Exchange mechanism of nonradiative energy transfer between rare-earth ions in crystals

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We investigated the change in the probability *W*(*R*) of energy transfer between rare-earth ions in $Y_3Al_5O_{12}$ crystals. The objects of the investigations were the ions Eu^{3+} (donor) and Yb^{3+} (acceptor), the energy level splitting schemes of which favor the observation of the mechanism of nonradiative energy transfer due to exchange interaction. The peculiarities in the formation of associates of impurity ions in the $Y_3Al_5O_{12}$ crystals were used to measure *W*(*R*) at concrete distances in the $Y_3Al_5O_{12}$ lattice. From the strong change in the value of *W*(*R*) on going from the first to the second cation coordination sphere around the donor it is concluded that an exchange-resonance mechanism of energy transfer between $Eu^{3+} \to Yb^{3+}$ exists in $Y_3Al_5O_{12}$. The absolute value of the probability of transfer with participation of the exchange mechanism over the shortest distance between these ions is obtained.

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Dexter[1] has considered various mechanisms of nonradiative energy transfer between ions in crystals. In the case of the inductive-resonant mechanism or the dipole-dipole, dipole-quadrupole, or quadrupole-quadrupole interactions, the variation of the transfer probability W(R) with changing distance R between the donor and acceptor should be proportional to R^{-6}, R^{-8}, and R^{-10}, respectively.

An investigation of nonradiative energy transfer in a system of rare-earth ions TR^{3+} has revealed the existence of donor-acceptor pairs for which the variation of W(R) agreed with the relations indicated above.[2-4] The conclusion that W(R) has a definite type of variation, and consequently that a multipole interaction takes place, was based on a comparison of the experimental data (the concentration dependences of the lifetime or the emission intensity of the donors) with a set of theoretical curves calculated for various types of interaction. These curves were calculated with approximate formulas which cannot include the real distances between the ions in the lattice. Average distances, which can be estimated from the activator concentrations, were usually employed. This approach is valid for cases when the transfer occurs over relatively large distances between the donors and acceptors, i.e., when their concentrations in the crystal are insignificant.

Yet it is known that the theory deals with an energy transfer mechanism (exchange) for which the variation of W(R) can be steeper than R^{-10}.[1] The exchange mechanism predominates in the case of forbidden electronic transitions, and the transfer probability depends on the overlap integral of the donor and acceptor electron clouds. This transfer mechanism should therefore be effective at quite short distances between the ions, and can consequently be observed at high activator concentrations.

The existence of an exchange mechanism of energy transfer between TR^{3+} ions is of particular interest because, in view of the depth of the electronic f-shells of Tr^{3+} ions, the wave-function overlap integral is negligible even when they are adjacent in the crystal.

Attempts to observe this transfer mechanism experimentally are few, and criteria other than the law governing the variation of W(R) were used for its identification, inasmuch as the procedure considered above cannot be used because of the need of taking into account the interaction at concrete distances between the ions in the crystal. Thus, Antipenko and Ermolaev[5,6] concluded that an exchange transfer mechanism can exist between TR^{3+} ions in solutions on the basis of an analysis of the selection rules in the acceptor.

In their known papers, Van Uitert and coworkers[7,8] resorted to the mechanism of exchange interaction via intermediate oxygen ions in order to explain the observed laws governing the energy transfer between like Eu^{3+} or Tb^{3+} ions in crystals. The basis for this was the dependence they observed of the transfer probability on the coordination number of the cation sphere closest to the donor, this number being determined by the structure of the crystal matrix. It should be noted that to identify the exchange transfer mechanism one can use the fact that it is short-range, i.e., that W(R) changes appreciably when the distance between the donor and acceptor is increased. For this purpose it is necessary, however, in contrast to the procedure used for long-range transfer mechanisms[2-4], to measure the value of W(R) at concrete distances between the ions in the crystal.

We were able to carry out investigations of this type by using the peculiarities in the production of various types of associates of TR^{3+} ions in the structure of aluminum garnet, and the possibility of their identification.

INVESTIGATED CRYSTALS, APPARATUS, AND EXPERIMENTAL PROCEDURE

The investigated crystals were grown by the Stockbarger and Czochralski methods. The following concentration series were synthesized: $(Y_{1-x}, Yb_x)_3Al_5O_{12}$–0.1% Eu^{3+}, $(Y_{1-x}, Lu_x)_3Al_5O_{12}$–1% Eu^{3+}, $(Y_{1-x}, Yb_x)_3Al_5O_{12}$–1% Eu^{3+} (x = 0 to 1), as well as the crystal $(Y_{0.9}Yb_{0.1})_3Al_5O_{12}$. The purity of the initial materials was 99.9999%.

The emission spectra of Eu^{3+} and Yb^{3+} were registered with a specially constructed high-sensitivity installation based on the DFS-12 spectrometer. The radiation receivers were the photomultipliers FÉU-79 and FÉU-62, cooled with liquid-nitrogen vapor. The photomultipliers operated in the photon-counter regime. The signal from the photomultiplier was fed to multichannel analyzer NTA-512B. The wavelength setting of the spectrometer was reconciled with the analyzer channel number by a coding device.

This system made it possible to operate in the signal accumulation regime by multipass registration of the spectrum, thus ensuring high sensitivity. The Eu^{3+} luminescence was excited with DRSh-1000 and DKSSh-1000 lamps through FS-7 and SZS-14 filters, and also through an MDR-2 monochromator. The spectra were registered at 4.2, 77, and 300°K. The EU^{3+} emission kinetics was investigated with an "Orion" TR-4401 oscilloscope, and the excitation source was an ISSh-100-3 flash lamp with flash duration ≈ 70 μsec.

The objects of the investigation were $Y_3Al_5O_{12}$ (YAG) crystals activated with Eu^{3+} and Yb^{3+}, and while the donor concentration (Eu^{3+}) did not exceed 1 at.%, the acceptor (Yb^{3+}) concentration ranged from 5 at.% to complete substitution of Yb^{3+} for Y^{3+}. This donor-acceptor pair, in our opinion, offers a number of advantages when attempts are made to investigate experimentally energy transfer via the exchange mechanism.

1. The energy level schemes of Yb^{3+} and Y^{3+}, based on an analysis of the luminescence and absorption spectra (Fig. 1),[1)] shows that the overlap integral of the donor emission spectrum and the acceptor absorption spectrum[1] differs from zero, and the $Eu^{3+} \rightarrow Yb^{3+}$ interaction can proceed with emission of a phonon of energy $\Delta E > 860\ cm^{-1}$.

2. It is seen from Fig. 1 that the transition $^5D_0 \rightarrow {}^7F_6$ of Eu^{3+} will take part in the transfer; the oscillator strength of this transition, according to our measurements, is the smallest among the radiative $^5D_0 \rightarrow {}^7F_J$ transitions (smaller by $\approx 10^3$ times than for the most intense transition $^5D_0 \rightarrow {}^7F_1$). Recognizing that the absolute probabilities of the forbidden transitions $^5D_0 \rightarrow {}^7F_J$ in Eu^{3+} and $^2F_{5/2} \rightarrow {}^2F_{7/2}$ in Yb^{3+} are in turn small (as indicated by the large lifetimes of the metastable levels of these ions, 4.2 and 1 msec, respectively), the relative contribution of the exchange mechanism of energy transfer at a short distance between the donor and acceptor can be predominant.

3. The scheme under consideration does not contain the migration of the excitation energy between the donor ions, in view of the extremely low probability of the $^5D_0 \rightarrow {}^7F_0$ transition ($\approx 0.1\ sec^{-1}$ according to our data) responsible for the energy transfer between Eu^{3+} ions at low temperatures. The low probability of the resonant $^5D_0 \rightarrow {}^7F_0$ transition makes migration between the Eu^{3+} ions almost impossible if the concentration of the latter does not exceed at most ≈ 1 at.%. This fact was established experimentally for $(Y_{1-x}, Yb_x)_3Al_5O_{12}$ crystals in which the Eu^{3+} concentration was varied from 0.1 to 1 at.%. No decrease in the lifetime of the Eu^{3+} was registered then. Further increase of the Eu^{3+} concentration in the $Y_3Al_5O_{12}$ crystals entails great difficulties, and in the present study we did not check on the Eu^{3+} concentration at which a shortening of the lifetime of the $^5D_0$ level takes place.

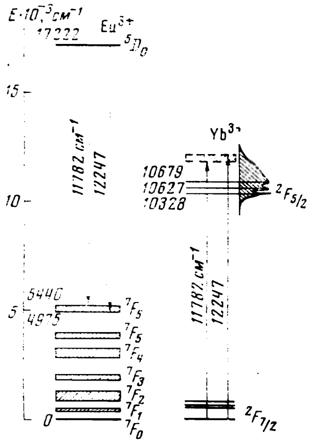

FIG. 1. Level splitting schemes of Eu^{3+} and Yb^{3+} in $Y_3Al_5O_{12}$ crystal at 77°K. The arrows show the energy resonance that can occur when energy is transferred between these ions.

4. In view of the peculiarities of the energy level scheme for the $Eu^{3+} \rightarrow Yb^{3+}$ pair, the reverse transfer $Yb^{3+} \rightarrow Eu^{3+}$ with excitation of the $^5D_0$ level of Eu^{3+} is possible only by a cooperative process whose probability is known to be negligibly small compared with the direct transfer probability.

The procedure proposed by us for measuring the transfer probability between the ions in the crystal makes use of the fact that location of the acceptor at a definite distance from the donor leads not only the quenching of the latter, but also to a shift of its spectral lines. As shown in[10], it is possible to separate in garnet crystal the spectra of the following ions: (a) with no other impurity ions in the first coordination sphere, i.e., the latter ions are located in the second and more remote spheres; (b) those having at least impurity ion in the first coordination sphere.

The possibility of separating the spectra of the donors located in the indicated activator centers enables us to measure separately, for each of them, such characteristics as the relative quantum yield η and the lifetime τ, with the aid of which it is then possible to obtain the transfer probability from the well-known formulas

$$\frac{1}{\tau} = \frac{1}{\tau_0} + W, \quad \eta = \frac{1}{\tau_0}\left(\frac{1}{\tau_0} + W\right)^{-1}, \tag{1}$$

where τ_0 is the radiative lifetime of the donor.

Since the distance R for the first and second cation coordination spheres in the garnet is known,[11] the variation of W(R) on going from the first to the second sphere can be obtained with sufficient accuracy.

The separation of the spectra of donors having different acceptor surroundings, and the calculation of the concentrations of various types of activator centers, were carried out by the procedure described in[10]. As shown there, the line shift of various activator centers (AC) in garnet crystals does not exceed 1–3 cm^{-1}. In view of the weak perturbation of the crystalline environment of the TR^{3+} upon formation of the associates, there is practically no change in the probability of the transitions of the TR^{3+} ions contained in the different AC. In turn, to register lines located at such short distances from one another, we need instruments with high resolution, which must furthermore be intended for the registration of weak light fluxes, since the luminescence intensity of the so-called "quenched" centers is extremely weak. These tasks can be well handled by the apparatus described above.

Since the procedure of AC separation is based on an investigation of the dependence of the spectral line intensities of various AC on the impurity concentration, we have investigated the concentration series of crystals $(Y_{1-x}, Yb_x)_3Al_5O_{12}$–$Eu^{3+}$. The series of crystals $(Y_{1-x}, Lu_x)_3Al_5O_{12}$–$Eu^{3+}$ was used to monitor the positions of the luminescence lines of the Eu^{3+} AC, which had, owing to the quenching processes, and extremely weak intensity in the $(Y_{1-x}, Yb_x)_3Al_5O_{12}$ crystals. The AC lines of Eu^{3+} + Lu^{3+} and Eu^{3+} + Yb^{3+} practically coincide. At the same time, inasmuch as Lu^{3+} does not have any electronic levels in the transparency region of the crystal, there is no quenching of Eu^{3+} in the Eu^{3+} + Lu^{3+} centers.

EXPERIMENT

The conclusion that nonradiative energy transfer takes place from Eu^{3+} to Yb^{3+} can be drawn from the experimentally observed fact that the emission intensity and the lifetimes of the excited Eu^{3+} ions decrease with increasing Yb^{3+} concentration. We registered also the luminescence of Yb^{3+} following excitation in the absorption band of Eu^{3+}; this luminescence was not observed in the $(Y_{0,9}Yb_{0,1})_3Al_5O_{12}$ crystal that did not contain Eu^{3+}.

Let us examine the connection between the change of the relative intensity of the luminescence of Eu^{3+}, on the one hand, and the structure and concentration of the AC present in a crystal with a definite number of acceptors (Yb^{3+}), on the other. According to the results of[10], at low (up to 30 at.%) amounts of Yb^{3+} (Lu^{3+}) in the $Y_3Al_5O_{12}$ crystals, the Eu^{3+} spectra should contain mainly lines of two types of AC, their models being: an Eu^{3+} ion without a neighboring Yb^{3+} in the first coordination sphere (N center), and an Eu^{3+} + Yb^{3+} (Lu^{3+}) pair (M center). As follows from Fig. 2a, which shows the luminescence spectra of the crystals $Y_3Al_5O_{12}$—10% Yb^{3+} (Lu^{3+})—Eu^{3+}, the luminescence of both N and M centers was observed only in crystals with Lu^{3+}. Only ‘‘isolated’’ N centers of Eu^{3+} luminescence in the $Y_3Al_5O_{12}$—Yb^{3+} crystal. This fact indicates that entry of even one Yb^{3+} ion into the first coordination sphere of Eu^{3+} causes practically complete quenching of the latter. At the same time, the presence of Yb^{3+} in the second and more remote spheres of Eu^{3+} has little effect on the luminescence intensity of the latter. As a result, in contrast to the $Y_3Al_5O_{12}$—Lu^{3+}—Eu^{3+} crystals, where the line intensities of the associates Eu^{3+} + Lu^{3+} increase with increasing Lu^{3+} concentration and these ‘‘crowd out’’ the N-center lines at a concentration as low as 30%, in the YAG:Yb^{3+} crystal the N lines could be registered up to 70 at.% Yb^{3+}. The dependence of the relative intensity of the N-center luminescence ($\xi = I_N/I_0$) on the Yb^{3+} concentration in the crystal (β) is illustrated in Fig. 3 (curve 2). Here I_N is the integrated intensity of the emission of the N centers of Eu^{3+} in the crystal of the series $(Y_{1-x}, Yb_x)_3Al_5O_{12}$, and I_0 is the emission intensity of the Eu^{3+} in the YAG. The Eu^{3+} concentration in the investigated series of crystals was the same. When plotting $\xi = f(\beta)$ it was possible to dispense with a correction for reabsorption, since the final level $^7F_1$ of the investigated luminescent transition $^5D_0 \to {}^7F_1$, located 300 cm^{-1} below the ground level, is not populated at 77 and 4.2°K.

Figure 3 shows also the dependence of the relative N-center concentration $\alpha(\beta)$ on β (curve 1). This curve was calculated by a formula that takes into account the statistical distribution of the ions in the garnet crystal, and is given in[10]. This formula can be used because, as shown in the cited paper, the distribution of the TR^{3+} ions in the garnet crystals is equiprobable.

A comparison of the functions $\alpha(\beta)$ and $\xi(\beta)$ (Fig. 3, curves 1 and 2) shows that the change of the relative emission intensity of the N centers correlates well with the change of their concentrations. At the same time, the $\xi(\beta)$ curve lies somewhat lower than the $\alpha(\beta)$ curve. This indicates that some insignificant quenching of the N centers of Eu^{3+} is produced by the interaction of the Yb^{3+} located at a distance larger than the Y^{3+} ion in the first coordination sphere. Were it not for this interaction, $\alpha(\beta)$ and $\xi(\beta)$ would be equal.

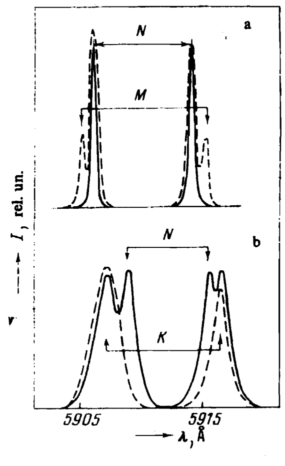

FIG. 2

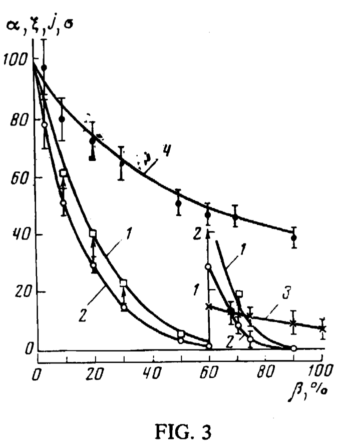

FIG. 3

FIG. 2. Luminescence spectra of Eu^{3+} in the $^5D_0 \to {}^7F_1$ group at 4.2°K in the crystals $Y_3Al_5O_{12}$—10% Yb(Lu) (a) and $Y_3Al_5O_{12}$—67% Yb(Lu) (b). Solid line—crystals with Yb, dashed—with Lu. The ordinate scale for case (b) in the $Y_3Al_5O_{12}$—67% Yb crystal is increased about 100 times compared with the $Y_3Al_5O_{12}$—67% Lu crystal.

FIG. 3. Dependence of the functions α, ξ, j, and σ on the total concentration of Yb^{3+} in the crystal (β): α—calculated plot of the relative concentration of centers of type N (curve 1); ξ—variation of the relative intensity of the N-center luminescence (curve 2), j—variation of the relative intensity of the K centers (curve 3); σ—calculated variation of the relative lifetime of the $^5D_0$ level of the N centers of Eu^{3+} (curve 4) (the experimental points are marked ●). The arrows show the change of curve 2 when a correction is introduced for the N-center quenching by the Yb^{3+} ions located outside the first coordination sphere. The ordinate scale for β>60% of curves 1, 2, and 3 is increased by 20%.

The presence in the crystal of Eu^{3+} activators centers characterized by different degrees of quenching should make itself manifest in measurements of the lifetime of the Eu^{3+} metastable level $^5D_0$. Thus, the lifetime of the M centers (τ_1) should be much less than the Eu^{3+} radiative decay time (τ_0), while the lifetime of the ‘‘isolated’’ N centers (τ_2) should remain of the same order as τ_0.

The experimentally measured change $\sigma^{\text{meas}} = \tau^{\text{meas}}/\tau_0$ of the lifetime with increasing Yb^{3+} concentration is shown in Fig. 3 (curve 4), where τ_0 is the lifetime of Eu^{3+} in $Y_3Al_5O_{12}$. The value of τ^{meas} was determined from the luminescence quenching curve, which turned out to be exponential. As seen from Fig. 3, the order of magnitude of the measured quantity τ^{meas} remained the same as that of τ_0 in a wide range of Yb^{3+} concentrations, up to 90%, i.e., until almost all the Y^{3+} sites of the crystals were occupied by the acceptor ions.

So slight a change allows us to conclude that we measured in the experiment the lifetime of the long-lived N centers of Yb^{3+} (τ_2^{meas}). Favoring this statement is the fact that if the $\xi(\beta)$ curve is corrected for the N-center quenching by using the values of τ_2^{meas}, then the $\xi(\beta)$ curve becomes identical with the $\alpha(\beta)$ curve (Fig. 3). For this calculation, we determined the values of the relative mean quantum yield of the emission of the N centers for different β, using the formula

$$\overline{\eta}_2=\tau_2^{\text{meas}}/\tau_0. \tag{2}$$

The reason why we did not register in the investigation of the decay kinetics of the metastable $^5D_0$ level the presence of "quenched" M centers is that the low value of τ_1 for these centers makes their observation by our apparatus impossible. According to a preliminary estimate, τ_1 should be $<70\ \mu$sec.

Since it was impossible to measure τ_1, the probability of energy transfer between Eu^{3+} and Yb^{3+} with the shortest distance between them was determined by another method.

In the investigation of the Eu^{3+} in crystals with small Yb^{3+} contents, it was impossible to observe the luminescence of the associates $Eu^{3+} + Yb^{3+}$, because of the extremely weak intensity of their spectral lines, both due to the low concentration of these centers and by virtue of the fact that their luminescence was strongly quenched. These lines could not be registered on the edge of the intense N lines. However, as Yb^{3+} increased with decreasing N-center concentration and with increasing concentration of the $Eu^{3+} + Yb^{3+}$ associates, it became possible to observe the lines of the Eu^{3+} centers (K centers) having in their nearest surrounding at least one Yb^{3+} ion. This case is illustrated in Fig. 2b for the $Y_3Al_5O_{12}$–67% Yb crystal. Besides the N lines, the positions of which were shifted somewhat relative to $Y_3Al_5O_{12}$ because of the change in the unit-cell parameter, we observed also the K-center lines. These lines were registered in YAG crystals with Yb^{3+} concentration from 60 to 100%, and the luminescence intensity of these centers is given by curve 3 of Fig. 3. It is seen that the equalization of the N- and K-center line intensities occurs in a crystal with 67% Yb^{3+}, where the Eu^{3+} concentration in the N centers is ≈1% of all the Eu^{3+} ions in the crystal. It is perfectly understandable that if the quenching of the Eu^{3+} were eliminated, say if Yb^{3+} were replaced by Lu^{3+} with the same concentration, then it would be impossible to observe simultaneously the emission of the N and K centers. This case is illustrated in Fig. 2b for the crystal $Y_3Al_5O_{12}$–67% Lu, the spectrum of which contains only K lines.

Using the equality of the intensities of the N and K centers in the YAG crystal with 67% Yb^{3+}, we can obtain the average relative quantum yield ($\overline{\eta}_1$) of the emission of K-type centers, from the formula

$$\overline{\eta}_1=\overline{\eta}_2(n_2/n_1). \tag{3}$$

The ratio of the N- and K-center concentrations is here (n_2/n_1) – 1/99 at the Yb^{3+} concentration 67%, and $\overline{\eta}_2$ is given by formula (2) with $\beta = 0.67$. It follows from (3) that the value of $\overline{\eta}_1$ of Eu^{3+} ions having at least one Yb^{3+} ion in the first coordination sphere is smaller by almost two orders than the relative quantum yield of the Eu^{3+} ions whose nearest sphere is free of Yb^{3+}. This enables us to ascribe the value of $\overline{\eta}_1$ determined from (3) exclusively to energy transfer from Eu^{3+} to Yb^{3+} located at the shortest distance from the Eu^{3+}. In this case we can calculate the transfer probability W_1 for the $Eu^{3+} + Yb^{3+}$ pair, if we take into account different variants of the disposition of the Yb^{3+} in the first coordination sphere at $\beta = 0.67$.

Using a statistical calculation, we can define the average value $\overline{\eta}_1$ as follows:

$$\overline{\eta}_1=\left[\sum_{l=1}^{k}\frac{W_0}{W_0+lW_1}C_k^l\beta^l(1-\beta)^{(k-l)}\right]\Big/\left[1-(1-\beta)^k\right]. \tag{4}$$

Here k is the coordination number of the first sphere and is equal to 4 for garnet crystals; l is the possible number of Yb^{3+} ions in this sphere (from 1 to 4); C_k^l is the number of combinations of k elements in groups of l.

Using formulas (2)–(4) with the values of τ^{meas}, n_1 and n_2 at $\beta = 0.67$, we find that $W_1 = (2.5 \pm 1.25) \times 10^{-4}\ \text{sec}^{-1}$. On the basis of this value we find that the lifetime τ_1 for Eu^{3+}, in centers with Yb^{3+} located at the shortest distance, should be ≈40 μsec. This is indeed too small to be observed in our experiments on the kinetics of luminescence damping.

DISCUSSION OF RESULTS

As shown above, the transfer probability between Eu^{3+} and Yb^{3+}, at the shortest distance $R = 3.67$ Å between these ions, is ≈100 times larger than the radiative-decay probability. We can also estimate the probability W_2 of transfer between the indicated ions when the distance between them increases to the radius of the second sphere (5.6 Å). We used for this purpose the lifetime τ_2^{meas} of the Eu^{3+} centers whose first sphere was not filled with Yb^{3+} (N centers).

Two cases must be considered in the calculation of W_2.

A. The observed shortening of the lifetime in the N centers with increasing β is due to interaction between Eu^{3+} and Yb^{3+} ions located only in the second sphere. This case is possible if the short-range transfer mechanism remains practically ineffective over a distance larger than to the first sphere. In this case the determined $Eu^{3+} \rightarrow Yb^{3+}$ energy transfer at the distance of the second sphere will have a maximum value W_2', since it is necessary to take into account in the calculation the averaging of the transfer to acceptors located only in the second coordination sphere.

B. If the N-center quenching is due to another mechanism, in which the interaction involves the acceptors located in some spherical volume around the donor, then in this case the calculated value of W_2 will be smaller than W_2'.

To determine the minimum possible value of W_2 (W_2'') it is necessary to consider the longest-range transfer mechanism (dipole-dipole). This mechanism is not excluded for the system under consideration, since we are dealing here with so-called induced electric dipole transitions due to mixing of the electronic configuration with odd parameters of the classical field.[12] In this approximation, on the one hand, the transfer probability is proportional to R^{-6},[12] and on the other hand its absolute magnitude remains extremely small. At the shortest distance between the ions, the effectiveness of this mechanism is negligible and the quenching can be due to the short-range mechanism. At larger distances, one should not exclude the existence of the dipole-dipole interaction.

The values of W_2' and W_2'' were determined by using the law governing the change of the relative number n(t) of exciting donors with time. To deduce this law it is necessary to average the action of the acceptors in the second coordination sphere for the case of excitation deactivation only through this sphere (case A), and in a certain volume around the donor in the case of the dipole-dipole mechanism (case B).

In the calculation we took into account the statistics of the acceptor distribution over the different coordination spheres, using the "binomial" distribution formula known from probability theory.[14] The functions n(t) for cases A and B are given by formulas (5) and (6) respectively:

$$n(t)=\sum_{l=0}^{k} C_k^l\beta^l(1-\beta)^{k-l}\exp(-W_0t-W_2'lt), \tag{5}$$

we use here the same notation as in (4), and k = 8 (the coordination number of the second sphere);

$$n(t)=\sum_i\prod_p C_{k_p}^{l_p}\beta^{l_p}(1-\beta)^{(k_p-l_p)}\exp[-W_0t-W_2''l_p(R_0/R_p)^6t],$$

$$\sum_i\prod_p C_{k_p}^{l_p}\beta^{l_p}(1-\beta)^{k_p-l_p}=1, \tag{6}$$

by virtue of the normalization, W_0 is the radiative-decay probability, k_p and l_p are respectively the coordination number and the number of acceptors in the p-th sphere (l_p ranges from 0 to k_p), and R_0 and R_p are the radii of the second and p-th spheres in the garnet crystals. The summation is over all possible variants (i) of the location of the acceptors in a certain region near the donors. The dimension of this region was limited by the number of coordination spheres that were taken into account in the calculation. The product was taken over the number of spheres (p), starting with the second and ending with the p-th.

W_2' and W_2'' were calculated by formulas (5) and (6) by choosing the corresponding quantities in such a way that the value of τ_2^{calc} determined with the aid of the calculated curve coincided at the obtained value of W_2 with the experimentally determined lifetime τ_2^{meas}. For τ_2^{meas} we used the lifetime measured in the crystal at β = 67%. We then plotted, for the obtained value of W_2 the function $\sigma^{\text{calc}} = \tau_2^{\text{calc}}/\tau_0 = f(\beta)$ for comparison with the experimental $\sigma^{\text{meas}}(\beta)$ plot. Since the procedure for selecting W_2 is quite cumbersome, especially using (6), the calculation was performed with an M-220 computer. The program was produced with the "MIR-2" computer with subsequent translation to the M-220 computer with the aid of the setup considered in[15].

The calculation by formula (6) was performed with various numbers of spheres. It turns out that the chosen value of W_2'' ceases to vary starting with the eighth sphere. This shows that the deactivation of the excitation, even in the case of the longest-range inductive-resonant mechanism, occurs in a crystal with a large number of acceptors mainly in a sphere of relatively small radius. This excludes the possibility of simplifying formula (6) by changing over from summation to integration as i → ∞, as was done in Förster's known paper.[16]

An analysis of the plots of n(t) has shown that they are well approximated by exponentials. The reason is the following: Our statistical calculation has shown that owing to the small radius of the quenching sphere due to the large acceptor concentration, the number of variants of the acceptor surroundings of the donor is limited, and most donors have in the main an almost equivalent surrounding which is most probable for the given Yb^{3+} concentration.

As shown in[17], in this case an exponential decay should be observed, i.e., τ_2 has the physical meaning of the lifetime of the Eu^{3+} ions in N centers having the most probable acceptor surrounding.

According to the calculation procedure presented above, W_2' and W_2'' are equal to 58 ± 20 and 28 ± 10 μsec, respectively. It is easily noted that these quantities are quite close. This causes the functions $\sigma^{\text{calc}}(\beta)$ calculated from the values of W_2' and W_2'' to coincide. Consequently, it is impossible to choose between the transfer mechanisms at the distance of the second coordination sphere by comparing the calculated and experimental σ^{calc} and σ^{meas}. A plot of $\sigma^{\text{calc}}(\beta)$ is shown in Fig. 3 (curve 4) and is seen from this figure to be in satisfactory agreement with experiment. Thus, the decrease of the Eu^{3+} lifetime in N centers with increasing Yb^{3+} concentration is explained by the growth of the number of acceptors in the second and more remote coordination spheres around Eu^{3+}.

Using the obtained values of W_2' and W_2'', we can estimate the minimum value of the relative decrease of the probability W_1/W_2 of the $Eu^{3+} \rightarrow Yb^{3+}$ transfer on going from the first to the second coordination sphere. It amounts to ≈200. In the approximation of the inductive-resonant transfer mechanism, the changes W_1/W_2 should be 13, 30 and 70 for the different cases of interaction like R^{-6}, R^{-8}, and R^{-10}, respectively.

Thus, a quantitative estimate of the change of S(R) with changing distance makes it possible to state with sufficient justification that nonradiative energy transfer between such TR^{3+} ions as Eu^{3+} and Yb^{3+}, at the shortest distances in the garnet crystals, is realized via the exchange mechanism.

It appears that the possibility of observing the exchange mechanism of energy transfer between TR^{3+} ions was due in our case not only to a successful choice of the donor-acceptor pair, but also to the peculiarities of the host itself. In particular, in $Y_3Al_5O_{12}$ crystals, by virtue of their structure, there is a realistic possibility of effecting the exchange-interaction scheme proposed in[7], when the overlap of the wave functions of the TR^{3+} ions is produced not directly by via intermediate oxygen ions.

An investigation of the character of the variation of W(R), besides the establishment of the existence of an exchange transfer mechanism between the rare-earth ions in the crystals, has made it possible to estimate the absolute value of the transfer probability via this mechanism for the shortest distance between the TR^{3+} ions. According to the value of W_1 determined above, the transfer probability can lie in the range 10^4–10^5 $\sec^{-1}$. This value is large enough to compete with other transfer mechanisms at the shortest distances.

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[1] We used the results of [9] to determine the position of the upper component of the $^2F_{5/2}$ level of the Yb^{3+} ion.

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