Concentration self-quenching

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Concentration self-quenching of excitations by cross-relaxation of energy between the impurity centers is considered. It is assumed that resonance-excitation migration over the impurities leads to an uncorrelated change of configuration of the surrounding particles after a jump. The self-quenching rate calculated in accordance with the theory of continuous random walks is found to be independent of resonant interaction between the centers. However, correction of the theory by partially taking into account the return of an excitation to the initial center restores the kinetic similarity of the quenching and self-quenching processes, the only difference being in the numerical values of the rate constants.

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INTRODUCTION

By concentration quenching is usually meant excitation quenching produced in solids or in very viscous liquid solutions when the activator (energy-donor) concentration $[D]=\rho$ is increased. This phenomenon is due to resonant transfer of energy from an excited donor to an unexcited one, a transfer that ensures spatial delocalization of the excitation migrating over identical impurity centers. The migration of the excitation does not by itself shorten its lifetime, but ensures transport of the energy to its sinks. These are the donors on which the excitation annihilates faster than on others. The most common cause of accelerated of energy dissipation on these donors is their proximity to acceptors—impurity centers to which the energy is transferred irreversibly. In such a case the quenching is enhanced not only with increasing ρ, but also when the energy-acceptor concentration $c=[A]$ is increased. As a result, the theory of concentration quenching should generally speaking consider the dependence of the pressure on two variable concentrations, ρ and c. It happens, however, that the same impurity centers are simultaneously both donors and acceptors of energy. This is possible if the interaction between them is capable of leading to irreversible replacement of one excitation by two that are approximately half as large, via a cross-relaxation mechanism (Fig. 1). This is the situation in crystals and glasses activated with neodymium ions, in the Stark-level system of which there are located states $4F^{3/2}$ suitable for cross-relaxation deactivation.[1–4] The symmetrical vibration of the CH_3 of the CH_3CCl_3 molecule is quenched in exactly the same manner in a liquid solution by changing into two low-frequency oscillations, identical or different, the sum of the energies of which is approximately equal to the initial excited value.[5] Self-quenching becomes forced with increasing impurity concentration, even if there is no resonant transfer of the excitation. But the latter is always present. By changing cross-relaxation partners with different distances to the excited donor, the migration modulates the rate of its quenching with time. Calculation of the resultant rate of this process is in fact the subject of the present paper.

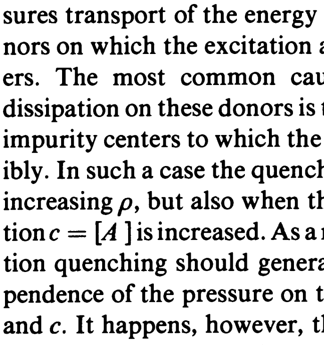

FIG. 1.

1. HOPPING QUENCHING

Concentration self-quenching of Nd^{3+} became the first object of application of the theory of hopping quenching,[1] even though the latter always dealt with donors and acceptors of different type.[6] It was implied that the hopping thoery describes self-quenching as a particular case in which $\rho\equiv c$. Actually, in principle acceptors and donors were treated in Ref. 6 differently. The acceptors were assumed to be distributed uniformly but randomly in space. The quenching probability of each donor by the aggregate of its surrounding acceptors

$$W=\sum_i w(r_i) \tag{1.1}$$

depended on the concrete configuration of the acceptors located at different distances r_i from the donor. On the contrary, the donors were assumed to be located at the sites of an "equivalent" lattice, whose period was equal to the average distance between them, $\lambda=\rho^{-1/3}$. For this reason, the rate of outflow from any site was assumed to be the same at

$$1/\tau_0=8\pi^3 C_{DD}\rho^2/27, \tag{1.2}$$

where C_{DD} is a constant that determines the probability of resonant dipole-dipole transfer of excitation from donor to donor:

$$u=C_{DD}/r^6. \tag{1.3}$$

Obviously, under these assumptions, the kinetics of the outflow (irreversible departure of excitation from its creation point) is always exponential

$$R_e=\exp(-t/\tau_0). \tag{1.4}$$

An entirely different kinetics is obtained for static (in the absence of migration) quenching of excitation by acceptors:

$$N_0=\langle\exp(-Wt)\rangle. \tag{1.5}$$

The averaging designated by the angle brackets, over different random configurations of the acceptors, transforms quenching into a non-exponential process. In particular, in dipole-dipole quenching, when

$$w=C_{DA}/r^6, \tag{1.6}$$

we obtain the well-known Förster result[7]:

$$N_0=\exp(-\sqrt{qt}), \quad q={}^{16}/_9\pi^3C_{DA}c^2. \tag{1.7}$$

According to the theory of hopping quenching[6], the kinetics of a migration-accelerated process $N(t)$ is described by the integral equation

$$N(t)=N_0(t)R_e(t)-\int_0^t N_0(t-t')\dot{R}_e(t-t')N(t')\,dt', \tag{1.8}$$

the kernel of which is the product of the function $N_0\dot{R}_e$. At $q\tau_0\ll 1$ this process develops exponentially over practically its entire extent, at a rate

$$\overline{W}=-\int_0^\infty\frac{\dot{N}_0R_e}{N_0}\frac{dt}{\tau_0}. \tag{1.9}$$

If both the transport and the quenching are dipole-dipole, using expressions (1.4) and (1.7) in (1.9), we obtain[6]

$$\overline{W}=(\pi q/4\tau_0)^{1/2}=\pi(2\pi/3)^{5/2}(C_{DA}C_{DD})^{1/2}c\rho. \tag{1.10}$$

It was indicated many times that the numerical coefficient in this formula should be corrected, particularly because the kinetics of the outflow $R(t)$, even in the case of ordered arrangements of the donors, coincides with (1.4) only during the initial state ($t\lesssim\tau_0$), when the return of the excitation to the initial center can be neglected. In fact, however, the number of excitations that return at least once to the point of creation is equal approximately to 25%. In the course of time, when the fraction of the excitations that do not leave the initial center becomes smaller than those returning after random walks over the crystal, the outflow kinetics becomes of the diffusion type: $R\propto 1/\rho(4\pi Dt)^{2/3}$ $(t\gg\tau_0)$. This difference between R and R_e lengthens the average time of stay of the excitation at its initial center:

$$\bar{\tau}=\int_0^\infty R(t)\,dt=\eta\tau_0. \tag{1.11}$$

For dipole-dipole transport, $\eta=1.266$ for a primitive cubic lattice, 1.214 for a body-centered lattice and 1.211 for a face-centered lattice.[8] Owing to the returns of the excitation, the modulation W in the course of the random walks is not strictly speaking a process without memory, as assumed in Ref. 6. It was established nevertheless in Ref. 9 that replacement of τ_0 by $\bar{\tau}$ in (1.10) is the only necessary refinement of this result in the case of ordered arrangement of the donors. This conclusion was subsequently confirmed in Ref. 10.

In the case of disordered donors, the kinetics of outflow is different from (1.4) even at the initial irreversible state of the process at $t\leqslant\tau_0$. The outflow probability

$$U=\sum_l u(r_l) \tag{1.12}$$

is different for different centers because of the different configurations of the surrounding donors. Outflow kinetics averaged over these configurations

$$R_0(t)=\langle\exp(-Ut)\rangle=\exp\left\{-\rho\int[1-\exp(-u(r)t)]d^3r\right\} \tag{1.13}$$

does not differ during this stage from the quenching kinetics from the viewpoint of the time dependence.[11] For dipole-dipole excitation transfer

$$R_0(t)=\exp(-\sqrt{6t/\tau_0}). \tag{1.14}$$

The average time of stay on the initial center, obtained from the equation

$$\tilde{\tau}=\int_0^\infty R_0(t)\,dt, \tag{1.15}$$

is one-third the value of τ_0 only because of the variance of the outflow probabilities. Consequently, this factor is at least just as important as the return of the excitation. In the next section we consider how it can be taken into account separately, and then introduce into the calculation a correction for the partial allowance for the return of the excitation.

2. UNCORRELATED CHANGE OF PROBABILITIES

From the very start, the theory of hopping quenching was constructed under the assumption that the probability of quenching after each hop of the excitation can be arbitrary, independent of the preceding value, in strict accordance with the equilibrium distribution $\varphi(W)$ of the donors over the quenching probabilities.[6] Such a change of $W(t)$ is known in the theory of Markov processes as uncorrelated. The memory function $f(W',W)$ which establishes the connection between the quenching probabilities before and after the hop, coincides in this case with φ, namely $f(W',W)=\varphi(W)$. The question of determining the corresponding function $f(U',U)$ did not arise, since it was assumed that $\varphi(U)=\delta(U-1/\tau_0)$.

As already indicated, for disordered systems this assumption is artificial, even if the return of the excitation to the initial center is neglected. The donor distribution in U is exactly the same as in W. However, any theory that makes possible the use of this distribution requires additional assumptions which are not always explicit, but are essentially connected with the correlation of U' and U, as well as of U and W. Such is, in particular, the presently very popular theory of "continuous-time random walks (CTRW). It was first used to describe dipole-dipole transport of excitation in a disordered system of centers by Vugmeĭster,[12] and then used many times for the same purpose by others.[13,14] Vugmeĭster derived in the same formalism an integral equation similar to (1.11), which describes the kinetics of the hopping quenching with allowance for the variance of the outflow probabilities. It was recently duplicated in Ref. 15, where the authors avoided the uncoupling procedure used in CTRW, assuming that not only $W(t)$ but also $U(t)$ varies with time in an uncorrelated manner, i.e., $f(U', U) = \varphi(U)$.

On the basis of this assumption, the validity of which we shall discuss later, it is easy to consider not only quenching but also self-quenching. The difference from the usual situation, in which the donors and acceptors are different particles, lies only in the fact that the averagings over U and W are not independent. To demonstrate this, we use an economical and effective method of summing over realizations, first used to obtain Eq. (1.8) (Ref. 6). All the realizations of a random process are broken down into subensembles, in which: a) not a single hop took place in the time interval $(0, t)$; b) only one hop took place at the instant t' in this interval; c) two hops occurred at the instants t'' and t' $(t'' < t')$, etc. The probability that the hop takes place in an interval dt near t is obviously $Ue^{-Ut}dt$, and the probability of quenching in this interval is either dependent (self-quenching) or independent of U (quenching). Reasoning in this manner, it is easy to specify $N(t)$ in the form of a series

$$\begin{aligned} N(t) = \langle e^{-(W+U)t}\rangle + \int_0^t \langle e^{-(W+U)(t-t')}\rangle \langle e^{-(W'+U')t'}U'\rangle dt' \\ + \int_0^t \langle e^{-(W+U)(t-t')}\rangle dt' \int_0^{t'} \langle e^{-(W'+U')(t'-t'')}U'\rangle \\ \times \langle e^{-(W''+U'')t''}U''\rangle dt'' + \dots \end{aligned} \tag{2.1}$$

The process must be uncorrelated for the averaging over the probabilities in each time interval between the successive excitation hops to be independent of the remaining ones. The expression (2.1) obtained in this manner can be represented in the form

$$N(t) = F(t) + \int_0^t F(t-t')P(t')dt', \tag{2.2}$$

in which $F = \langle \exp[-(W+U)t]\rangle$, and P satisfies the equation

$$P(t) = \Phi(t) + \int_0^t \Phi(t-t')P(t')dt', \tag{2.3}$$

where

$$\Phi(t) = \langle U \exp[-(W+U)t]\rangle.$$

Taking the Laplace transform of Eqs. (2.2) and (2.3), it is easy to obtain

$$\tilde{N}(s) = \tilde{F}(s)[1+\tilde{P}(s)], \quad \tilde{P}(s) = \tilde{\Phi}(s)/[1-\tilde{\Phi}(s)]. \tag{2.4}$$

Eliminating $\tilde{P}(s)$ from these equations, we have

$$\tilde{N}(s) = \tilde{F}(s) + \tilde{\Phi}(s)\tilde{N}(s). \tag{2.5}$$

Returning to the temporal variables, we find ultimate

$$N(t) = F(t) + \int_0^t \Phi(t-t')N(t')dt'. \tag{2.6}$$

To obtain from this an equation that describes the concentration quenching, it suffices to recognize that the distributions of the donors and acceptors in space are not correlated. This makes it possible to average over W and U independently, and calculate F and Φ:

$$F(t) = \langle e^{-Wt}\rangle\langle e^{-Ut}\rangle = N_0(t)R_0(t), \tag{2.7}$$

$$\Phi(t) = -\langle e^{-Wt}\rangle \left\langle \frac{d}{dt} e^{-Ut}\right\rangle = -N_0(t)\dot{R}_0(t). \tag{2.8}$$

Substituting these results in (2.6) we obtain indeed the Vugmeĭster equation[12,15]:

$$N(t) = N_0(t)R_0(t) - \int_0^t N_0(t-t')\dot{R}_0(t-t')N(t')dt', \tag{2.9}$$

which differs from (1.8) in that R_e is replaced by R_0. This difference can be traced all the way to the formula that determines the rate of the hopping quenching, which was first obtained by a different method in Ref. 16:

$$\overline{W} = -\int_0^\infty \frac{\dot{N}_0 R_0}{N_0}\frac{dt}{\tilde{\tau}} = -\frac{1}{\tilde{\tau}}\int_0^\infty \ln N_0 \dot{R}_0\, dt.$$

The difference of this result from (1.9) does not reduce to replacement of τ_0 by $\tilde{\tau}$. The averaging is carried out here over a non-exponential distribution of the times $\psi(t) = -\dot{R}_0(t)$, which distinguishes in principle the CTRW theory from the Markov theory. Nonetheless, the quenching rate differs only numerical coefficients from its Markov analog (1.10):

$$\overline{W} = \left(\frac{q}{2\tilde{\tau}}\right)^{1/2} = \frac{8\pi^3}{9}(C_{DA}C_{DD})^{1/2}c\rho. \tag{2.10}$$

When estimating with the aid of these formulas the self-quenching rate, the usual assumption[2–5] is that $\rho \equiv c$, which yields the experimentally observed quadratic dependence of the rate on the activator density. However, the application of the Markov theory to this problem seems inconsistent, since it is necessary to regard the same particles as arranged both in order and randomly, depending on whether they serve to transport or quench the excitation. Utterly inapplicable in the CTRW theory is also Eq. (2.10), no matter how it is derived. Although it takes into account the scatter, over the states, of both the acceptors and the donors, the averaging over either type of particle located around the excitation is carried out in (1.5) and (1.13) quite independently. But if the donors and acceptors are identical particles, they are distributed in like manner around the excited center.

In other words, in the course of migration the probabilities W of the self-quenching and U of the outflow vary in a correlated manner: they increase or decrease together when the excitation hops over from one center to another. This is in principle compatible with the fact that their new values are not dependent in any way on the preceding ones. However, the separate averaging over W and U, assumed in (2.7) and (2.8), is inadmissible. There is a single distribution of N particles in the volume V, which at moderate $\rho = N/V$ is multiplicative over the distributions of each individual particle:

$$dW = \prod_{i=1}^{N} (d^3r_i/V).$$

It is this distribution that must be used to calculate the functions $F(t)$ and $\Phi(t)$, going to the limit as $N \to \infty$, $V \to \infty$, and $\rho = \text{inv}$, as in usually done.[17] Taking (1.11) and (1.12) into account, we have

$$F = \lim_{N,V\to\infty} \left\langle \exp\left\{-\sum_{i=1}^{N} (w_i+u_i)t\right\}\right\rangle = \exp\{-\rho I\},$$

$$I = \int [1-e^{-(w+u)t}]d^3r. \tag{2.11}$$

Somewhat more complicated is also the averaging of the quantity

$$\Phi = \lim_{N,V\to\infty}\left\langle \sum_{i=1}^{N} u_i \exp\left\{-\sum_{i=1}^{N} (w_i+u_i)t\right\}\right\rangle$$

$$= \lim_{N,V\to\infty} \sum_{i=1}^{N} \int u_i \exp\left\{-(w_i+u_i)t\right\} \frac{d^3r}{V} \left\langle \prod_{l}{}' \exp\{-(w_l+u_l)t\}\right\rangle.$$

Here $W_i = w(r_i)$ and $u_i = u(r_i)$, while the prime of the product symbol means that the ith factor is missing from the product. The last circumstance becomes meaningless when the limit is taken, as a result of which the following relation is established between the sought functions:

$$\Phi(t) = \rho \int ue^{-(w+u)t}d^3r \cdot F(t). \tag{2.12}$$

If the impurity centers are subjected to inhomogeneous broadening, the exponent in (2.11) should be averaged not only in space but also over the distribution of the detunings of the resonance in the channels of the transport and quenching of the energy, which can also be uncorrelated. The same applies to the integrand of (2.12). Substituting the expressions obtained in this manner for $f(t)$ and $\Phi(t)$ in (2.6) we solve in principle the problem of concentration self-quenching in the most general form at any interaction that effects quenching and transport.

We defer, however, the discussion of the general case to the future and consider a particular but quite common situations, in which both the transport and the quenching are due to the interaction of like multipolarity. If there is no inhomogeneous broadening in such a situation, we have

$$W = zU, \tag{2.13}$$

where $z = C_{DA}/C_{DD}$. This simplifies substantially the formal description of the phenomena, since

$$F(t) = R_0([1+z]t), \tag{2.14}$$

$$\Phi(t) = -dR_0([1+z]t)/d[1+z]t. \tag{2.15}$$

Substituting these functions in (2.6) and changing over to a new variable $\tau = (1+z)t$, we obtain the equation

$$N(\tau) = R_0(\tau) - \frac{1}{1+z}\int_0^{\tau} \dot{R}_0(\tau-\tau')N(\tau')d\tau'. \tag{2.16}$$

At $z = 0$ it is obviously satisfied by the solution $N = \text{const}$, since there is no quenching. If, however, $z \ll 1$ but not zero, self-quenching takes place mainly exponentially at a rate $\overline{W}$. To verify this it suffices to take the exact Laplace transform of (2.16):

$$\tilde{N}(s) = \frac{1+z}{z\tilde{R}_0^{-1}(s)+s}. \tag{2.17}$$

At small s this solution has a simple pole, which in fact determines the sought quantity

$$\overline{W} = z/\tilde{R}_0(0) = z/\tilde{\tau}. \tag{2.18}$$

The physical meaning of this result is clear. At $z \ll 1$ the quenching is weak. In the interval between two successive hops it is on the average small: $W\bar{t} = W/U = z$. Thus, a fraction z of the excitation is lost at each center visited in the course of migration, regardless of the configuration of the surrounding particles. Multiplying by the number of hops per unit time, which is in fact $1/\tilde{\tau}$, we obtain (2.18).

Let us apply (2.18) to the dipole-dipole interaction, using in it (1.15):

$$\overline{W} = 3z/\tau_0 = {}^8/_9\pi^3 C_{DA}\rho^2. \tag{2.19}$$

We took into account here the definition $z = C_{DA}/C_{DD}$ and the definition given in (1.2) for $1/\tau_0$. The result is quadratic in the density of the impurity centers, as expected. It is qualitatively different, however, from what can be obtained from (1.10) or (2.10) by putting $c = \rho$. The difference is that it does not depend on C_{DD}, i.e., on the rate of the donor-donor transport, about which we know only from the conditions of the applicability of (2.19) that it is large:

$$C_{DD} \gg C_{DA}. \tag{2.20}$$

In this sense this result is similar to the kinetic limit (ultrafast migration), which is also reached when the quanching becomes weak.[6]

The long-term asymptotic form of the self-quenching process is therefore given by

$$N = e^{-\overline{W}\tau} = e^{-\overline{W}(1+z)t}. \tag{2.21}$$

Since $z \ll 1$ the rate of the process is determined in fact by (2.19). These results, however, do not extend to the initial nonstationary state of the process. To obtain an idea of the latter, it suffices to put $N(\tau) = 1$ in the right-hand side of (2.6). The very first iteration gives

$$N = \frac{1+zR_0(\tau)}{1+z} \approx 1 - \left(\frac{6z^2t}{(1+z)\tau_0}\right)^{1/2} \approx \exp\{-(zqt)^{1/2}\}. \tag{2.22}$$

We have thus at first a pseudo-Förster decay of the excitation with a parameters smaller by a factor z than in (1.7). The quenching rate during this stage, equal to $-\dot{N}(t)$, decreases monotonically until it becomes comparable with W. The equality $-\dot{N}(t_b) = W$ determines the temporal boundary t_b

between the initial (2.22) and concluding (2.21) stages of the process. It is obviously equal to

$$t_r=9/16\pi^3C_{DD}\rho^2,$$

i.e., it is smaller by a factor $6/\pi$ than the corresponding time in the theory of ordinary quenching.

Thus, self-quenching is not a particular case of quenching within the framework of the approach used here, which is equivalent to the CTRW theory. The difference between the latter and the Markov theory, which in the case of quenching reduces to correction of the numerical coefficient, becomes functional when self-quenching is considered. The dependence of the rate of the process on the microparameters C_{DA} and C_{DD} turns out to be different both in the stationary and the nonstationary stages of the process. It would be premature, however, to review from this point of view the extensive experimental material whose interpretation within the framework of the usual premises has raised no difficulty so far. The assumption that the variations two probabilities are not correlated is too strong and does not correspond fully to the physics of the process. The change of the probability of the quenching can be reasonably assumed to be uncorrelated when it is small. But if it is large, the main reason is that the cross-relaxation partner is alongside, "paired." The probability of exchange of excitation within such a pair is very high, and its contribution to U is decisive. This excitation exchange, however, does not modulate the rate of its decay, i.e., the change of W is strongly correlated and insignificant—only on account of the modulation of the distance to the particles surrounding the pair. The simplest consequence of this is the lengthening of the time of preservation of the quenching probability when the excitation lands on closely located centers. It leads to an increase of the "action" $\overline{Wt}$, which can become quite strong thereby destroying the validity of the usual picture of hopping quenching. We shall verify below that even partial allowance for the return, from only the nearest neighbors, confirms these arguments.

3. PARTIAL ALLOWANCE FOR THE RETURN OF THE EXCITATION

The outflow kinetics lends itself to direct experimental investigation in experiments on selective excitation of luminescence of the activator with inhomogenous broadened spectrum.[18,19] A definite idea concerning this kinetics is obtained also from computer simulation of the migration of the excitation in the disordered system.[19] In the course of these investigations it became clear that to regard the outflow process as an irreversible one even during the initial stage is incorrect. Much better agreement with laboratory and computer experiment is reached by making the following substitution:

$$\exp(-Ut)=\prod_l \exp\{-u(r_l)t\}\to\prod_l n(r_l,t), \tag{3.1}$$

and assuming that

$$n(r_l,t)={}^1/_2+{}^1/_2\exp\left[-u(r_l)t\right]. \tag{3.2}$$

Obviously, $n(r_l,t)$ is the population of the excited state of the donor, which decreases with time from 1 to 1/2 as a result of the intermixing of the excitation between it and its partner located at a distance r_l. Equation (3.2) would take quite rigorously into account the return of the excitation if there were only two particles. If, however, the outflow is to many surrounding particles, it is possible to regard this process as multiplicative, as in (3.1), only if it develops exponentially through all channels. Therefore the use of (3.2) in (3.1) is an approximate semiphenomenological artifice. Proceeding in manner, we expect to take correctly into account the return at least from the nearest neighbor, and it is not likely that there will be two or more nearest ones in a dilute solution. As for the more remote neighbors, we have for them

$$n(r_l,t)\approx1-u(r_l)t\approx\exp(-u_lt),$$

i.e., everything is favorable. This device, proposed by Huber, has fully justified itself.[20–22] Using (3.1) in (1.13) we obtain

$$R(t)=\left\langle\prod_l n(r_l,t)\right\rangle=\exp\left\{-\frac{\rho}{2}\int\left[1-e^{-2u(r)t}\right]d^3r\right\}. \tag{3.3}$$

This result differs from (1.13) only in that the parameters are redefined, namely $\rho\to\rho/2$ and $C_{DD}\to2C_{DD}$. Therefore the outflow kinetics with partial allowance for the return remains the same as before, although its rate becomes different. In dipole-dipole interaction we obtain

$$R(t)=\exp\left(-\sqrt{t/\tilde{\tau}}\right), \tag{3.4}$$

and

$$\bar{\tau}=\int_0^\infty R(t)\,dt=2\tilde{\tau}={}^2/_3\tau_0 \tag{3.5}$$

takes on a value closer to τ_0. It is clear that allowance for return from more remote neighbors decreases even more the difference between them.

The constructive improvement proposed by Huber is used at the present time extensively to correct the results that depend on the outflow kinetics. It was used, in particular, to refine the coefficient of diffusion over a disordered system, which is obtained in the CTRW[13] and in the Green's function formalism.[23] If it is used in Eqs. (2.7) and (2.8), the situation reduces to a simple replacement of R_0 by R, after which we obtain in place of (2.9) the following kinetic equation for the quenching:

$$N(t)=N_0(t)R(t)-\int_0^t N_0(t-t')\dot{R}(t-t')N(t')\,dt'. \tag{3.6}$$

It can be seem that partial allowance for the return in this case does not lead to any qualitative changes, and merely corrects the numerical coefficient in the quenching rates obtained from (3.6):

$$\overline{W}=\left(\frac{3q}{4\tau_0}\right)^{1/2}=\frac{8\pi^3}{9\sqrt{2}}(C_{DA}C_{DD})^{1/2}c\rho. \tag{3.7}$$

This brings us back in fact to the intial result (1.10), which is only $(\pi/3)^{1/2}$ larger than (3.7).

A much more radical influence is that of partial allowance of the return on the self-quenching. Making the substitution (3.1) in (2.11) and averaging, we get

$$F = \exp\left\{-\frac{\rho}{2}\int\left[(1-e^{-wt})+(1-e^{-2ut-wt})\right]d^3r\right\}$$

$$= N_0\left(\frac{\rho}{2},\, t\right)R\left(t\left[1+\frac{z}{2}\right]\right), \qquad (3.8)$$

where $N_0(\rho/2, t)$ is obtained from (1.7) which c replaced by $\rho/2$.

We calculate in the same manner also

$$\Phi = \lim_{N,V\to\infty}\left\langle\sum_i^N(-\dot{n}_i)\exp\left\{-\sum_l^N w_l\right\}\prod_l{}' n_l\right\rangle$$

$$= \rho\int u\exp\{-(2u+w)t\}\,d^3r\cdot F. \qquad (3.9)$$

Taking (3.8) and (3.3) into account, we obtain hence

$$\Phi = -\frac{dR}{dt}\left(t\left[1+\frac{z}{2}\right]\right)N_0\left(\frac{\rho}{2},\, t\right). \qquad (3.10)$$

Using (3.8) and (3.10) in (2.6) we get ultimately

$$N(t) = N_0\left(\frac{\rho}{2},\, t\right)R\left(t\left[1+\frac{z}{2}\right]\right)$$

$$-\int_0^t \dot{R}\left([t-t']\left[1+\frac{z}{2}\right]\right)N_0\left(\frac{\rho}{2},\, t-t'\right)N(t')\,dt'. \qquad (3.11)$$

This equation, which describes self-quenching, differs from Eq. (3.6) in the hopping limit, when $z\ll 1$, only in that c is replaced by $\rho/2$. We therefore obtain in place of (3.7) for the rate of hopping self-quenching

$$\overline{W} = \frac{4\pi^3}{9\sqrt{2}}(C_{DA}C_{DD})^{1/2}\rho^2. \qquad (3.12)$$

If, however, $z\gg 1$ only the free term in (3.11) is significant and this term, as can be seen, is transformed into $N_0^2(\rho/2, t) = N_0(\rho, t)$, which corresponds to a static collective quenching on account of cross relaxation

$$N = N_0(\rho, t) = \exp\left\{-\left(\frac{16\pi^3}{9}C_{DA}\rho^2 t\right)^{1/2}\right\}.$$

In fact, there is no place left for diffusion self-quenching.

CONCLUSION

It can be stated that at present two different viewpoints have been formed concerning the manner of correctly estimating the rate of hopping quenching in a disordered system of centers. One of them starts out in fact from the concept of an equivalent regular lattice, which is the basis of the initial Markov theory. The quenching rate in this case is always determined by Eq. (1.9), and what matters is only that the migration time over the equivalent structure be correctly determined. Sometimes one proposed to replace τ_0 by $\bar{\tau}$ from (1.11) (Refs. 9 and 10), but more frequently by $\tilde{\tau}$ (Refs. 24–26, 19). Favoring the latter is the agreement between the results obtained by two independent statistical methods: secularization of the t-matrix[25] and the coherent-potential method.[26] The other viewpoint is contained in the papers discussed in Sec. 2, which are based on the concept of uncorrelated variation of both probabilities (of the quenching and of the transport).[12,15,16] The quenching rate (2.10) obtained in these papers differs numerically from the Markov estimate (1.10), even if one puts in the latter $\tilde{\tau}$ in place of τ_0. Since the difference is only numerical and small, it had not been regarded as significant before. However, an analysis of self-quenching, carried out in that paper, shows that this difference is fundamental. From the statistical point of view self-quenching turns out to be a more subtle phenomenon than quenching at a result of formulation of transport and cross-relaxation processes. To eliminate the qualitative differences in its description it was necessary to take semiphenominologically into account the return effect. One must not lose sight, however, of the fact that this effect was taken into account only partially and only partial allowance was made for the correlation of the quenching probability, namely only for excitations that return to the initial center. In fact, however, the excitation has exactly the same (and not arbitrary) probability of becoming quenched when located on the other center of the pair. From the equivalent-lattice, point of view, excitation transitions between the pair particles do not exist at all as a process that modulates the quenching probability; this makes it possible to take better account of the correlation where this is most necessary. On the other hand, the subdivision of identical particles into two kinds, those belonging to the equivalent lattice over which the excitation is transported and those not belonging to it but participating only in the cross-relaxation, seems quite arbitrary. It is therefore not quite clear at present which viewpoint should be given preference.

In this connection, a third path is attractive: expansion of the solution is a series in the impurity density, which in principle makes it possible to carry out a consistent averaging over the configurations in any order. A linear theory of this kind was proposed in Ref. 27, but it is valid only for short times ($t\lesssim\tau_0$). To get an idea of the long-time asymptotic form, with parameter $\overline{W}$, of the process it is necessary to sum this series, at least in part. Two such methods were recently developed, two-particle and three-particle,[28] but only the latter is acceptable, since it is the only one capable of reproducing the statice (Förster) kinetics of the quenching, at least at short times, and reflects the difference between the diffusion and hopping quenching ($z\lesssim 1$).[29] There exists also other methods which are contrasted in the theory of disordered systems to the CTRW,[30] but their effectiveness as applied to migration and quenching problems has not been demonstrated even once.

In conclusion, the author considers it his duty to note that he is indebted to the formulation of the present problem to very useful discussions during the time of the Seventh All-Union Symposium on the Spectroscopy of Crystals Activated with Rare-Earth and Transition-Metal Ions (Leningrad,

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