τ_1^c. This time strictly determines mean exciton dynamics in disordered systems and its calculation is of central importance in any question of one-dimensional energy transfer. Fig. 2(a) illustrates the process. τ_1^c depends on the number of trap molecules over which the exciton may delocalize S_1, the barrier transmission coefficient T, and the intermolecular transfer frequency, $\nu=\nu_r$ or ν_c in the case of diffusive or coherent propagation, respectively.

The exciton begins its migration thru the interval from a site adjacent to the barrier through which it has just passed. If the motion is completely coherent, the exciton is reflected back and forth with constant absolute momentum between the two barriers, colliding with a barrier every S_1 jumps. However, if the motion is random, probability theory predicts that the exciton, beginning from a site adjacent to a barrier, will still collide with some barrier every S_1 jumps[12]. This may be seen as the average of many collisions with the near barrier requiring only one or a few jumps and a few collisions with the far barrier requiring approximately S_1^2 jumps. In either the coherent or random walk limit, the average number of intermolecular jumps can be expressed as

$$\langle S\rangle = \sum_{i=1}^{\infty} T(1-T)^{i-1}(iS_1) \Big/ \sum_{i=1}^{\infty} T(1-T)^{i-1} = \frac{S_1}{T} \qquad (7)$$

where iS_1 is the number of jumps completed after i collisions and $T(1-T)^{i-1}$ is the probability of transmission on the i th collision which is used to derive the weighted average of i S_1. The product of the average number of jumps before barrier transmission, $\langle S\rangle$, and the time per jump between band molecules, ν^{-1}, gives the effective jump time between intervals, τ_1^c :

$$\tau_1^c = \nu^{-1} \langle S\rangle = S_1/T\nu \qquad (8)$$

The physical significance of the expression is quite simple. $T\nu$ is the probability of transmission per unit time from a molecule adjacent to the barrier, but the effective tunneling time is increased by the S_1 molecules on which the exciton may sit. The exciton diffusion coefficient, which describes exciton dynamics, is

$$D = \frac{1}{2}(S_1 \underset{\sim}{a})^2/\tau_1^c = \frac{1}{2}\underset{\sim}{a}^2 S_1 T\nu \qquad (9)$$

which differs for the random walk and coherent limits only so far as ν differs.

One important assumption has masked differences in the functional dependence of the diffusion coefficient between the random walk and coherent migration limits. We have assumed that the likelihoods of transmission through each of the two barriers on the interval are equal, independent of the initial position or momentum of the exciton. Given a sufficiently long exciton lifetime within the interval, this condition is met but a relatively large transmission coefficient will cause a significant change in exciton dynamics by allowing a high probability of escape from the interval before a symmetric population density is achieved.

B. Exciton Diffusion: Random Walk Limit

In the random walk limit, uniform population population density in an interval S_1 molecules wide is effectively achieved in S_1^2 jumps, as illustrated in Fig. 3. The exciton begins its movement in the interval from a site adjacent to the barrier through which it has just passed from an adjacent interval. It will collide with this "near" barrier several times during the first S_1^2 jumps before it sees the "far" barrier, making the likelihood of passage back through the near barrier greater than for the far barrier. The resulting correlation between successive jumps[13] acts to keep the exciton in the vicinity of the near barrier. The problem is treated by calculating how many collisions with the near barrier occur during the initial S_1^2 jumps and allowing successful transmission during these jumps to cancel out the previous jump into the interval, thus decreasing the overall frequency of migration between intervals, $1/\tau_1^c$. This corresponds to finding the number of returns to origin in S_1^2 jumps, $\langle N\rangle$, where the origin is the site adjacent to the near barrier, and the average number of collisions with the barrier at each return to origin, C, where

$$\langle C\rangle = \sum_{i=o}^{\infty} i/2^{i+1} = 1 \tag{10}$$

Eq. (10) is an average of the number of collisions with the barrier for each return to origin, i, weighted by the probability of that number of collisions, $\left(\frac{1}{2}\right)^{i+1}$. For example, the exciton has a 50% probability (probability = $\frac{1}{2}$) of jumping away from the barrier on its first jump with zero barrier collisions, a probability = $\frac{1}{4}$ of reflecting off the barrier once and then jumping away for a total of one collision, and so forth. Follow this reasoning, $\langle N\rangle$is given as

$$\langle N\rangle = \sum_{N=0}^{S_1^2/2} N \left(\frac{1}{2}\right) S_1^{2-N} \left(\frac{(S_1{}^2-N)!}{(S_1{}^2/2)\,!\,(S_1{}^2/2-N)!}\right)$$

$$\Bigg/ \sum_{N=0}^{S_1^2/2} \left(\frac{1}{2}\right) S_1{}^2{-}N \left(\frac{(S_1{}^2-N)!}{(S_1{}^2/2)\,!\,(S_1{}^2/2-N)!}\right) \tag{11}$$

The term repeated in numerator and denominator is the probability of N returns to origin in $S_1{}^2$ jumps[14], so eq. (11) is a simple weighted average of N. <N> cannot be simplified in the general form, but a numerical solution in the range $S_1^2 = 10\text{-}50$ gives a simple form linear in S_1

$$\langle N\rangle \cong 0.75\, S_1 - 0.675 \tag{12}$$

The probability of escape from the interval before a symmetric population density is achieved is defined as P_e and is given by:

$$P_e = \sum_{N=1}^{\langle N\rangle} \left(T(1-T)^{N-1}\right) \simeq \langle N\rangle T \text{ for } T \ll 1 \tag{13}$$

By allowing each barrier jump which occurs before symmetric population density is achieved to cancel out the barrier jump directly preceding it, the effective jump frequency between intervals is decreased and in a periodic perturbed potential.

$$\left(1/\tau_1{}^c\right)_{eff} = \left(1-2P_e\right)\left(1/\tau_1{}^c\right) \tag{14}$$

In such cases the random walk diffusion coefficient, is given by:

$$D_r = \frac{1}{2}\left(S_1 a\right)^2 \ (1-2\langle N\rangle T)/\ \tau_1^c \tag{15}$$

C. Exciton Diffusion: Coherent Limit

In the perfect coherent limit, the delocalized wavepacket can elastically scatters off the two barriers alternately. The probability of passing through the far barrier, P_f, which always undergoes the initial collision because of the wave vector momentum carried over from the last barrier transmission, will be greater than P_n, the probability of passing through the near barrier. The far barrier withstands the first, third, fifth, and succeeding alternate collisions with probability of transmission T on the first collision, R^2T on the third, R^4T on the fifth, and so forth. Likewise, the near barrier feels the second, fourth, sixth, etc. collisions with similar progression in transmission probabilities. Therefore,

$$P_f = T + R^2T + R^4T + \ldots\ldots = \frac{1}{2-T} \tag{16a}$$

$$P_n = RT + R^3T + R^5T + \ldots\ldots = \frac{1-T}{2-T} \tag{16b}$$

The effect on the diffusion coefficient of the correlated transfer between the intervals due coherent transfer within intervals is to lengthen the effective jump distance, λ_{eff}.

$$\lambda_{eff} = \left(1 + (P_f - P_n) + (P_f - P_n)^2 + \ldots\right) S_1 \underset{\sim}{a}$$

$$= \frac{2-T}{2-2T} S_1 a \qquad [17]$$

The term $P_f - P_n$ gives the probability of travelling a second interval coherently due to the correlated motion. $(P_f - P_n)^2$ and higher order terms allow for three or more intervals to be passed through coherently and these terms converge quickly for moderate T to the value given, which is greater than the length of a single interval. The probability of making the second correlated jump falls exponentially with time, so two correlated barrier jumps, if they occur, will take little longer than a single barrier jump. τ_1^c still provides a time base on which to define the equivalent of a diffusion coefficient for coherent propagation, D_c.

$$D_c = \frac{1}{2} \lambda_{eff}^2 / \tau_1^c = \frac{1}{2} \left(\frac{2-T}{2-2T}\right)^2 S_1^2 a^2 / \tau_1^c \qquad [18]$$

D_c is a limiting value. If the exciton coherence is lost in a time short with respect to τ_1^c but long with respect to ν_c^{-1}, the coherence length lies between $S_1 \underset{\sim}{a}$ and $\underset{\sim}{a}$, but exciton dynamics approach the random walk limit very slowly due to the greater delocalization efficiency of even partially coherent migration. Both eq. [15] and [18] reduce to eq. [9] for uncorrelated motion in the small T limit, but it should be noted the D_c and D_r have different dependences on both S_1 and T in the large T limit. Fig. 4 shows the particularly interesting T dependence of diffusion, where correlated motion due to coherence produces a slight increase in the diffusion coefficient over the uncorrelated model, while correlated motion due to the random walk produces a sharp decrease. An experiment where T can be varied, such as a temperature variation where thermal promotion over barriers is important, should distinguish between the two models.

III. ENERGY TRANSFER IN DISORDERED SYSTEMS WITH A STATISTICAL DISTRIBUTION OF PERTURBED POTENTIALS.

In this portion of the paper, we apply these insights to more complex disordered systems, differentiating between mechanisms of energy transfer within the context of the energy partitioning experiments which are the standard probes of such systems[15]. The limiting cases of tunneling and thermal promotion (as well as a hybrid case) are illustrated for a range of physically realistic parameters. Experimental results for singlet and triplet exciton migration in a disordered pseudo-one-dimensional molecular crystals follow in a separate paper[16].

A. Direct Transfer

Physically realistic and useful models of exciton transfer in a two-component substitutionally disordered system must hold over the entire concentration range. Increased barrier molecule concentration leads to the formation of a statistical distribution of aggregate barriers of two, three or more adjacent barrier molecules and the nature of the transmission process which sets the relative transmission coefficients for the different barriers becomes extremely important. At sufficiently low temperatures, exciton transfer between localized trap states is determined by resonant tunneling. Fig. 5 illustrates this process for tunneling from single traps.

If the intermolecular interaction, β, is the same for both components, as in isotopic mixtures, the interaction energy between two traps separated by n barrier molecules[17] is

$$\beta_n = \beta^{n+1} \Delta^{-n} \tag{19}$$

where Δ is the trap depth. A simple quantum mechanical resonance model predicts a transfer time across the barrier.

$$\tau_n = h/4\beta_n \tag{20}$$

Because the width of the barriers is so critical to the transmission time, the system may be treated within the concept of a hierarchy of barriers. The interval between single barriers will contain S_1 unperturbed trap molecules,

$$S_1 = x^{-1} \tag{21}$$

where x is the barrier molecule mole fraction. A random isotopic distribution is assumed. On the next step of the hierarchy, the interval between double barriers contains S_1 intervals bounded by two single barriers or a single barrier and a double barrier, as in Fig 2 (b). Likewise, the interval between triple barriers contains S_1 intervals bounded by double barriers and so forth. The important requirement in order to apply this framework to exciton dynamics is that the matrix element for tunnelling through a barrier n molecules wide,

β_n, is so much larger than the matrix element for passing through a barrier n-1 molecules wide, that all smaller intervals within a larger interval will be visited by the exciton before it escapes from the larger interval. This equivalent to the requirement that $T \ll 1$ where $T \cong \beta/\Delta$, so that no correlated motions need be considered and exciton transfer between intervals may be treated by simple random walk statistics.

In the first section, an expression for the effective tunneling time thru a single barrier, τ_1^c, was derived. According to the hierarchy of barriers argument, the expression for a double barrier, τ_2^c, can be derived assuming that the basic unit between two couble barriers is not a single trap molecule, but an extended trap state between two single barriers. In such cases:

$$\tau_2^c = \tau_1^c \ \langle S \rangle = h\Delta^2/4\beta^3 \ x^2 \tag{22}$$

The higher terms are derived analogously, with the tunneling time across an n molecule wide barrier determined by a random walk between intervals surrounded by n-1 molecule wide barriers. The general term is given by:

$$\tau_n^c = \frac{h}{4\beta}\left(\frac{\Delta}{\beta x}\right)^n \tag{23}$$

B. Energy Partitioning Between Mobile and Stationary States.

The tunneling model with its characteristic times can be applied to the problem of energy partitioning between[15] "mobile" trap states, out of which the exciton may tunnel, and "stationary" trap states, in which the exciton is trapped over the excited state lifetime. Figure 6 shows schematically the potential surface of such a ternary system. The model proposes that excitons are unable to pass through barriers n+1 or more host molecules wide during the excited state lifetime. The excitons sample intervals between barriers of n hosts according to random walk statistics with a characteristic jump time τ_n^c, and a limiting excited state lifetime, T. The effect of smaller barriers is incorporated within τ_n^c. The fraction of exciton population reaching a stationary trap is a function of the number of sites visited and the site probability (or mole fraction) of the stationary trap, x_s.

Let c_n be the fraction of excitons which do not have access to a stationary trap unless they cross an n+1 molecule wide barrier and t_n be the concentration of barriers n+1 molecules wide or wider. c_n and t_n are given by:

$$t_n = x^{n+1}(1-x) \tag{24}$$

$$c_n = \left[(t_n'-1)/t_n'\right]^{x_s} \tag{25a}$$

while,

$$x_s'/t_n' = x_s/t_n \quad x_s' \quad t_n' << 1, \tag{25b}$$

and c_n converges rapidly for large x'_s and t'_n. X'_s and t'_n are the number of stationary traps and impassable barriers, respectively, in an arbitrarily large volume of the system. t'_n is also the number of intervals between impassable barriers. The probability that one such interval in the arbitrarily large volume will not contain a stationary trap is the number of ways of distributing x'_s traps in all the other $t'_n - 1$ intervals, $(t'_n - 1)^{X'_s}$, divided by the number of ways of distributing these traps in all the intervals, $t'_n{}^{X'_s}$. If x'_s, $t'_n >> 10^3$, c_n will be very close to the infinitely large volume result.

The average number of intervals between n-wide barriers sampled is estimated[18] as 1.60 T/τ_n^c, so the number of sites sampled, N is

$$N = 1.60 \sqrt{T/\tau_n^c}\, x^{-n}(1-x)^{-1} \qquad (26a)$$

The number of sites between the two impenetrable n+1-molecule wide barriers is given by N_2 (and represents) the maximum number of sites an exciton may sample within this model. This is given by:

$$N_2 = t_n^{-1} \qquad (26b)$$

so the smaller of the two quantities, N_{min} must be used to derive the percentage of population that reaches a stationary trap before decaying, $\left(\frac{N_{stat}}{N_{total}}\right)$. If unit trapping efficiency is assumed, then the normalized population "probe"[15] (stationary site) is given as:

$$(N_{stat}/N_{total}) = (1-c_n) \sum_{i=0}^{N_{min}} x_s (1-x_s)^i \qquad (27)$$

where $(1-c_n)$ is a factor that accounts for those excitons which do not have a stationary trap accessible to them.

If the fractional population of the stationary trap is plotted against the guest mole fraction, the statistical treatment of the tunneling model is characterized by a sharp transition from low to high stationary trap population as shown in Figure 7. These curves are surprisingly similar to those for the onset of macroscopic[10] percolative conduction in two- and three-dimensional systems. Figure 7 shows that when the stationary trap population, x_s, is reduced, approaching a limit where the exciton must travel a macroscopic distance to reach a stationary trap, the transition threshold becomes more sharply defined. In percolation theory, a similar sharpening takes place as the size of the interconnected clusters increases. Variations of other parameters, such as excited state lifetime, T, or barrier size limit, n, does not qualitatively change the nature of the single sharp concentration threshold . This is illustrated in Figure 8.

C. Indirect Transfer in Substitutionally Disordered Systems.

Thermal detrapping and migration along host band states is an important alternative mechanism for exciton transfer along a substitutionally disordered potential surface. Fayer and Harris[9] proposed a two-step model for thermal promotion where the trapped exciton is first promoted to a state degenerate with the host band and then decays into the manifold of band states, with the combined rate given by

$$K_{\varepsilon k} = \frac{2\pi}{h} \langle n(\varepsilon)\rangle_T \; |\langle \tau P(\varepsilon)|H_{TP}|\tau_i \; P(\varepsilon - E_i)\rangle|^2$$

$$\cdot \, |\langle \tau_i \; P(\varepsilon - E_i)|H_{TE}|kP(\varepsilon - E_i)\rangle|^2 \; \rho(E_i) \qquad [28]$$

where the matrix elements represent coupling of exciton with phonon and exciton-phonon complex with band, respectively. τ is the trap state,

τ_i is the exciton-phonon excited state, and k is a host band state.

The rate of thermal promotion to the band must be distinguished from the rate of exciton migration to another trap. Few experimental determinations[19] of the ratio of these rates given by the migration efficiency α are available. If the problem of migration through the real barrier band states is treated as a one-dimensional random walk with absorbing barriers i.e. the trap states, the efficiency α is given by,

$$\alpha = \frac{1}{n+1} \tag{29}$$

where n is the barrier width. One notes that α increases as the barrier width n decreases or as the exciton coherence length in the band increases. Since the coherence length is a strong function of exciton-phonon coupling and therefore of temperature, α is temperature dependent as well as concentration-dependent. This effect will not be considered in detail here although it can be incorporated parametrically into the equations.

An energy partitioning model for transfer by thermal promotion can be proposed which is a one-dimensional random walk where the characteristic effective jump time across an <u>average</u> barrier is $\langle K_{\varepsilon k}^{-1} \alpha^{-1} \rangle$. Certain assumptions are made. (i) $K_{\varepsilon k}$ is independent of barrier width and may be expressed as a constant times a Planck distribution function for the phonon density of states at the barrier height Δ; i.e.

$$K_{\varepsilon k} = H_e{}^{-\Delta/kT} \tag{30}$$

(ii) α is averaged over a statistical distribution of barrier widths;

$$\langle\alpha\rangle = \sum_{i=1}^{\infty} \left(\frac{1}{i+1}\right) x^{i}(1-x)^{2} \Big/ \sum_{i=1}^{\infty} x^{i}(1-x)^{2} \qquad (31a)$$

$$\langle\alpha\rangle = \frac{1-x}{x^{2}} \left[\ln \left(\frac{1}{1-x} \right) -1 \right] \qquad (31b)$$

and (iii) unit trapping efficiency is assumed. As in the tunneling model, the number of jumps made is the exciton lifetime divided by the jump time $\langle K_{\varepsilon k}^{-1} \alpha^{-1}\rangle$. Finally, (iv) thermal promotion is the rate limiting step in exciton transfer, as opposed to diffusion within trap or band. The number of intervals sampled goes as the square root of the number of jumps, and the number of sites sampled, N, is

$$N = 1.60 \sqrt{T K_{\varepsilon k} \langle\alpha\rangle}\; x^{-1}(1-x)^{-1}, \qquad (32)$$

hence,

$$\frac{N_{stat}}{N_{total}} = \sum_{i=0}^{N} x_{s}(1-x_{s})^{i} \qquad (33)$$

Representative curves are shown in fig 9. Note that N_{stat}/N_{total} is now temperature dependent with an activation energy of $\Delta/2$ because of the square root in N. In these cases the temperature dependence of the "probe" site would show a composition <u>independent</u> activation energy $\Delta/2$.

D. Hybrid Transfer

As we have shown resonant tunneling between exciton-phonon complexes across a barrier contributes significantly to the overall tunneling rate. However as the population of phonon states decreases with increasing energy, fewer states are promoted. The decrease in effective barrier height upon promotion results in an enhanced tunneling rate. This effect becomes more important as the barrier width increases. The quantum mechanical rate, $k(n,\varepsilon)$, from an energy ε above the original trap state (fig. 10), is given as the Boltzmann average over ε from 0 to $\Delta-\delta$, where $\Delta-\delta$ is some energy below the barrier band states. Equations (19) and (20) still hold in this case and hence the averaged rate is given by:

$$\langle k(n)\rangle_{\varepsilon} = \int_0^{\Delta-\delta}\left[\frac{h}{4\beta^{n+1}}\,(\Delta-\varepsilon)^{n}\right]^{-1} e^{-\varepsilon/kT}\,d\varepsilon \Bigg/ \int_0^{\Delta-\delta} e^{-\varepsilon/kT}\,d\varepsilon \qquad [34]$$

The hierarchy of barriers argument used in section IIIA must be envoked in the limit where $kT \ll \Delta$, if it is valid for the same parameters in the pure tunneling model. In the high temperature limit, the thermal promotion model of section IIIB is more appropriate and the escape time from an interval bounded by -n- molecule wide barriers is given as

$$\tau_n^c = x^{-n}/\langle k(n)\rangle_{\varepsilon} \qquad (35)$$

Equations (24) through (27) may be used to calculate the energy partitioning ratio incorporating equation τ_n^c of equation (35). Representative curves are shown in Fig. 11. An interesting result of this model is that the tunneling model now shows an activation energy and the value experimentally measured will be a function of concentration (Fig. 12). This may be seen physically as follows. A wide barrier will show a larger effective activation energy, $<\varepsilon>$ than a small barrier. Quantitatively, $<\varepsilon>$ is given as:

$$<\varepsilon> = \int_0^{\Delta-\delta} (\varepsilon)\ k(n,\varepsilon) e^{-\varepsilon/kT} d\varepsilon \Bigg/ \int_0^{\Delta-\delta} k(n,\varepsilon) e^{-\varepsilon/kT} d\varepsilon \qquad (36)$$

because activated tunneling becomes more favorable as n increases. As the barrier molecule concentration, x, grows, the effective activation energy averaged over the statistical distribution of barriers, $<<\varepsilon>>_n$, grows

$$<<\varepsilon>>_n = \sum_{n=1}^{\infty} <\varepsilon>\ x^n (1-x)^2 \Big/ \sum_{n=1}^{\infty} x^n (1-x)^2 \qquad [37]$$

because the distribution shifts to larger n and more wide barriers. Similarly, Fig. 12 shows that this expression for the average activation energy will be a strong function of temperature. Higher temperatures will increase transmission rates through wide, high activation energy barriers disproportionately, thus increasing the average activation energy. The net result is that the transfer of excitations proceeds via tunneling at the low barrier limit to thermal promotion at the other limit. This is the physical basis for the apparent activation energy being dependent on the composition of the crystal. This is an important prediction and will be dealt with in a more detailed fashion in the forth coming[16] experimental study of energy transfer in one-dimensional disordered system.

IV. DISCUSSION AND SUMMARY

Explicit expressions for energy-partitioning ratios in a quasi-binary (low stationary trap concentration) system derived in the previous section draw a sharp distinction between the thermal promotion model, on one hand, and the pure and hybrid tunneling models, on the other. The enhancement of communication between localized trap states by exciton tunneling through virtual states of the host is a strong function of the width of the intervening barriers and shows a relatively sharp concentration dependence. The detrapping model and its energy partitioning ratio depend primarily on the number of barriers, which is symmetric in the guest-host composition, and only secondarily on the barrier widths. The problem may be reduced to an average barrier width (and average trap width) much like the simple disordered system of section II. Averaging procedures in all models require, of course, that the exciton visit many sites before decaying.

We have not dealt with the effects of coherence and incoherence in heavily disordered systems. Incoherent effects at barrier is expected to be extremely important in such cases, severly limiting long range exciton diffusion. The effect of coherent wavepacket propagation will be attenuated by the high concentration of scatterers resulting in a localization of k states even within the intervals of pure guest or host molecules.

In practice, both models of exciton migration may be simultaneously effective and should properly be treated as competing processes. Realistically, the tunneling model must include the occasional detrapping event which does not behave within the hierarchy of barriers structures and the thermal promotion model should include the correlations induced by the remaining bias towards transmission through the smaller of two confining barriers. Additionally, both models lose validity as the amalgamation limit is approached closely. The question of coherent migration in amalgamated bands is of particular interest and will be dealt with later. Here we have dealt implicitly with the region where $\beta<<\Delta$, but extension to an intermediate bandwidth region requires only an additional averaging for promotion or tunneling rates convolved with a Boltzmann distribution of initial and final states. The flexibility of the models proposed here, which include the quantum mechanical wavepacket properties of energy transfer, allows treatment of ternary and more complex systems. The energy transfer properties of any one-dimensional substitutionally disordered system in which the interactions between low energy or conducting sites are known are accessible. A future paper in the series[16] will deal with experimental results for singlet and triplet exciton transfer in an isotopically mixed pseudo-one-dimensional conductor, 1,2,4,5-tetrachlorobenzene. We note also that some of the ideas presented here, when extended to random walks in two or three dimensions may be useful in understanding energy transfer in higher-dimensional systems where the mobile trap concentration is well below the percolation threshold and transfer between clusters is mediated by host barriers of varying width.

V. ACKNOWLEDGEMENT

This research was supported by the U. S. Energy Research and Development Administration, Division of Physical Sciences under the auspices of the Lawrence Berkeley Laboratory, Molecular and Materials Research Division.

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15. Of the available probes for studying disordered systems only two seem to be very extensively used in molecular solids. The first is the observation of the relative emission from deep traps which are in dilute concentration in the lattice (cf. Reference 9) The second involves the use of optically detected electron spin coherence (cf. W. G. Breiland, H. C. Brenner and C. B. Harris, J. Chem. Phys. 62, 3458 (1975) and is only useful for triplet migration.

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18. The mean maximum position reached from the origin in n hops will be $\sqrt{\frac{2n}{\pi}}$ sites for an unrestricted symmetric random walk, because the probability that $Z>0$ will be the maximum goes as $\sqrt{\frac{2}{\pi n}}\, e^{-Z^2/2n}$ (Feller I, p 89, 357) and

$$\langle \max \rangle = \int_0^\infty z\sqrt{\frac{2}{\pi n}}\, e^{-Z^2/2n}\, dZ \Bigg/ \int_0^\infty \sqrt{\frac{2}{\pi n}}\, e^{-z^2/2n}\, dZ$$

$$= \sqrt{\frac{2n}{\pi}}$$

By symmetry, the mean minimum is $-\sqrt{\frac{2n}{\pi}}$. Although the variables are not independent, the mean of the difference between maximum and minimum is the difference of the means. The average number of different sites visited in n hops is $2\sqrt{\frac{2n}{\pi}} = 1.60\sqrt{n}$. In this case, n equals the lifetime of the exciton divided by the time per hop, T/τ_n^c.

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Figure 1: Model of disordered system with periodic distribution of potential barriers. Crosses represent molecular sites along a one-dimensional cyrstal lattice axis.

Figure 2: (a) Escape process from interval bounded by monomer barriers. (b) Escape process from interval bounded by dimer barriers.

Figure 3: Population distribution for one-dimensional random walk with reflecting barriers. N equals number of jumps. Interval width (S_1 molecular sites) is 10 for purposes of illustration. Exciton position is 0 for N = 0.

Figure 4: Diffusion coefficients vs. barrier transmission probability for one dimensional simple disordered system.

Figure 5: Resonant tunneling between traps separated by one, two, and three host molecules.

Figure 6: Model of potential surface for energy-partitioning studies. Depth of stationary trap is much greater than kT.

Figure 7: Resonant tunneling model: fraction of population reaching stationary trap vs. mobile trap mole fraction. Stationary trap concentration is varied. ($n = 4$, $\beta = 0.3\ cm^{-1}$, $\Delta = 21\ cm^{-1}$, $T = 25$ msec.)

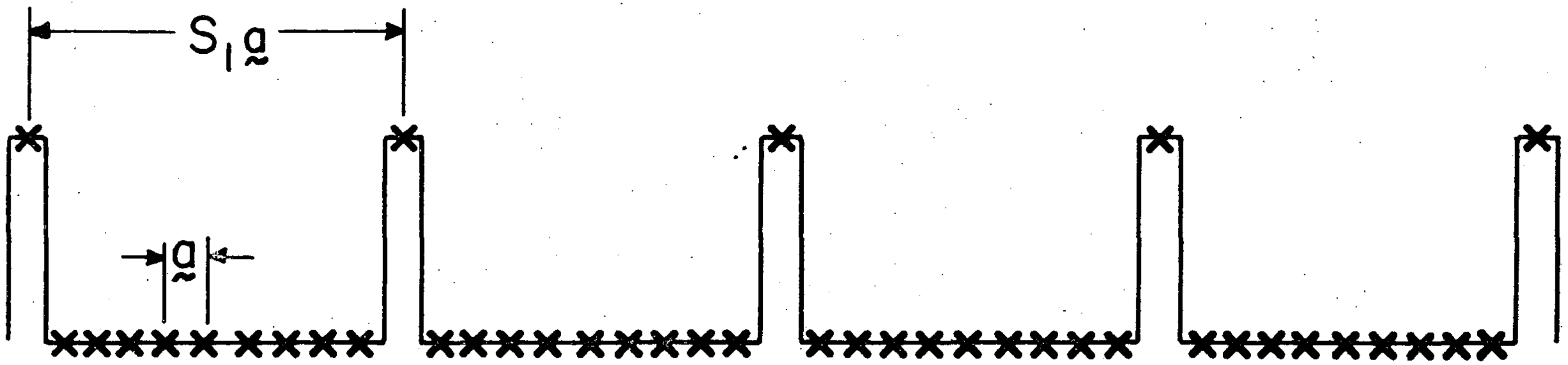
Figure 8: Resonant tunneling model; fraction of population eaching stationary trap vs. mobile trap mole fraction. Excited state lifetime and maximum penetrable barrier size are varied. ($x_s = 0.002$, $\beta = 0.3\ cm^{-1}$, $\Delta = 21\ cm^{-1}$; for $n = 3$, $T = 25$ msec)

Figure 9: Thermal detrapping model; fraction of population reaching stationary trap vs. mobile trap mole fraction. Temperature is varied ($x_s = 0.002$, $H = 3 \times 10^{10} S\text{-}1$, $\beta = 0.3\ cm^{-1}$, $\Delta = 21\ cm^{-1}$, $T = 25$ msec)

Figure 10: Model for hybrid tunneling.

Figure 11: Hybrid tunneling model; fraction of population reaching stationary trap vs. mobile trap mole fraction temperature is varied ($x_s = 0.002$, $\beta = 0.3\ cm^{-1}$, $\Delta = 21\ cm^{-1}$, $T = 25$ msec, $n = 4$)

Figure 12: Calculated activation energy for hybrid tunneling. (parameters are the same as in Figure 11)



XBL 768-7373

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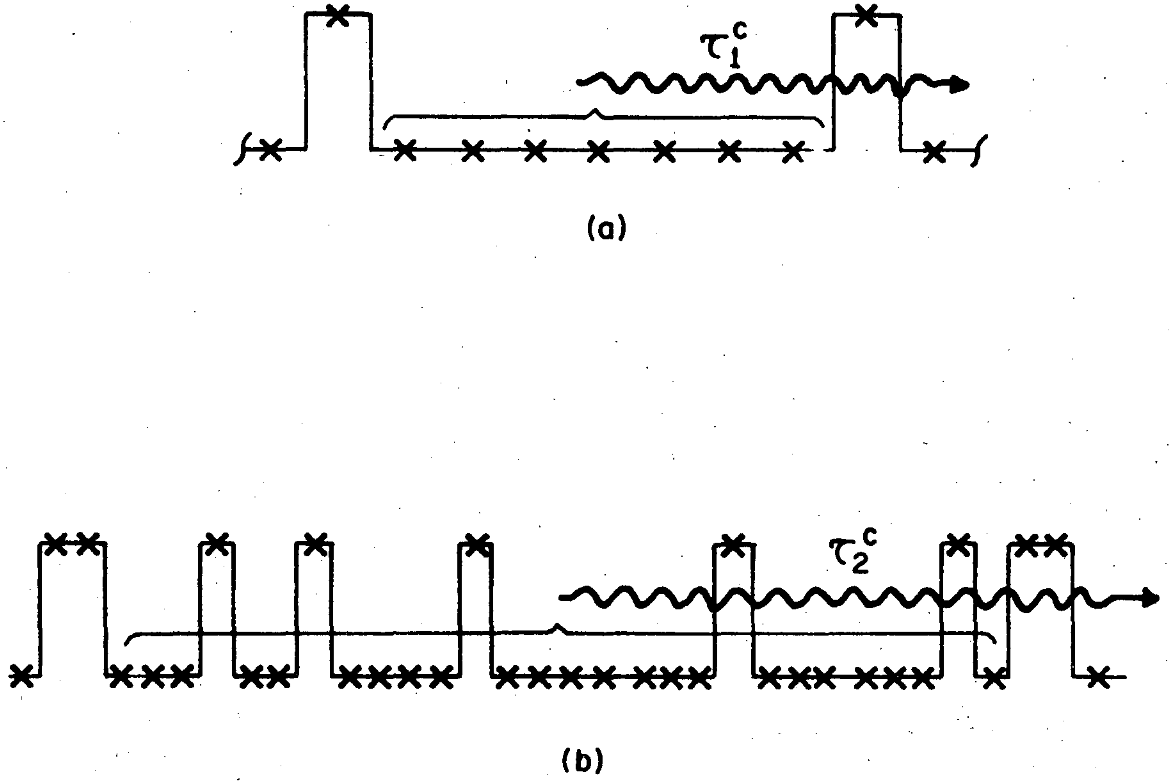
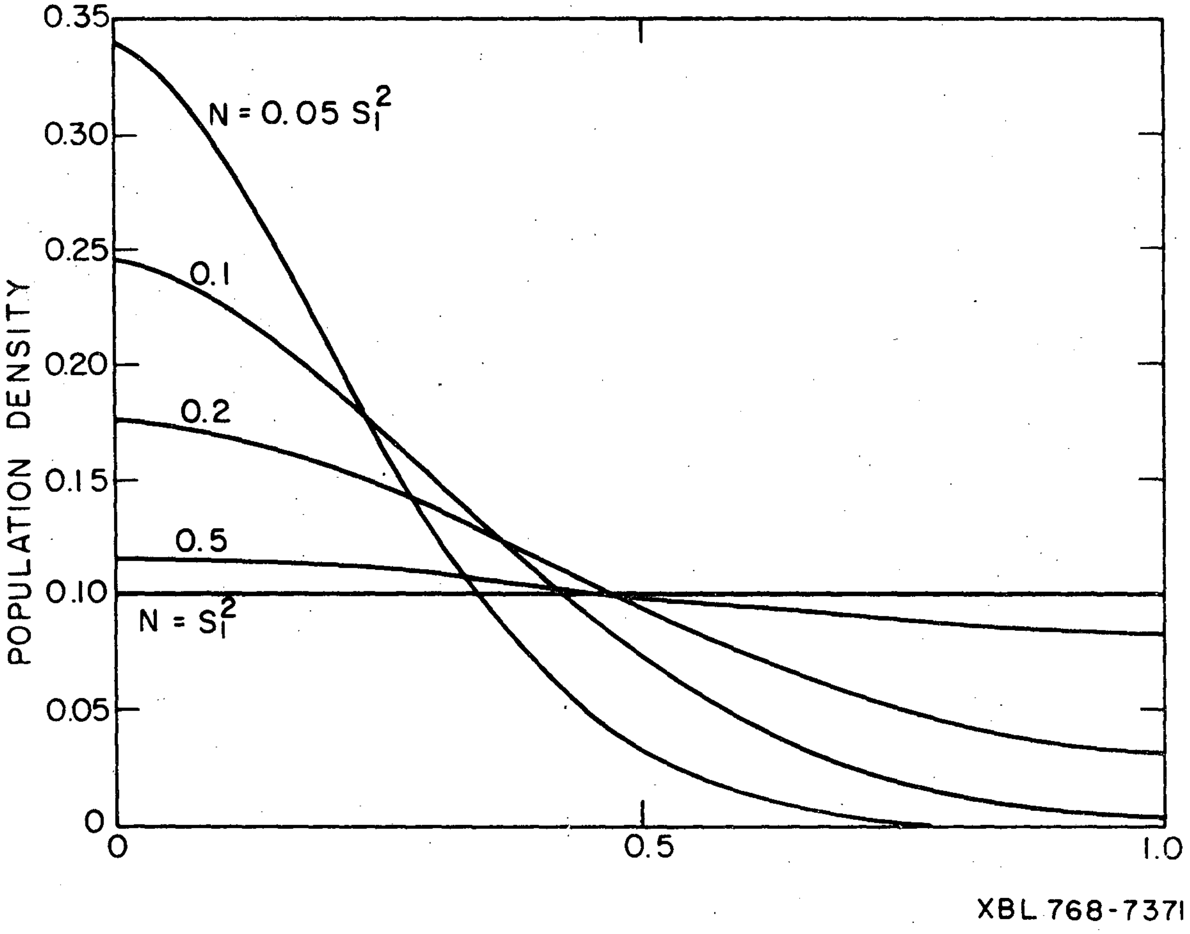


XBL 766-7117

Fig. 2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0.20
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0.10
0.05
0
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$N = S_1^2$
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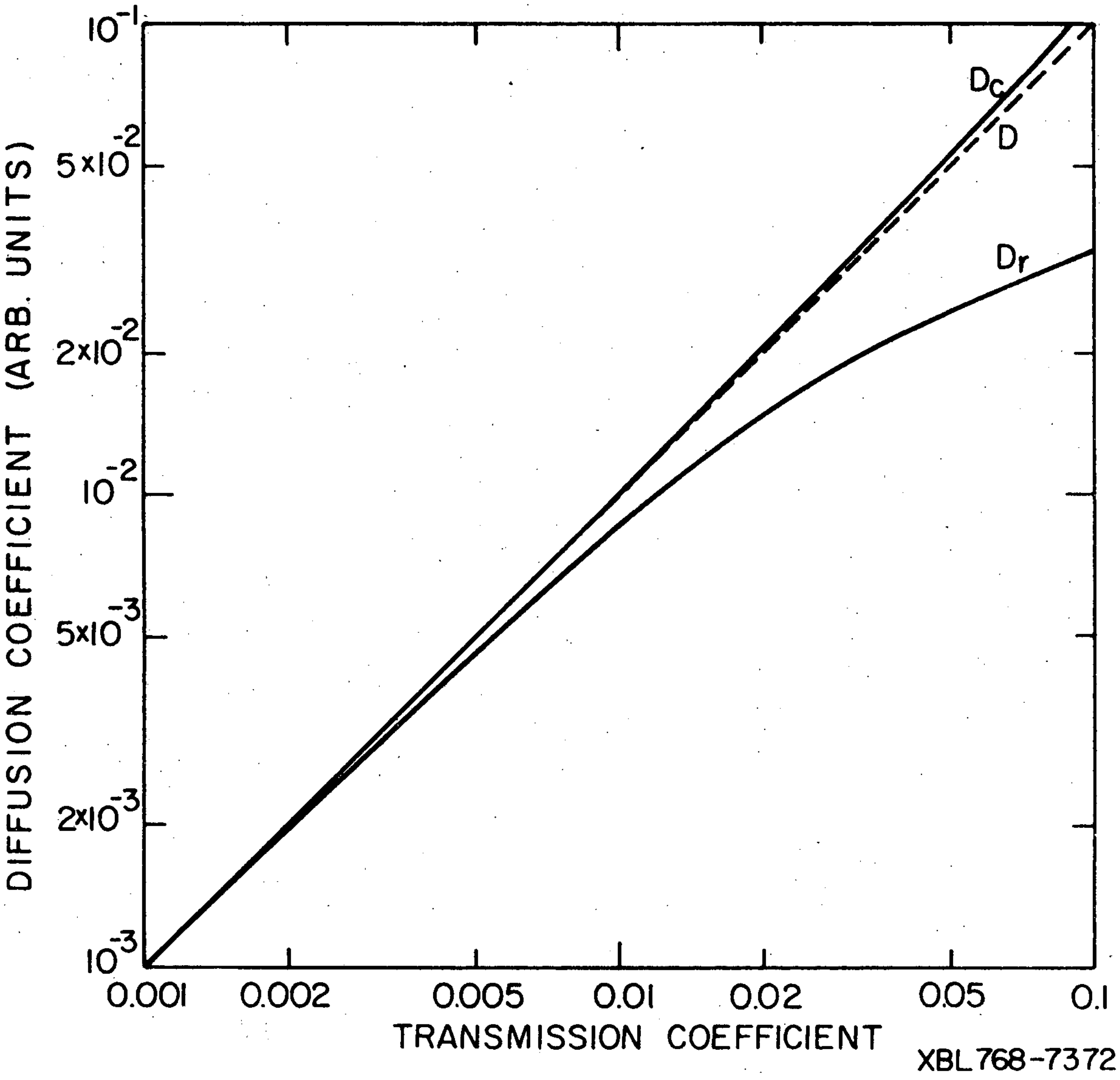
0.5
1.0
XBL 768-7371

Fig. 3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0.002
0.005
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0.1
TRANSMISSION COEFFICIENT
D_c
D
D_r
XBL 768-7372

Fig. 4

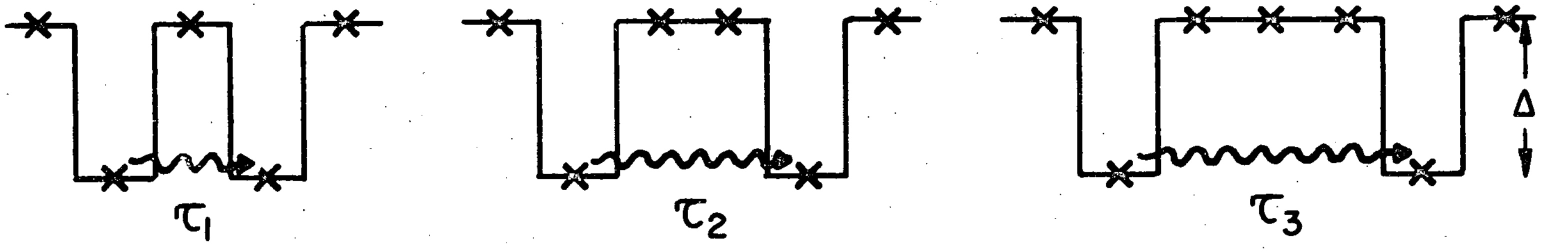

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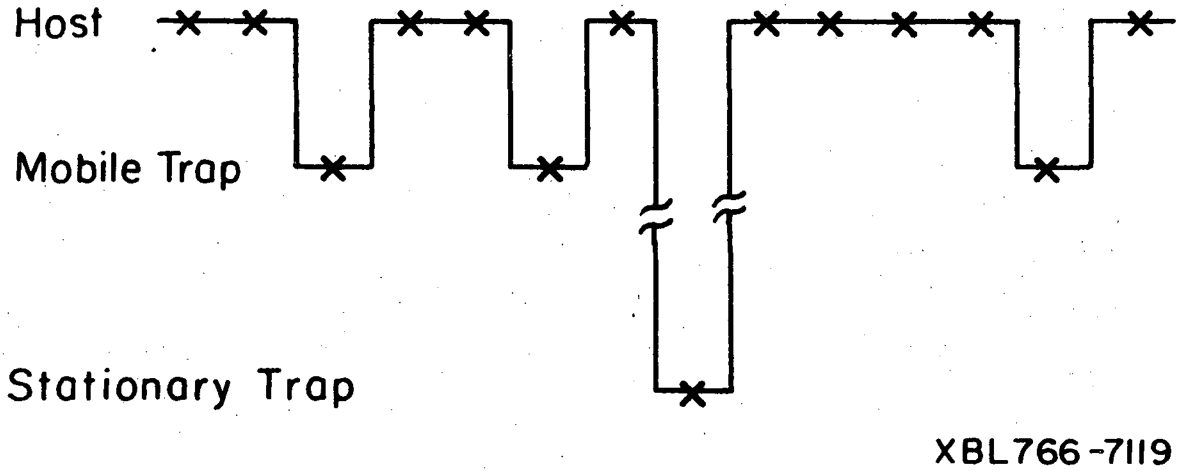
Fig. 5



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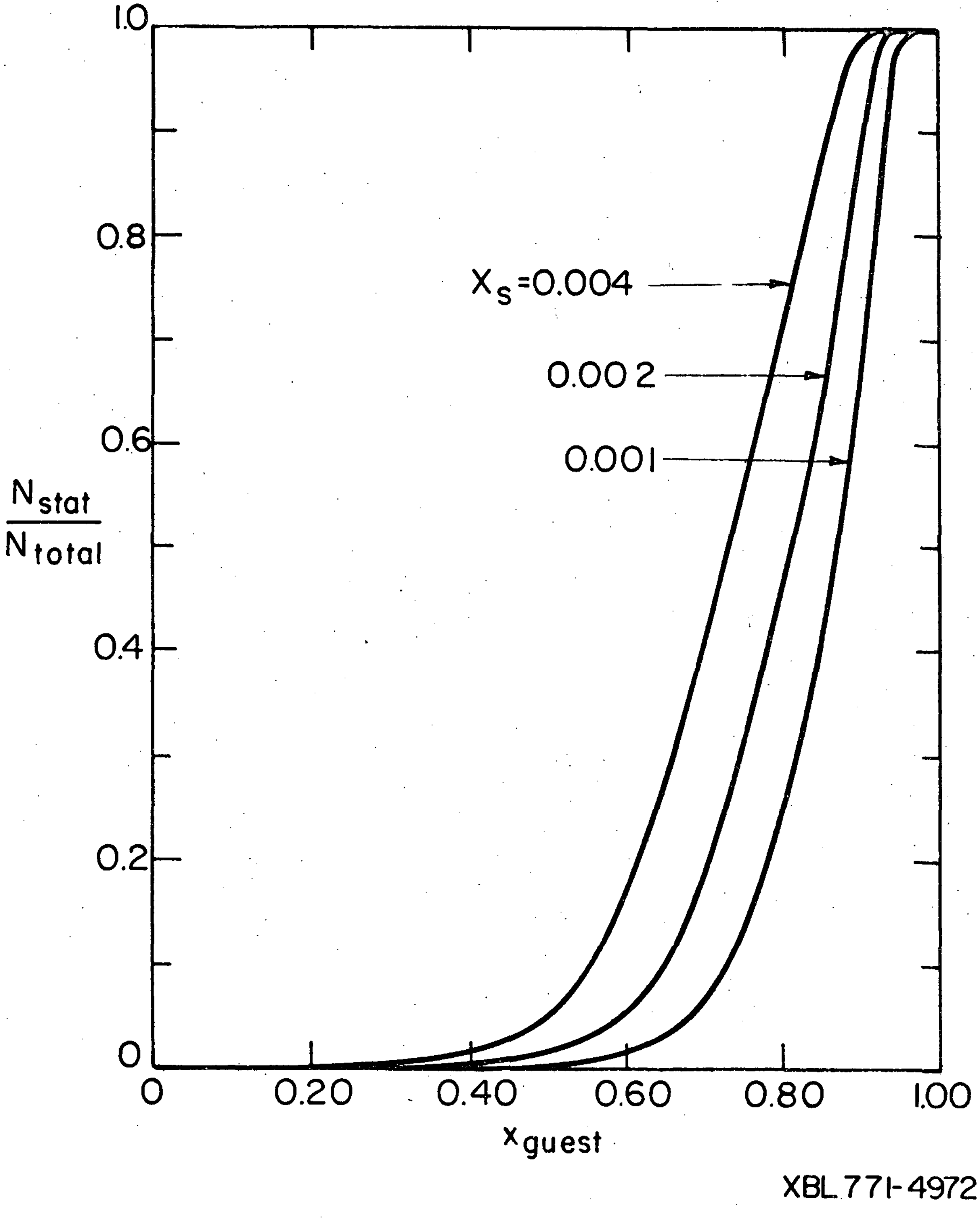
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0.4
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0
$\frac{N_{stat}}{N_{total}}$
0
0.20
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1.00
x_{guest}
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XBL 771-4972

Fig. 7

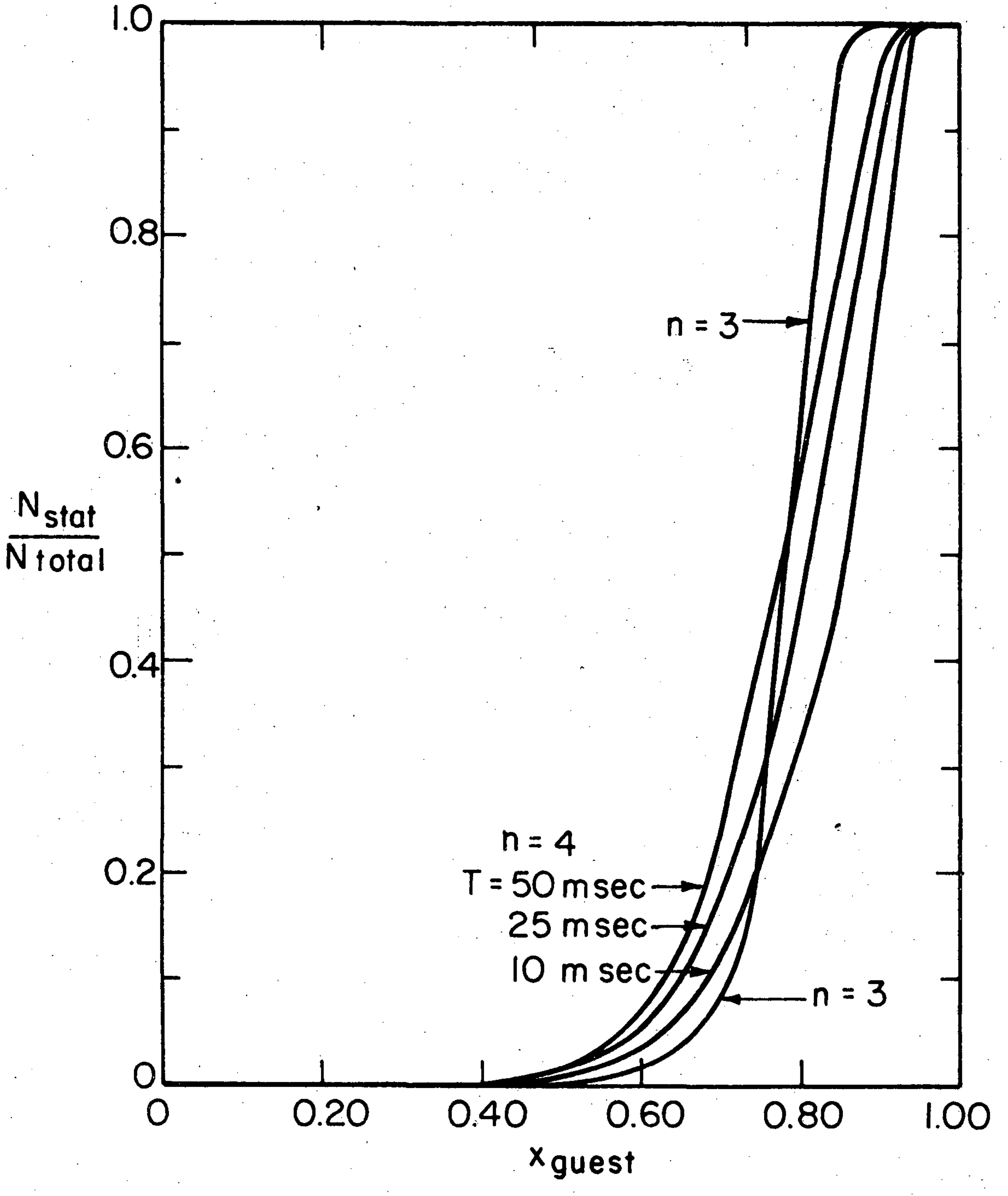

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Fig. 8

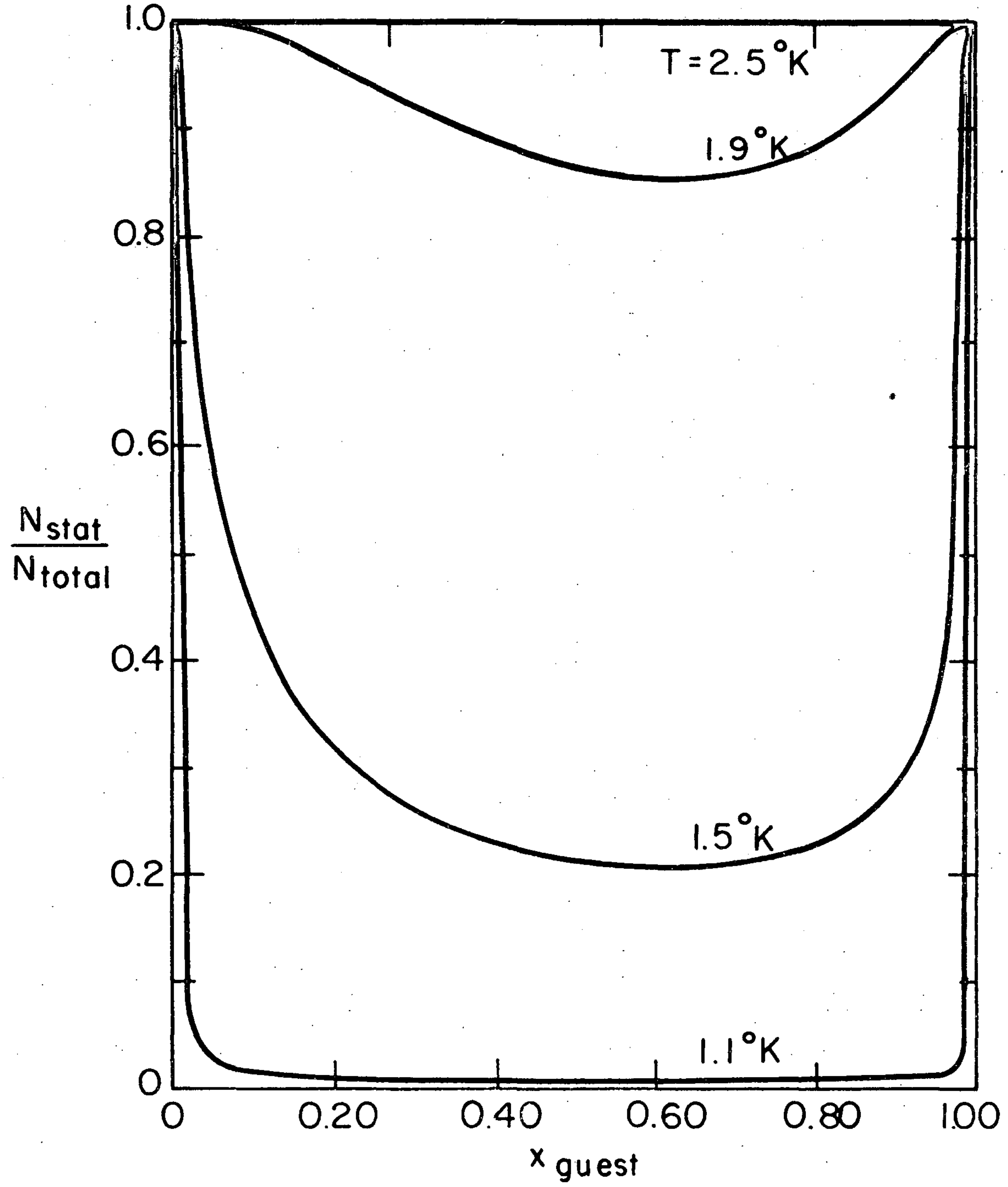

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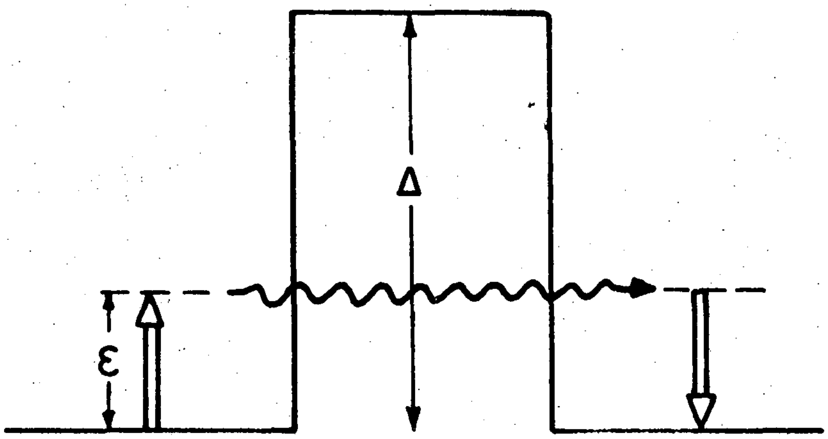
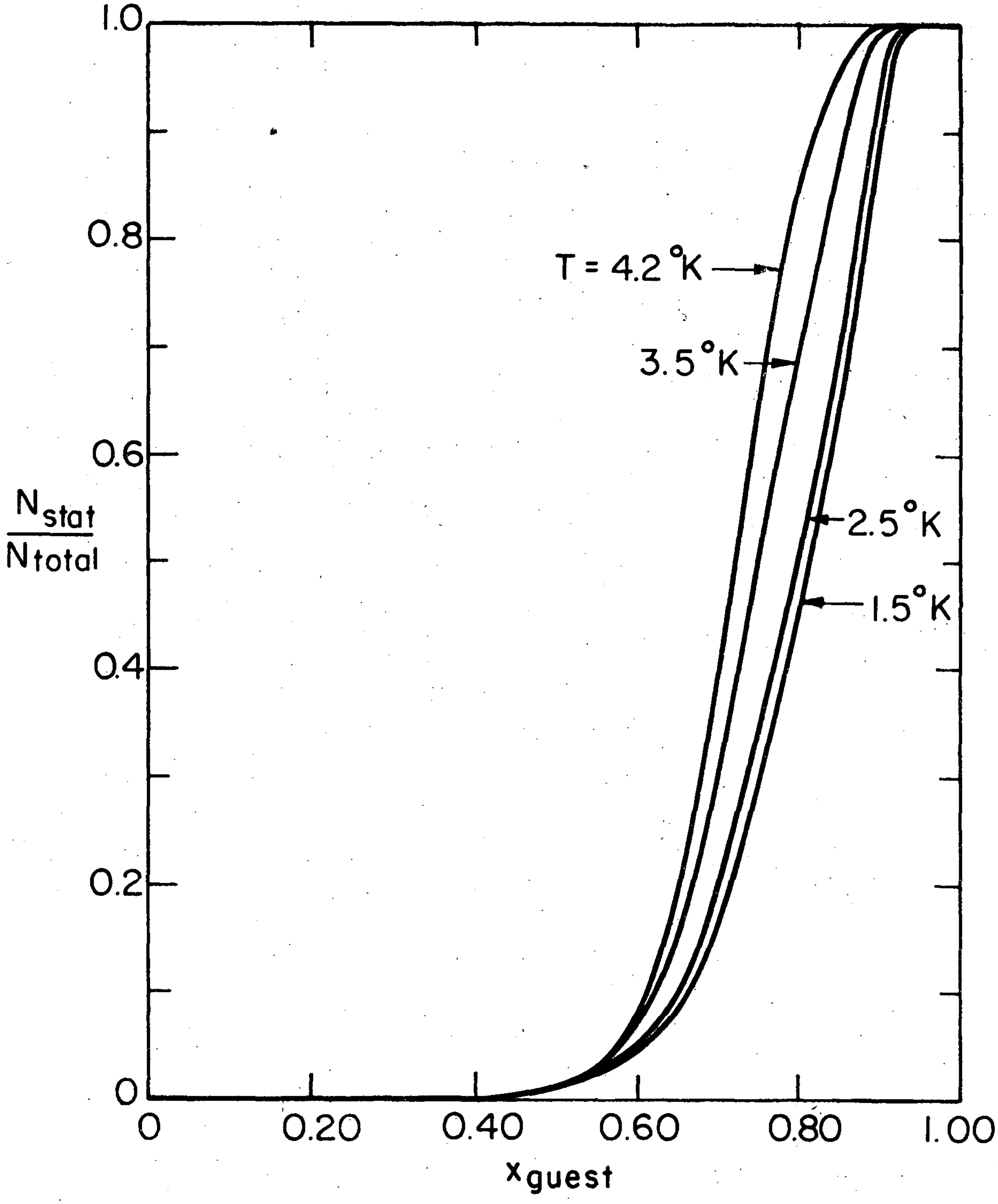
Fig. 9



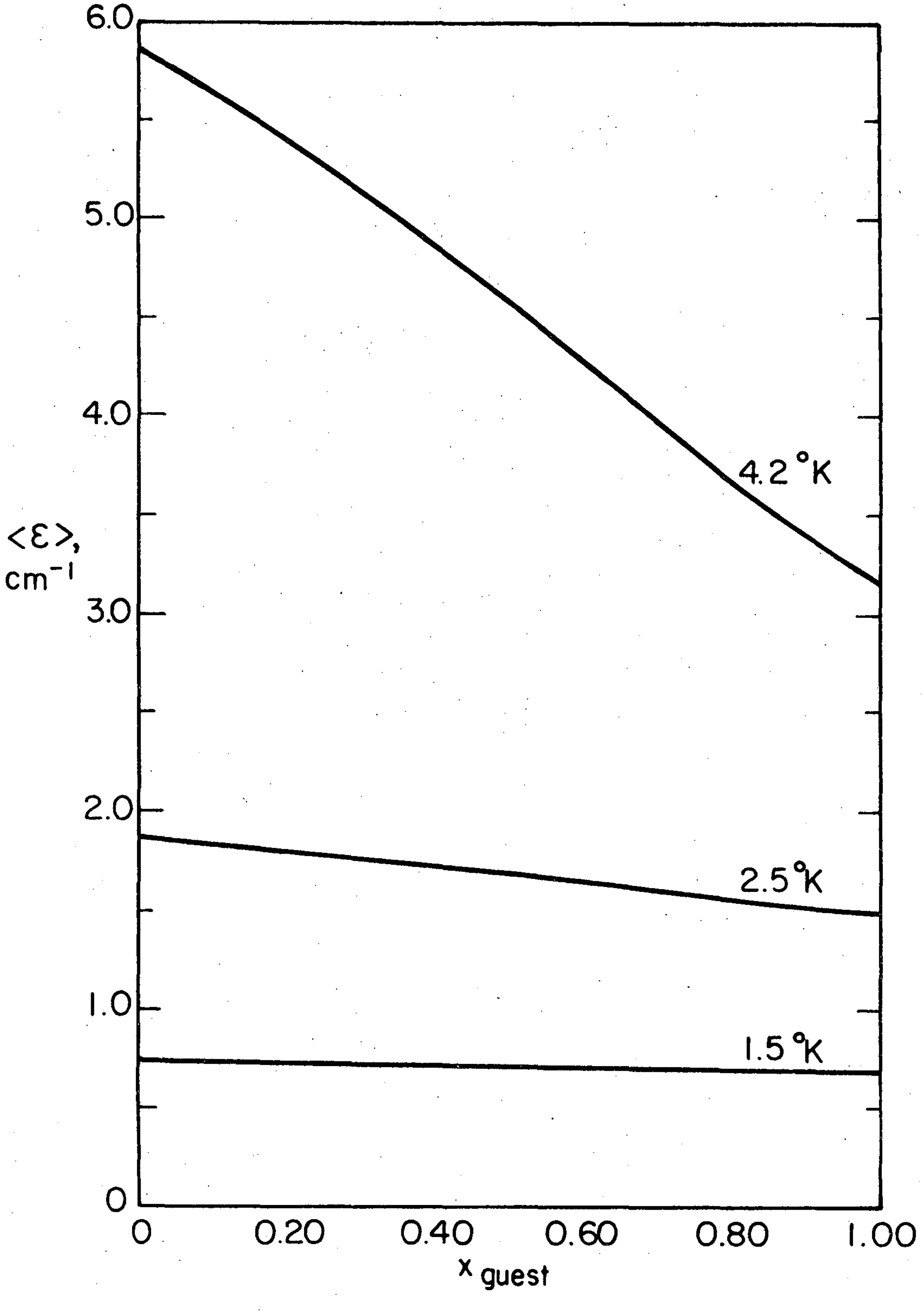
XBL 771-4970

Fig. 10



XBL 771-4975

Fig. 11



XBL771-4971

Fig. 12

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