Effect of donor-donor and donor-acceptor interactions on the decay kinetics of the metastable state of Nd $^{3+}$ in crystals

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The decay kinetics of the metastable state of Nd^{3+} is investigated with a tunable laser at various activator concentrations and at temperatures between 4.2 and 77°K. The relevant theoretical results are analyzed. The donor-donor and donor-acceptor interaction parameters are determined both as averaged over space and time and as reflecting elementary processes. The donor-donor and donor-acceptor interactions are shown to possess a single multiplicity and to be dipole-dipole. The migration mechanism over the Nd^{3+} ions is discontinuous and cannot be described by the diffusion equations. The concentrations of excitations which can be destroyed by various mechanisms are found. It is shown that the migration and cross-relaxation probabilities are functions of the temperature.

INTRODUCTION

The nonradiative transfer of the electron excitation energy due to the multipole interaction between particles lies at the basis of many physical, photochemical, and biophysical phenomena. The interaction between activator ions in condensed media may give rise to the following effects.

1. The energy of a single excited ion may be transferred to the same level of an identical ion (energy migration). For example, in doped molecular crystals this effect is manifested in the polarization characteristics of their luminescence.[1] In activated ionic crystals the migration of the excitation energy between identical particles is very difficult or impossible to observe.

2. An excited donor particle may transfer some of its energy to an identical unexcited particle which acts as an energy acceptor. Both the donor and acceptor are then in lower excited states than the initial state of the donor (cross relaxation). If the two states which are populated by this interaction are radiative, a "photon subdivision" takes place. If both these states or one of them are non-radiative, the energy or some part of it is degraded into heat. Similar processes also occur between unlike donors and acceptors.

3. The interaction between particles in excited states results in the population of higher electron states, both real and virtual, and this may be accompanied by a strong anti-Stokes luminescence or quenching. These processes are of considerable interest and are being investigated intensively.[2-7] They can be resonant or nonresonant in nature, i.e., they may take place without or with the participation of the lattice phonons.

The migration of energy does not affect directly the nature of deactivation of an excited state but reduces the radius of the interactions of the second and third types discussed above and thus raises considerably the probability of such interactions.[6,8,9] In particular, the migration of energy affects considerably the laser emission from the Nd^{3+} ions.[10-13] Studies of crystal matrices activated with Nd^{3+} are of considerable interest because each Nd^{3+} ion (like many other trivalent rare-earth ions TR^{3+}) can act both as a quenching particle, i.e., an acceptor (Nd^{3+} ions undergo effective cross relaxation), or as an energy carrier (donor). This situation has been investigated theoretically.[14-16]

The present paper reports a study of the kinetics of the decay (deactivation) of a metastable state of Nd^{3+} in $YAlO_3$ crystals which has been found to be highly sensitive to the influence of the interactions between such ions. These crystals represent one of the most efficient laser materials [17] and are characterized by a special splitting of the Nd^{3+} levels, which may help in the interpretation of the observed effects.[18,19]

EXPERIMENTAL METHOD

Crystals of $YAlO_3:Nd^{3+}$ were grown by the Czochralski method. The concentration of Nd^{3+} ranged from 0.05 to 2.5 at.%. Special attention was paid to the purity of the original materials. The total concentration of accidental impurities did not exceed 10^{-5}. The luminescence was excited by applying radiation pulses generated in a rhodamine 6G laser with a tunable wavelength in the 5600-6200 Å range. This dye laser was pumped by the second harmonic of a Q-switched Nd^{3+}-glass laser. The pulse duration was $\sim 5 \times 10^{-8}$ sec and the radiation power was 10^6 W. This excitation method enabled us to study the kinetics of the decay of an excited state of Nd^{3+} in the initial stages of the decay and to observe the luminescence of ions which was strongly quenched and could not be observed under normal excitation condition, i.e., we were able to record the luminescence of centers with a very low quantum efficiency.

Our $YAlO_3:Nd^{3+}$ crystals were excited in the absorp-tion band corresponding to the $4I_{9/2} \rightarrow 2G_{7/2}, 4G_{5/2}$ (5720-5940 Å) transition. The absorption spectrum of a $YAlO^3$: Nd^{3+} crystal and the emission line of the tunable dye laser (Fig. 1) were determined using a PGS-2 spectrograph in the first order (dispersion 5 Å/mm). It was found that the dye laser line, whose width was 20 Å, coincided with the 5726 Å Stark component. The luminescence signal was recorded at 8756 Å (it corresponded to a transition between the Stark components of the levels $4F_{3/2}$ and $4I_{9/2}$). The low optical density of our samples excluded the influence of the reabsorption on the kinetics of decay of the excited state under investigation. A DFS-12 spectrometer, operated in the first order (dispersion 10 Å/mm) was used as a monochromator. An FEU-22 photomultiplier, cooled with liquid nitrogen, was used as a detector. A time scan of the luminescence signal was provided by an ORION-EMG-1546 oscillograph of the TR-4401 type. This oscillograph was triggered by a G5-7A pulse generator. A typical decay curve

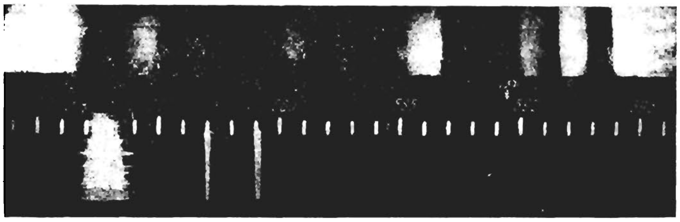

FIG. 1. Absorption spectrum of Nd^{3+} in $YAlO_3$. Transition $^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$, T = 77°K, C = 2.5 at.% Nd^{3+}. The lower part of the figure represents the emission spectrum of a tunable laser. The calibration is provided by mercury lines at λ = 5769.59 Å and λ = 5790.65 Å. The wavelength scale in nm is also included in the figure.

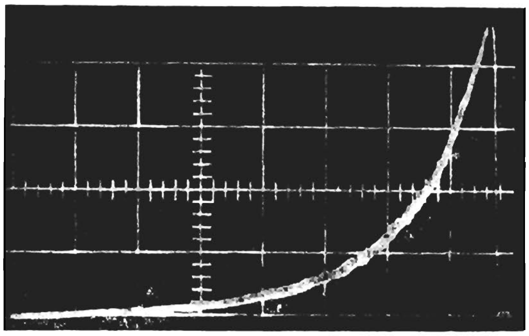

FIG. 2. Characteristic decay curve of the excited state. T = 77°K, C = 0.9 at.% Nd^{3+}. One square represents 100 μsec.

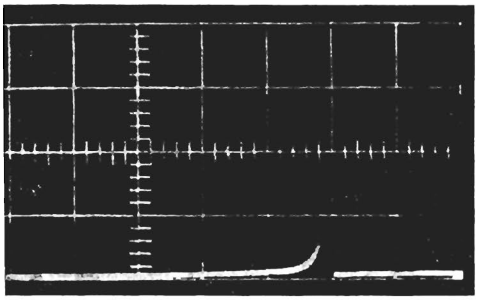

FIG. 3. Laser pulse, one square represents 5 μsec. Duration of the signal is a measure of the time resolution of the detector system.

is plotted in Fig. 2. The method employed allowed us to display on the oscillograph screen various parts of the curve in Fig. 2 on an enlarged time scale. The time resolution of the detector was at least 0.5 μsec (Fig. 3). The time needed for the relaxation from the absorption band ($^4I_{9/2} \rightarrow {}^2G_{7/2}, {}^4G_{5/2}$) to a metastable level $^4F_{3/2}$, represented by the time of rise of the population at this level (Fig. 2), was found to be short (< 10^{-6} sec) and it did not affect the decay curve in the range of time intervals of interest to us. This was in agreement with the results obtained for other matrices containing oxygen and having an extended phonon spectrum. [20,21]

The sample was kept at a constant temperature by a combination of a cryostat capable of thermal regulation and an automatic temperature stabilization unit of the UTREKS type, which enabled us to vary smoothly the temperature of the sample from 4.2 to 300°K and to stabilize at any particular value to within 0.05°K. Our measurements were carried out at T = 4.2 and 77°K.

THEORY

We shall consider how the ratio of the interaction parameters C_{DD} (this parameter describes the migration of energy between donor ions denoted by D) and C_{DA} (this parameter represents additional channel for the relaxation of donors by the interaction with acceptors by A) affects the decay curve of an excited state and its temperature dependence. We shall consider the specific excited metastable state $^4F_{3/2}$ of the Nd^{3+} ion, which is split by the crystal field into two components. In this case, the parameter C_{DA} is governed by the cross relaxation via excited nonradiative levels of the ground multiplet ^4I. [19]

The parameters C_{DD} and C_{DA} are related to the probabilities of migration W_m and cross relaxation W_{cr}:

$$W_m = C_{DD}/R^n, \quad W_{cr} = C_{DA}/R^n,$$

where R is the distance between the interacting ions; n = 6, 8, or 10 for the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively. The parameters C_{DD} and C_{DA} are functions of the oscillator strengths of the interacting transitions and of the overlap integrals of the luminescence spectrum of the donor and the absorption spectrum of the acceptor. [22,23] Basic difficulties are encountered in the experimental determination of these parameters by the standard methods because of the special properties of the TR^{3+} ions.

1. $C_{DA} = 0$. If the luminescence spectrum is Lorentzian, the decay is exponential. We can then have $C_{DD} \neq 0$ and excitation jumps between the donor ions may take place but there is no directional migration of the excitation. As a rule, there is no intracenter nonradiative relaxation from the $^4F_{3/2}$ level in crystals activated with Nd^{3+} provided the temperature is not too high, so that in this case the decay constant τ is equal to the radiative time. [18] The decay time may vary with temperature: [24,25]

$$\tau_0 = \Big(\sum_p A_{gr}\Big)^{-1} [1 + e^{-\Delta E/kT}] \Big[1 + e^{-\Delta E/kT} \sum_p A_{er} \Big/ \sum_p A_{gr}\Big]^{-1}, \qquad (1)$$

where $\sum A_{gr}$ and $\sum A_{er}$ are the sums of the probabilities of radiative transitions from the ground ($\sum A_{gr}$) and excited ($\sum A_{er}$) components of the state $^4F_{3/2}$ to all the levels p of the ground multiplet ^4I; ΔE is the splitting of the $^4F_{3/2}$ level. If $\sum A_{gr} \neq \sum A_{er}$ and $\Delta E \sim kT$, the temperature dependence of τ is unrelated to the interaction between the activator ions.

2. $C_{DD} = 0$, $C_{DA} \neq 0$. Under these conditions, if the probability of cross relaxation is $W_{cr} \sim 1/\tau_{eff}$ (τ_{eff} is an effective lifetime of the level in question), the deexcitation may occur at the same center at which the excitation is generated or as a result of interaction with one ion. Because of the differences between the acceptor environments of different donors, there is a distribution of the deactivation probabilities $\varphi(W_{cr})dW_{cr}$. In this case, the decay of an assembly of donors is nonexponential and if the interaction is of the dipole-dipole type, the decay curve is [26,27]

$$N(t) = \int_0^\infty \exp(-W_{cr}t)\varphi(W_{cr})dW_{cr} = \exp(-\gamma t^{1/2}), \qquad (2)$$

where $\gamma = (4/3)\pi^{3/2} n_A C_{DA}^{1/2}$, n_A is the number of acceptors (A) per 1 cm^3, and

$$\varphi(W_{\mathrm{cr}}) = \gamma\left(\frac{1}{4\pi W_{\mathrm{cr}}{}^{3}}\right)^{1/2} \exp\left(-\frac{\gamma^{2}}{4W_{\mathrm{cr}}}\right)$$

A decay of the type described by Eq. (2) is known as the Förster decay. Equation (2) has already been criticized by Sveshnikov. [28] However, Konobeev [29] gives the luminescence decay law of donors obtained as a result of rigorous averaging of the various positions of a donor and an acceptor. It is found that if $n_D(4/3)\pi R^3 \ll 1$, where n_D is the donor concentration and R is the distance between the interacting ions, [29] the decay law assumes the form given by Eq. (2). Sakun [16] obtained an expression for the quenching law, including terms of the higher order in respect of the acceptor concentration n_A. He estimated the times and concentrations for which the transfer of energy would not be affected by the disorder in the acceptor environment and the decay would be exponential. The possibility of an exponential region in the early stages of the decay, resulting from the strong donor-acceptor interaction, was also pointed out by Burshteĭn and Konyshev. [14,30] A strong interaction may arise between a donor and an acceptor located close to one another, for example, at neighboring sites in the crystal lattice. This is difficult to study experimentally because of the low concentration of such luminescence centers and the low quantum efficiency of these centers.

The temperature dependence of C_{DA} may be related to the thermal population of the excited Stark components of the ground and excited states. This gives rise to additional interactive transitions. The efficiency of this mechanism is determined by the relative positions of the levels governing the cross relaxation process. In the nonresonant interaction we may observe the phonon stimulation effect. [25,31-33] The temperature dependence of C_{DA} can be described by the general formula

$$C_{\mathrm{DA}} = F(n_0, n_e)\left\{\begin{matrix} n_p \\ n_{p+1} \end{matrix}\right., \tag{3}$$

where $F(n_0, n_e)$ is a function of the populations of the Stark components of the ground and excited states; $n_p = [\exp(\Delta E_p/kT - 1]^{-1}$ is the occupation number of the phonon states whose detuning energy is ΔE_p. The factor $n_p + 1$ corresponds to the processes accompanied by the emission of a phonon, and the factor n_p to the processes accompanied by the absorption of a phonon; C_{DA} depends on T provided

$$\Delta E_i \approx kT, \quad E_p \approx kT, \tag{4}$$

where ΔE_i represents the energies of the Stark splitting of the ground and excited states. The dependence (3) was interpreted by us in some specific cases. [25,31]

3. $C_{DA} \neq 0$, $C_{DD} \neq 0$. If the probabilities of migration and transfer of energy to an acceptor are high, the decay kinetics of a donor level is governed by the decay kinetics of an acceptor level. [34,35] This case has been observed for the Nd^{3+} ions [36] in MeF_2 crystalline matrices (Me = Ca, Sr, Ba) in which the Nd^{3+} ion experiences a considerable inhomogeneous splitting of the levels. At high excitation intensities and migration rates we may encounter additional nonradiative losses whose probability is a nonlinear function of the excitation intensity (nonlinear quenching). [6]

The more general case, not restricted to large values of W_m and W_{cr} of the decay kinetics, has been studied by several workers. [14-16] According to the more general theory, the donor-donor and donor-acceptor interactions are assumed to be of the dipole-dipole nature although the treatment can be generalized also to other types of interaction. These theoretical papers are concerned with a particular excitation and give the probability that this excitation is not quenched up to a moment t. Then, the decay curve N(t) is given by

$$N(t) = \left\langle \exp\left\{-4\pi n_A \int_0^\infty R^2\,dR\left[1 - \exp\left(-\int_0^t W_a[R(t')]\,dt'\right)\right]\right\}\right\rangle \tag{5}$$

where $W_a[R(t')]$ is the probability of quenching by the a-th acceptor; the angular brackets represent the averaging over the ensemble of the realizations of trajectories. If the quenching predominates over the migration processes, i.e.,

$$W_{\mathrm{cr}} \gg W_{\mathrm{m}}, \tag{6}$$

we find

$$N(t) = \exp\left\{-4\pi n_A \int_0^\infty R^2\,dR[1 - e^{-W(R)t}]\right\}. \tag{7}$$

In the case of the dipole-dipole interaction, Eq. (7) reduces to Eq. (2). If allowance is made for the migration process, Eq. (2) is obtained for small values of t. In the final stage the process becomes exponential:

$$N(t) = e^{-\overline{W}t}, \tag{8}$$

where $\overline{W}$ is governed by the migration of the excitations which are quenched on reaching the sphere where the donor-acceptor interaction D-A is strong. The radius of this sphere, R_W, is found from the condition:

$$\frac{C_{\mathrm{DA}}}{R_m{}^6}\xi = 1, \tag{9}$$

where ξ is the time needed for the excitation to travel across the sphere. If the excitation can leave or enter the strong-quenching sphere in one jump, the migration mechanism is called discontinuous. If many jumps are needed, the migration is regarded as a quasidiffusion process. According to the estimates given in the cited papers, the first case corresponds to

$$C_{\mathrm{DA}} \leqslant C_{\mathrm{DD}}, \tag{10}$$

and the second to

$$C_{\mathrm{DA}} \gg 2C_{\mathrm{DD}}. \tag{11}$$

In both cases, the theory predicts that the excited state decays in accordance with Eq. (8).

In the case of the Nd^{3+} ions, the condition (11) and the consequent decay (8) are in conflict with the decay described by Eq. (2) which is obtained from Eq. (5) subject to the condition (6). This is because each Nd^{3+} ion can act as an energy carrier or absorber (quenching center), i.e., we cannot increase the donor concentration without increasing the acceptor concentration and conversely. Therefore, the relationship between C_{DD} and W_m and between C_{DA} and W_{cr} can be expressed in terms of the same interaction radius R:

$$W_{\mathrm{m}} = C_{\mathrm{DD}}/R^6, \quad W_{\mathrm{cr}} = C_{\mathrm{DA}}/R^6. \tag{12}$$

Consequently, the condition (11) is analogous to the condition (6) which gives rise to a decay curve of the type given by Eq. (2) and not by Eq. (8).

The condition $W_m \gg W_{cr}$ in the $C_{DD} \ll C_{DA}$ case can be satisfied if the donor and acceptor in question are unlike ions, i.e., we must have $n_D \gg n_A$. In this case, it is meaningful to speak of the diffusion of the excitation energy. If the excitation of the Nd^{3+} ions is lost only as a result of interaction over very short distances (interacting ions located at neighboring sites in the crystal lattice) and the energy can migrate over long distances, we cannot speak of the diffusion because this mechanism yields the condition (10) which presupposes the discontinuous migration mechanism. Therefore, according to the theory discussed here, there should be no diffusion of the excitation energy between the Nd^{3+} ions: we can only have the discontinuous migration mechanism.

Calculation of $\overline{W}$ of Eq. (8) and γ of Eq. (2), subject to the possibility of an inhomogeneous broadening of the lines, gives (see [15]):

$$\overline{W} = \pi(2\pi/3)^{5/2} K_1 K_2 n_A n_D, \tag{13}$$

$$\gamma = {}^4/_3 \pi^{3/2} K_1 n_A, \tag{14}$$

where

$$K_1 = \int C_{DA}^{1/2}(\nu) f(\nu)\, d\nu, \quad K_2 = \int C_{DD}^{1/2}(\nu') f'(\nu')\, d\nu',$$

$\nu = \nu_A - \nu_D$ is the difference between the transition frequencies of the interacting donor-acceptor ions; $f(\nu)$ is the density of the distribution of the difference; ν' and $f'(\nu')$ are the corresponding quantities for the donor-donor interaction.

We shall introduce the notation

$$\int C_{DA}^{1/2}(\nu) f(\nu)\, d\nu = (C'_{DA})^{1/2}, \quad \int C_{DD}^{1/2}(\nu') f'(\nu')\, d\nu' = (C'_{DD})^{1/2}. \tag{15}$$

This approach makes it possible to allow not only for the inhomogeneous line broadening but for the more important (in the case of a crystal activated with TR^{3+} ions) nonresonant interaction case when the detuning of the transitions of the interacting ions exceeds considerably the line width. In this case, $f(\nu)$ and $f'(\nu')$ are the phonon distribution functions.

Sakun [16] also obtained an expression for N(t) subject to $C_{DD} \neq 0$ and $C_{DA} \neq 0$. We shall not give this expression because it is cumbersome but we must mention that it consists of two terms. The first term describes the Förster process of the donor quenching [see Eq. (2)], whereas the second term describes the "mixing" action of the migration of energy in a donor system. It also follows from Sakun's theory [16] that if the decay kinetics is governed by the second term, it should be exponential. The conditions for an exponential decay are

$$\frac{n_A}{n_D}\left(\frac{C'_{DA}}{C'_{DD}}\right)^{5/6} < 1 \text{ for } C'_{DD} \ll C'_{DA}, \tag{16}$$

i.e., we must have $n_D \gg n_A$, or

$$\frac{n_A}{n_D}\left(\frac{C'_{DA}}{C'_{DD}}\right)^{1/2} < 1 \text{ for } C'_{DD} \gg C'_{DA}, \tag{17}$$

which are similar to the conditions discussed earlier.

Sakun [16] discussed the cases when the interactions C_{DA} and C_{DD} have different multipole orders. This gives rise to a power exponent of t in Eq. (8) which differs from unity and is a fraction. The temperature dependence of W_m has been explained [9,37,39] by mechanisms leading to the temperature dependence of C_{DD} and, consequently, of W_m. In all cases, this dependence is associated with an inhomogeneous line broadening.

EXPERIMENTAL RESULTS AND DISCUSSION

Figures 4 and 5 show the decay curves of the investigated metastable state of Nd^{3+} in $YAlO_3$ crystals, obtained at various temperatures and for different activator concentrations C. We can see that the exponential decay of the luminescence is observed throughout the investigated range of time. Such decay is obtained for 0.05% Nd^{3+} at both temperatures and for 2.5% Nd^{3+} at T = 77°K. In other cases, the exponential decay is observed only in the final stages. The decay times τ are listed in Table I for T = 77°K and 4.2°K. The decay time τ = 175 μsec, obtained for C = 0.05% Nd^{3+} (T = 4.2 and 77°K) and for C = 0.9% (T = 4.2°K) can be regarded—on the basis of the results of Weber et al. [18,40]—as the radiative decay time τ_0. Since τ_0 is independent of temperature, it follows that $\sum A_{gr}$ and $\sum A_{er}$ are equal [see Eq. (1)].

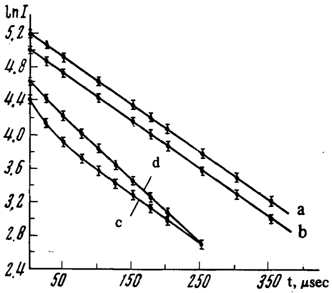

FIG. 4. Decay curves of the excited state (ln I plotted against t): a) T = 4.2°K, C = 0.05 at.%; b) T = 77°K, C = 0.05 at.%; c) T = 4.2°K, C = 0.9 at.%; d) T = 77°K, C = 0.9 at.%.

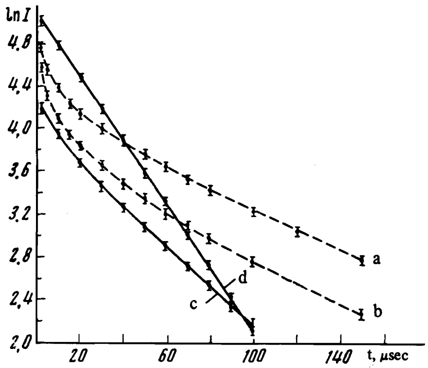

Fig. 5. Decay curves of the excited state (ln I plotted against t): a) T = 4.2°K, C = 1.8 at.%; b) T = 77°K, C = 1.8 at.%; c) T = 4.2°K, C = 2.5 at.%; d) T = 77°K, C = 2.5 at.%; the points are the experimental values and the dashed curves are calculated using Eq. (18) and the parameters listed in Table II.

The deviations from the exponential decay are slight for C = 0.9% (T = 4.2°K) and C = 1.8% (T = 77°K) and, therefore, in these cases there is no point in analyzing quantitatively the initial decay stages. However, in the case of C = 1.8 and 2.5% and T = 4.2°K (curves a and c in Fig. 5), the deviations are much greater and such an analysis is possible.[1)] We carried out such an analysis by subtracting the exponential dependences, corresponding to the final stages, from the general decay curve. In this way, we obtained curves which were again nonexponential but could be represented in the form $\ln[\ln(I_0/I_i)] = f(\ln t)$. The results of this analysis are presented in Fig. 6 (curves c and d). The slope of the obtained dependences is close to 1 at low values of t; as t increases, the slope tends to 1/2. The exponential decay for C = 0.05 and 0.9% at T = 77°K can be plotted using the same coordinates. In these cases, the slope is naturally equal to 1.

Thus, it is clear that the decay curves a and c in Fig. 5 are exponential in the initial and final stages. The Förster mechanism makes a considerable contri-

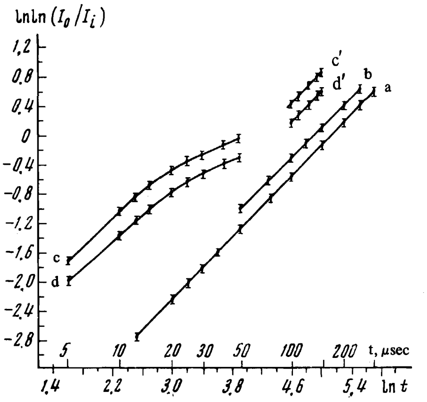

FIG. 6. Decay curves renormalized and plotted as the dependences $\ln[\ln(I_0/I_i)] = f(\ln t)$: a) T = 77°K, C = 0.05 at.%; b) T = 77°K, C = 0.9 at.%; c) T = 4.2°K, C = 2.5 at.% (the exponential dependence in the final stages of the process is subtracted from the general curve); c′) T = 4.2°K, C = 2.5 at.% (the decay curve corresponding to the final stage of the process); d) T = 4.2°K, C = 1.8 at.% (the exponential dependence corresponding to the final stages is subtracted from the general curve); d′) T = 4.2°K, C = 1.8 at.% (the decay curve corresponding to the final stage of the process).

TABLE I

C, at.%	τ, μsec	$\overline{W}$, sec^{-1}	τ, μsec	$\overline{W}$, sec^{-1}	C, at.%	τ, μsec	$\overline{W}$, sec^{-1}	τ, μsec	$\overline{W}$, sec^{-1}
	T = 77° K		T = 4.2° K			T = 77° K		T = 4,2°K	
0.05 0.9	175±5 137±5	0 1.5·10^3	175±5 173±5	0 0	1.8 2.5	55±5 34±3	1.25·10^4 2.37·10^4	120±5 100±5	2.62·10^3 4.28·10^3

TABLE II

C, at.%	A	B	C	τ$_1$, μsec	τ$_2$, μsec	γ, sec^{-1}	A + + B + + C
1.8	55	48	18	120±5	7	0.25·10^3	121
2.5	40	35	25	100±5	7	0.29·10^3	100

TABLE III

C, at.%	n$_D$ × 10^{-20}, cm^{-3}	n$_A$ × 10^{-20}, cm^{-3}	K$_1$ × 10^{19}, sec$^{-1/2}$·cm^3	K$_2$ × 10^{19}, sec$^{-1/2}$·cm^3
1.8	3.6	3.6	0.9	0.18
2.5	5	5	0.8	0.16
1.8	0.36	3.24		1.8
2.5	0.65	4.35		1.5

bution in the time interval 20-50 μsec. A qualitative analysis of the decay curves corresponding to this interval was carried out on a BESM-4 computer. It was found that these curves could be described by the expression:

$$I(t)=A\exp\left(-\frac{t}{\tau_1}\right)+B\exp(-\gamma t^{1/2})+C\exp\left(-\frac{t}{\tau_2}\right).\tag{18}$$

The values of the parameters in the above equation are listed in Table II. The calculated dependences are represented by the dashed curves in Fig. 6.

The relationship between the parameters A, τ$_1$, and B, γ is such that the second term in Eq. (18) does not distort the exponential decay in the final stages. It should be noted that the second term in Eq. (18) has a diverging derivative at $t \neq 0$. However, it follows from the physics of the process that the divergence cannot exist because of an upper limit to the probability of interaction for minimal distances between a donor and an acceptor.[14,16] Formally, the third term in Eq. (18) decays faster than the second term in the time interval 5-10 μusec (for the calculated values of B, γ and C, τ$_2$). Thus, the experimental curves are described by Eq. (18) for the only possible combination of the parameters listed in Table II.

The experimentally obtained quantities A, B, and C have a definite physical meaning for the excitation method used in our investigations. They represent the relative concentrations of the excitations which are destroyed by various methods. For example, the quantity C represents the relative concentration of the excitations destroyed by a strong interaction at fixed distances. The relative values of C are 25% for 2.5 at.% Nd^{3+} and 16% for 1.8 at.% Nd^{3+} (see Table II). If we assume that the distribution of impurity ions is random, which is true in our case, the number of ions which have neighbors at the nearest lattice sites is given by a well-known formula for repetitive sampling:[41]

$$C_n=\frac{a!}{n!\,(a-n)!}\beta^{n+1}(1-\beta)^{a-n},\tag{19}$$

where a is the number of sites in the first coordination sphere of an impurity ion (in our case a = 12); n is the number of sites in the same sphere occupied by such ions; β is the fraction of sites occupied by impurity ions.

Calculations show that the parameter C is equal to the fraction of the ions which have a neighbor at the nearest lattice site (27% for 2.5 at.% Nd^{3+} and 18% for 1.8 at.% Nd^{3+}), i.e, τ = 7 μsec, which corresponds to the exponential region of the decay curve at low values of t (the corresponding probability is $W^*_{cr} = 0.143 \times 10^6$ sec^{-1}), is the decay time of the excited ions which have a neighbor at the nearest lattice site. The quantity B is the relative concentration of the ions whose excited state decays in accordance with the Förster law (2); A is the concentration of the ions which decay in accordance with an exponential law that describes radiative decay and migration accompanied by quenching.

We shall now estimate the interaction parameters quantitatively. The value of $C'_{DA}(K_1)$, which represents the donor-acceptor interaction, can be found using the value obtained for the probability of cross relaxation in a pair W^*_{cr} (0.143×10^6 sec^{-1}) and the known distance R between the interacting ions (5.2 Å):[17]

$$C_{DA}'=W_{cr}\cdot R^n,\tag{20}$$

where n = 6, 8, or 10, depending on the multipole order of the interaction. The parameter C'_{DA} is found to be 0.3×10^{-38} sec^{-1}·cm^6 ($K_1 = 0.55 \times 10^{-19}$ sec$^{-1/2}$·cm^3), 7×10^{-54} sec^{-1}·cm^8 ($K_1 = 2.65 \times 10^{-27}$ sec$^{-1/2}$·cm^4), 2.2×10^{-68} sec^{-1}·cm^{10} ($K_1 = 1.48 \times 10^{-34}$ sec$^{-1/2}$·cm^5) for the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively. The value of K$_1$ for the dipole-dipole interaction can also be determined in a different way using the experimental value of γ and the formula (14). The results obtained are listed in Table III. We can see from this table that the agreement is quite satisfactory. Equation (14) is transformed somewhat in the case of interactions of higher multipole orders. The constant factors and the power exponent of n$_A$ also change slightly. For example, in the case of the dipole-quadrupole interaction this exponent is 4/3, whereas for the quadrupole-quadrupole interaction it is 5/3. The agreement between the values of C'_{DA} obtained by the two methods described below is much poorer for the interactions of higher multipole orders. The difference is a factor of 10 for the dipole-quadrupole interaction and a factor of 45 for the quadrupole-quadrupole interaction. This allows us to assume that the cross relaxation of the ${}^4F_{3/2}$ excited state of Nd^{3+} is due to the dipole-dipole interaction and the exponential decay in the final stages of the process suggests that the donor-donor and donor-acceptor interactions are of the same multipole order. [16]

The quantity K_2 can be found using Eq. (13) and the experimentally determined value of W at 4.2°K (Table I). The presence of a large number of paired ions and their exponential decay in the early stages (small t) makes it necessary to consider two cases.

1. The excitation is destroyed before reaching a pair. In this case, the exponential region corresponding to large t is governed by the migration and destruction of the excitation in a strong-quenching sphere of a sufficiently large radius. We must substitute $n_A = n_D = n_0$, where n_0 is the total activator concentration, in Eq. (13). The results obtained are represented by the first and second rows in Table III. It is found that $C'_{DD} \ll C'_{DA}$.

2. Exponential decay at large t due to the quenching in and the migration of excitation to a pair. This case presupposes the presence of two types of acceptor in the system, i.e., acceptors appearing as single ions and as pairs. The conclusion that single ions act as energy acceptors follows directly from the experimental observations of the Förster decay. However, we shall assume that the main contribution to the quenching is made by pairs. Then, using Eq. (13), we can select n_A to be half the concentration of ions having neighbors at the nearest lattice site, i.e., one of the ions in a pair acts as a donor and the other as an acceptor. The results obtained for this case are given in the third and fourth rows of Table III. In this case, $C'_{DD} > C'_{DA}$. This case and that discussed above clearly represent the extremes.

Thus, the results of measurements at T = 4.2°K allow us to determine accurately the parameter $C'_{DA} = 0.3 \times 10^{-38}$ $sec^{-1} \cdot cm^6$ and the range of possible values of $C'_{DD} = 2.5 \times 10^{-40}$–$3.2 \times 10^{38}$ $sec^{-1} \cdot cm^6$. When the temperature is raised to 77°K, the decay curve for C = 2.5 at.% Nd^{3+} is exponential (see Fig. 5, curve d). It follows from the theory that, in this case, one of the conditions (16) and (17) should be satisfied. In the case under discussion the condition (16) cannot be satisfied because the inequality $n_D \gg n_A$ is not obeyed and, consequently, the condition for the exponential decay is (17). The experimental situation is close to case 2 and the real values of K_2 are close to the values in the third and fourth rows of Table III. The disappearance, on increase of T, of the fast exponential stage corresponding to small values of t is evidence of an increase in C'_{DA}. In fact, we cannot observe the luminescence of pairs if $W^*_{cr} \geq 10^6$ sec^{-1}. Consequently, the value of C'_{DA} should rise to at least 10^{-38} $sec^{-1} \cdot cm^6$. Using $\overline{W}$ for C = 2.5 at.% at T = 77°K (Table I), we can determine the value of C_{DD} from Eq. (13). It is found that, in this case, C_{DD} is 20×10^{-38} $sec^{-1} \cdot cm^6$. The following condition (16) is then satisfied:

$$\frac{n_A}{n_D}\left(\frac{C'_{DA}}{C'_{DD}}\right)^{1/2} = 0{,}03 < 1 \text{ for } C'_{DD} \gg C'_{DA}.$$

This situation occurs only if we assume that at T = 77°K the quenching is due to the Nd^{3+} ions located at neighboring lattice sites.

Using the values of $\overline{W}$ for C = 1.8 and 0.9 at.% at T = 77°K, we can show that as the temperature rises C'_{DA} does not exceed 10^{-38} $sec^{-1} \cdot cm^6$ and the parameters C'_{DA} and C'_{DD} at 77°K are, respectively, 10^{-38} $sec^{-1} \cdot cm^6$ and 20×10^{-38} $sec^{-1} \cdot cm^6$. In fact, substituting these values and the corresponding parameters n_A and n_D, we find that $\overline{W} = 1.45 \times 10^3$ sec^{-1} for C = 0.9 at.% and $\overline{W} = 10^4$ sec^{-1} for C = 1.8 at.%, which is in good agreement with the results of measurements (Table I). Thus, we can find accurately the parameters C'_{DA} and C'_{DD} at 4.2 and 77°K (Table IV). This permits us to determine W_{cr} and W_m for the average distances. These values are listed in Table V. For the sake of comparison, Table V also includes the probabilities of the radiative and measured deactivation.

TABLE IV

T, °K	C'_{DD}, $sec^{-1} \cdot cm^6$	C'_{DA}, $sec^{-1} \cdot cm^6$
4.2	$2.2 \cdot 10^{-38}$	$0.3 \cdot 10^{-38}$
77	$20 \cdot 10^{-38}$	10^{-38}

TABLE V

C, at.%	W_m, sec^{-1}	W_{cr}, sec^{-1}	W_{deac}, sec^{-1}	$1/\tau_0$, sec^{-1}
		$T = 4.2°$ K		
0,05	2.2	0.3	$5.7 \cdot 10^3$	$5.7 \cdot 10^3$
0.9	$6.9 \cdot 10^2$	$0.94 \cdot 10^2$	$5.7 \cdot 10^3$	
1.8	$2.8 \cdot 10^3$	$0.38 \cdot 10^3$	$8.3 \cdot 10^3$	
2.5	$5.5 \cdot 10^3$	$0.75 \cdot 10^3$	10^4	
		$T = 77°$ K		
0,05	20	1	$5.7 \cdot 10^3$	$5.7 \cdot 10^3$
0.9	$6.3 \cdot 10^3$	$3.15 \cdot 10^2$	$7.3 \cdot 10^3$	
1.8	$2.56 \cdot 10^4$	$1.28 \cdot 10^3$	$1.82 \cdot 10^4$	
2.5	$5 \cdot 10^4$	$2.5 \cdot 10^3$	$2.94 \cdot 10^4$	

We can see that the probabilities obtained describe well the situation observed experimentally. In fact, in the cases when $W_m \ll 1/\tau_0$, we do not observe experimentally a reduction in τ (see Tables I and V). Moreover, the relationships between W_m and W_{deac} confirm our conclusion, drawn from an analysis of the theory, that the excitation energy cannot diffuse between the Nd^{3+} ions and the migration mechanism is discontinuous. Calculations of W_m for the average distances in the dipole-quadrupole and quadrupole-quadrupole interactions give values smaller than $1/\tau_0$. For example, in the dipole-quadrupole interaction the value of W_m for C = 1.8 at.% and T = 4.2°K is 2×10^2 sec^{-1} (W_{cr} is correspondingly smaller). In this situation τ should not decrease, which is in conflict with the experimental results. This confirms the conclusion that the interaction of the Nd^{3+} ions is of the dipole-dipole type. Our results indicate that C'_{DD} and C'_{DA} are functions of the temperature and in our specific case the temperature dependence of C'_{DD} is stronger (Table IV).

We shall not consider the mechanism responsible for the temperature dependence of C'_{DD}. Possible mechanisms are discussed in [9,37–39]. However, the temperature dependence of C'_{DA} cannot be explained on the basis of the available theories. The crystal splitting of the ${}^4I_{9/2}$, ${}^4I_{13/2}$, ${}^4I_{15/2}$, and ${}^4F_{3/2}$ levels of Nd^{3+} (Fig. 7) [18] excludes the conditions under which C'_{DA} could depend on the temperature [se Eq. (3)]. In fact, the maximum energy of the ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ (5659 cm^{-1}) transition is less than the minimum energy of the ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$ (5760 cm^{-1}) transition. The populations of the Stark components in the T = 4.2–77°K range also cannot give rise to cross relaxation involving these transitions. The effective nonresonant cross relaxation may involve two intermediate states ${}^4I_{13/2}$ and ${}^4I_{15/2}$ (${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ and ${}^4I_{9/2} \rightarrow {}^4I_{15/2}$).

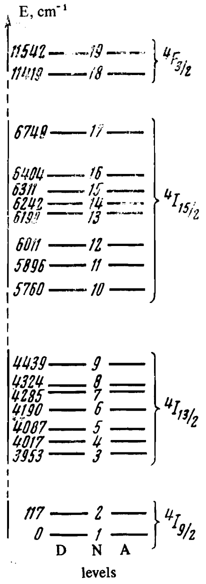

FIG. 7. Crystal splitting of the $^4I_{9/2}$, $^4I_{13/2}$, $^4I_{15/2}$, $^4F_{3/2}$ levels of Nd^{3+} in a $YAlO_3$ crystal. [18].

The Stokes detuning of the resonance lies in the 232–2706 cm^{-1} range. Experiments show that such nonresonant cross relaxation gives rise to a strong quenching. The population of the Stark components does not increase the detuning because $\Delta E_{12} \approx \Delta E_{19,18} \approx \Delta E_{8,9}$ (see Fig. 7). Moreover, $\Delta E_p > kT$ in the investigated range of temperatures and, consequently, the conditions (4) for the appearance of $C_{DA} = f(T)$ in Eq. (3) are not satisfied. In this case, the temperature dependence is due to an increase in the absorption at the detuning frequency. It follows from Bosomworth's investigation [42] that this effect is very considerable if the temperature is increased from 4.2 to 77°K.

The main results of our investigation can be summarized as follows.

The parameters of the donor-donor and donor-acceptor interactions have been found as averages over space and time and as characteristics representing elementary processes.

The concentrations of the excitations destroyed by various mechanisms have been determined. It has been shown that the interaction of the Nd^{3+} ions is of the dipole-dipole type.

The probabilities of migration and cross relaxation are functions of the temperature. At different temperatures the mechanisms of nonradiative losses from the investigated metastable level of Nd^{3+} are different.

The migration of excitation between the Nd^{3+} ions is discontinuous and cannot be described by the diffusion equation.

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[1)] It should be noted that curves a and c in Fig. 5 resemble superficially the corresponding dependences under nonlinear quenching conditions. [6] However, the decay kinetics does not change with the excitation intensity and, consequently, the interaction between the excited states does not occur.

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