Effect of broadening of spectral lines on the migration of electron excitation along impurity centers in crystals

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The effect of spectral line broadening on electron-excitation migration along the active ions in crystals is investigated theoretically and experimentally. It is shown that in the case of uniformly broadened spectral lines the broadening results in a weakening of the migration effect. A criterion that depends on the nature of spectral line broadening is discussed for the validity of the usual diffusion procedure used to describe excitation migration along like ions. The relation between the migration probability and ratio of the uniform and nonuniform widths ($b = \delta/\Delta$) is obtained by calculations based on the linear model of excitation migration. The dependence is nonmonotonic and has a peak at $b = 0.43$. The temperature dependence ($T = 4.2$–300°K) of excitation migration along the Yb^{3+} ions in the $(Y_{0.46}Yb_{0.54})_3Al_5O_{12}$ + 0.06 at.% Eu system is investigated experimentally. The correlation predicted between the migration probability and nonuniformity factor b for spectral line broadening is observed. Satisfactory quantitative agreement between the experimental and theoretical dependence is obtained in the high temperature range ($T > 130$°K) in which the diffusion approach for describing migration is valid.

Interactions between impurity ions in crystals provide an additional channel for the relaxation of the excited state of the activator, and by the same token influence the kinetics of the decay of an excited level. The large amount of theoretical material that has now been accumulated and the use of modern techniques of physical experiment make it possible to form a qualitative, and in some cases also a quantitative, picture of the processes that occur in an activated crystal when it is excited.

The results of many theoretical papers[1-3] point to a strong connection between the probability of the elementary excitation and the character and magnitude of the broadening of the spectral lines. It makes sense to search for a manifestation of this connection in the temperature dependences of the probability of deactivation of the electron excitation and of the broadening of the spectral lines of the interacting ions. There are at present no published experimental data on such a correlation, although many papers have been devoted to investigation of the temperature dependences of the electron-excitation deactivation probability[4-8]. These papers did not deal with the influence of various types of spectral-line broadenings on the general picture of deactivation of the excited states of impurity ions. The present paper is devoted to an analysis of the influence of broadenings in a system in which the deactivation of the excited state is due to migration of a large number of identical ions (donors) towards a certain quencher (acceptor).

We chose for the investigations a mixed yttrium-ytterbium garnet crystal. The Yb^{3+} ions are convenient because interactions between them (donor-donor) cannot cause loss of the excitation, but merely displace it in space. In addition, the large Stark splittings of the ground and excited levels of the Yb^{3+} ion in the garnet allows us to exclude the influence of the underpopulation of the excited Stark components on the temperature dependence of the probability of the migration over the Yb^{3+} ions.

INVESTIGATED CRYSTALS AND EXPERIMENTAL PROCEDURE

Crystals of $Y_3Al_5O_{12}$ + 0.07 at.% Yb and $(Y_{0.46}Y_{0.54})_3Al_5O_{12}$ + 0.06 at% Eu were grown from the melt by the Czochralski method.

The absorption and luminescence spectra of the Yb^{3+} ions in the crystals (transition $^2F_{5/2} - {}^2F_{7/2}$) were registered with a DFS-12 spectrometer with resolution no worse than 0.15 cm^{-1}. A unified thermostating system of the UTREKS type, which made it possible to vary the temperature of the sample smoothly in the wide temperature range from 4.2 to 300°K and to stabilize it with accuracy 0.1°, was used to investigate the samples in that range.

Pulsed excitation of the luminescence of the Yb^{3+} ions in the crystals was by means of radiation from an organic-dye-solution laser pumped by a Q-switched ruby laser. The dye laser generated a 10^5-W light pulse at the wavelength $\lambda = 9400$ Å, which is in good correspondence with the transition between the lower Stark sublevel of the ground state $^2F_{7/2}$ and the second Stark component of the excited state $^2F_{5/2}$ of the Yb^{3+} ion.

The generated-pulse duration was 50 nsec. The individual luminescence lines of the $^2F_{5/2} - {}^2F_{7/2}$ transition were separated by an MDR-2 monochromator. The temporal decrease of the luminescence of the Yb^{3+} ions was registered with an FÉU-62 photomultiplier followed by photography from the screen of a Tr4401 oscilloscope. Time resolution of the recording apparatus was no worse than 1 μsec. The thickness of the $(Y_{0.46}Yb_{0.54})_3Al_5O_{12}$ + 0.06 at.% Eu crystal was chosen such that the damping time was not affected by reabsorption of the radiation, and amounted to h = 0.3 mm. The use of a Tr4401 oscilloscope, which has good sweep linearity and good accuracy of the vertical-deflection amplifier, made it possible for us to determine the damping times with accuracy no worse than 5%.

THEORETICAL ANALYSIS

The most widely used approach for the description of the decay of donor excitation as a consequence of energy migration to the acceptors is the use of the diffusion equation. In the absence of direct quenching interaction between the excited donors and the acceptors, the diffusion equation takes the form[9-11]

$$\partial\Psi(r,t)/\partial t=-A\Psi(r,t)+D\Delta\Psi(r,t), \quad (1)$$

where $\Psi(r, t)$ is the density of the donor excitations, A is the probability of radiative decay of the donors, and D is the diffusion coefficient.

The solution of this equation with allowance for the boundary condition $\Psi(r, t)|_a = 0$ leads to a donor-excitation decay kinetics in the form

$$n_D(t)=n_D(0)\exp[-(A+W_M)t-W_M a(t/\pi D)^{1/2}]. \quad (2)$$

The first term in the argument of the exponential in (2) is responsible for the exponential kinetics of the emission of the donors, and corresponds to a stationary solution of the diffusion equation

$$W_M=4\pi n_A Da, \quad (3)$$

where W_M is the migration probability, n_A is the acceptor concentration, and a is the characterized scattering length of the excitation. The second term corresponds to the nonstationary solution of the diffusion equation and leads to nonexponential behavior of the initial section of the donor damping. This nonexponential behavior is usually manifest only in the case of small diffusion coefficients[11,12]. Let us estimate the conditions under which the nonstationarity can be neglected.

The general form of the donor-damping kinetics (2) can be rewritten as

$$n_D(t)=n_D(0)\exp\{-(A+W_M)t-S[(A+W_M)t]^{1/2}\}, \quad (4)$$

$$S=4a^2 n_A[D\pi/(A+W_M)]^{1/2}. \quad (5)$$

From the data of[10] we see that at $S \leq 0.2$ the contribution of the nonexponential behavior to the damping kinetics is negligibly small. Using expressions (3) and (5), we can represent the parameter S in the form

$$S=2[a^3 n_A W_M/(A+W_M)]^{1/2}. \quad (5')$$

In this case the condition that the donor-state decay be exponential takes the form

$$R_A \geqslant 5a,$$

where $R_A = n_A^{-1/3}$ is the mean distance between the acceptors. The kinetics of the decay is then given by

$$n_D(t)=n_D(0)\exp[-(A+W_M)t].$$

The most important parameter that determines the migration probability W_M and the mechanism of the deactivation process is the diffusion coefficient D.

For the case of donors that form a regular lattice, the diffusion coefficient can be written as

$$D=\sum_{i=1}^{n} P_i n_i r_i^2; \quad (6)$$

here n_i is the number of donor ions in the i-th coordination sphere around the excited donor, r_i is the radius of the i-th coordination sphere, and P_i is the probability of interaction between the pair of donors at the distance r_i. The quantities n_i and r_i for the garnet lattice can be found in[13].

The relative contribution made to the diffusion coefficient by the interaction with the i-th sphere is given by

$$d_i=D_i/D=P_i n_i r_i^2 \Big/ \sum_{i=1}^{n} P_i n_i r_i^2.$$

The table lists the values of n_i, r_i, and d_i for the coordination spheres of the garnet lattice. In the calculation of d_i, the summation in the denominator was limited to n = 22, and it was also assumed that $P_i \propto r^{-6}$, corresponding to a dipole-dipole interaction between the donors. It is seen from the table that the main contribution to the diffusion coefficient is made by the first sphere. In the case when the diffusion of the excitation is due to interactions of higher multipolarity, say dipole-quadrupole (r^{-8}) or quadrupole-quadrupole (r^{-10}) interactions, the contribution of the first sphere to the diffusion coefficient is even more appreciable. In this case the diffusion can be regarded in the short-range approximation, i.e., at a strictly fixed distance $r_1 = 3.7$ Å.

The second important parameter in expression (3) for the migration probability is the characteristic excitation scattering length a. This parameter can be introduced in two ways, depending on the experimentally realized quenching of the donor excitation by the acceptor. If the donor-acceptor interaction parameter ($C_{DA} = P_{DA}r^6$) is much larger than the donor-donor interaction parameter ($C_{DD} = P_i r^6$), the loss of the excitation occurs in a certain sphere whose radius a depends on the diffusion coefficient[9]

$$a=0.68(C_{DA}/D)^{1/4}.$$

Not all the donor excitations are lost as a result of migration over like ions to the quenchers. A definite fraction of the excitations is lost as a result of direct interaction with the acceptors, so that the exponential kinetics of the excited-state decay, for which the migration is responsible, is preceded by a nonexponential Forster decay due to direct donor-acceptor interactions at various distances[4,5,14-16].

Another case can be encountered in the presence of dependences of the donor-donor and donor-acceptor interactions on the distance. If the quenching probability from the second sphere surrounding the acceptor is smaller than the probability of entry into the first sphere by diffusion and quenching in this sphere, then the following short-range approximation is satisfied for the quenching act[9-11]:

$$a=\text{const}=r_0,$$

where r_0 is the distance to the donor closest to the acceptor. In this case the quenching can proceed only via migration of the excitation over the donor subsystem, and the kinetics of the decay of the donor excitations takes an exponential form.

i	n_i	r_i/r_1	d_i, %	i	n_i	r_i/r_1	d_i, %
1	4	1	45.6	12	16	3.0	2.3
2	8	1.53	16.6	13	16	3.22	1.7
3	2	1.63	3.4	14	6	3.28	0.6
4	8	1.82	8.4	15	8	3.44	0.7
5	4	1.92	3.5	16	8	3.61	0.5
6	8	2.24	3.6	17	8	3.65	0.5
7	4	2.31	1.6	18	16	3.74	0.9
8	12	2.52	3.3	19	20	3.78	1.0
9	8	2.77	1.5	20	16	3.96	0.7
10	8	2.83	1.4	21	8	4.0	0.4
11	8	2.9	1.3	22	8	4.12	0.3

For the two cases considered above, the connection between the migration probability and the diffusion coefficient is different. In the first case (a depends on the diffusion coefficient) we have

$$W_{\text{м}}=8.5n_AC_{DA}^{1/4}D^{3/4},$$

and in the second (a is constant)

$$W_{\text{м}}=4\pi n_A r_0 D.$$

Analyzing the temperature dependences of the migration probability, we can obtain the information of interest to us concerning the mechanism of the interaction between the donors. This interaction usually has a resonant character with participation of various Stark sublevels of the ground and excited states[4,5,7]. In addition, in[6,17,18] there is assumed a possibility of nonresonant donor-donor interaction with participation of an excited Stark sublevel of the ground state and with release of the excess energy in the form of a phonon.

The influence of the temperature on the interaction between the donors can manifest itself in two ways. First, a change in temperature can lead to a change in the electron-vibrational interaction, i.e., to a change in the relaxation level width of the transitions that participate in the interaction; second, a temperature-induced underpopulation of the excited Stark sublevels can be observed and can lead to a temperature dependence when the oscillator strengths and transition line widths differ.

In many published experimental papers the temperature dependences of the migration probability are attributed to the appearance of new interacting transitions of resonant[4,5] or nonresonant[6,17,18] character. In either case, the temperature dependence of the resonant interaction as a result of the broadening of the spectral lines is neglected without justification. In the analysis that follows we shall be interested in precisely this dependence. Its existence was first pointed out by Dexter in his basic paper on the transfer of electron-excitation energy[1].

The expression for the probability of multipole interaction between a pair of identical ions with homogeneous width δ and with resonance detuning ϵ_i due to the difference between the local electric fields in the crystal, takes the following form[2]:

$$P_i=K_i\frac{2\delta}{4\delta^2+\varepsilon_i^2}. \tag{7}$$

Here K_i is a coefficient that does not depend on the temperature and includes the oscillator strengths of the transitions and the dependence on the distance. Substituting (7) in (6), we obtain for the diffusion coefficient

$$D=\sum_{i=1}^{n}K_i\frac{2\delta}{4\delta^2+\varepsilon_i^2}n_ir_i^2. \tag{8}$$

In this case we do not consider the degree of multipolarity of the interaction between the donors, inasmuch as the interaction probability is proportional to the overlap integral in any order of multipolarity. It is seen from (8) that if the homogeneous broadening exceeds the inhomogeneous broadening, i.e., $\delta > \epsilon_i$, then the overlap integral is

$$I=2\delta/(4\delta^2+\varepsilon_i^2)=1/2\delta$$

and does not change from one pair of interacting donors to another. Taking this integral outside the summation sign, we obtain for the diffusion coefficient and for the migration probability

$$D=\frac{1}{2\delta}\sum_{i=1}^{n}K_in_ir_i^2, \tag{9}$$

$$W_{\text{м}}=4\pi n_A a\frac{1}{2\delta}\sum_{i=1}^{n}K_in_ir_i^2. \tag{10}$$

It is seen from (10) that for homogeneously broadened donor lines, an increase of the line width leads to an appreciable decrease of the migration probability.

The diffusion approach developed above describes well the process of excitation migration over a donor subsystem only if the homogeneous broadening of the donor lines exceeds the inhomogeneous broadening due to the presence of defects and stresses in the crystal. It is precisely in this case that the entire excitation-migration process is described by a single diffusion coefficient which is the same over the entire crystal. But if the inhomogeneous broadening of the lines exceeds the homogeneous broadening, i.e., $\epsilon_i > \delta$, then D depends significantly on the set of detunings ϵ_i of the pairs of interacting donors.

Indeed, as is seen from the table, the value of D is determined mainly by the interaction with a limited number of ions (4 to 12). Recognizing also that the detunings ϵ_i have a Gaussian distribution with a half-width Δ (the inhomogeneous width of the transition line), we can easily see from (8) that when the homogeneous width is decreased, $\delta < \Delta$, the value of D can decrease and does not remain constant over the entire crystal. This indicates that when the excitation moves over the donor subsystem its velocity is not constant (described by a single diffusion coefficient), but is modulated as a function of the ratio of the homogeneous and inhomogeneous broadenings. The migration probability then has a complicated dependence on the spectral broadening of the donor line. To determine the qualitative form of this dependence, let us consider a simplified case wherein the excitation migrates over a linear chain of donors and is subsequently quenched by an acceptor.

We assume that each donor of the chain interacts only with its two neighbors, which are located at a distance r_0 (the short-range approximation). We are interested in an expression for the probability of deactivation of an excitation that is initially at the m-th donor. We start our analysis with the chain donor closest to the acceptor. The solution for the probability of deactivation of donor excitation as a result of resonant1) interaction with the acceptor was derived in[19], namely

$$w_D=P_{DA}\omega/(P_{DA}+\omega), \tag{11}$$

where P_{DA} is the probability of donor-acceptor interaction and ω is the probability of deactivation in the acceptor.

From (11) we obtain for the two limiting cases

$$w_D=P_{DA}\ \text{at}\ \omega\gg P_{DA},$$
$$w_D=\omega\ \text{at}\ P_{DA}\gg\omega.$$

These limiting cases conform to the considerations used in the "bottleneck" model, since it is the slowest process, the one that limits the deactivation rate, which always becomes manifest in the kinetics of the donor-excitation decay (w_D). We generalize expression (11) to the case of a chain. Then w_{D_1} [Eq. (11)] is the probability of deactivation of the excitation from the donor closest to the acceptor. Assuming that the role of the acceptor for the next donor D_2 is assumed by the first donor D_1 (with the deactivation probability w_{D_1}), we obtain for the probability of deactivation from the second donor

$$w_{D_2}{}^{-1}=P_1{}^{-1}+w_{D_1}{}^{-1}=P_1{}^{-1}+P_{DA}{}^{-1}+\omega^{-1}. \tag{12}$$

Here P_1 is the probability of the interaction between the donors. Analogously, for the probability of deactivation of the excitation of the m-th donor via migration over the chain to the acceptor, we obtain

$$w_{D_m}^{-1}=\sum_i P_i{}^{-1}m_i+P_{DA}^{-1}+\omega^{-1}. \tag{13}$$

To take into account the radiative channel for the decay of the excited donor state it is necessary to add to the deactivation probability (13) the probability A of spontaneous donor emission.

The first term in (13) has the meaning of the time of excitation migration or the reciprocal probability of migration over a chain of m donors:

$$w_m^{-1}=\tau_m=\sum_i P_i{}^{-1}m_i, \tag{14}$$

where m_i is the number of migration acts with probability P_i. It is seen from (13) that in the case when the donor-acceptor interaction probability P_{DA} and the probability ω of nonradiative transitions in the activator are much larger than the migration probability w_m, then the probability of deactivation of the donor excitation is determined by the slowest process, i.e., by the migration over the chain of donors:

$$w_{D_m}=w_m=\Big(\sum_i P_i{}^{-1}m_i\Big)^{-1}. \tag{15}$$

For the case of identical probabilities of the interaction between different donors of the chain, $P_1 = P_2 = P_m = P$, we have

$$w_{D_m}=\Big(P^{-1}\sum_i m_i\Big)^{-1}=P/m, \tag{16}$$

which agrees with the result obtained in[20] for the diffusion mechanism of excitation transfer from the donor to the acceptor. In the most general case, the probability of interaction P_i between donors is different for different donor pairs, and, as seen from expression (7), is determined only by the relation between the homogeneous width δ and the detuning from resonance ϵ_i. Let us substitute (7) in (15), assume that the distribution of m_i over the detunings ϵ_i is Gaussian, and replace the sum for large m by an integral. As a result we obtain for the migration probability

$$\frac{1}{w_m}=\frac{1}{K}\left[2\delta m+\frac{m}{2\delta}\left(\frac{\ln 2}{\pi}\right)^{1/2}\frac{1}{\Delta}\int_{-\infty}^{\infty}\varepsilon_i{}^2\exp\left\{-\frac{\varepsilon_i{}^2\ln 2}{\Delta^2}\right\}d\varepsilon_i\right]. \tag{17}$$

Here m is the number of donors in the chain and Δ is the half-width of the inhomogeneously broadened line.

The final connection between the migration probability and the inhomogeneity parameter $b = \delta/\Delta$ turns out to be

$$w_m=\frac{K}{2m\Delta}\frac{b}{b^2+0.181}. \tag{18}$$

A plot of $w_m(b)$ is shown in Fig. 1. We see that the maximum of the migration probability corresponds to $b = 0.43$, i.e., $\delta = 0.43\Delta$. With increasing homogeneous width, at values close to the inhomogeneous width ($\delta > \Delta$), the migration probability decreases like $w_m \propto 1/b$, in full agreement with the previously obtained expression (10). When the homogeneous width becomes smaller than the inhomogeneous width, the migration probability also decreases, since $w_T \propto b$. Relations similar to that considered above were previously obtained in[2,3,21] for models in which direct donor-acceptor interactions were responsible for the deactivation of the donor excitation. In these papers it is likewise indicated that the efficiency of excitation transfer is maximal in the case when the homogeneous widths are of the same order as the inhomogeneous ones.

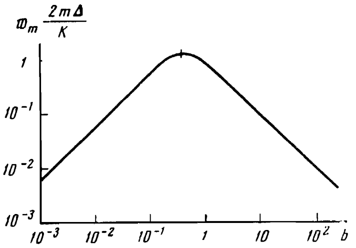

FIG. 1. Dependence of the migration probability on the inhomogeneity parameter $b = \delta/\Delta$ in the linear-chain model.

It is interesting to note another limiting case that follows from expression (13) at very high migration probability $w_m \gg P\omega_{DA}$, ω (super-migration). In this case the probability of deactivation of the donor excitation is also determined by the slowest process limiting the rate at which the excitation is taken out of the system:

$$w_{D_m}=P_{DA}\omega/(P_{DA}+\omega). \tag{19}$$

Equation (13) can probably be used also in the case of spatial migration, taking the migration time to be the average time of spatial migration of the excitation to the acceptor. In other words, by increasing the migration probability in the experiment, it is possible to observe finite donor-acceptor interaction acts or finite probabilities of deactivation (radiative or nonradiative) in the acceptors.

RESULTS OF EXPERIMENTS AND DISCUSSION

The scheme for the crystal splitting of the energy levels of the Yb^{3+} ions in a garnet lattice, as given in[22,23], is shown in Fig. 2. Our measurements of the absorption and luminescence spectra have confirmed this level scheme and the weak dependence of the Stark splitting on the concentration of the Yb^{3+} ions. It is seen from Fig. 2 that the only possible interaction between the Yb^{3+} ions at low temperatures is resonant interaction via the transition 1—5.

We have investigated the temperature dependences (T = 4.2 to 300°K) of the absorption and luminescence of this transition in the crystal $Y_3Al_5O_{12}$ + 0.07 at.% Yb. Measurement of the integral cross section of this transition has shown it to be independent of the temperature. At T < 77°K, the line is inhomogeneously broadened and has a Gaussian shape. In the region T = 77—140°K the line broadens and its shape is well described by a convolution of a Lorentz function with a Gauss function (the Voigt contour)[24]. At temperatures above 140°K, the homogeneous width greatly exceeds the inhomogeneous width and the spectrum becomes Lorentzian.

The dependence of the half-width Δ^* of the investigated line on the temperature is shown in Fig. 3. The data of[24] make it possible, knowing the temperature-independent inhomogeneous broadening Δ, to separate

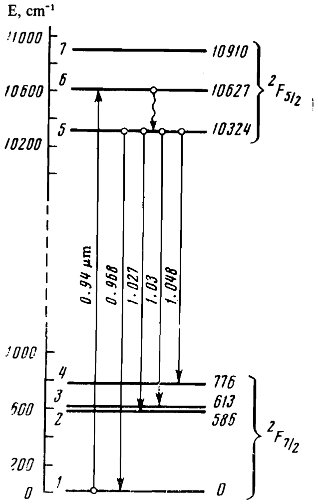

FIG. 2

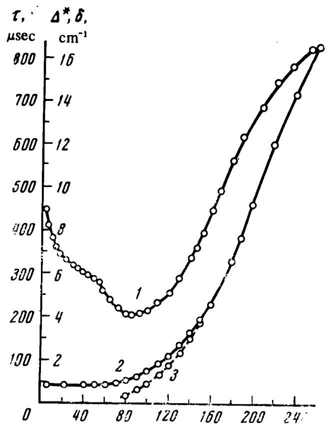

FIG. 3

FIG. 2. Scheme of crystal splitting of the levels $^2F_{7/2}$ and $^2F_{5/2}$ of the Yb^{3+} ion in a garnet.

FIG. 3. 1) Temperature dependence of the lifetime τ of the excited state of Yb^{3+} ions in a $(Y_{0.46}Yb_{0.54})_3Al_5O_{12}$ + 0.006 at. % Eu crystal; 2) dependence of the half-width Δ^* of the line of the 1-5 transition on the temperature for the crystal $Y_3Al_5O_{12}$ + 0.07 at. % Yb; 3) temperature dependence of the half-width δ of the homogeneous component of the same line.

from the complex Voigt contour the homogeneous component of the broadening δ, which is a function of temperature. The result of this reduction is also shown in Fig. 3 in the form of the function $\delta(T)$ (curve 3). This curve is described with accuracy better than 10% via the relation $\delta \propto (e^{\Delta E/kT} - 1)^{-1}$, which is typical of single-phonon relaxation processes with absorption of a phonon of energy $\Delta E = 303\ cm^{-1}$, which is equal to the energy gap between the levels 5 and 6 (Fig. 2).

We measured the radiative lifetime of the metastable state $^2F_{5/2}$ of the Yb^{3+} ions in the same $Y_3Al_5O_{12}$ + 0.07 at.% Yb crystal, and found it to be $\tau_0 = 1/A$ = 1.17 msec and independent of the temperature in the range of interest to us. The investigation of the influence of the temperature on the electron-excitation migration probability in a $(Y_{0.46}Yb_{0.54})_3Al_5O_{12}$ + 0.06 at.% Eu crystal was based on the analysis of the form and temperature dependence of the damping kinetics of the emission of the Yb^{3+} ions. The time dependence of the emission damping of this crystal was strictly exponential in the entire range from 4.2 to 300°K.

Figure 3 shows the temperature dependence of the damping time τ. An examination of this dependence shows that the maximum quenching of Yb^{3+} luminescence is observed at T = 90°K. When the temperature is raised to 300°K, an appreciable increase of τ is observed, indicating an appreciable weakening of the quenching. Lowering the temperature to that of liquid helium also leads to a weakening of the luminescence quenching. A comparison of plots 1 and 3 reveals that the maximum quenching is observed near the temperature at which the homogeneous broadening of the spectral line of the 1—5 transition becomes comparable with the inhomogeneous broadening.

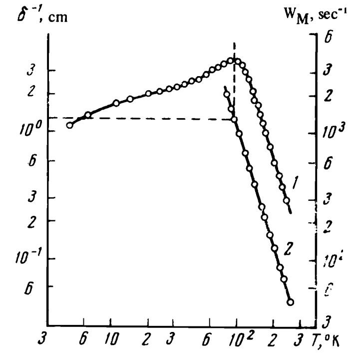

FIG. 4. 1) Temperature dependence of the migration probability W_M; 2) temperature dependence of the reciprocal of the homogeneous line half-width.

Figure 4 shows the temperature dependence of the probability W_M of excitation migration over the Yb^{3+} ions, calculated from the formula

$$W_M = 1/\tau - 1/\tau_0. \qquad (20)$$

As seen from the figure, the migration probability has a clearly pronounced maximum at T = 90°K. The same figure shows for comparison a plot of $\delta^{-}(T)$. The horizontal line marks the value of $(0.43\Delta)^{-1}$. The inhomogeneous width Δ for this crystal was estimated by using the known width for yttrium-aluminum garnet and the data of[25]. It was found to be $\Delta = 2\ cm^{-1}$. A comparison of curves 1 and 2 of Fig. 4 shows that the migration probability has a maximum at the temperature at which $\delta = 0.43\Delta$, in agreement with the result of the theoretical analysis (Fig. 1 and formula (18)).

In the crystal $(Y_{0.46}Yb_{0.54})_3Al_5O_{12}$ + 0.06 at.% Eu the concentration of the donors (of the Yb^{3+} ions) is at least three orders of magnitude larger than the concentration of the acceptors (Eu^{3+} ions and impurities that cannot be controlled). This circumstance and the presence of fixed distances between the Yb^{3+} ions make it possible to use, at temperatures when $\delta > \Delta$, the diffusion approach for the description of excitation migration over the donors. The exponential character of the donor decay indicates that the quenching can occur only via migration over the donor subsystem to the acceptors, and that the diffusion has a stationary character (2).

As indicated above, the use of the diffusion equation in the usual form is valid only at $\delta > \Delta$, i.e., in our case at T > 130°K. The connection between the migration probability and the homogeneous width, when this condition is satisfied, is given by expression (10). From a comparison of the slopes of curves 1 and 2 (Fig. 4) in the region T > 130°K we see that the migration probability is inversely proportional to the homogeneous line width of the resonant transition 1—5. This experimental result is in full agreement with the theoretical result (10) for the case of a constant excitation scattering length a, when the migration probability is proportional to the first power of the diffusion coefficient.

Thus, the universally accepted diffusion approach describes only a part of the experimentally observed temperature dependence. Its application to the low-temperature region T < 130°K leads to results that differ qualitatively from experiment. The simple model of energy migration over a linear chain that we proposed above leads (in the high-temperature region) to results that agree with those obtained from the diffusion theory, and, in addition, makes it possible to explain the dependence of the migration probability in the region where ordinary diffusion theory is not valid (T < 130°K). Indeed, as already indicated above, the main contribution to the migration probability is made by a small number of ions situated in the first and second coordination spheres (see the table). As a result, a decrease of the homogeneous width $\delta < \Delta$ decreases the number of possible resonances, and by the same token also the probability of interaction with this nearest surrounding, which in turn is manifest in a decrease of the migration probability W_M.

Owing to the lack of exact data on the homogeneous broadening at $T < 80°K$, a comparison of experiment with theory in this region was carried out only qualitatively. However, from EPR investigations[26] it is known that on going from nitrogen to helium temperatures the homogeneous width decreases by approximately two or three orders of magnitude. It is seen from Fig. 1 that in our model this should lead to a weakening of the migration probability by approximately the same amount. In fact, the decrease of the migration probability is much less pronounced (see Fig. 4). This difference is the result of the fact that the linear-chain approximation is not quite exact for description of the experimental situation that obtains in the $(Y_{0.46}Yb_{0.54})_3Al_5O_{12}$ crystal. Thus, the presence of not one but several neighbors in the nearest surroundings leads to a weakening of the $W_M(\delta/\Delta)$ dependence because the probability of finding a closer resonance among them is higher. In addition, allowance for the contribution to the migration probability from interactions with remote spheres can also lead to a certain weakening of the dependence of the migration probability on the inhomogeneity parameter.

Thus, the use of the diffusion approach and of the simplified description in the linear-chain model enables us to understand the qualitative picture of the influence of the varying nature and magnitude of spectral-line broadening on the probability of migration over like ions (and even the quantitative picture at high temperatures ($T > 130°K$)), and to interpret the temperature dependence of the migration probability in the entire investigated temperature range.

A donor-lifetime temperature dependence similar to ours (Fig. 3) and having a clearly pronounced minimum at $T = 60°K$ was observed earlier[6] in an investigation of excitation migration over Er^{3+} ions in garnet. It was treated by using the diffusion equation for the change in the migration probability in the low-temperature region $T < 60°K$. In the cited paper, as we have already indicated, no account was taken of the magnitude and character of the broadenings of the spectral lines, and the increased quenching on going from 4.2 to 60°K was explained by resorting to a nonresonant migration mechanism with participation of an excited Stark component of the ground state and with emission of a phonon at the difference frequency. On the other hand, the decrease of the quenching with increasing temperature above 80°K, which is frequently observed in experiment, was not explained in the literature at all.

Our experimental results and their good agreement with the theoretical calculations make it possible to treat unambiguously the mechanism of interaction between the Yb^{3+} ions, which leads to migration of the excitation, as a pure resonance mechanism with participation of only the transition 1—5.

Thus, we have observed experimentally a connection between the efficiency of the interaction and the broadening of the spectral line of the transition that takes part in the interaction.

We chose a criterion for the applicability of the usual diffusion approach and showed that in the temperature region where it is satisfied, the migration probability is directly proportional to the diffusion coefficient D and inversely proportional to the homogeneous line width δ of the resonant transition, i.e., it is connected with the homogeneous broadening in exactly the same manner as the probability of the elementary resonant excitation for the case of two ions.

In addition, we have proposed a simple model that gives calculated results in good agreement with those obtained from the diffusion theory (where the latter is applicable) and explains qualitatively the experimental results at $\delta \leq \Delta$, where the diffusion theory is not valid.

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[1)] In the case of nonresonant interaction between the donor and acceptor, with large detuning $\Delta E \gg kT$, the inverse transfer from the acceptor to the donor becomes impossible. Then the entire analysis becomes identical with that given in the paper (formulas (11)–(19), in which we put $\omega = \infty$).

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