Investigation of the processes of relaxation of electron excitation in crystals for arbitrary relationships between interaction microparameters and concentrations of energy donors and acceptors

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An analysis is made of the time dependences of the populations in a donor subsystem interacting with energy acceptors. Various methods of transport of the excitation to the region where it is lost in a solid are considered. The criteria of validity of various models of energy relaxation in a set of noncoherently interacting particles at macrolevels and microlevels are considered. It is shown that in addition to the familiar relaxation mechanisms (diffusion, mixed, and hopping) there is a new transition mechanism distinguished by a characteristic population profile of the donor subsystem in the region of an energy acceptor. This mechanism is a consequence of the discrete nature of the structure and corresponds to a wide range of parameters in the theory of energy transport in solids. This transition model is used to obtain expressions for the steady-state rate of energy relaxation in a regular donor lattice in a real crystal. Similar expressions are obtained also for the mixed mechanism. A report is given of a study of the evolution of the population of a metastable state of donors in $La_{1-x-y}Nd_xDy_yP_5O_{14}$ crystals. All the characteristic parameters in the theory of energy transport are determined for this system and the transition relaxation model is confirmed. The nature of kinetics of nonradiative energy transport in a set of interacting particles is established for the whole time scale. A quantitative agreement between the theoretical and experimental results is obtained.

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Relaxation of electron excitation in a set of interacting particles in a solid is a superposition of a large number of elementary energy transport events of two types. These are events resulting in migration of excitation between metastable donor (D) states and events resulting in the transfer of excitation from donors to acceptors (A). The probabilities of the occurrence of these elementary events (per unit time) are[1,2]

$$W_{DD}=C_{DD}f_{DD}(R),\quad W_{DA}=C_{DA}f_{DA}(R),\tag{1}$$

where C_{DD} and C_{DA} are the microparameters of the D–D and D–A interactions; R is the internal distance in a pair of interacting particles; $f_{DD}(R)$ and $f_{DA}(R)$ are the functions whose form is governed by the nature of the D–D and D–A interactions.

The quantities C_{DD} and C_{DA} are governed by the crystal basis and by the properties of transitions responsible for the transport of excitation. Consistent theories revealing the functional relationship between the rate of loss of excitation in a set of interacting particles, the properties of these particles in a given crystal basis, and their concentrations have been developed for two limiting situations, for which the criteria

$$C_{DA}\gg C_{DD}\tag{2a}$$

(Refs. 1, 3, and 4) and

$$C_{DD}\gg C_{DA}\tag{2b}$$

(Refs. 1 and 4–6) are largely intuitive. Other restrictions have been assumed also in the theories of Refs. 1 and 3–6 and these we shall consider later.

The fullest experimental investigations have been made of the situation in which direct loss of excitation occurs via an intermediate nonradiative state (cross relaxation). In this case each particle can act as an energy donor and as an enercy acceptor, i.e., the concentrations of energy donors and acceptors are the same and equal to the total concentration ($n_A=n_S=n$).

It would be interesting to investigate the processes of relaxation of the energy of electron excitation in a set of interacting particles at general relationships between C_{DD} and C_{DA}, and also between the concentrations of donors and acceptors in a crystal.

This problem was tackled in the present study by synthesizing a large number of $La_{1-x-y}Nd_xDy_yP_5O_{14}$ pentaphosphate crystals, in which the donars are neodymium ions and the acceptors are Dy^{3+} ions. These crystals provide a convenient model for investigating relaxation processes because the lattice structure of these pentaphosphate crystals is well known, and the neodymium and dysprosium ions are incorporated isomorphously in the lanthanum sublattice up to complete replacement of the lanthanum ions. It is thus possible to vary in an arbitrary manner the concentrations of the energy donors and acceptors within the same crystal structure. Changes in the population of a metastable state of Nd^{3+} with time were investigated in a wide range of neodymium and dysprosium concentrations.

The transfer of energy from a metastable state of neodymium ions to Dy^{3+} may occur along several channels[7] and the value of the microparameter C_{DA}(Nd–Dy) is the sum over all possible channels. The most important circumstance is that the Nd–Dy transfer is irreversible. This simplifies greatly the interpretation of the results.

The selected energy donors (Nd^{3+}) and acceptors (Dy^{3+}) can be used to model situations not investigated earlier and this can be done by varying their concentra-

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tions. It is important to note that in all cases the following conditions of noncoherence of the transport processes are obeyed:

$$\Gamma \gg W_{DA},\ W_{DD},\ 1/\tau_0, \tag{3}$$

where Γ is the line width in the optical spectra and τ_0 is the intrinsic lifetime of the excited states. In the case of trivalent rare-earth ions the conditions of Eq. (3) are always satisfied.[8] In the case of our system this allows for the use of the probabilistic approach of Eq. (1) to the theoretical interpretation of the relationship obtained by us.

SYNTHESIS OF INVESTIGATED CRYSTALS

We synthesized complex phosphates of the following compositions: $Nd_{0.1}La_{0.9-y}Dy_yP_5O_{14}$ (where $y=0.001$, 0.005, 0.01, 0.02, 0.05, and 0.1); $Nd_{0.5}La_{0.5-y}Dy_yP_5O_{14}$ ($y=0.01$, 0.02, and 0.05); $Nd_{1-y}Dy_yP_5O_{14}$($y=0.001$, 0.005, 0.01, 0.02, 0.05, 0.1, 0.3, and 0.5); the synthesis method was that described in Ref. 9. The starting materials were lanthanum, neodymium, and dysprosium oxides, containing 99.900–99.999% of the main substance, and phosphoric acid of 86% concentration. It was reported earlier[10] that La and Nd pentaphosphates have the same structure characterized by the monoclinic system with the space group $P2_1/c$. According to our results, Dy pentaphosphate may crystallize (depending on the synthesis conditions) in two structures which both belong to the monoclinic system but have different space groups ($P2_1/c$ and $C2/c$). The presence of two other components (La and Nd) in the synthesis of these mixed pentaphosphates causes them to crystallize in the structure with the space group $P2_1/c$, giving rise to continuous series of solid solutions. The existence of these solid solutions in the investigated $Nd_{0.1}La_{0.9-y}Dy_yP_5O_{14}$; $Nd_{0.5}La_{0.5-y}Dy_yP_5O_{14}$, and $Nd_{1-y}Dy_yP_5O_{14}$ systems was confirmed by x-ray diffraction.

KINETICS OF DECAY OF DONOR EXCITATIONS

The existence of the donor–donor (DD) and donor–acceptor (DA) interactions in a set of particles gives rise to a complex evolution of the population of the excited state of the donor subsystem. However, in all cases of practical importance the process of excitation decay has the following characteristic stages.

Before the populations of the various donors begin to differ significantly (ordered stage of static decay), the decay process is exponential (Refs. 2 and 4):[1)]

$$N_d(t) \sim \exp\Big(-tyC_{DA}\sum_i R_i^{-6}\Big), \tag{4}$$

where y is the relative concentration of acceptors and $\sum_i R_i^{-6}$ is the sum over all the lattice sites accessible to A. The duration τ_1 of the static ordered decay stage is governed by the reciprocal of the scatter of the rates of static deactivation in a system of many donors D and acceptors A, and it is estimated from the expression[4]

$$\tau_1 = \left\{\frac{y}{|\ln(1-y)|}W_{max}\right\}^{-1}, \tag{5}$$

where W_{max} is the maximum possible rate of energy transfer in a DA pair, i.e., $W_{max}=C_{DA}/R_0^6$, where R_0 is the minimum possible distance between D and A in a crystal.

After a time τ_1 the difference between the acceptor environments begins to tell and, consequently, the rates of decay of different donors become significant; therefore, the populations begin to fluctuate greatly from one donor to another. The static ordered stage of Eq. (4) is followed by a static disordered decay stage[11,12]

$$N_d(t) \sim \exp(-\gamma t^{1/2}), \tag{6}$$

$$\gamma = {}^4/_3\pi^{3/2} n_A C_{DA}^{1/2}. \tag{7}$$

In the absence of migration of excitation in the donor subsystem, the loss of excitation should occur in accordance with Eq. (6), irrespective of time. Energy migration, which frequently takes place in real systems, influences the nature of decay kinetics of donor excitations in the $\tau > \tau_1$ case. It has been established[2] that the experimentally observed nonradiative decay curves of an excited neodymium state under conditions of energy migration can be described satisfactorily by the following expression valid in the interval $\tau_1 < t < \tau_2$:

$$N_d(t) \sim \exp[-(\gamma t^{1/2} + \overline{W}t)], \tag{8}$$

where $\overline{W}$ is the steady-state rate of loss of excitation at the acceptors because of migration of energy to the acceptors from the donors. The moment τ_2 can be estimated from

$$\tau_2 \sim (\gamma/\overline{W})^2. \tag{9}$$

Eventually, this migration of energy between excited donor states results in decay of the exponential type (migration-limited relaxation).

It has also been found experimentally[2] that in the case of migration-limited relaxation the kinetics of the energy transfer process at times $t > \tau_2$ is described well by the expression

$$N_d(t) \sim \exp[-(\overline{W}t + \Delta)], \tag{10}$$

where $\exp(-\Delta)$ is the proportion of excitation not lost statistically.

Determination of the dependence of the steady-state rate of loss of excitation $\overline{W}$ on C_{DA}, C_{DA}, n_D, and n_A, together with determination of the general nature of the decay kinetics throughout the whole time scale represent some of the main tasks in the study of energy transfer in a set of interacting particles.

A very important auxiliary role in finding this rate dependence is played by the concept of a sphere of strong quenching surrounding A. The radius of the sphere R_W is given by

$$C_{DA}\tau_W/R_W^6 \approx 1, \tag{11}$$

where τ_W is the time that an excitation spends inside a sphere of radius R_W in the absence of an acceptor.

The mechanism of steady-state migration quenching in a set of interacting particles is governed by the ratio $R_W/\overline{\lambda}$, where $\overline{\lambda} = n_A^{-1/3}$ is the average distance between the donor particles, i.e., the characteristic length of a migration jump. The condition

$$R_W \gg \bar{\lambda} \tag{12}$$

means that the density of the donor excitations at neighboring donors differs only slightly, so that a continuous distribution of this density can be assumed in the kinetic equations. We can then speak of the diffusion of the excitation energy to an acceptor.[13] It follows that in the diffusion quenching mechanism the value of R_W is given by

$$R_W \equiv R_W{}^{\mathrm{d}} \approx (D\tau_W)^{1/2}, \tag{13}$$

where

$$D \approx C_{\mathrm{DD}}/\bar{\lambda}^4 \tag{14}$$

is the diffusion coefficient. It follows from Eqs. (11), (13), and (14) that

$$C_{\mathrm{DA}}/C_{\mathrm{DD}} \approx (R_W{}^{\mathrm{d}})^4/\bar{\lambda}^4. \tag{15}$$

It is clear from Eq. (15) that the condition (12) is satisfied if

$$C_{\mathrm{DA}}^{1/4} \gg C_{\mathrm{DD}}^{1/4}. \tag{16}$$

Doktorov, Kipriyanov, and Burshteĭn[14] obtained a more rigorous criterion of the validity of the diffusion theory, which is as follows:

$$\bar{\lambda} \ll \delta_{R_W}, \tag{16a}$$

where $\delta_{R_W} = R_W/m$ (m is the multipole order of the interaction; in our case $m = 6$) is the thickness of the quenching layer. The condition (16a) is a consequence of the fact that in the diffusion model the complete quenching of an excitation occurs already on the boundary of a sphere of radius R_W in a layer of thickness δ_{R_W}. The passage through this layer is by diffusion, i.e., it occurs by a large number of jumps. The layer thickness $\delta_{R_W} = R_W/m$ is the distance to the boundary of the sphere in which the probability of excitation loss decreases by a factor of e. Clearly, it is meaningful to speak of diffusion-limited relaxation only if $n_{\mathrm{D}} \gg n_{\mathrm{A}}$, since in the opposite case the condition (16) has the effect that the decay is hardly accelerated by energy migration and may remain purely static.

The condition

$$R_W \ll \bar{\lambda} \tag{17}$$

means that the excitation cannot migrate by jumps inside the sphere and a single jump is sufficient to enter or leave the sphere (hopping energy relaxation mechanism). The time for the transfer of excitation between particles separated by a distance $\bar{\lambda}$ is

$$\tau_W \approx \bar{\lambda}^6/C_{\mathrm{DD}}. \tag{18}$$

Thus, it follows from Eqs. (11) and (18) that the condition (17) implies

$$C_{\mathrm{DD}}^{1/6} \gg C_{\mathrm{DA}}^{1/6}. \tag{19}$$

The rise of the donor concentration reduces both $\bar{\lambda}$ and R_W. The inequality

$$R_W \ll R_0 \tag{20}$$

means that the density of donor excitations remains constant in space and that it varies with time in accordance with the exponential law (4), i.e., rate of decay over the whole time scale is equal to the rate of decay during the initial stage when the donor density is low. This situation is known as relaxation under supermigration conditions. We shall call it the kinetic limit. Clearly, the conditions (12) and (20) are mutually contradictory. This means that the kinetic limit cannot be reached within the framework of the diffusion approach. It can be reached only when the condition (12) is reversed. In fact, it follows from Eqs. (11) and (18) that in the hopping model, we have

$$R_W{}^{j} \approx \bar{\lambda}(C_{\mathrm{DA}}/C_{\mathrm{DD}})^{1/6}, \tag{21}$$

and if the condition (19) is obeyed, we can satisfy not only Eq. (17) but also Eq. (20) even when $x \ll 1$ (x is the relative concentration of the donors).

In the first approximation the condition for attaining the kinetic limit can be expressed as follows in terms of microparameters[2]

$$C_{\mathrm{DD}}/\bar{\lambda}^6 \gg C_{\mathrm{DA}}/R_0{}^6, \tag{22}$$

which means that the rate of migration in the average distance must be greater than the rate of loss of excitation in the minimum possible distance between the interacting particles. It is important to note that in a set of interacting particles the most probable migration rate $\tilde{W}$ is greater than the rate of excitation jumps over distances $\bar{\lambda}$ given by Eq. (18):

$$\tilde{W} = {}^1/_6\left({}^4/_3\pi^{3/2} n_{\mathrm{d}} C_{\mathrm{DD}}^{1/2}\right)^2 \approx 9 C_{\mathrm{DD}} n_{\mathrm{d}}{}^2, \tag{23}$$

which makes it easier to reach the kinetic limit, and the condition (22) becomes less stringent:

$$C_{\mathrm{DD}} \gg C_{\mathrm{DA}}/x^2. \tag{24}$$

This condition is satisfied when a certain critical donor concentration x^* is reached.[2]

An allowance for the fact that the most probable migration rate $\tilde{W}$ is a set of particles is greater than the rate of migration over a distance $\bar{\lambda}$ results in a significant easing of the condition of validity of the hopping model when

$$y \ll x \ll 1. \tag{25}$$

In this case the criterion of validity of the hopping mechanism can be written as follows:

$$9 C_{\mathrm{DD}} n_{\mathrm{d}}{}^2 \gg C_{\mathrm{DA}}/\bar{\lambda}^6, \tag{26}$$

from which it follows automatically that, when the composition obeys Eq. (25), the hopping mechanism is obtained if

$$C_{\mathrm{DD}} \gg C_{\mathrm{DA}}. \tag{27}$$

The transition from Eq. (19) to Eq. (27) when the condition (25) is satisfied represents reformulation of the definition R_W (Ref. 1), so that in Eq. (11) we substitute not Eq. (18) but $\tilde{W}$ defined by Eq. (23), and this gives rise to a numerical factor of ~10. In other words, in contrast to Eq. (12), the condition (17) is not rigorous.

The relationship between the rate of relaxation $\overline{W}$ due to energy migration to an acceptor was established in Refs. 1, 4–6, and 15 for microparameters of the energy transfer process typical of the hopping mechanism. This relationship is

$$\overline{W}=\pi\left(\frac{2\pi}{3}\right)^{5/2}n_{\mathrm{A}}n_{\mathrm{d}}C_{\mathrm{DA}}^{1/2}C_{\mathrm{DD}}^{1/2}P_0^{1/2}, \tag{28}$$

where P_0 is the probability that during a random walk on a lattice a particle never returns to the starting point.$^{2)}$ This formula is derived without allowance for fluctuations of the donor–donor distances. An attempt to allow for these fluctuations was made by Vugmeĭster[16] and it resulted in a slight increase in the numerical coefficient in Eq. (28). It is essential to stress the following point. Equation (28) is derived on the assumption that the donor–acceptor distance fluctuates in different quenching spheres. In a crystal lattice, when both donors and acceptors replace the same ion in the matrix, this is valid only in the case of low concentrations of the active particles, i.e., when the condition (17) is satisfied, but the number of points of rest in a sphere of radius R_W is large.

The rate of nonradiative relaxation in the diffusion model can easily be calculated using the formalism of Eq. (11) and the procedure described in Ref. 14. The steady-state solution of the diffusion equation is of the form

$$\overline{W}=4\pi n_{\mathrm{A}}DR_W{}^{\mathrm{d}}. \tag{29}$$

According to Ref. 14, we have

$$R_W{}^{\mathrm{d}}\approx\left(\frac{C_{\mathrm{DA}}}{m^2D}\right)^{1/(m-2)}. \tag{30}$$

Substituting Eq. (30) into Eq. (29), we obtain

$$\overline{W}=0{,}4\cdot4\pi n_{\mathrm{A}}D^{3/4}C_{\mathrm{DA}}^{1/4}. \tag{31}$$

This result is in good agreement with the exact solution[3] in which the numerical coefficient 0.4 is replaced with the coefficient 0.676. This difference is the consequence of using the formalism of a strong quenching sphere whose radius is given by Eq. (30) and it is not exactly the quantity which should be substituted in Eq. (29). However, this formalism is useful because it makes it possible to analyze the criteria of validity of various models and to estimate the energy relaxation rate for any value of R_W and $\overline{\lambda}$. Moreover, the formalism of this sphere allows us to give a simple interpretation of the expressions for the nonradiative relaxation rate $\overline{W}$. According to this interpretation, $\overline{W}$ is the product of the volumes of the quenching spheres and the frequency of arrival of excitations in these spheres:

$$\overline{W}={}^4/_3\pi R_W{}^3n_{\mathrm{A}}/\tau_W. \tag{32}$$

The knowledge of the exact expressions for $\overline{W}$ in the hopping[6] and diffusion[3] models allows us to determine accurately the radii of the spheres R_W, which can be done by comparing the expression (32) and the exact solutions. The resultant correction of Eq. (11) is unimportant and it does not affect our analysis of the validity criteria of the various models.

In specifying the value of D we should bear in mind that the correct formula of the relationship between D and the microparameter C_{DD} in the case of the dipole–dipole interaction is available only for a regular donor lattice and homogeneous broadening of the spectral lines. It then follows from Ref. 13 that

$$D=\frac{1}{6}C_{\mathrm{DD}}\sum_i\frac{1}{R_i{}^4} \tag{33}$$

(R_i is the distance to the i-th donor; summation is carried out over all the donors in the lattice) and the expression (31) including the correction in the definition of R_W can be rewritten in the form

$$\overline{W}=0{,}676\cdot4\pi n_{\mathrm{A}}C_{\mathrm{DA}}^{1/4}\left(\frac{1}{6}C_{\mathrm{DD}}\sum_i\frac{1}{R_i{}^4}\right)^{3/4}. \tag{34}$$

At low donor concentrations there is some scatter of D due to fluctuations of the donor–donor distances. In this case an expression analogous to Eq. (3) becomes[14]

$$D=\lambda^2/6\tau_0, \tag{35}$$

where λ is the average scale of a jump and τ_0 is the time between successive jumps. There is some arbitrariness in the definition of λ and τ_0. For example, the mean-square value of the jump length λ^2 is given by

$$\lambda^2=\int_0^\infty R^4f(R)\,dR\Big/\int_0^\infty R^2f(R)\,dR, \tag{36}$$

which becomes meaningless in the case of the dipole–dipole interaction because the integrals in Eq. (36) then diverge.$^{3)}$ A rigorous definition of τ_0 is also lacking. There are several ways of overcoming these difficulties.

a. Introduction of the diffusion coefficient by means of an integral is proposed in Ref. 1:

$$D=\frac{4\pi}{6}n_{\mathrm{d}}\int_\lambda^\infty\frac{C_{\mathrm{DD}}}{R^2}dR, \tag{37}$$

which is an expression that can be obtained from Eq. (33) by changing from summation over i, i.e., over the sites occupied by the donors, to integration with respect to R. The resultant divergence is suppressed by introducing a cutoff factor λ. This factor can be $\overline{\lambda}=n_{\mathrm{D}}^{-1/3}$.

b. One can use Eq. (35) in which in accordance with Ref. 12 the value of $\tau_0=\overline{W}^{-1}$ is substituted from Eq. (23) and it is also assumed that $\lambda^2=n_{\mathrm{D}}^{-2/3}$.

c. One can also follow Eq. (33), i.e., assume that the distribution of donors is regular even at low concentrations and that the distance between donors is $\overline{\lambda}=n_{\mathrm{D}}^{-1/3}$.

d. A rigorous solution of the problem of disorder in the donor system was attempted by Vugmeĭster[16] who allowed for the effects of disorder in the initial kinetic equations.

All these cases give the following expression for the diffusion coefficient:

$$D=AC_{\mathrm{DD}}n_{\mathrm{d}}^{4/3}, \tag{38}$$

but the value of the coefficient A varies. The values of A for the various ways of allowing for the disorder in the donor subsystem are as follows:

a	b	c	d
2.1	1.5	2.6	4.13

It follows that in the calculation of the numerical coefficients by means of the expression $\overline{W}=f(n_A, n_D, C_{DD}, C_{DA})$ in the $x<1$ case considered in the diffusion model there is some indeterminacy because the procedures **a**, **b**, and **c** are to some extent speculative, and the claim in Ref. 16 to give a correct allowance for the disorder effect is unjustified. In fact, an analysis shows that the result of Ref. 16 is an increase in D, i.e., acceleration of migration in a disordered system compared with a regular lattice, for the same donor concenteration. This is in conflict with the existing ideas[17] according to which one can expect slowing down of such motion in disordered media. This comment applies also to the hopping model, for which allowance for disorder in Ref. 16 also increases the rate of migration, although by a very small amount. Bearing the points made above in mind and substituting Eq. (38) into Eq. (31), we obtain

$$\overline{W}=A^{3/4}\cdot 0.676\cdot 4\pi n_A n_d C_{DA}^{1/4} C_{DD}^{3/4}. \tag{39}$$

It should be stressed that introduction of the concept of a quenching layer makes the criterion of the diffusion model more stringent compared with Eq. (16), namely

$$Z=C_{DA}/C_{DD}\geqslant 10^7. \tag{40}$$

A mixed energy degradation mechanism is proposed in Ref. 14 and its range of validity is given by

$$R_W/m\ll\lambda\ll R_W, \tag{41}$$

where R_W is defined in the dame way as for the hopping model:

$$C_{DA}(R_W)^{-6}\overline{W}^{-1}\approx 1. \tag{42}$$

The essence of this mechanism is that the motion of an excitation obeys the diffusion laws and the passage of a distance equal to the thickness of a quenching layer R_W/m occurs in one jump. Bearing in mind that the hopping criterion of Eq. (17) is not rigorous, we can make the inequality (41) less stringent:

$$R_W/m<\lambda\ll R_W. \tag{43}$$

The value of $\overline{W}$ is calculated in Ref. 14 for the mixed mechanism on the assumption that one can use the diffusion formula (29) in which the diffusion coefficient is substituted in accordance with the diffusion theory [Eq. (38)], and R_W is defined in accordance with the hopping model [Eq. (42)]. Bearing in mind that in the case of a regular donor lattice the time for a single jump is

$$\tau_W=\left(C_{DD}\sum_i\frac{1}{R_i^6}\right)^{-1}, \tag{44}$$

and the diffusion coefficient is given by Eq. (33), we obtain

$$\overline{W}=\frac{2\pi}{3}n_A C_{DD}^{5/6} C_{DA}^{1/6}\left(\sum_i\frac{1}{R_i^4}\right)\left(\sum_i\frac{1}{R_i^6}\right)^{-1/6}. \tag{45}$$

In the calculation of $\overline{W}$ for the mixed mechanism when $x\ll 1$ we again face the problem because of the indeterminacy of the diffusion coefficient. Bearing this point in mind, we find that the substitution of Eqs. (38) and (42) into Eq. (29) gives

$$\overline{W}=0.7\cdot 4\pi A n_A n_d C_{DD}^{5/6} C_{DA}^{1/6}. \tag{46}$$

The conditions of validity of the mixed relaxation mechanism, Eqs. (43) and (42), indicate that in the case of the dipole–dipole interaction the range of this mechanism is very narrow; it is then given by

$$10^5\leqslant Z\leqslant 10^7. \tag{47}$$

It is important to stress also that correction of the validity criteria of the diffusion model and the proposal of the mixed mechanism[14] in the case of solid discrete structures have in now way reduced the region lying between the hopping and diffusion models. The mixed mechanism simply displaces the range of validity of the diffusion model to even lower values of $Z=C_{DA}/C_{DD}$.

This analysis shows that a study of the decay kinetics of the donor excitations makes it possible to determine the value of C_{DA} by two independent methods using the nature of the kinetics during the stages described by Eqs. (4) and (6). However, difficulties are encountered in the establishment of the migration-limited relaxation mechanism and determination of the value of C_{DD} because the ratio R_W/λ is not known. The situation is further worsened by the fact that the existing theories do not allow us to go from one model to another. Nevertheless, in the limit $x\to 1$ it is possible to obtain an expression for $\overline{W}$ which is valid irrespective of the value of the ratio C_{DA}/C_{DD} provided the lattice structure is known, i.e., provided the coordinates of all the donor sites are known, and the acceptor concentration is low.

The relevant calculation reduces to finding the donor population in the case of steady-state energy flow to the acceptors, i.e., it reduces to solution of the system of equations

$$-n_i\left(\sum_k W_{ik}+W_{iA}\right)+\sum_k n_k W_{ki}=0 \tag{48}$$

subject to the boundary condition that $n_i\to 1$ when $i\to\infty$ (i and k label the donor sites; W_{ik} is the probability of a migration jump of an excitation from a donor i to a donor k, and W_{iA} is the probability of a jump to an acceptor). The required rate $\overline{W}$ is then

$$\overline{W}=y\sum_i W_{iA}n_i. \tag{49}$$

Solution of this problem becomes much easier if $Z\leqslant 10$. This restriction is due to the fact that the function W_{iA} decreases rapidly on increase in the distance of a donor i from an acceptor A. Consequently, we can simplify Eq. (49) retaining only the terms corresponding to the interaction between the acceptors and donors in the first coordination sphere. Then,

$$\overline{W}=yKW_{1A}n_1, \tag{50}$$

where W_{1A} and n_1 are, respectively, the deactivation probability and the population of the donors in the first coordination sphere; K is the coordination number of the acceptors. The approximation (50) is justified only if even the second coordination sphere satisfies the inequality

$$\sum_k W_{ik}\gg W_{iA}. \tag{51}$$

In the case of a simple cubic lattice the condition (51) reduces to $9C_{DD} \gg C_{DA}/8$, i.e., $C_{DA}/C_{DD} \ll 70$, and this defines the region where finite results can be applied to describe the migration-limited relaxation in a cubic lattice. We can assume (see the Appendix) that the solution of the system (48) is in this case

$$n_i = 1/(1+\xi Z), \tag{52}$$

and the expression for $\overline{W}$ becomes

$$W = yKW_{iA}/(1+\xi Z), \tag{53}$$

where ξ is some numerical coefficient. It is thus clear that at low values of Z the above formula reduces to that for the kinetic limit obtained in the hopping theory.

We shall apply the same procedure but to the lattice of a pentaphosphate NdP_5O_{14} crystal. We shall assume that an acceptor "senses" six of the nearest donors located at distances 5.2, 5.9, 6.6, 6.6, 6.8, and 7.4 Å. These distances are deduced from the results of Ref. 18 and agree with those of Ref. 19. In the case of the seventh donor site, located at 8.8 Å from the energy acceptor, the probability of the interaction with the acceptor for $Z = 10$ is an order of magnitude less than the probability that an excitation escapes from this donor site without loss; the population at this donor site can be regarded quite accurately as equal to the population at the more distant donors. Solution of the system (48) under the above assumptions gives the following expression for $\overline{W}$ (C_{DA} is in units of cm^6/sec):

$$\overline{W}[\mathrm{c}^{-1}] = 1.32 y C_{DA} \cdot 10^{44} \left[\frac{0.51}{1+0{,}51Z} + \frac{0.23}{1+0.18Z} + \frac{0.12}{1+0.09Z} + \frac{0{,}12}{1+0{,}09Z} + \frac{0{,}1}{1+0{,}07Z} + \frac{0.06}{1+0.04Z} \right]. \tag{54}$$

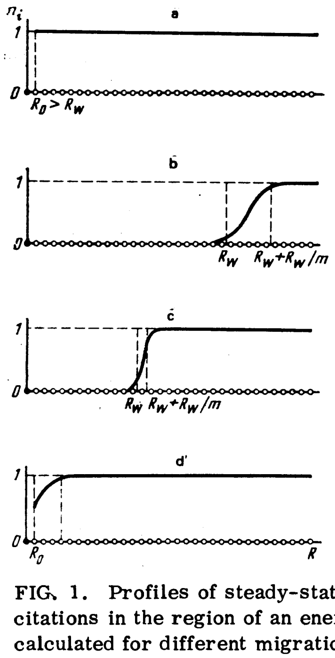

FIG. 1. Profiles of steady-state populations n_i of donor excitations in the region of an energy acceptor in the limit $x \to 1$ calculated for different migration mechanisms of energy relaxation; a) kinetic limit; b) diffusion mechanism; c) mixed mechanism; d) transition mechanism. Here, ● represents an acceptor and ○ are donors.

In the limit $Z \to 0$ the expression (54) reduces to that for the kinetic limit. The fact that we have ignored the difference bewteen the populations at the donors located further than 7.4 Å sets the limit of validity of Eq. (54):

$$Z \ll 10^2. \tag{55}$$

The differences between the various mechanisms of the migration-limited relaxation are due to the different profiles of the donor populations in a certain region near an acceptor. This is demonstrated in Fig. 1 for the $x \to 1$ case. It should be stressed that the transition mechanism, like the kinetic limit, appears because the minimum approach distance between excitations R_0 is comparable or greater than the radius of the strong-interaction sphere R_W, and this is characteristic of solids.

EXPERIMENTAL RESULTS AND DISCUSSION

The results of measurements of the decay curves of the $^4F_{3/2}$ metastable state of neodymium in $La_{1-x}Nd_xP_5O_{14}$ crystals with $x = 0.1$, 0.2, 0.5, 0.9, and 1 confirmed the earlier results. For practically any value of x, the decay curves were exponential with the nonradiative decay constant

$$W = 1/\tau_{\mathrm{meas}} - 1/\tau_0 \tag{56}$$

($\tau_0 = 310$ µsec is the radiative lifetime and τ_{meas} is the measured lifetime of a sample with a given composition), directly proportional to x. This was explained earlier[20] by the fact that the mutual quenching of neodymium ions as a result of the cross-relaxation mechanism ($n_A = n_D = n$) in pentaphosphate crystals makes it possible to reach the kinetic limit even at low neodymium concentrations and the observed decay kinetics can be described by

$$I(t) = I(0) \exp\left(-\frac{t}{\tau_0} - x C_{DA}(\mathrm{Nd-Nd}) \sum_i \frac{1}{R_i^6} t \right). \tag{57}$$

Our calculation of the lattice sum showed that its value is 1.5×10^{44} cm^{-6}. Hence, the microparameter C_{DA}(Nd–Nd) is 3.7×10^{-41} cm^6/sec.

Figures 2(a) and 2(b) show the decay curves of the $^4F_{3/2}$ excited neodymium state for various concentrations of the neodymium and dysprosium ions in $La_{1-x-y}Nd_xDy_yP_5O_{14}$ crystals. In each case we have included also the decay curves of the excited neodymium state in dysprosium-free crystals. We can see that for all the investigated concentrations the dysprosium ions reduce the duration of luminescence of neodymium and the kinetics of decay is nonexponential obeying

$$I(t) = I(0) \exp\left\{ -\left[\frac{t}{\tau_0} + x C_{DA}(\mathrm{Nd-Nd}) \sum_i \frac{1}{R_i^6} t + \Phi(t) \right] \right\}, \tag{58}$$

where $\Phi(t)$ is a function describing the kinetics of energy transfer from the neodymium to the dysprosium ions.

Some conclusions can be drawn even from a qualitative analysis of the results in Figs. 2(a) and 2(b). Further stages of the decay of all the curves are characterized by exponential asymptotics, indicating that some excitations are lost at the dysprosium ions having migrated first between the neodymium ions.

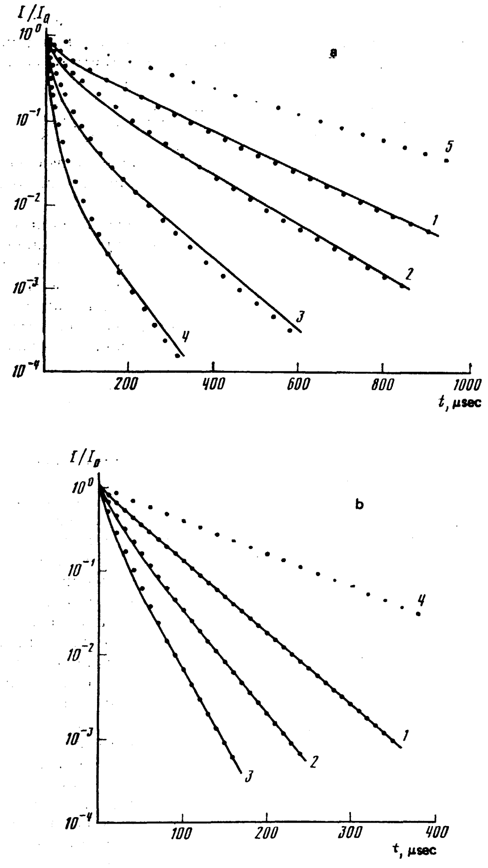

FIG. 2. Decay curves of the $^4F_{3/2}$ metastable state of neodymium in a $La_{1-x-y}Nd_xDy_yP_5O_{14}$ crystal at 300 K; the points are the experimental results and the curves are theoretical. **a**: $x = 0.1$; *1)* $y = 0.01$, *2)* $y = 0.02$, *3)* $y = 0.05$, *4)* $y = 0.1$, *5)* $y = 0$. b: *1)* $x = 0.995$, $y = 0.005$; *2)* $x = 0.99$, $y = 0.01$; *3)* $x = 0.98$, $y = 0.02$; *4)* $x = 1.0$, $y = 0$.

A strictly exponential decay is not observed at any concentration of neodymium or dysprosium, including in the limit $x \to 1$ [Fig 2(b)] and this is true over the whole time scale. Consequently, in the process of quenching of the neodymium by the dysprosium ions an increase in the donor concentration makes it impossible to reach the kinetic limit, whose existence is postulated in the hopping model. Hence, it follows that $C_{DA}(Nd-Dy) > C_{DD}(Nd-Nd)$ and the hopping mechanism should be rejected in the present case. On the other hand, if $x = 0.1$ and $y \neq 0$ [Fig. 2(a)], exponential asymptotics is observed during the latter stages of the relaxation process and the measured exponential decay time τ_{meas} is then considerably less than the time τ in a sample with $x = 0.1$ and $y = 0$. It follows that the relaxation due to migration to the dysprosium ions does occur in this case. It would seem that when the inequalities of (47) are obeyed, and particularly those of Eq. (40) (they represent the conditions of validity of the mixed and diffusion mechanisms, respectively), and if $x = y$, such migration should not occur because then excitations would have been lost statistically in the interaction with the dysprosium ions and after a moderately long time the decay curve for a sample with $x = 0.1$ would have had the form

$$I(t) = I(0)\exp\left\{-\left[\gamma(\mathrm{Nd-Dy})t^{1/2} + 0.1C_{DA}(\mathrm{Nd-Nd})\sum_i \frac{1}{R_i^6}t + \frac{t}{\tau_0}\right]\right\}. \tag{59}$$

The experiments show that the constant $\tau_{meas.}$ obtained during the later stages is then less:

$$\tau_{meas}^{-1} > 0{,}1C_{DA}(\mathrm{Nd-Nd})\sum_i \frac{1}{R_i^6} + \frac{1}{\tau_0} \tag{59a}$$

[see Fig. 2(a)].

We can thus see that qualitative considerations demonstrate that we are dealing with an intermediate case when the application of the diffusion, mixed, and hopping mechanisms is not justified.

We shall now analyze qualitatively the decay curves using the theoretical ideas put forward in the preceding section.

Figure 3 shows the forms of the function $\Phi(t)$ plotted as the dependences $\ln\Phi(t) = f(\ln t)$ during the initial stage of the decay process. They are obtained by subtracting the initial decay curves, plotted on a logarithmic scale, for samples without and with dysprosium and with the same neodymium concentrations. We can see that the dependences obtained are near-linear and the slope is close to unity. Consequently, the law of nonradiative decay of the neodymium ions interacting with the dysprosium ions is initially near-exponential. Figure 4 shows the dependence of the rate of this decay on the dysprosium concentration for various neodymium concentrations. We can see that, in accordance with the theory described by Eq. (4), the decay rate is independent of the concentration of the energy donors (neodymiun ions) and is directly proportional to the concentration of the energy acceptors (dysprosium ions). Hence, we may conclude that initially the decay of the neodymium ions interacting with the dysprosium ions is of the static ordered nature and during this stage the general decay curve is described by the expression

$$I(t) = I(0)\exp\left\{-\left[yC_{DA}(\mathrm{Nd-Dy})\sum_i \frac{1}{R_i^6} + xC_{DD}(\mathrm{Nd-Nd})\sum_i \frac{1}{R_i^6} + \frac{1}{\tau_0}\right]t\right\}. \tag{60}$$

This result and Eq. (4) yield the value of the microparameter $C_{DA}(Nd-Dy)$, whose value is 2×10^{-38} cm^6/sec.

We shall identify the region of static disordered decay in accordance with the procedure of Ref. 2, which involves subtraction of the exponential component (applicable during the later stages of the process) from the

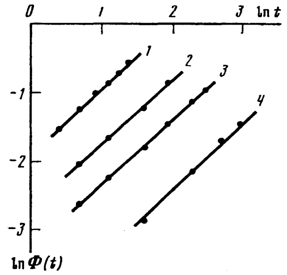

FIG. 3. Forms of the function $\Phi(t)$ during the initial stage of decay in $La_{1-x-y}Nd_xDy_yP_5O_{14}$ crystals at $T = 300$°K. *1)* $x = 0.5$, $y = 0.05$; *2)* $x = 0.99$, $y = 0.01$; *4)* $x = 0.995$, $y = 0.005$.

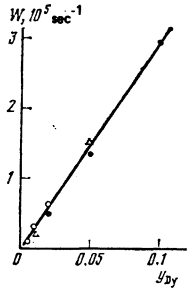

FIG. 4. Dependence of the rate of static ordered decay on the dysprosium concentration in $La_{1-x-y}Nd_xDy_yP_5O_{14}$. ●) $x = 0.1$; ○) $x \approx 1$ (0.995, 0.99, 0.98); △) $x = 0.5$.

general decay curve plotted on a logarithmic scale. This gives the component of the kinetics of energy transfer from the neodymium to the dysprosium ions in the form of Eq. (6). The values of γ are directly proportional to the dysprosium concentration and independent of the neodymium concentration (Fig. 5). Then, using Eq. (7), we can obtain C_{DA}(Nd–Dy) by another (independent) method, which gives 2×10^{-38} cm^6/sec, which is identical with the result obtained from the initial static ordered part of the decay curve. We can thus see that in a certain time interval the observed decay curve is described by

$$I(t)=I(0)\exp\left\{-\left[xC_{DA}(\mathrm{Nd-Nd})\sum_i\frac{1}{R_i^6}t+\gamma(\mathrm{Nd-Dy})t^{1/2}+\overline{W}t+\frac{t}{\tau_0}\right]\right\}. \quad (61)$$

The process of relaxation entirely due to migration during the latter stages of decay gives rise to an exponential law, i.e., the decay rate is given by

$$\overline{W}=\frac{1}{\tau_{\mathrm{meas}}}-xC_{DA}(\mathrm{Nd-Nd})\sum_i\frac{1}{R_i^6}-\frac{1}{\tau_0}. \quad (62)$$

Clearly,

$$xC_{DA}(\mathrm{Nd-Nd})\sum_i\frac{1}{R_i^6}+\frac{1}{\tau_0}=\frac{1}{\tau}, \quad (63)$$

where τ is the lifetime of the excited neodymium state for a given value of x in a sample free of dysprosium. Thus, the exponential decay kinetics observed during the later stages is

$$I(t)=I(0)\exp\left\{-\left[\frac{t}{\tau_0}+\overline{W}t+\Delta+xC_{DA}(\mathrm{Nd-Nd})\sum_i\frac{1}{R_i^6}t\right]\right\}. \quad (64)$$

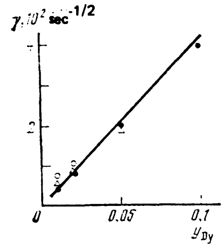

FIG. 5. Dependence of the parameter of static disordered decay on the dysprosium concentration in $La_{1-x-y}Nd_xDy_yP_5O_{14}$ crystals. ●) $x = 0.1$; ○) $x \approx 1$ (0.99, 0.98); △) $x = 0.5$.

An analysis of the experimental dependences (58), (60), (61), and (64) suggests the empirical form of the function $\Phi(t)$, which provides a good quantitative description of the observed decay of the excited donor state over the whole time scale:

$$\Phi(t)=yC_{DA}\sum_i\frac{1}{R_i^6}t\exp\left(-\frac{t}{\tau_1}\right)+[\gamma(\mathrm{Nd-Dy})t^{1/2}+\overline{W}t]\left[1-\exp\left(-\frac{t}{\tau_1}\right)\right]\exp\left(-\frac{t}{\tau_2}\right)+(\overline{W}t+\Delta)\left[1-\exp\left(-\frac{t}{\tau_2}\right)\right], \quad (65)$$

where τ_1 is the time for transition from the static ordered decay to the static disordered decay, and τ_2 is the time of the transition from the static to the steady-state migration decay. Figures 2(a) and 2(b) show the curves plotted on the basis of Eq. (65) and they agree well with the experimental results. The times τ_1 and τ_2 can be found by fitting the theoretical and experimental results. Thus, the decay process described by Eq. (60) is localized in time up to τ_1; the decay of the type given by Eq. (61) occurs between τ_1 and τ_2, whereas the decay given by Eq. (64) occurs after τ_2.

We now face the question of the mechanism of the migration-limited relaxation and determination of the microparameter C_{DD}. Substituting the values of $\overline{W}$ determined experimentally for $x = 0.1$ and various values of y [Fig. 2(a)] into the equation (28) for the hopping quenching mechanism and using the value C_{DA}(Nd–Dy) $= 2\times10^{-38}$ cm^6/sec obtained earlier, we find that C_{DD}(Nd–Nd) $= 7.6\times10^{-40}$ cm^6/sec, i.e., the condition of validity (27) of the hopping model is clearly not obeyed.

Application of the formulas for the diffusion and mixed mechanisms also gives values of C_{DD} which are in conflict with the conditions (40) and (47). A calculation of C_{DD} on the basis of Eq. (54) for the transition mechanism in the limit $x \to 1$ gives C_{DD}(Nd–Nd) $= 5\times10^{-39}$ cm^6/sec, which satisfies the condition (55) and supports the transition mechanism.

The results obtained allowed us to calculate all the characteristic parameters of the theory and to analyze quantitatively the energy relaxation process in the investigated crystals.

1. *Energy Relaxation in Neodymium Ions.* As expected, the ratio

$$Z=\frac{C_{DA}(\mathrm{Nd-Nd})}{C_{DD}(\mathrm{Nd-Nd})}=\frac{3.7\cdot10^{-41}}{5\cdot10^{-39}}\approx0.7\cdot10^{-2}$$

lies in this case in the range where the hopping model applies.

Figure 6 shows the dependences of R_W^i(Nd–Nd) and $\bar{\lambda}$ on the neodymium ion concentration. For $Z \approx 10^{-2}$, which applies in this case, the condition $R_W^i < \bar{\lambda}$ is always obeyed. The point of intersection of the dependences $R_W^i(x)$ with the line R_0 [Fig. 6(a)], corresponding to the critical concentration, separates the regions of the migration-limited relaxation and of the kinetic limit. For $x = 0.05$, the excited state lifetime τ differs slightly from the radiative lifetime $\tau_0 = 310$ μsec, i.e., quenching is unimportant in the region of the migration-limited relaxation. Figure 6(a) demonstrates clearly the fact that practically throughout the range where the concentration quenching of the neodymium luminescence is exhibited by pentaphosphate crystals, the energy relaxation occurs in the kinetic

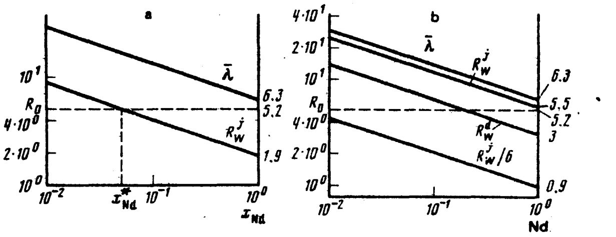

FIG. 6. Dependences of the characteristic parameters of the theory (Å) on the donor concentration in a pentaphosphate crystal: a) Nd—Nd interaction; b) Nd—Dv interaction.

limit regime and the decay of the excited state is described by Eq. (57). Then, the population profile in the donor subsystem has the form shown in Fig. 1(a). This situation, which is characteristic of the linear concentration dependence of the nonradiative relaxation rate (4), is exhibited by a wide range of neodymium-activated materials in which the concentration quenching effect is anomalously weak.[21]

2. *Relaxation of Energy of Neodymium Ions Interacting with External Acceptors.* Figure 6(b) shows the dependence of R_W^j(Nd–Dy) on the concentration x plotted on the basis of the results obtained ($Z=4$) for the case when R_W^j(Nd–Dy) is determined using the hopping model. We can see that $R_W^j(\text{Nd–Dy}) \sim \bar{\lambda} > R_0$ applies at all values of x, including the limit $x \to 1$. Consequently, the kinetic limit cannot be reached in the investigated crystal lattice, which is confirmed experimentally.

The same figure gives also the dependences of R_W^j(Nd–Dy)/6 and of R_W^d(Nd–Dy) on the concentration x. We can see that the condition $R_W^d \gg \bar{\lambda}$ is not obeyed. It follows that the diffusion and mixed mechanisms do not occur either in the investigated crystal. The steady-state population of the donor nearest to an acceptor is ~0.3, i.e., the donor population profile is that expected of the transition relaxation mechanism (Fig. 1). Then, for any donor concentration we are dealing with the migration (and not the diffusion) control of the nonradiative relaxation rate during the later stages of the decay. The transition energy relaxation mechanism occurs in real crystals because of the existence of the minimal approach distance R_0 between an excitation and an energy acceptor, which is ignored in the theory of Ref. 14.

In conclusion, the authors which to express their gratitude to V. A. Myzina for an analysis of the composition of the samples using a Camevax system.

APPENDIX

The steady-state rate of deactivation of a donor excitation can be found by solving the following infinite system of equations:

$$\sum_{k'=1} W_{kk'} n_{k'} = 0, \tag{A.1}$$

where k and k' label the coordination spheres of an acceptor,

$$W_{kk'} = \Big[W_{DA}(k,0) + \sum_{k''} W_{DD}(k,k'')\Big]\delta_{kk'} - W_{DD}(k',k),$$

$W_{DA}(k,0)$ and $W_{DD}(k,k')$ are the total probabilities of excitation transfer from the donors belonging to the k-th coordination sphere of an acceptor to the acceptor in question and to the donors located in the k'-th coordination sphere of the acceptor. The system (A.1) must be solved subject to the boundary condition

$$\lim n_k = 1, \quad k \to \infty, \tag{A.2}$$

and then the required donor deactivation rate is

$$W = C_A \sum_k W_{DA}(k,0) n_k.$$

It follows from the condition (A.2) that the system (A.1) and (A.2) is identical with the solution of a finite system of equations in which it is assumed that $n_k = 1$ at values of k somewhat greater than K, and then K is allowed to become infinite, i.e.,

$$n_k = \lim n_k(K), \quad K \to \infty,$$

where $n_k(K)$ is found from the equations

$$\sum_{k' \leqslant K} W_{kk'} n_{k'}(K) = -\sum_{k'' > K} W_{kk''}. \tag{A3}$$

Solution of the system (A.3) gives

$$n_{k'}(K) = \Delta_{k'}(K)/\Delta(K), \tag{A.4}$$

where $\Delta(K)$ is the determinant of a matrix block composed of elements $W_{kk'}$ with $(k,k') \leqslant K$ (K block of a matrix) and $\Delta_{k'}(K)$ is the determinant of the K block of a matrix deduced from the matrix $W_{kk'}$ by replacing in it the column K' with a column of elements given by $-\sum_{k''>k} W_{kk''}$.

When excitation transfer to an acceptor occurs only in its first coordination sphere, Eq. (A4) is easily transformed to

$$n_1(K) = [1 + \varkappa W_{DA}(1,0)]^{-1}, \tag{A.5}$$

where $\varkappa = \Delta_{D1}^1(K)/\Delta_D(K)$, $\Delta_D(K)$ is the determinant of the K block of a matrix $W_{kk'}$ in which it is assumed that $W_{DA}(1,0) = 0$, and $\Delta_{D1}^1(K)$ is the minor of the (1, 1) element of this matrix. If the DA and DD transfer processes are of the dipole-dipole nature, Eq. (A5) becomes

$$n_1(K) = [1 + \xi(K)(C_{DA}/C_{DD})]^{-1},$$

where

$$\xi(K) = R_1^{-6} \mathscr{R}_1^1(K)/\mathscr{R}(K),$$

R_1 is the radius of the first coordination sphere of the acceptor, whereas $\mathscr{R}(K)$ and $\mathscr{R}_1^1(K)$ are obtained from $\Delta_{D1}^1(K)$ and $\Delta_D(K)$, respectively, by the formal substitution $C_{DD} \to 1$. Thus, the quantity ξ is governed by the geometry of the lattice composed of the donor sites. In the case of a simple cubic lattice, we have $\xi(1) = 0.2$; as K increases, the function $\xi(K)$ rapidly (for $K \sim 7$) reaches a plateau and we have $\xi(10) \approx 0.37$. Thus, in this case we obtain

$$W \approx 6 C_A C_{DA}/a^6 (1 + 0.37\, C_{DA}/C_{DD}),$$

where a is the lattice constant.

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[1] Here and later, we shall consider specifically the dipole–di-

pole interactions, which are characterized by $f_{DD}(R) = f_{DA}(R) = f_{DA}(R) = R^{-6}$.

[2)] In the case of the simplest random three-dimensional walk, we have $P_0 \approx 0.66$, i.e., allowance for the fact that an excitation may escape from the range of influence of an acceptor without being lost gives rise to a numerical coefficient which differs little from unity.

[3)] It is possible to calculate λ^2 for the exchange interaction.[14]

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