Role of the crystal structures in the hopping models of luminescence extinction

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By using numerical methods we carried out the solution of the integral equation which describes a nonradiative excitation energy transfer within the framework of the hopping mechanism. We used various models for the excitation outflow in a disordered collection of donors with and without inclusion of the crystal lattice geometry, and we considered various values of the parameters which characterize the theory. We conducted an analysis of the results. We revealed the main characteristics which arise in the kinetics of the hopping luminescence extinction when the crystal structure is taken into account.

One of the problems which arise when investigating processes of nonradiative energy transfer in a collection of interacting particles is the determination of microscopic donor-donor (C_{DD}) and donor-acceptor (C_{DA}) interaction parameters which reflect the processes of ion-ion interactions at a microscopic level. Investigations, having this aim, of the decay curves of the donor excited state after the sample has been excited by a short light pulse is as a rule limited by the characteristic time intervals, including the limit as $t \to \infty$. Generally speaking, this complicates extraction of the information about various stages of the process of nonradiative energy transfer.[1] These stages could significantly superimpose onto each other so that experimental decay curves reflect a superposition of different processes rather than their individual manifestations which are described by various theoretical models. The time hierarchy needed in these conditions by the theory to describe the experimental results is often not clear beforehand. The most adequate, even though cumbersome, approach to the solution of this problem is to analyze, within the framework of an appropriate model of the extinction, the experimental decay kinetics over the whole investigated time scale, rather than to use only its characteristic intervals. A necessary step in this direction is to account for the geometry of the crystal lattice, that is, to change from integral formulas to their analogs that account for the crystal structure.

It was shown in Refs. 2 and 3 that the kinetics of the hopping migration-accelerated energy transfer for samples excited by short light pulses is described by the integral equation

$$N(t)=N_0(t)R(t)-\int_0^t N_0(t-t')\dot{R}(t-t')N(t')\,dt'. \qquad (1)$$

Here $N(t)$ is the number of excitations which are not lost by the time t, the function $R(t)$ describes kinetics of the excitation outflow (escape) to unexcited donors, and the quantity $N_0(t)$ characterizes the kinetics of the static excitation extinction. Since, as mentioned above, breaking up of the decay processes into characteristic stages can turn out to be difficult in certain cases, it is of some interest to describe the decay process in a unified way as the result of the solution of Eq. (1).

For low acceptor concentrations and for the dipole-dipole interaction which will be considered below the quantity $N_0(t)$ is usually written in an integral form:[4]

$$N_0(t)=\exp(-\gamma_a t^{1/2}), \quad \gamma_a={}^4/_3\pi^{3/2}n_A C_{DA}^{1/2}, \qquad (2)$$

where γ_a is the microscopic parameter of the static disordered decay (n_A is the acceptor concentration). From the viewpoint of accounting for the crystal structure it is clear that the following exact expression for $N_0(t)$, valid for all acceptor concentrations, should be used:[5,6]

$$N_0(t)=\exp\left\{\sum_i \ln[1-y+y\exp(-W_{DA(i)}t)]\right\}, \qquad (3)$$

where the sum extends over all sites of the acceptor sublattice, $y=n_A/N_A$ is the relative concentration of the acceptors (N_A is the concentration of the acceptor sites), $W_{DA}=C_{DA}/r^6$, and r is the distance between the interacting particles.

A choice of the outflow function $R(t)$ is not unique. In the early works[2,7] an equivalent regular lattice of donors with some average spacing was considered. In this case the outflow kinetics was exponential:

$$R(t)=\exp(-t/\tau_0), \quad \tau_0=({}^8/_{27}\pi^3 C_{DD}n_D^2)^{-1}, \qquad (4)$$

where τ_0 is the most probable time for the donor-donor transfer[2,7] and n_D is the donor concentration. An account for the return of an excitation to its initial center during a random walk over the lattice somewhat increased the total time that an excitation would spend at the initially excited center.[8–10]

In Ref. 3 an integral expression of the form (1) was obtained with the function $R(t)$ accounting for the dispersion of the probabilities for the excitation extinction in the disordered donor subsystem. Using Ref. 11 we have[3] for $R(t)$

$$R(t)=\exp(-\gamma\, t^{1/2}), \quad \gamma_d={}^4/_3\pi^{3/2}n_D C_{DD}^{1/2}. \qquad (5)$$

The "structure" analog of (5) has clearly the form[5,6]

$$R(t)=\exp\left\{\sum_i \ln[1-x+x\exp(-W_{DD(i)}t)]\right\}, \qquad (6)$$

where the sum is over all sites of the donor sublattice, $x=n_D/N_D$ is the relative donor concentration (N_D is the concentration of the donor sites), and $W_{DD}=C_{DD}/r^6$.

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An account of the reversibility of the excitation flow in ordered as well as disordered donor systems was made in Refs. 12–15. In particular, a model was investigated in which an excitation is "distributed" between two donors—the initially excited one and the nearest unexcited one. Such a "partial" account of the return is fully justifiable at small concentrations of donors when the probability of finding a donor having two or more nearest neighbors is small. In this case the outflow function has the form

$$R(t)=\exp\left\{\sum_i \ln\left[1-x+x\exp(-W_{DD(i)}t)\cosh(W_{DD(i)}t)\right]\right\}. \tag{7}$$

According to Ref. 2, accounting for the reversibility of the excitation loss reduces to substituting in Eq. (1) the appropriate outflow function $R(t)$.

It is of interest to compare the results of the solution of Eq. (1) for different functions $N_0(t)$ and $R(t)$ (without subdividing the decay curve into characteristic intervals[7]) and to quantitatively assess the influence of the crystal structure characteristics on the donor excitation decay kinetics for various combinations of $N_0(t)$ and $R(t)$. With this aim, Eq. (1) was numerically solved with a computer for the following combinations of the functions $N_0(t)$ and $R(t)$:

$N_0(t)$ (Eq. (3)), $R(t)$ (Eq.(4)) (8)
$N_0(t)$ (3), $R(t)$ (6) (9)
$N_0(t)$ (3), $R(t)$ (7) (10)
$N_0(t)$ (2), $R(t)$ (4) (11)

Therefore, with the use of the exact equation (3) for the static energy-transfer function, the cases (8), (9), and (10) have different outflow functions $R(t)$: exponential in the equivalent donor lattice model (8); one that accounts for the disorder of the donors (9); and one that accounts for the partial return of the excitations in the disordered donor system (10). In the case (11) the Förster expression (2) is used for the static transfer function $N_0(t)$ and exponential outflow function is used for $R(t)$.

Precisely the last case as the simplest one is usually employed for the analysis of the experimental data in investigations of the asymptotics of the decay curves. We compare below the results of calculations for this case with the results obtained with account of the crystal structure. We remark that Eq. (1) with the condition (11) was solved in Ref. 16 by numerical methods.

Besides this, time evolutions of the donor-excited-state populations were calculated with the use of a relationship obtained in Ref. 17 within the framework of the approach of Ref. 18:

$$W(t)=\frac{n_A}{N_D}\sum_i W_{DA(i)}n(r_i,t), \tag{12}$$

where the sum is over the sites of the donor sublattice while

$$N(t)=\exp\left(-\int_0^t W(t')dt'\right)$$

and $n(r_i,t)$ are determined in accordance with Ref. 18.

We remark that a drawback of the developed approach is that accounting for the crystal structure can make it difficult to obtain in a general form some of the results, particularly the dependence of the rate of extinction on the particle density. However, this is necessary in order to formulate the conditions of applicability and correct description of the experimental results within the framework of analytical model relationships which assume a possibility of isolating various stages from the general experimental excited-state decay curves.

It is clear from Refs. 2, 3, 7, and 15 that the above mentioned dependences remain when going over from the exponential outflow to a nonexponential one. Nevertheless, as we shall show below, disregard of the structure of a real crystal can lead to quantitative as well as qualitative disagreements between the theory and a real situation.

We have also calculated the decay curves of the excited donor states using the results of Ref. 18. In this reference the kinetics of the luminescence extinction was determined over the entire time scale within the framework of the hopping mechanism for the extinction. They considered the case $n_A R_w^3 < 1$, where R_w is the effective-extinction-sphere radius, and they assumed $r_1 = 0$ (r_1 is the minimal donor-acceptor distance). The corresponding expressions had the form

$$N(t)=\exp\left[-\Pi(t)\right],$$

$$\Pi(t)={}^2/_3\pi^2 n_A (C_{DA}\tau_0)^{1/2}\{{}^1/_2\Phi[(t/\tau_0)^{1/2}]+(t/\tau_0)\Phi[(t/\tau_0)^{1/2}] + (t/\pi\tau_0)^{1/2}\exp(-t/\tau_0)\}, \tag{13}$$

where

$$\Phi(x)=\frac{2}{\pi^{1/2}}\int_0^x e^{-z^2}dz.$$

We conducted calculations for a simple cubic lattice according to (1) in the cases (8), (9), and (10), as well as according to (12), assuming that donors and acceptors can be situated at the same sites. As the dimensionless time we chose the quantity

$$\tau=t/\tau_1, \quad \tau_1^{-1}=C_{DA}/r_1^6.$$

When using (11) and (13) the dimensionless time was chosen equal to $\tau = t/\tau_0$ because in this case it is assumed that $r_1 = 0$ and the time τ_1 looses its meaning.

In Fig. 1a the results of the numerical solution of (1) with the conditions (8), (9), and (10) are given. As can be easily shown in general, in the initial intervals of the excited donor state decay curves ($t \ll \tau_1$) the extinction rates are the same in all three cases (8), (9), and (10) and equal[1,2]

$$W_m = yC_{DA}\sum_i \frac{1}{r_i^6} \tag{14}$$

(the sum is over the sites of the acceptor sublattice). Immediately afterwards, the curves diverge significantly because the donor excited state populations differ in various models by a quantity of order 50% already to first order.

We remark that the maximal extinction rate, which is realized for short times ($t \ll \tau_1$) and at the kinetic stage,[2] when obtained by using the expression (3) for $N_0(t)$ with $y = x/2$ in

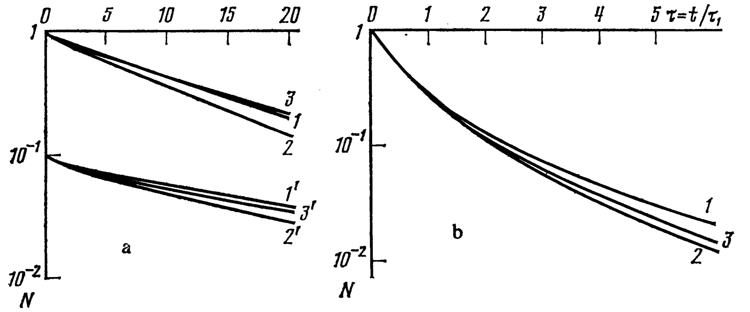

FIG. 1. Time evolutions of the donor excited state populations calculated: (a) according to the formulas (1) and (8) (curves 1 and 1'), (1) and (9) (curves 2 and 2'), (1) and (10) (curves 3 and 3'), where $z = C_{DA}/C_{DD} = 0.2$, $y = 0.02$, $x = 0.1$ (curves 1–3), and $x = 0.05$ (curves 1'–3'); (b) according to the formulas (1) and (8) (curve 1), (1) and (9) (curve 2), (1) and (10) (curve 3), where $z = 0.2$, $y = 0.2$, and $x = 0.033$.

the Burshteĭn integral equation for self-extinction of impurities,[2] is two times smaller than the one obtained from (14).

With an increase in the acceptor concentration y (a decrease of donor concentration x) the obtained decay curves converge due to an increase in the static extinction contribution and a decrease in the migration-accelerated one (Fig. 1b), i.e., a more distinct separation of one of the extinction stages takes place, namely that of the static decay stage.

We used the exact static energy transfer function (3) when solving the integral equation (1) with allowance for the crystal lattice geometry. Clearly, the results of the solutions should, generally speaking, depend on the lattice type and on the properties of the function (3). As it was shown in Ref. 19, for a given function (with log t as the independent variable) it is possible that "oscillations," i.e., sign reversals of the second derivative, take place in contrast to the integral analog in (2). The plots given in Ref. 19 can create the impression that the population $N_0(t)$ oscillates. Nevertheless, it can be easily shown that the second derivative of the function (3) with respect to time (rather than with respect to log t) is always positive. That is, no such oscillations occur in the usual time scale and the indicated effect is purely a scale effect. We remark that the extinction rate calculated for the disordered donors according to (9) is higher than for the equivalent regular lattice, although it would seem that the highest migration extinction rate should correspond to the ordered distribution of the donors.[20]

If the disordered donors whose concentration is n_D are to be placed on the sites of a simple cubic lattice with the period $n_D^{-1/3}$, the rate of the excitation outflow $\approx 8.4 C_{DD} n_D^2$ would be even smaller than τ_0^{-1}. Correspondingly, the migration extinction rate would be also smaller than if the expressions (5) and (6) were used for the outflow function of the real, disordered distribution of the initial donors. This may be due to neglect of the correlations in donor as well as acceptor surroundings of various donors. This is particularly important for donors at small distances from each other because fast excitation transfer between them does not lead to a real transport of excitations through the donor subsystem and it practically does not modulate the rate at which the excited state decays. It can be seen from Fig. 1a that a partial account of the return[12–15] reduces the decay rate owing to the reduction in the rate of the real displacement of excitations through the donor subsystem. In this case (see Fig. 1a) there is a crossing of the decay curves calculated for the equivalent regular donor lattice (8) and for the disordered distribution of donors accounting for the return (10) (curves 1 and 3, respectively; curves 1' and 3' intersect at the later time than the times shown in the figure). This circumstance is clearly related to the fact that the returns start to play a significant role only at relatively large times.

It is also necessary to remark on a certain inconsistency of the approach, due to inclusion of the return in the final equation obtained by assuming the process to be uncorrelated. Apparently, direct inclusion of the return of the excitations in the derivation of the basic equation would be more correct. This is an independent problem which is not solved at present.

Figure 2 shows the results of the solutions of Eq. (1) with the conditions (8) and (11), that is, with and without inclusion of the crystal lattice geometry. The relative time t/τ_0 is the abscissa. The degree of discrepancy of these results depends on the ratio τ_1/τ_0. It amounts to $\approx 60\%$ for $\tau_1/\tau_0 = 0.5$ ($x = 0.1$, $y = 0.05$) and to $\approx 100\%$ for $\tau_1/\tau_0 = 1$ ($x = 0.15$, $y = 0.075$) within the dynamical range of the donor excited state population variation, which comprises two orders of magnitude.

As demonstrated in Ref. 2, for sufficiently large concentrations of donors, when the transition into the kinetic limit regime takes place, the use of the expression (2) for $N_0(t)$ in equation (1) is not valid. In order to obtain from equation (1) the kinetic regime limit it is necessary to replace the function $N_0(t)$. With the help of Refs. 2 and 18 it is easy to show that generally even when $N_0(t)$ is replaced with the expression (3) in the limit $\tau_0/\tau_1 \to 0$ (which corresponds to the approach to the kinetic limit regime) the rate of the stationary migration extinction approaches the initial rate W_m (14). That is, a crossover to the extinction within the regime of rapid excitation energy migration through the donor subsystem automatically takes place in this case.

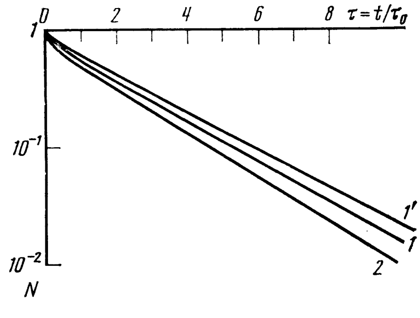

FIG. 2. Equations (1) and (8) lead to the curves 1 and 1' for the values of $z = 0.2$, $y = 0.05$, $x = 0.1$ and $z = 0.2$, $y = 0.75$, $x = 0.15$, respectively. Equations (1) and (11) lead to the curve 2.

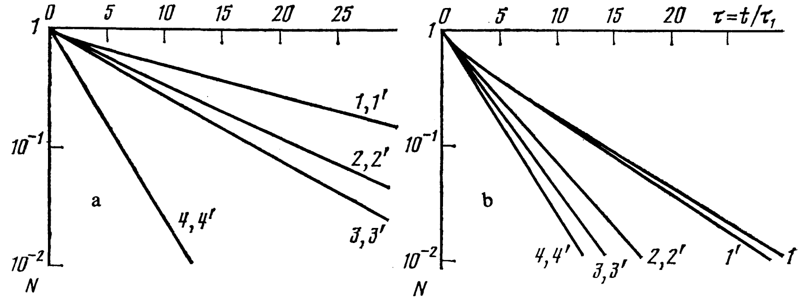

FIG. 3. Time evolutions of the donor excited state populations calculated according to the formulas (1) and (8) (curves with an unprimed number) or (12) (curves with a primed number), and for $z = 0.2$ $\tau_0/\tau_1 = 4$ (curves 1 and 1'), $\tau_0/\tau_1 = 1$ (curves 2 and 2'), $\tau_0/\tau_1 = 0.5$ (curves 3 and 3'), and $\tau_0/\tau_1 = 0.2$ (curves 4 and 4'). In (a) $y = 0.02$, while in (b) $y = 0.05$.

Since Eq. (1) is valid for all values of the parameter[2]

$$q=(\tau_0\Delta)^{1/2}, \qquad \Delta={}^{16}/_{9}\pi^3 n_A{}^2 C_{DA},$$

while the approach presented in Ref. 18 is based on an expansion in the small parameter $n_A R_w^3$ which is valid[18] for $\tau_0\Delta < 1$, it was of interest to make precise the limits of applicability of the results obtained within the framework of such an approach. In Figs. 3a and b we show calculations of the evolutions of the donor excited state populations for $y = 0.02$ (a) and 0.05 (b) and for various values of τ_0/τ_1 (R_w/R_1, correspondingly). Clearly, within the dynamical range for the change in the donor excited state population, which covers two orders of magnitude, the calculated values of the population are in agreement within $\sim 10\%$, as is usual in experiments at $q \lesssim 0.7$ which corresponds to Ref. 18.

We should remark in conclusion that our numerical solution of Eq. (1) with account taken of the crystal structure allows us to obtain a number of principal results and to determine the microscopic interaction parameters without sometimes unjustifiable division of the donor excited state decay process into characteristic stages. At the same time, it is obvious that this approach is cumbersome, in contrast to the presently accepted methods for the analysis of the asymptotics. Of course, the choice of one or another method of the analysis of experimental data is determined by the specifics of the investigated objects and by the concrete experimental problem.

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