Models for energy transfer in solids

H. C. Chow and Richard C. Powell
Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74078
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Two new approaches for describing the dynamics of energy transfer in solids have been developed and are described here. The first is a method for treating the case in which weak direct sensitizer-activator interaction acts as a small perturbation on energy transfer by diffusion among sensitizers. A technique involving a propagator expansion and the Born approximation in the interaction strength is used to solve this problem. The second approach is a Monte Carlo technique to simulate the migration of energy on a random distribution of sensitizers. The predictions of both these models are compared to experimental results and to the predictions of other theoretical models. In their regions of validity they predict significantly different results than those of the models commonly used. The models developed here are applicable to many important materials such as those used for rare-earth lasers.

I. INTRODUCTION

The transfer of electronic excitation energy between ions or molecules in a solid has been the subject of many investigations for over forty years. Recently there has been increased interest in characterizing this process in materials used for laser and phosphor applications. Energy transfer can be used to increase the pumping efficiency of the active ions or molecules in these materials but it can also cause decreased fluorescence emission through concentration quenching interactions. Despite the significant amount of interest and research activity in this area there are still some important aspects to the problem of energy transfer which are not well characterized and understood. The work described here treats two aspects of this problem which have not been satisfactorily accounted for in previous developments.

Energy transfer is generally treated in one of two limiting cases. The first is a direct transfer from an excited "sensitizer" to an unexcited "activator." The theory describing this "single-step process" has been developed in the classic papers of Förster[1] and Dexter[2] with problems such as the effect of random disorder being attacked recently.[3-5] The second case is that of energy transfer to activators after multistep diffusion among sensitizers. The description of this "exciton" diffusion energy transfer was first developed by Frenkel,[6] Trlifaj,[7] and Förster.[1] A major problem in studying diffusional energy transfer is how to separate the properties of diffusion among sensitizers and the properties of trapping at an activator site from the total energy-transfer properties which are measured. Several theories have been proposed to account for simultaneous sensitizer energy diffusion and sensitizer-activator interaction[8-10] but the final solutions of each of these theories involve assumptions which limit their validity to specific cases. One

important case to which the currently available theories do not apply is one in which the direct sensitizer-activator interaction is smaller than the diffusional term but not small enough to be negligible. A theoretical description of this case is developed in Sec. II of this paper and several cases where it may apply are discussed.

A second problem involving multistep migration of energy concerns the spatial distribution of sensitizers. All the standard theories assume a uniformly distributed lattice of sensitizers so that the random walk of the exciton can be described by a single average hopping time. This picture should be valid for "host-sensitized" energy transfer or other situations involving high concentrations of sensitizers but it is certainly a poor approximation if the sensitizers are randomly distributed impurities with low concentrations. In Sec. III of this paper we describe a Monte Carlo treatment of this problem and compare the results to predictions of existing theories and experimental results.

II. EFFECTS OF DIRECT SENSITIZER-ACTIVATOR INTERACTION ON DIFFUSIONAL ENERGY TRANSFER

In this section we consider the situation in which energy transfer includes both diffusion among sensitizers and single-step resonant transfer between sensitizer-activator pairs. Yokota and Tanimoto[8] treated the limiting case in which the one-step transfer is dominant and the diffusive contribution is a small perturbation. They developed an interpolation scheme for the time dependence of the excited sensitizer concentration in this limit. On the other hand, if diffusion is the more important of the two transfer processes, the usual treatment[10,11] is to as-

sume some finite trapping radius for the activators outside of which diffusion takes place, while neglecting any direct, single-step sensitizer-activator interaction. Here we will consider the fast-diffusion regime and specifically examine what effects the single-step transfer might have on the time development of the excited sensitizer concentration otherwise depleted by diffusion.

The equation governing the excited sensitizer concentration $n(\vec{r},t)$ including both diffusion and single-step transfer is

$$\partial n(\vec{r},t)/\partial t = -\beta n(\vec{r},t) + D\nabla^2 n(\vec{r},t)$$
$$- \sum_i v(\vec{r} - \vec{R}_i)n(\vec{r},t) \quad . \tag{1}$$

Here β is the intrinsic decay rate of the sensitizers, D is the diffusion coefficient, $\vec{R}_i$ is the position vector for a given activator, and $v(\vec{r} - \vec{R}_i)$ is the interaction strength for a given sensitizer-activator pair. In this development the interaction is taken to be of the common electric dipole-dipole type, and thus $v(\vec{r} - \vec{R}_i)$ varies inversely as the sixth power of $|\vec{r} - \vec{R}_i|$. The solution to Eq. (1) must eventually be averaged over the configuration of activator distributions, which is a difficult task. With the assumption of a uniform activator distribution, however, Yokota and Tanimoto[8] have shown that the problem is reduced to averaging the solution of a single-center problem, in which an activator acting as an absorber is located at $\vec{r} = 0$. For this case

$$\partial n(r,t)/\partial t = -\beta n(r,t) + D\nabla_r^2 n(r,t) - v(r)n(r,t) \quad , \tag{2}$$

where

$$\nabla_r^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$$

is the isotropic Laplacian operator. The general solution to Eq. (2) can be written as

$$n(r,t) = \sum_k \exp(-\beta t - Dk^2 t)\phi_k(r) \tag{3}$$

with $\phi_k(r)$ obeying the eigenvalue equation

$$[\nabla_r^2 + k^2 - D^{-1}v(r)]\phi_k(r) = 0 \quad . \tag{4}$$

Because of the assumed r^{-6} dependence of $v(r)$, no solution to Eq. (4) can be found that is regular at $r = 0$. Nevertheless, it is possible[12] to employ the

Fermi pseudopotential method to find the lowest eigenvalue and eigenfunction, k^2 and $\phi_k(r)$, respectively, which according to Eq. (3) determine the asymptotic behavior of the excited sensitizer concentration. In this approach $\phi_k(r)$ thus determined is identically zero for a finite distance, $0 \leq r \leq a$, the so-called scattering length.

The above remarks serve to justify the use of an approximate potential in lieu of the exact dipole-dipole interaction. Namely, we let

$$v(r) \cong v_0(r) + u(r) \tag{5}$$

in which

$$v_0(r) = \begin{cases} 0, & r > a \ , \\ \infty, & r \leq a \ , \end{cases}$$
$$u(r) = \begin{cases} 0, & r \leq a \ , \\ \alpha/r^6, & r > a \ . \end{cases} \tag{6}$$

With the use of this approximate potential, the kinetic Eq. (2) is solved exactly except for $u(r)$ which is treated in the Born approximation. Such a solution clearly corresponds to the case in which energy transfer via diffusive migration is stronger than transfer by single-step electric dipole-dipole resonant transfer.

The method of solution is based on the well-known propagator expansion.[13] Upon writing $n(r,t) = e^{-\beta t}\psi(r,t)$, it is seen because of the linearity of the operations in Eq. (2) that the temporal and spatial development of $\psi(r,t)$ is governed by

$$\psi(r,t) = \int G(r,t|r_0,t_0)\psi(r_0,t_0)\,dr_0 \tag{7}$$

in which the propagator or Green's function $G(r,t|r_0,t_0)$ obeys the equation

$$[-\partial/\partial t + D\nabla_r^2 - v(r)]G(r,t|r_0,t_0)$$
$$= \delta(r-r_0)\delta(t-t_0) \quad , \tag{8}$$

where $\delta(x)$ is the Dirac δ function. If instead of the full electric dipole-dipole interaction, one solves for the Green's function for the approximate potential $v_0(r)$

$$[-\partial/\partial t + D\nabla_r^2 - v_0(r)]G_0(r,t|r_0,t_0)$$
$$= \delta(r-r_0)\delta(t-t_0) \tag{9}$$

then the objective enunciated in the preceding paragraph is accomplished by obtaining

$$\psi(r,t) \cong \psi_0(r,t) + \psi_1(r,t)$$
$$= \int G_0(r,t|r_0,t_0)\psi(r_0,t_0)\,dr_0 - \int G_0(r,t|r_1,t_1)u(r_1)G_0(r_1,t_1|r_0,t_0)\psi(r_0,t_0)\,dr_1\,dt_1\,dr_0 \quad . \tag{10}$$

We determine $G_0(r,t|r_0,t_0)$ by the method of image. Upon writing

$$G_0(r,t|r_0,t_0) = r^{-1}\bar{G}(r,t|r_0,t_0)$$

Eq. (8) reads

$$[-\partial/\partial t + D(\partial^2/\partial r^2) - v_0(r)]\bar{G}(r,t|r_0,t_0) = r_0\delta(r-r_0)\delta(t-t_0) \quad . \tag{11}$$

The effect of $v_0(r)$ is accounted for if it is required that $\bar{G}(r,t|r_0,t_0)$ vanishes for $r \leq a$. This may be accomplished by introducing a source of strength r_0 at $r=r_0$ and an image source at $r=2a-r_0$, leading to

$$G_0(r,t|r_0,t_0) = \frac{r_0}{r}\frac{\theta(t-t_0)}{[4\pi D(t-t_0)]^{1/2}}\{\exp[-(r-r_0)^2/4D(t-t_0)]$$

$$-\exp[-(r+r_0-2a)^2/4D(t-t_0)]\}, \quad r,r_0 \geq a \quad , \tag{12}$$

where $\theta(t)$ is a unit Heaviside step function. For uniform initial excitation of sensitizers, $\psi(r_0,t_0) = n_0$ at $t_0=0$, the result is

$$\psi_0(r,t) = n_0\left[1 - \frac{a}{r} + \frac{a}{r}\,\text{erf}\left[\frac{r-a}{(4Dt)^{1/2}}\right]\right] \quad , \tag{13}$$

which is identical to the result[11] describing the diffusive migration of excited sensitizers in the presence of a trap of radius a.

The effect of concurrent single-step electric dipole-dipole resonant transfer from sensitizer to activator is contained in the next term in the Born approximation

$$\psi_1(r,t) = \int dr_1 u(r_1)K(r,t|r_1) \quad , \tag{14}$$

where

$$K(r,t|r_1) = \frac{n_0}{(4\pi D)^{1/2}}\frac{r_1}{r}\int_0^t \frac{d\tau}{(t-\tau)^{1/2}}\{\exp[-(r-r_1)^2/4D(t-\tau)]-\exp[-(r+r_1-2a)^2/4D(t-\tau)]\}$$

$$\times\left[1 - \frac{a}{r_1} + \frac{a}{r_1}\,\text{erf}\left[\frac{r_1-a}{(4D\tau)^{1/2}}\right]\right] \quad . \tag{15}$$

Further progress can be made with the aid of the following integrals (which are derivable from the results in the appendix of Ref. 13):

$$\int_0^t \frac{d\tau}{(t-\tau)^{1/2}}\exp[-|\beta|^2/4D(t-\tau)] = 2\sqrt{t}\exp(-|\beta|^2/4Dt) - \left(\frac{\pi}{D}\right)^{1/2}|\beta|\,\text{erfc}\left[\frac{|\beta|}{(4Dt)^{1/2}}\right]$$

$$\int_0^t \frac{d\tau}{(t-\tau)^{1/2}}\exp[-|\beta|^2/4D(t-\tau)]\,\text{erf}\left[\frac{r-a}{(4D\tau)^{1/2}}\right]$$

$$=\text{erf}\left[\frac{r-a}{(4Dt)^{1/2}}\right]\left[2\sqrt{t}\exp(-|\beta|^2/4Dt) - \left(\frac{\pi}{D}\right)^{1/2}|\beta|\,\text{erfc}\left[\frac{|\beta|}{(4Dt)^{1/2}}\right]\right]$$

$$+\frac{(r-a)}{(\pi D)^{1/2}}E_1\left[\frac{(r-a)^2+\beta^2}{4Dt}\right]$$

$$-\frac{4|\beta|}{(\pi D)^{1/2}}\int_{(r-a)/(4Dt)^{1/2}}^\infty dy\, e^{-y^2}\int_{|\beta|y/(r-a)}^\infty dx\, e^{-x^2}$$

in which $E_1(x) = \int_x^\infty e^{-t}t^{-1}\,dt$ is an exponential integral. Then Eq. (15) can be written as

$$K(r,t|r_1) = \frac{n_0}{(4\pi D)^{1/2}}\frac{a}{r}\sum_{i=1}^3 [F_i(r-r_1) - F_i(r+r_1-2a)] \quad , \tag{16}$$

where

$$F_1(x) = \left[\frac{r_1}{a} - 1 + \mathrm{erf}\left(\frac{r_1-a}{(4Dt)^{1/2}}\right)\right]\left[2\sqrt{t}\,e^{-x^2/4Dt} - (\pi/D)^{1/2}|x|\,\mathrm{erf}\left(\frac{|x|}{(4Dt)^{1/2}}\right)\right] ,$$

$$F_2(x) = \frac{r_1-a}{(\pi D)^{1/2}}E_1\left[\frac{x^2+(r_1-a)^2}{4Dt}\right] ,$$

$$F_3(x) = \frac{-4|x|}{(\pi D)^{1/2}}\int_{r_1-a/(4Dt)^{1/2}}^{\infty} dy\, e^{-y^2}\int_{(|x|/|r_1-a|)y}^{\infty} dz\, e^{-z^2} .$$

Rather than finding the explicit space and time dependence of the excited sensitizer concentration which entails a further integration in Eq. (14), it is expedient to obtain the time-dependent energy-transfer rate $k(t)$ which is also accessible experimentally. The latter is related to the total amount of excitation $N(t)$ via[14]

$$\tilde{N}(t) \equiv N(t)e^{\beta t} = N_0\exp\left[-\int_0^t k(t')\,dt'\right] . \quad (17)$$

It is also customarily treated as the quantity that appears in the rate equation

$$d\tilde{N}(t)/dt = -k(t)N_0 . \quad (18)$$

It is clear that the two definitions are equivalent only in the limit that $\int_0^t k(t')dt'$ is much less than unity.

To proceed further, Eq. (2) is integrated over the volume of the sample Ω and the first identity of Green invoked to obtain

$$\partial\tilde{N}(t)/\partial t = -4\pi a^2 D\left(\frac{\partial\psi}{\partial r}\right)_{r-a} - \int u(r)\psi(r,t)\,d\Omega . \quad (19)$$

Comparison between Eqs. (18) and (19) leads to the expression for the time-dependent energy-transfer rate for the case of N_a activators per unit volume, correct to the first Born approximation

$$k(t) = \frac{N_a\Omega}{N_0}\left[4\pi a^2 D\left(\frac{\partial\psi_0}{\partial r} + \frac{\partial\psi_1}{\partial r}\right)_{r-a}\right.$$
$$\left. + \int u(r)\psi_0(r,t)\,d\Omega\right] . \quad (20)$$

The three factors that appear in Eq. (20) have rather obvious physical interpretations. The first factor has the explicit form

$$k_0(t) = 4\pi DaN_a[1 + a(\pi Dt)^{-1/2}] \quad (21)$$

and is simply the rate at which excitations arrive diffusively at the surfaces of the activator traps. It has been used as the standard result[11,14] for the time-dependent energy transfer in the fast diffusion regime. The generalized random-walk model[10] which includes an extended trapping region yields the same

time dependence with a somewhat different interpretation of the physical parameters involved. The last factor in Eq. (20) is the integrated amount of excitations weighted with the probability per unit time of making a single-step transfer to an activator. This represents the rate of energy transfer by a single-step resonant process. The presence of such single-step transfer has the consequence of diminishing the amount of excitations available for transfer by diffusive migration. This is accounted for by the second factor in Eq. (20) which is intrinsically negative by virtue of the fact that

$$\left(\frac{\partial\psi_1}{\partial r}\right)_{r-a} = -\frac{n_0}{D}\int_a^\infty dr\, u(r)\,\mathrm{erfc}\left(\frac{r-a}{(4Dt)^{1/2}}\right)$$
$$\times\left[\frac{r}{a} - \frac{1}{2}\mathrm{erfc}\left(\frac{r-a}{(4Dt)^{1/2}}\right)\right] . \quad (22)$$

Thus the time-dependent energy-transfer rate for the case considered here may be written as $k(t) = k_0(t) + k_1(t)$ with k_0 being the usual diffusion expression given in Eq. (21) and k_1 accounting for the two effects of direct sensitizer-activator interaction discussed above. For electric dipole-dipole interaction the latter term becomes

$$k_1(t) = \frac{4\pi N_a\alpha}{3a^3} + 2\pi N_a a^2\int_a^\infty dr\frac{\alpha}{r^6}\left[\mathrm{erfc}\left(\frac{r-a}{(4Dt)^{1/2}}\right)\right]^2$$
$$- 8\pi N_a a\int_a^\infty dr\frac{\alpha}{r^5}\left[\mathrm{erfc}\left(\frac{r-a}{(4Dt)^{1/2}}\right)\right] . \quad (23)$$

At this point it is necessary to use numerical integration to extract the explicit time dependence of this additional contribution to the energy-transfer rate. However, since it is readily seen that the magnitude of $k_1(t)$ varies from $4\pi N_a\alpha/(3a^3)$ at $t=0$ to $-4\pi N_a\alpha/(15a^3)$ as $t\to\infty$, a measure of the optimal significance of the effects of single-step transfer in the fast-diffusion regime may conveniently be chosen as the ratio $k_1(t=0)/k_0(t\to\infty) = \alpha/(3Da^4)$. Table I[15-17] lists values of this ratio for a number of systems for which fast diffusion has been identified.

It should be pointed out that in the absence of any other theoretical considerations, the values of α, a,

TABLE I. Estimated importance of direct sensitizer-activator interaction on energy transfer in the fast-diffusion regime.

System	α (cm^6/sec)	D (cm^2/sec)	a (cm)	$\dfrac{k_1(t=0)}{k_0(t\to\infty)}$
Tb$_3$Al$_5$O$_{12}$[a]	1.2×10^{-35}	1.25×10^{-11}	2.1×10^{-7}	1.65×10^2
Y$_{0.84}$Yb$_{0.1}$Ho$_{0.05}$F$_3$[b]	1.8×10^{-41}	2.2×10^{-11}	2.03×10^{-8c}	1.61
Eu, Cr: Glass[d]	5.0×10^{-38}	6.0×10^{-10}	1.2×10^{-7}	0.134
Anthracene in fluorene[e]	1.74×10^{-32}	3.4×10^{-7}	3.69×10^{-8}	9.2×10^3
Tetracene in anthracene[e]	1.78×10^{-32}	3.1×10^{-5}	1.84×10^{-6}	1.67×10^{-5}
Tetracene in naphthalene[e]	3.52×10^{-35}	3.1×10^{-6}	1.37×10^{-6}	1.07×10^{-6}

[a]Reference 16.   [d]Reference 15.
[b]Reference 17.   [e]Reference 14.
[c]Estimated using $a=0.676(\alpha/D)^{1/4}$ from Ref. 8.

and D listed in Table I have been determined by fitting the experimental data with the standard diffusion theory and are therefore not totally reliable for establishing or dismissing the importance of single-step transfer in the fast-diffusion regime. [Note the inconsistency indicated by the fact that the parameter $\alpha/(3Da^4)$ is larger than unity in several cases.] The present calculation hopefully can provide some criteria for assigning the values of these physical quantities and for assessing the significance of resonant transfer either by using an independently determined set of parameters or by comparing the full time dependence of the energy-transfer rate to the experimental results.

III. HOPPING ON A RANDOM LATTICE

Another phenomenological approach to the treatment of energy transfer which also enjoys rather frequent use is based on the physical picture of excitations hopping among sensitizers and from sensitizers to activators. In the limit of many steps the results of this random-walk approach are equivalent to those of the diffusion approach. The basic premises of random-walk treatments will now be briefly reviewed.[9,18] Let $\rho_j(t)$ denote the probability that an excited sensitizer is located at $\vec{R}_j$ at time t, the equation for excitation migration is

$$\frac{d\rho_j(t)}{dt} = -\beta\rho_j(t) - \sum_i v(\vec{R}_i-\vec{R}_j)\rho_j(t) \quad . \quad (24)$$

The meanings of the other symbols are the same as those encountered in the last section except that $\vec{R}_i$ now denotes the position vector for either an activator or a sensitizer. The solution to Eq. (24) must be averaged over the configuration of activator-sensitizer distributions and the result designated by $\phi(t)$ may

be correlated to, for example, the luminescence emitted by the sensitizer. It should be noted that Eq. (24) neglects the effects of back transfer from activator to sensitizer ions. This is justified for systems in which relaxation processes on the activator take the excitation out of resonance with the sensitizer which is true for many cases that have been investigated. For systems where back transfer is not a negligible process an additional term is present in Eq. (24).

If the excitations are incapable of migration among the sensitizers themselves, it is possible to solve Eq. (24) and carry out an ensemble average over the uniform distribution of activators and the result, $\bar{\rho}(t)$, for electric dipole-dipole interaction is[1]

$$\bar{\rho}(t) = \exp[-\beta t - (C_a/C_0)(\pi\beta t)^{1/2}] \quad , \quad (25)$$

where C_a is the activator concentration and the "critical concentration" is $C_0=(\frac{4}{3}\pi R_0^3)^{-1}$. Here R_0 is defined as the distance between sensitizer and activator at which the rate of energy transfer is equal to the intrinsic decay rate; i.e., $v(\vec{R}) = \beta(R_0/R)^6$. If, however, the excitations may hop among sensitizers, the interaction strength $v(\vec{R})$ that appears in Eq. (24) abruptly changes each time a hopping takes place and is therefore a random variable. By assuming that the duration over which the interaction strength $v(\vec{R})$ does not change is distributed according to $\tau_0^{-1}\exp(-t/\tau_0)$, and thus identifying τ_0 as the mean hopping time, Burshtein[9] was able to arrive at an equation governing $\phi(t)$

$$\phi(t) = \bar{\rho}(t)e^{-t/\tau_0} + \tau_0^{-1}\int_0^t \phi(t')\bar{\rho}(t-t')e^{-(t-t')/\tau_0}dt' \quad . \quad (26)$$

The solution for Eq. (26) can be obtained by numerical methods[19] and gives results equivalent to those of the Yokota-Tanimota[8] theory in the appropriate limit. On the other hand, if Eq. (24) is to be augmented

with an additional term to account for the back transfer from activator to sensitizer ions, the problem is significantly more complicated[4] and indeed no analytic solution has yet been found.

The merit of Burshtein's approach lies in its simplicity and its relative ease for numerical solution. It remains, however, an approximation. For example, it is easily seen from the probability distribution for dipole-dipole interaction in a random system[20] that the corresponding hopping time distribution is proportional to $t^{-1/2}\exp(-\lambda t)$, where λ is a constant for a given concentration of sensitizers. For a small or moderately large concentration of sensitizers this function falls off much slower than the approximation used by Burshtein. The underlying difficulty in studying hopping motion on a random lattice as described above is this possible wide distribution of hopping times. In the absence of better theoretical techniques to handle such situations, we have resorted to Monte Carlo methods to study this problem. As will be seen, our study leads to rather different results from those predicted by Eq. (26).

The essence of the Monte Carlo calculation will now be described. We generate a finite number of excited sensitizers, allow the excitations to hop around on a matrix of prespecified concentrations of sensitizer and activator sites, and count the fractional excitations that survive at various times. Intrinsic decay of the excitations is easily accounted for and thus is not explicitly considered in this treatment. The disappearance of excitations therefore occurs solely as the result of a jump onto an activator site which has a jump probability dependent upon the fractional occupation of sites by activators. The physical nature of the random distributions of the sensitizers and activators and the ion-ion interaction mechanism can be simulated by the generation of a weighted set of random numbers to be used for hopping times. The standard set of random numbers generated by the computer are uniformly distributed and must be transformed to have the desired characteristics. For example, the sensitizers must obey the law of distribution of the nearest neighbor in a random distribution of available sites (the Hertzian distribution).[11] This law, in the representation of the number of available sites, y, in a sphere centered on a sensitizer site and interior to the nearest-neighboring sensitizer, is $c\exp(-cy)$, where c is the fractional sensitizer occupancy of sites. The sequence of numbers having such a feature is obtained from a sequence of uniformly distributed random numbers r via the expression $y = c^{-1}\ln(1-r)$. (The last relation follows from equating the cumulative distributions of the two sequences.) In a similar manner, we require that the sequence of numbers reflects the nature of an electric dipole-dipole interaction (which falls off as r^{-6}) in addition to that of a random distribution of sensitizers of a given concentration. The

set of weighted random numbers constructed in this way are then used as hopping times for the simulated random walk.

A computer simulation is thus constructed which "observes" the hopping of each generated excitation having first insured that the excitation was not created on an activator site. The time for each hop is selected from the weighted set of random numbers generated by the method described above. This allows the excited sensitizer on each step of the random walk to interact with any of the other randomly distributed sensitizer and activator ions which reflects the electric dipole-dipole nature of the interaction. In this manner any spatial correlation is accounted for. Hopping is allowed to continue until either of the following two events takes place: an activator site is encountered or a particular hop takes a longer time than the time of interest (in the present study, about ten times the intrinsic lifetime). The survival time of each excitation is determined by calculating the sum of all its previous hopping times before being terminated by one of the two criteria mentioned previously. In the end, a bin sort is performed to determine the fractional number of excited sensitizers that have succeeded in avoiding any activator site at various times. To ensure that correct random-number sequences are used in the calculation, the sequences are tested and seen to obey the Hertzian distribution. Furthermore, the results are compared to test whether they are insensitive to different arbitrary cutoffs in the random numbers used in the calculation, as they should be if the proper distribution characteristics are built into the hopping time and sensitizer position distributions.

The results of some typical Monte Carlo calculations of this type are shown in Fig. 1. For each run an average hopping time is determined and is used as an input in Watts's program[19] for integrating Burshtein's equation. The predictions of the Burshtein approach, after being multiplied by $\exp(\beta t)$, are also shown in Fig. 1 for comparison. In general, for the same interaction strength, the Burshtein approach predicts a faster decrease in the excited sensitizer population than does the Monte Carlo simulation. Note that the concentrations used in curve (a) are those of a typical case of energy transfer among Nd^{3+} ions in yttrium gallium garnet crystals which has been investigated recently.[21] The data shown in Fig. 7 of Ref. 21 consist of the time evolution of the intensity ratios of emission centers at two different crystal-field sites. Ions in one type of site are selectively excited by the specific laser frequency used, and energy transfer occurs to ions in the other type of site. The intensity ratios for the three different sets of spectral transition shown in the figure are fitted with the same theoretical parameters. A good fit to experimental data under discussion occurs for either the Monte Carlo simulation with an interaction distance of 20 Å or the
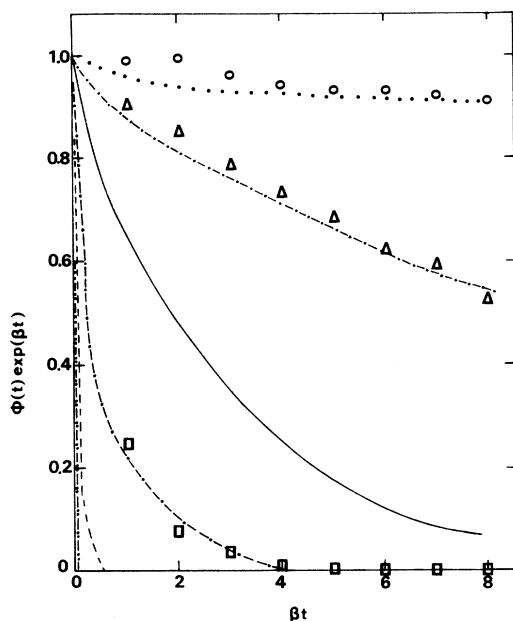
FIG. 1. Comparison of Monte Carlo predictions of excitation survival probability, $\phi(t)e^{\beta t}$, with the predictions of Burshtein's theory. (a) For $C_s = 8.33 \times 10^{-3}$, $C_a = 1.67 \times 10^{-3}$, $\beta^{-1} = 2.5 \times 10^{-4}$ sec, and $R_0 = 20$ Å, O gives the Monte Carlo predictions and —— gives the Burshtein-theory prediction. ... gives the Burshtein theoretical prediction for the same concentrations but with $R_0 = 11$ Å. (b) For $C_s = 8.33 \times 10^{-2}$, $C_a = 1.67 \times 10^{-3}$, $\beta^{-1} = 2.5 \times 10^{-4}$ sec, and $R_0 = 20$ Å, Δ gives the Monte Carlo predictions and — — — is the prediction of the Burshtein theory. For the same concentrations but $R_0 = 12$ Å the Burshtein-theory prediction is given by —·—·. (c) For $C_s = 8.33 \times 10^{-2}$, $C_a = 1.7 \times 10^{-2}$, $\beta^{-1} = 2.5 \times 10^{-4}$ sec, and $R_0 = 20$ Å, □ represents the Monte Carlo results and —·· gives the Burshtein results. —·— gives the prediction of the Burshtein theory for the same concentrations but with $R_0 = 12$ Å.

Burshtein theory with a critical interaction distance of 11 Å. Theoretical estimates for R_0 for this system are closer to the larger value but this must be considered as only a rough approximation because of the complicated nature of the phonon-assisted diffusion enhanced energy transfer in this system.[21]

IV. DISCUSSION AND CONCLUSIONS

A rigorous, complete solution to the problem of energy transfer among randomly distributed sensitizers and activators is still lacking. This is especially true if the additional complications of back transfer from activators to sensitizers and random distributions of transition energies are included. Recently there have appeared a significant number of theoretical works on these and related subjects, among which

may be mentioned the papers of Haan and Zwanzig,[5] Huber,[4] and Holstein, Lyo, and Orbach.[3] These generally use more powerful mathematical techniques and starting with the elemental interactions among sensitizers and activators, they seek to elucidate the connection between the behavior on the microscopic scale and the somewhat more phenomenological diffusion and random-walk models. The final exact solution to this complicated physical problem has not yet been obtained. In the preceding sections we have concerned ourselves with several aspects of both the diffusion and random-walk models of the energy problem with the objective to supplement and clarify some aspects of these existing models. The virtue of these models has been their capability of being brought into direct comparison with experimental results and the more fundamental theories[4,5] by and large confirm in the appropriate limits the validity of these phenomenological models. This provides the justification and possible usefulness of the present work.

We have developed here two important aspects of the energy-transfer problem. The first is a theoretical expression for treating the case: The direct sensitizer-activator interaction is a small perturbation on the transfer of energy by diffusion among the sensitizers. The second is a Monte Carlo approach to simulate the migration of excitations on a random distribution of sensitizers. It should be pointed out that the approach to the Monte Carlo simulation used here is similar to the continuous-time random-walk model developed to explain anomalous transit-time dispersion for charge carriers in amorphous solids.[22,23] It attempts to account for the possibility of transfer from an excited sensitizer to any other sensitizer in the system at each step in the random walk by using the configuration-averaged distribution of hopping times at each site. This is different from the Monte Carlo procedure used previously[3] which generates a specific lattice topology, assumes only first nearest-neighbor steps and then forms a configuration average of the results. In that study[3] which correlates the decrease in fluorescence emission from ions in selective excited sites due to energy migration to ions in different types of neighboring sites, care must be exercised in dealing with excitations hopping back to the original site since this offsets the time-dependent line-narrowing effect. This clearly presents no particular problem in the present study; a return to the original site has no distinguishable effects from hopping to a fresh sensitizer site.

Table II compares the commonly used phenomenological models of energy transfer and indicates the physical situation in which each model is valid. This shows the important areas of usefulness for the two theoretical treatments developed here. It should be stressed that each of these models should be applied only to the physical situations in which they are valid;

TABLE II. Phenomenological models for the dynamics of energy transfer.

Model	Region of applicability	Ref.
Förster-Dexter	Direct s-a interaction; no sensitizer energy diffusion	1, 2
Yokota-Tanimota	Strong s-a interaction; weak sensitizer energy diffusion	8, 1
Chow-Powell	Weak s-a interaction; strong sensitizer energy diffusion	This paper
Burshtein	Equivalent to Yokota-Tanimota model and diffusion/random-walk model in the appropriate limits	9
Soos-Powell	Strong sensitizer energy diffusion with the effects of extended trapping regions	10, 14
Diffusion-random walk	No direct s-a interaction; energy transfer by hopping onto an activator site	7, 11
Monte Carlo	No direct s-a interaction; transfer by energy diffusion on a random lattice	3, this paper

this has not generally been true in the past. For example, the results of the preceding section show that, if data involving energy migration on a random distribution of sensitizers are analyzed with the Burshtein model, the interaction strength one obtains is approximately a factor of 2 smaller than the value found from the Monte Carlo treatment which accounts for the random distribution of hopping times. Note that the Burshtein model is equivalent to the Yokota-

Tanimota model in the weak-diffusion limit and equivalent to the standard diffusion result in the strong-diffusion limit. However, it does not correctly account for the effects of direct sensitizer-activator interaction when it is not negligible in the fast-diffusion regime and it does not correctly account for the distribution of hopping times when hopping takes place on a random lattice. The models developed here are most applicable in these regions where the Burshtein approach fails. Also, of course, there are special situations where none of the models in Table II apply. An example of this is when high-resolution laser experimental techniques, such as fluorescence line narrowing are used and theories accounting for differences in transition energies must be employed.

In summary, we have developed two new approaches to the problem of energy transfer of solids which allow for the treatment of physical situations involving strong diffusion with weak direct sensitizer-activator interaction and migration of energy on a random distribution of sensitizers. Both of these situations have important applications to impurity-doped laser materials and many of the previous results on these materials should be reinterpreted using the new models described here.

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