Reversible nonradiative excitation-energy transfer in a system of strongly interacting particles

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We study nonradiative excitation-energy transfer between impurity ions in crystal matrices. The case of excitation-energy transfer between two species of ions is considered in the presence of an energy mismatch (ΔE) between metastable states of these ions. It is shown on the basis of theoretical calculations and experimental investigations that the character of reversible excitation-energy transfer between assemblies of ions is determined not only by the quantity $\Delta E/kT$ (kT is the temperature activation energy) but also by the ratio of the densities of the different ion species. A shift of the low-temperature limit of reversible excitation-energy transfer in systems of strongly interacting particles is observed experimentally for the first time and explained. The investigations reported are important for gaining an insight into the nature of nonradiative excitation-energy relaxation in crystals. The results of the paper should also be taken into account in the design of laser matrices based on the principle of sensitization of active ions.

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INTRODUCTION

Nonradiative energy transfer between particles in condensed media plays an important role in the sensitization and quenching of active ions in laser matrices.

Interest has increased recently in high working-ion density laser materials in which the so-called case of "strong coupling"[1)] can take place and the energy-transfer probability is much higher than the probability of the decay of the excited states of the active particles in the system.[1] The investigation of the reversible energy transfer between ions in the strong-coupling case has revealed many phenomena that are of interest from both the physical and practical viewpoints.[2–4] It must be noted, however, that the objects considered in these researches were subject to the condition $\Delta E \ll kT$. Here ΔE is the energy gap between the excited states of the interacting particles, and kT is the temperature activation energy. This variant is possible in the case of resonant interaction or at high temperatures. The probabilities of the direct (p) and reverse (h) energy transfer are equal in this case.

Another variant occurs when the condition $\Delta E \gg kT$ holds—the case of directed energy transfer from one species of ions to the other, when h is zero. Naturally, with increasing temperature the directed transport can go over into reversible energy transfer. The present study is aimed at theoretical and experimental investigations of the change of this character of nonradiative energy transfer with temperature, both for a system of two interacting particles and for assemblies of ions in the strong-coupling approximation.

ANALYSIS OF TEMPERATURE DEPENDENCE OF THE PROCESSES OF REVERSIBLE EXCITATION-ENERGY TRANSFER

The temperature dependence of the decay of two interacting ion species can be obtained by solving the Boltzmann transport equations, which are in general complicated. Simplification is possible in two cases: an isolated pair of ions N and A, or two interacting subsystems.

In Ref. 2, collective transport equations were used to describe interactions between subsystems of ions N and A. The first case can occur at low density of the activator ions in the crystal and the second, conversely, at high impurity density. According to Ref. 4, there exist two conditions for the applicability of the kinetic transport equations: 1) when the probability of transfer from any ion N and A to all the particles of the other species is the same, or 2) when the change of the population of the excited states of the particles, due to the rapid migration of the excitation over the subsystems N and A, is only a function of the time and does not depend on the position of the ion in the lattice.

These situations can be supplemented by a third, wherein the first condition is satisfied for one of the impurity subsystems and the second for the other. This can occur, for example, if the density of the ions N is much higher than that of A, and the ions N occupy practically all the sites of the regular lattice of the crystal. Rapid migration is possible then only in the subsystem N, whereas the ions A have identical environments of particles N, so that the probabilities of transfer from all the A ions to the N particles in the system are equal.

Solution of the system of collective transport equations yields the time dependences of the ion populations $C_A(t)$ and $C_N(t)$ in the following forms[4]:

$$C_A(t)=-K_1e^{-\lambda_1 t}+K_2e^{-\lambda_2 t},\qquad C_N(t)=-K_3e^{-\lambda_1 t}+K_4e^{-\lambda_2 t},\qquad (1)$$

where K_1 to K_4 are coefficients independent of t,

$$\lambda_{1,2}={}^1/_2(\alpha+\gamma+\overline{P}+\overline{H}\pm[(\alpha+\gamma+\overline{P}+\overline{H})^2-4\overline{H}(\alpha-\gamma)]^{1/2}),\qquad (2)$$

α and γ are the probabilities of the deactivation of the excited states in the ions N and A, respectively, and $\overline{P}$ and $\overline{H}$ are the probabilities of the transfer from any ion (N or A) to an as-

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sembly of particles of the other species.

Taking into account the conditions for the applicability of the collective transport equations, we can identify the quantity $\overline{P}$ (or $\overline{H}$) with the probability of the decay of a donor system in which ultrafast migration takes place, or else with the probability of static decay of donors in a crystal strongly doped with acceptors. The equations for the decay probabilities are then equal in the multipole approximation,[1] so that we can write

$$\overline{P}=p\beta_A\sum_i 1/R_i^l, \quad \overline{H}=h\beta_N\sum_j 1/R_j^l. \tag{3}$$

Here p and h are the probabilities of the direct and reverse energy transfer between the ions N and A over the shortest distance in the lattice, β_N and β_A are the relative densities of the ions N and A, and l is the multipolarity parameter. The summation is over all the crystal-lattice sites occupied by these ions.

If it is assumed that the sublevel of the excited state in the ion A lies lower than in the in N by an amount equal to the energy gap ΔE, the connection between p and h for the case of equal degeneracy multiplicity of the interacting states is then

$$h=p\exp(-\Delta E/kT). \tag{4}$$

Substituting (4) in (3) and carrying out the summation for a specific crystal lattice, say for the garnet structure, we obtain the connection between $\overline{P}$ and $\overline{H}$ in the form

$$\overline{H}=\overline{P}(n_N/n_A)\exp(-\Delta E/kT). \tag{5}$$

The constant λ_1 in (2) describes the initial section of the decay, which in the case $p\gg\alpha$ and $p\gg\gamma$ is short in time, after which the deactivation of both the N and A ions should proceed at the same rate, equal to λ_2. Using the strong-coupling condition $p\gg\alpha, \gamma$ we can obtain for λ_2 an expression independent of p and h:

$$\lambda_2=[\alpha n_N\exp(-\Delta E/kT)+\gamma n_A]/[n_A+n_N\exp(-\Delta E/kT)]. \tag{6}$$

The formulas for the decay of $C_N(t)$ and $C_A(t)$ for the model with an isolated pair made up of ions N and A with the shortest spacing in the lattice is obtained from (2) and (3) by replacing $\overline{P}$ by p and $\overline{H}$ by h. The connection between p and h is then given by Eq. (4). Let us analyze the relations obtained for the kinetics of the decay of $C_N(t)$ and $C_A(t)$ for the models with the pair and with the assembly of interacting particles.

Equations (4) and (5) lead to the interesting conclusion that replacement of the reversible transfer by a directed transfer of energy from the impurity subsystem N to the subsystem A can set in at much lower temperature than for a pair of ions N and A. This is due to the presence of the factor n_N/n_A in (5). If this factor is large (10^2–10^3), $\overline{H}$ turns out to differ from zero at temperatures at which a directed energy transfer should exist for the pair-interaction model.

In Ref. 3 was observed experimentally the so-called "excitation trapping" for the case of resonant interaction of two impurity assemblies of ions having different lifetimes. As a result, the lifetime of the level of the rapidly relaxing particle is increased because the excitation is trapped by ions with longer lifetimes. It is naturally of interest to analyze the manifestation of this effect in an interaction between an assembly of particles when there is an energy mismatch in the system. Let the energy of the lower component of the metastable level of the ion A be lower than that of ion N by an amount ΔE, and let the lifetime of this level be longer for the ion A than for N. Using Eqs. (1), (2), and (5) we have calculated the decay kinetics of the rapidly relaxing particles as a function of temperature at various ratios n_N/n_A and $\overline{P}$. The results of these calculations are shown in Fig. 1. It can be seen from this figure that for the case $n_N\gg n_A$ the temperature dependence of $C_N(t)$ varies greatly in our system. At high temperature the particle decay is exponential and corresponds to the radiative lifetime of the centers of type N. Cooling the sample leads to quenching of the type-N centers [the area under the nonexponential $C_N(t)$ curve decreases] and to an increase of the lifetime $\tau_N = 1/\lambda_2$ measured on the final exponential section of the decay. The "excitation trapping" effect manifests itself thus in our system only at low temperatures. The reason can be easily explained by considering the change of the probabilities of the direct and reverse excitation-energy transfer between the N and A particles. At high temperature when the condition $\Delta E < kT$ holds, the probabilities of the direct (p) and reverse (h) energy transfer from N to A are equal. In this case the presence of a low concentration of long-lived A ions has no effect whatever on the decay kinetics; in particular, λ_2 of (2) is determined by the deactivation rate (α) of the rapidly relaxing type-N centers. In the case of considerable cooling, when $p\gg h$, the population in the system of N ions decreases strongly and the trapping of the excitation by the slowly relaxing centers becomes noticeable. It is important to note that the quantity n_N/n_A influences strongly the change of the character of the decay of the type N centers. Thus, an increase of this quantity, as follows from Fig. 1, leads to an increase in the number of excited ions of type N at the instant of the transition from the fast section to the stage of low exponential decay. This makes it possible to observe in experiment the section of the slow decay of $C_N(t)$ at lower temperatures.

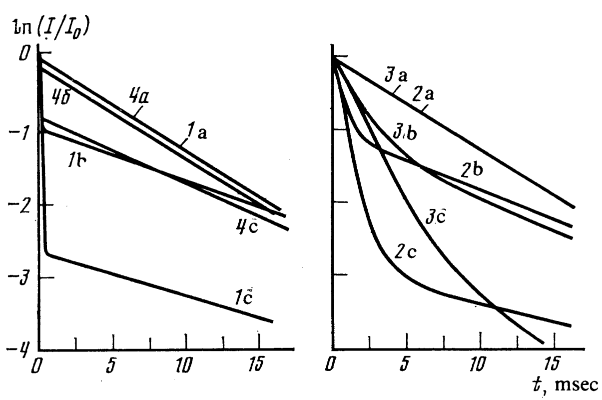

FIG. 1. Calculated dependences of the kinetics of the decay of ions of type N for different temperatures: a) 10 K, b) 4.2, c) 2.8. The values of $\overline{P}$ are 1 and 4) 10^4 sec^{-1}, 2) 10^3, 3) 10^2. The ratio n_N/n_A is 10^2 for curves 1, 2, and 3, and 10^3 for curves 4. The energy gap is $\Delta E = 21$ cm^{-1}, $\alpha = 125$ sec^{-1}, and $\gamma = 56$ sec^{-1}.

EXPERIMENTAL INVESTIGATION OF REVERSIBLE NONRADIATIVE ENERGY TRANSFER BETWEEN Er³⁺ IONS IN GARNET-STRUCTURE CRYSTALS

A good object for the investigation of nonradiative transfer between systems of two different types of ion are crystals of the solid solutions erbium-gadolinium-gallium and erbium-yttrium-aluminum garnets synthesized from the melt. Synthesis from the melt causes the Er^{3+} ions to enter not only in the "traditional" c-type sites with dodecahedral surroundings (Er_N^{3+}) but also in to a-type sites at octahedrally coordinated Al^{3+} or Ga^{3+} (Er_A^{3+}) (Ref. 5). Since the crystal fields in the surroundings of the Er_N^{3+} and Er_A^{3+} have different symmetries, the splitting of their energy levels is substantially different (Fig. 2), as a result of which an energy mismatch ΔE exists in the considered $Er_N^{3+} \to Er_A^{3+}$ interaction schemes in the transition $^4I_{15/2} \to {}^4I_{13/2}$. This gap varies in the range 21–55 cm^{-1}, depending on the type of garnet. Table I lists the absolute relative densities and the ratios of the densities of the N and A ions, calculated from the spectra of these ions in accord with the procedure of Ref. 6. We identify crystals with definite Er^{3+} density by using the values of β_N, since in the main the Er^{3+} replace c-sites of the lattice. Since the luminescence spectra of the Er_N^{3+} and Er_A^{3+} ions are strongly shifted for the $^4I_{13/3} \to {}^4I_{15/2}$ transition it is easy to record separately the emission kinetics of these two types of ion by using a monochromator with relatively low resolution (MDR-2).

The luminescence was excited in our experiment in the region $\lambda < 0.6\ \mu m$ using a DKsShR flash lamp with SZS-21 and SZS-26 filters. The use of wavelengths with $\lambda < 0.6\ \mu m$ causes the excitation energy to land on the Er_A^{3+} ions only as a result of nonradiative transfer from the Er_N^{3+} ions, since the absorption by the Er_A^{3+} ions is negligible in all the transitions except $^4I_{15/2} \to {}^4I_{13/2}$ (the 1.6-μm region), owing to the hindrance imposed on the electrodipole transitions by the presence of an inversion center in the surrounding crystalline polyhedron.[5] The considered crystal base is convenient because it is possible to vary purposefully the densities of the Er_A^{3+} and Er_N^{3+} ions by varying only the total Er^{3+} density or by introducing special impurities (the "mutual influence" effect[5]). By the same token it is possible to obtain crystals with different values of the ratio n_N/n_A (from 10 to 1000) and with different average distances between the Er_N^{3+} and Er_A^{3+}. A change of n_N/n_A is reflected in the probabilities of the migration between the ions and makes it possible to stimulate different variants of the energy-transfer processes. At a low Er^{3+} density (of the order of tenths of one percent), when the migration of the excitation energy over the impurity ions has little effect, transfer from Er_N^{3+} and Er_A^{3+} is possible in an isolated pair. At the same time, at high impurity densities (tens of percent) reversible transfer between assemblies of Er_A^{3+} and Er_N^{3+} becomes possible. In this case the Er_N^{3+} ions can fill the garnet c sublattice practically completely, causing rapid energy migration over the Er_N^{3+} impurity system. This case can be described with the aid of collective transport equations, since the third condition for their applicability is satisfied here. Actually, the appreciable filling of the c sublattice by Er_N^{3+} ions causes, on the one hand, rapid migration of the excitation energy over the Er_N^{3+} subsystem, and on the other causes each Er_A^{3+} ion to have, at the shortest distances from it, an identical surrounding of Er_N^{3+} ions.

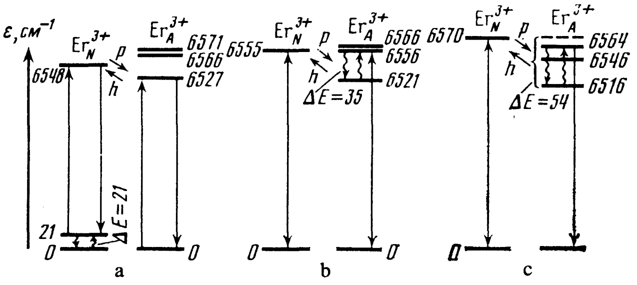

FIG. 2. Level schemes for nonradiative energy transfer between the ions Er_N^{3+} and Er_A^{3+} in crystals of various garnets. a) Series of solid solutions of yttrium-erbium-aluminum garnets, b) gadolinium gallium garnet + 0.3% Er^{3+}, c) erbium gallium garnet. The energy mismatch values ΔE are indicated in cm^{-1}.

An analysis of the experimental kinetics of the decay of the excited states of the ions Er_A^{3+} and Er_N^{3+} ions has shown that they are not exponential in the density region $\beta_N < 30\%$ and exponential at $\beta_N > 30\%$. Typical of $\beta_N < 30\%$ is a rapid decrease of the population of the levels of the Er_N^{3+} ions, which gives way to an exponential dependence at the final stage of the decay. The impossibility of recording the fast section of the decay of crystals with $\beta_N \geqslant 30\%$ is due to the limited time resolution of the PbS receiver, which cannot record damping times shorter than $10^2\ \mu$sec.

Figures 3, 4, and 5 illustrate the variation of the lifetimes τ_N of the Er_N^{3+} ions and τ_A of the Er_A^{3+} ions measured during the final stages of the decay, as functions of temperature, for crystals with various Er^{3+} densities. Starting from the regularities in the change of the quantities $\tau_N(T)$ and $\tau_A(T)$, the investigated gadolinium-gallium (GGG) and yttrium-aluminum (YAG) garnets should be divided into samples with low ($\beta_N = 0.3\%$), medium ($\beta_N = 20–30\%$) and high ($\beta_N = 100\%$) Er^{3+} density.

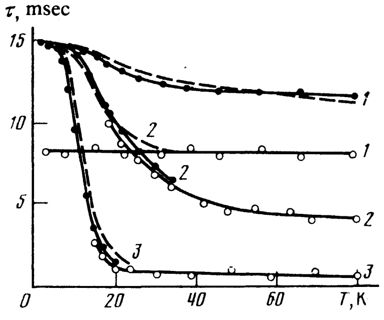

FIG. 3. Temperature dependences of the lifetimes τ_N of Er_N^{3+} ions (○) and τ_A of Er_A^{3+} ions (●) in gadolinium-gallium garnet crystals with different Er^{3+} densities: 1—0.3%, 2—30%, 3—100%. The dashed lines show the calculated $\tau_A(T)$ dependences for a crystal with $\beta_N = 0.3\%$ assuming the model with a pair of Er_N^{3+} and Er_A^{3+} ions, and for the remaining samples assuming the model of interacting particle assemblies [Eq. (6)]. The following parameters were used in the calculations: 1) $\Delta E = 35\ cm^{-1}$, $\alpha = 125\ Sec^{-1}$, $\gamma = 66\ Sec^{-1}$; 2) $\Delta E = 40\ cm^{-1}$, $\alpha = 125\ Sec^{-1}$, $\gamma = 66\ Sec^{-1}$, $n_N/n_A = 12$; 3) $\Delta E = 55\ cm^{-1}$, $\alpha = 10^3\ Sec^{-1}$, $\gamma = 66\ Sec^{-1}$, $n_N/n_A = 25$.

INTERACTION IN CRYSTALS WITH LOW Er^{3+} DENSITY

It follows from experiments on selective laser excitation[5] that in crystal having low density (GGG), $\beta_N = 0.3\%$) the probability of excitation-energy migration over the Er_N^{3+} is low, and it is this which causes the difference in pair interaction between the Er_N^{3+} and Er_A^{3+} ions. The pairs $Er_N^{3+} + Er_A^{3+}$ can be formed in the crystal as a result of accidental landing of the Er^{3+} ions in neighboring lattice sites a and c. Starting with a statistical calculation, the number of Er_N^{3+} and Er_A^{3+} ions combined into such pairs in a GGG crystal with 0.3% Er^{3+} is approximately 1%. Thus, emission of 1% of Er_A^{3+} ions from $Er_A^{3+} + Er_N^{3+}$ pairs should be observed in experiment, since the remaining 99% Er_A^{3+} will not be exposed to excitation energy for the reasons indicated above. As for the Er_N^{3+} ions, the dominant emission will be from the bulk of the ions, which are not contained in pairs, since it was impossible in our case to separate spectrally the emission of an isolated ion from the emission of an erbium ion contained in a pair. Experimental plots of $\tau_A(T)$ and $\tau_A(N)$ are shown in Fig. 3 for the crystal GGG + 0.3% Er^{3+}, confirm the existence of excitation-energy transfer in an isolated pair of ions Er_N^{3+} and Er_A^{3+}. The lifetime τ_N is found to be independent of temperature, since it characterizes the luminescence of the Er_N^{3+} ions not involved in the $Er_N^{3+} \leftrightarrow Er_A^{3+}$ interaction, whereas the τ_A dependence exhibits the regularity typical of the pair interaction model. This is confirmed by calculation of the $\tau_A(T)$ dependence in accord with Eq. (2). In the calculation, the interaction probability $\overline{P}$ was estimated from the section of the fast decay on the luminescence damping curve, and the deactivation probabilities were assumed to be $\alpha = 1/\tau_N^1$ and $\gamma = 1/\tau_A^1$ (τ_N^1 and τ_A^1 are the radiative lifetimes for the Er_N^{3+} and Er_A^{3+} ions). This choice of the values of α and γ is justified: the probabilities of the intracenter nonradiative processes of energy dissipation from the level $^4I_{13/2}$, just as the probability of the quenching of the Er^{3+} ions by the extraneous impurities, will be small. The former because of the large ($\approx 6000\ cm^{-1}$) energy gap between the levels $^4I_{13/2}$ and $^4I_{15/2}$, and the latter because of the low density of the Er^{3+} in the crystal. The value of τ_N corresponds to the temperature-independent lifetime τ_N^1 of the isolated Er^{3+} ions Fig. 3). The value of τ_A^1 can be determined on the section of the low-temperature plateau on the $\tau_A(T)$ curve (Fig. 3). At these temperatures, radiation is observed only from the Er_A^{3+} ions in crystals with high Er^{3+} density, since the luminescence of the Er_N^{3+} particles is fully quenched. This situation corresponds to directed energy transfer from the Er_N^{3+} to the Er_A^{3+} ions. It is seen from Figs. 3–5 that in crystals with both low and extremely high density of Er^{3+} the $\tau_A(T)$ curves reach a plateau with a value τ_A^1. In other words, in the absence of reverse transfer no quenching of the Er_A^{3+} ions by extraneous impurities is observed even in totally substituted garnets.

Experimental investigations of the transfer processes in crystals with low density could be carried out only in gallium garnets, where the number of Er_A^{3+} ions was large enough to produce such a density of $Er_A^{3+} + Er_N^{3+}$ pairs that made it possible to register the emission from the Er_A^{3+} ions they contained. As seen from Table I, the probability of finding Er^{3+} ions at a sites of aluminum garnets is much lower than for gallium garnets. Therefore in aluminum garnets the luminescence of the Er_A^{3+} ions could be observed at a density $Er^{3+} > 15\%$, when the excitation-energy migration processes already come into play. We cite therefore only the calculated $\tau_A(T)$ dependence for the model of pair interaction in aluminum garnets (Fig. 4).

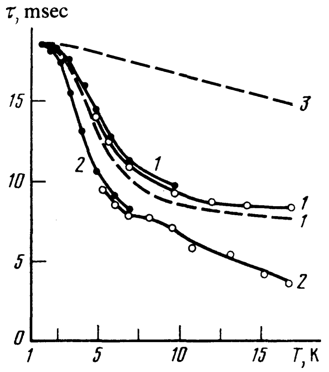

FIG. 4. Dependences of the lifetimes τ_n (○) and τ_A (●) in aluminum garnets with densities 20% (1) and 30% (2). Dashed lines—calculated $\tau_A(T)$ dependences): 1) from Eq. (6) for a crystal with $\beta_N = 20\%$ ($\Delta E = 21\ cm^{-1}$, $\alpha = 125\ sec^{-1}$, $\gamma = 56\ sec^{-1}$, $n_N/n_A = 10^2$); 3) for the pair model ($\Delta E = 21\ cm^{-1}$, $\alpha = 125\ sec^{-1}$, $\gamma = 56\ sec^{-1}$).

TABLE I. Densities of Er_N^{3+} and Er_A^{3+} ions in garnet-structure crystals with different total Er^{3+} densities.

Host	Total Er^{3+} density in crystal, $10^{22}\ cm^{-3}$	Relative (β) absolute (n) Er^{3+} ion densities in sites of type a and c				n_N/n_A ratio
		c sites		a sites		
		β_N, %	n_N, $10^{22}\ cm^{-3}$	β_A, %	n_A, $10^{20}\ cm^{-3}$	
YAG	0.27	22	0,27	0.3	0,27	10^2
YAG	0.41	34	0,41	0,45	0.41	10^2
YAG	1.37	100	1.37	1.5	1.37	10^2
YAG – 2% Sc^{3+}	1.37	100	1.37	0.15	0.14	10^3
GGG	$0.36 \cdot 10^{-2}$	0.17	$0.18 \cdot 10^{-2}$	0.21	0.18	1
GGG	0.26	19	0.24	2.4	2	12
GGG	1.3	100	1.25	5.9	5	25

INTERACTION IN CRYSTALS WITH MEDIUM Er^{3+} DENSITY

The character of the temperature dependence of the interaction processes in crystals with $\beta_N = 20$–30% differs substantially from the regularities of the variation of $\tau_A(T)$ and $\tau_N(T)$ considered above for the pair model. Thus, τ_A and τ_N begin to increase, when the crystal is cooled, at lower temperatures than for the pair model (Figs. 3 and 4). Our analysis has shown that with increasing Er^{3+} density conditions for the interaction between the collective Er_A^{3+} and Er_N^{3+} ions begin to be satisfied, and this interaction is described by Eqs. (5) and (6). Calculation of the $\tau_A(T)$ and $\tau_N(T)$ dependences from these equations has shown that the shift of the $\tau_A(T)$ plots into the region of lower temperatures is indeed due to the presence of the factor n_N/n_A in Eq. (5).

The calculated dependences shown in Figs. 3 and 4 were obtained under the assumption that the Er^{3+} ions do not interact with other quenching centers. Yet, as indicated earlier in Refs. 7 and 8, at densities 20–30% Er^{3+} quenching of luminescence from the $^4I_{13/2}$ level is observed in YAG crystals. This quenching is due to excitation-energy migration over the metastable Er^{3+} levels to the quenching centers, which are ions of uncontrollable impurities. The crystals investigated in the cited references were YAG-Er^{3+} synthesized from a solution in the melt, and these crystals, according to Ref. 5, can contain only Er_N^{3+} ions, so that the $Er_N^{3+} \leftrightarrow Er_A^{3+}$ interaction processes observed in the objects investigated by us are impossible in such crystals.

It can be seen from Figs. 3 and 4 that at Er^{3+} densities $\beta_N = 30\%$ the experimental $\tau_A(T)$ and $\tau_N(T)$ plots of both YAG and GGG lie somewhat lower than the calculated curves obtained for the model with interaction of Er_A^{3+} and Er_N^{3+} subsystems in the absence of extraneous quenching centers. At a lower density $\beta_N = 20\%$ one observes in YAG a close agreement between the experimental and calculated curves, and with increasing temperature the $\tau_N(T)$ curve reaches a temperature plateau corresponding to the radiative lifetime of the Er_N^{3+} centers.

It can thus be concluded that the uncontrollable impurities begin to play a role in our crystals at an Er^{3+} density higher than 20%.

It must be noted that the number of Er_A^{3+} crystals in the crystals investigated in the present study does not exceed several percent even at the maximum Er^{3+} ion density in the host (see Table I). Therefore it seems rather unlikely that the Er_A^{3+} ions interact with the uncontrollable impurities by the mechanism proposed in Refs. 7 and 8 and observed for Er_N^{3+} subsystems. The Er_A^{3+} ions can nonetheless be made to interact with extraneous impurities via the Er_N^{3+} subsystem owing to the reversible $Er_N^{3+} \leftrightarrow Er_A^{3+}$ transfer.

Since the $Er_N^{3+} \leftrightarrow Er_A^{3+}$ interactions and the interactions of the Er_N^{3+} ions with extraneous impurities are temperature dependent in close temperature intervals at medium Er^{3+} densities, it is impossible to determine the behavior of the $\tau_A(T)$ and $\tau_N(T)$ curves with allowance for the influence of the additional quenching centers. Such calculations, however, can be carried out for fully substituted garnet crystals, as will be shown below.

An analysis of the form of the nonexponential decay kinetics obtained for Er_N^{3+} ions in an experiment on a YAG crystal with $\beta_N = 20\%$ at various temperatures (Fig. 6) has shown them to agree with calculations performed for the interacting particle-assembly model (Fig. 1). Thus, τ_N was observed to increase on the exponential section of the decay when the crystal was cooled. It follows from Eq. (3) that this growth of τ_N can reach the value τ_A^1. Since the radiative lifetime τ_A^1 of the Er^{3+} ions is 18 msec for aluminum and 15 msec for gallium garnets, while τ_N^1 in both hosts amounts to 7–8 msec, the increase of τ_N with temperature can be easily observed in the YAG:30% Er^{3+} crystal. The value $\tau_N = 15$ msec observed in this crystal at 3 K is almost twice as large as τ_N^1. Cooling the crystal below 3 K makes it possible to observe the emission from the Er_N^{3+} ions. Therefore the breaks in the plots of Figs. 3–5 in the low-temperature region are due to the existence of a temperature limit for the registration of the luminescence from Er_N^{3+} ions. The $\tau_A(T)$ plots also have a temperature limit at which the spectra of the Er_A^{3+} ions can be registered but now when the crystal is heat-

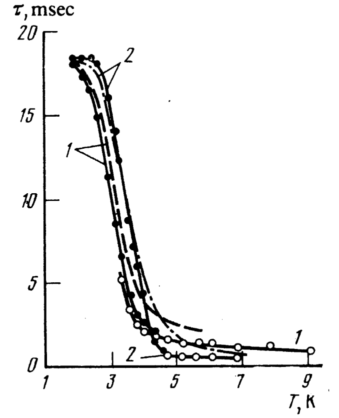

FIG. 5. Change of the temperature dependences of the lifetimes τ_N(○) and τ_A(●) with changing ratio n_N/n_A: 1) erbium-aluminum garnet with 2% Sc^{3+}, $n_N/n_A = 10^3$, 2) erbium-aluminum garnet, $n_N/n_A = 10^2$. Dashed and dash-dot lines—dependences calculated from Eq. (6) ($\Delta E = 21$ cm^{-1}, $\gamma = 56$ sec^{-1}, $\alpha = 10^3$ sec^{-1}—curve 1, $\alpha = 2 \times 10^3$ sec^{-1}—curve 2).

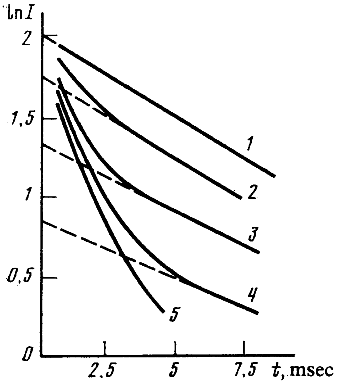

FIG. 6. Experimental kinetics of the decay of Er_N^{3+} ions in an yttrium aluminum garnet with 20% Er^{3+} at various temperatures: 1—10 K, 2—5.2, 3—4.2, 4—3.6, 5—2.8.

ed. In this case the intensity of the emission from the Er_A^{3+} ions decreases with increasing T because the transfer $\mathrm{Er}_A^{3+} \to \mathrm{Er}_N^{3+}$ prevails over $\mathrm{Er}_N^{3+} \to \mathrm{Er}_A^{3+}$.

INTERACTION IN CRYSTALS WITH HIGH Er^{3+} DENSITY

This case takes place in crystals of fully substituted erbium-aluminum and erbium-gallium garnets, in which the *c* sublattice is completely filled with Er^{3+} ions. These objects are of interest because they satisfy most accurately the third condition for the applicability of the collective transport equations for the description of the transfer between the Er_N^{3+} and Er_A^{3+} impurity subsystems. In crystals with $\beta_N = 100\%$ the quenching of the Er^{3+} ions by controllable impurities becomes particularly noticeable, as a result of which τ_N is 6–8 times smaller at high temperatures than the radiative value. It can be seen from Figs. 3 and 5 that both in erbium-aluminum and erbium-gallium garnets the $\tau_N(T)$ plot has a plateau up to the temperature at which the quenching of the Er_N^{3+} ions sets in because of the directed transfer $\mathrm{Er}_N^{3+} \to \mathrm{Er}_A^{3+}$. This circumstance makes it possible to regard the quenching of Er_N^{3+} ions by extraneous impurities as temperature-independent, and to take this quenching into account by introducing into the expresion for the probability of the excitation energy dissipation in the Er_N^{3+} impurity system a term W denoting the probability of the interaction of the Er_N^{3+} ions with the extraneous impurities. Then $\alpha = 1/\tau_N^1 + W$ and this quantity can be obtained by measuring the value of τ_N on the section of the high-temperature plateau (Figs. 3 and 5).

Calculations performed for fully substituted garnets describe well the experimental results for both aluminum and gallium garnets (Figs. 3 and 5).

A clear-cut demonstration of the effect of the ratio n_N/n_A on the irreversible transfer was obtained for erbium-aluminum garnet crystals. It is seen from Table I that n_N/n_A in GGG:Er^{3+} crystals can be changed by varying the total density of the Er^{3+}. This, however, changes the value of ΔE and the conditions for the $\mathrm{Er}_N^{3+} \leftrightarrow \mathrm{Er}_N^{3+}$ and $\mathrm{Er}_N^{3+} \leftrightarrow \mathrm{Er}_A^{3+}$ interactions because of the change of the distance between the ions. The ratio n_N/n_A in erbium-aluminum garnet was changed by introducing Sc^{3+} ions (approximately 2 at.%) in the crystal during its growth. This decreased the density of the Er_A^{3+} ions by 10 times (see Table I), while ΔE and the conditions for the interaction between the Er_N^{3+} and Er_A^{3+} remained the same as in the pure erbium-aluminum garnet, since the *c* sublattice of the crystal with Sc^{3+} remained completely filled with Er^{3+} ions. According to calculation (Fig. 6), the increase of the ratio n_N/n_A should have shifted the $\tau_A(T)$ curve into the region of lower temperatures, as was indeed observed in experiment. It is also seen from Fig. 5 that in the crystal with Sc^{3+} the emission from the Er_N^{3+} ions is registered up to temperatures 3.2 K, whereas the luminescence intensity of these ions in the sample without Sc^{3+} is practically zero already at 4.4 K. This is evidence that at the instant of transition from the fast to the exponential decay section the number of excited Er_N^{3+} ions increases with increasing n_N/n_A, in agreement with the calculations illustrated by Fig. 1.

CONCLUSION

The foregoing theoretical and experimental results have revealed an interesting feature of the reversible energy transfer in a system of two interacting species of particles. In the case when the interaction involves assemblies of impurity particles and the strong-coupling conditions are satisfied, the condition for the transition from the reversible transfer to the directed one upon cooling of the crystal is determined not only by the quantity $\Delta E/kT$, but also by the ratio n_N/n_A of the densities of these two species. When n_N/n_A reaches a value 10^2–10^3 the temperature limit of this transition can be shifted towards extremely low temperatures (3 K at an energy gap 21 cm^{-1}). In this case the low value of the temperature activation kT compared with ΔE is offset by the large degree of degeneracy of the system in the state with higher energy. This is an important result, since usually the existence of reversible transfer in a definite system is adduced only on the basis of an estimate of $\Delta E/kT$. It must be noted that in the present paper it was not our purpose to determine the character of the temperature dependence of the parameters of the interaction of the probabilities of the migration over the Er_N^{3+} ions and of the $\mathrm{Er}_N^{3+} \leftrightarrow \mathrm{Er}_A^{3+}$ interaction. It is natural to expect that when T is lowered they can decrease because of the deformation of the Lorentz contours of the lines of the interacting ions.[9] Our experiments on YAG and GGG crystals with high Er^{3+} densities, and their comparison with the calculated curves, show that the model of interacting particle assemblies is justified, and the decrease of the interaction probabilities with temperature does not reach a limit that prevents the description of the processes considered here with the aid of collective transport equations.

[1)] When considering in this paper processes that take place in this approximation we shall assume that the probability of interaction between the ions remains much less that the rate of phase relaxation in the system. This approach is well-founded for rare-earth ions[3] and permits the use of the transport equations for the calculations.

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