NONRESONANCE EXCITATION ENERGY TRANSFER BETWEEN IMPURITY RARE-EARTH IONS

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Transfer of energy between Er^{3+} and Tu^{3+} or Er^{3+} and Ho^{3+} ions in $Y_3Al_5O_{12}$ crystals, and concentration quenching of luminescence of Nd^{3+} ions in $Y_3Al_5O_{12}$, $Y_3Ga_5O_{12}$, and LaF_3 crystals are studied at temperatures between 2 and 300°K. The weakening of quenching or transfer observed in the investigated systems at helium temperatures is attributed to the decreased efficiency of excitation-energy migration along donor ions to the quenching centers or acceptor ions. It is shown that the mean migration probability $(\overline{W}_M)$ at temperatures between 2 and 77°K depends on the population of the first excited level of the donor ion ground state, $\overline{W}_M \propto e^{-\Delta/2kT}$ where Δ is the distance to this level. In the indicated temperature range, the decisive role in migration processes is played by nonresonance interactions between donor ions. The mean lifetime of the donor ions is calculated by taking into account the excitation-energy migration. The theoretical temperature dependence of the lifetime is the same as the experimental one. Experiments on monochromatic excitation of glasses containing Yb^{3+} were performed at low temperatures and confirmed the dependence of the nonresonance transfer on the phonon frequency.

NONRADIATIVE energy-transfer processes play an important role in the effective laser materials containing several alloying impurities. These processes lead also to concentration quenching of the luminescence. The already developed theory of non-radiative energy transfer[1] pertains to the case of resonance of the ion-donor and ion-acceptor transitions, when there is at least partial overlap of the donor luminescence lines and of the acceptor absorption lines. Experiments, however, have revealed cases of effective nonradiative energy transfer between ions even when there was no overlap of the donor and acceptor transitions (see, for example,[2]). Apparently these processes occur with phonons taking part. It is of considerable interest to investigate experimentally the characteristic features of nonresonant transfer: its efficiency, its dependence on the frequency of the phonons that take part in the transfer process, etc.

It is shown in the present paper that at low temperatures, when the lines in the spectra of the rare-earth ions in the crystals are inhomogeneously broadened, the resonant transfer processes are ineffective. At low temperatures, the principal role in the transfer between rare-earth ions is played by nonresonant processes in which phonons take part. The investigation of these processes reported in the present paper has made it possible to establish the connection between the nonresonant transfer probability and the frequency of the phonon that takes part in the process. We investigated the temperature dependence of the excitation energy transfer between Er^{3+} and Tu^{3+} ions and between Er^{3+} and Ho^{3+} ions in yttrium-aluminum garnet crystals (YAG) and the concentration quenching of the luminescence of Nd^{3+} ions in crystals of YAG, yttrium-gallium garnet (YGG), and LaF_3. We have shown earlier[3] that on going from nitrogen to helium temperatures the interactions between the rare-earth ions in the crystals becomes greatly weakened, leading to a deterioration of the excitation-energy transfer of

the acceptor to the ions or to a decrease of the concentration quenching. Such a weakening was attributed in[3] to the temperature dependence of the processes of migration of the excitation energy along the donor ions to the acceptor ions or to the quenching centers. In the present paper we report a more detailed investigation of the temperature dependences of the transfer in a large number of objects and in a wider temperature interval (2–300°K).

INVESTIGATION PROCEDURE

To obtain information concerning the energy transfer in the systems YAG: Er^{3+}, Tu^{3+} and YAG: Er^{3+}, Ho^{3+}, we measured the lifetime τ of the Er^{3+} ions at the $^4I_{13/2}$ level in a series of crystals having a constant content[1] of Er^{3+} (1%) and a variable concentration of Tu^{3+} or Ho^{3+}. In the study of the concentration quenching we measured the lifetimes of the Er^{3+} ions at the $^4I_{13/2}$ level and of Nd^{3+} at the $^4F_{3/2}$ level in a number of crystals with variable concentrations of Er^{3+} and Nd^{3+}.

The luminescence lifetime τ was measured at both fixed temperatures (4.2, 77, and 300°K) and with continuous variation of the temperature from 2 to 300°K. To this end, the crystals were placed in a massive copper block with apertures for excitation and observation. The block was cooled with liquid-nitrogen or liquid-helium vapor. The temperature in the 4.2−60°K range was monitored with a carbon resistance and in the 60−300°K with a copper-constantan thermocouple. In the former case the resistance was recorded by a null method, the working current through the resistance not exceeding 30 μA. The accuracy with which the sample temperature was measured by the carbon resistance was 0.5°. Cooling to a temperature below

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1) The impurity concentrations are indicated in at. % throughout.

$4.2°$K was by pumping off the helium. The temperature was monitored against the liquid-helium vapor pressure.

The luminescence was excited by an ISSh-100 flash lamp with a flash duration ~ 15 μsec. The luminescence signals of the Er^{3+}, Tu^{3+}, and Ho^{3+} ions were separated by an IKS-12 prism monochromator, with a PbS photoresistor placed behind the output slit of the monochromator. In the investigation of crystals activated with Nd^{3+}, the luminescence light was focused on the slit of a grating monochromator with dispersion 40 Å/mm, and was recorded with an FÉU-28 photoreceiver. The signal from the photomultiplier or photoresistor was fed to the input of an S1-19B oscilloscope.

The lifetime τ of the luminescence was measured for crystals ~ 1 mm thick. The lifetime measurement accuracy was 10%.

To obtain information concerning the relative positions of the levels of the ions Er^{3+}, Tu^{3+}, and Ho^{3+} in the YAG crystals, we investigated the absorption and luminescence spectra of singly-activated crystals in the $1.4-2.2$ μ region. The published data concerning these spectra[4-6] are incomplete; in particular, data are missing on the luminescence spectrum of Er^{3+} in YAG crystals in the 1.6 μ region. The absorption and luminescence spectra were investigated with the aid of a MDR-2 diffraction monochromator with a grating of 300 lines/mm and dispersion 80 Å/mm. The spectra were recorded with a resolution not worse than 2 cm^{-1}. It is difficult to investigate the absorption spectrum of Ho^{3+} in the 1.8 μ region (transition $^5I_8 \rightarrow {}^5I_7$) with the aid of the MDR-2 instrument, owing to the strong absorption of the atmosphere. The spectrum was therefore recorded with the aid of a double-beam prism spectrophotometer (SP-700) with a resolution not worse than 10 cm^{-1}.

In addition, we measured the width of the resonance absorption lines of the Nd^{3+} ions in various bases in the 0.87 μ region (transition $^4I_{9/2} \rightarrow {}^4F_{3/2}$). The measurements were made at 4.2 and 77°K with the aid of a DFS-12 diffraction spectrometer with dispersion 10 Å/mm and resolution ~ 0.2 cm^{-1}.

EXPERIMENTAL RESULTS

1. Energy Transfer from Er^{3+} to Tu^{3+} and Ho^{3+} in YAG Crystals

The investigation of YAG crystals with a single

activator (Er^{3+}, Tu^{3+}, or Ho^{3+}) has shown that the ions excited at high energy levels $(10,000-25,000$ $cm^{-1})$ experience rapid relaxation to the metastable levels $^4I_{13/2}(Er^{32})$, $^4H_4(Tu^{3+})$, and $^5I_7(Ho^{3+})$. Therefore the energy transfer takes place mainly between these levels.

Figure 1 shows the spectra of luminescence of Er^{3+} ions (transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$) and absorption of Tu^{3+} ions (transition $^3H_6 \rightarrow {}^3H_4$) and Ho^{3+} ions ($^5I_a \rightarrow {}^5I_7$) in YAG crystals at 77°K. We see that there is overlap of the spectra in the $Er^{3+} - Tu^{3+}$ pair, but not in the $Er^{3+} - Ho^{3+}$ pair. The energy of the lower level of the $^4I_{13/2}$ of the Er^{3+} terms in the YAG crystals was 6.549 cm^{-1}, and that of the upper level of the term $^4I_{15/2}$ was 572 cm^{-1}. Therefore the frequency of the shortest-wavelength line in the emission spectrum of Er^{3+} is 5.977 cm^{-1}. The highest level of the $^5I_7$ term of the Ho^{3+} ions in the YAG crystal has an energy ~ 5450 cm^{-1}. Thus, in order to effect the transfer of the excitation energy from the Er^{3+} ions to the Ho^{3+} ions it is necessary to emit phonons with frequency greater than 530 cm^{-1}.

Figure 2 shows the dependence of the luminescence lifetime of erbium in a series of crystals with constant content of Er^{3+} (1%) and variable concentration of Tu^{3+} $(0.2-1\%)$. The curves offer evidence of effective nonradiative energy transfer to the Tu^{3+} ions; this transfer depends strongly on the temperature. The transfer proceeds effectively at 77°K and weakly at 4.2°K. For the crystal activated with 1% Er^{3+} and 0.2% Tu^{3+}, we plotted the dependence of the lifetime τ of the Er^{3+} on the temperature T with continuous variation of the latter, as shown in Fig. 3. We see that $\tau(T)$ has a non-monotonic character. At temperatures $2-4.2$°K the lifetime does not change, and then it begins to shorten rapidly, and at 25°K it ceases to depend on the temperature. When the temperature increases from
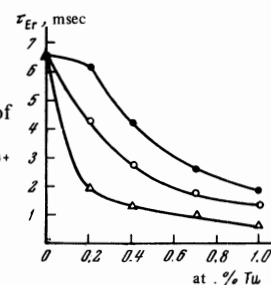
FIG. 2. Dependence of the lifetime of the luminescence from the $^4I_{13/2}$ level of the Er^{3+} ions in YAG crystals on the Tu^{3+} concentration at 300°K (O), 77° K (Δ), and 4.2° K (●).
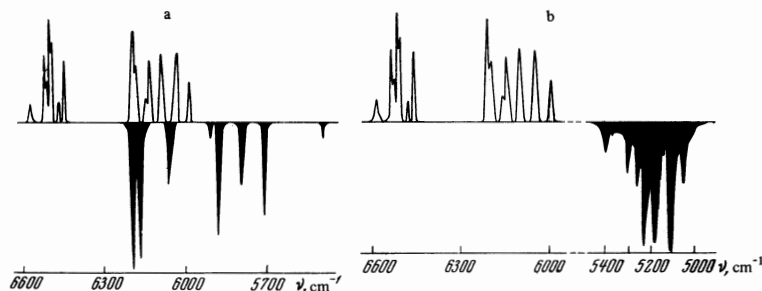
FIG. 1. Luminescence spectrum of Er^{3+} ions (top) and absorption spectrum of Tu^{3+} ions (a) and Ho^{3+} (b) in YAG crystals; T = 77° K.
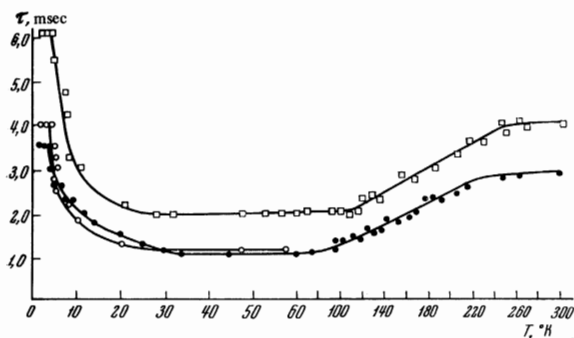
FIG. 3. Dependence of τ of Er^{3+} on the temperature in the temperature interval $2 - 300°K$ in YAG crystals activated with: $\square$ — 1% Er^{3+}, 0.2% Tu^{3+}; ● — 1% Er^{3+}, 0.5% Ho^{3+}; ○ — 20% Er^{3+}.

FIG. 4. Concentration dependence of the lifetime of the luminescence of Er^{3+} ions from the level $^4I_{13/2}$ in YAG crystals at 300°K (○), 77°K (Δ), and 4.2°K(●).
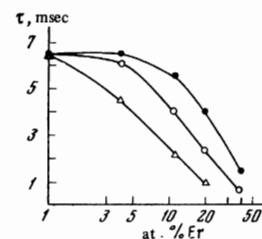

FIG. 5. Concentration dependence of the lifetime of the luminescence of Nd^{3+} ions from the $^4F_{3/2}$ in YAG crystals at 77°K (●) and 4.2°K (Δ).
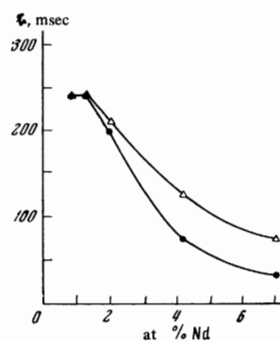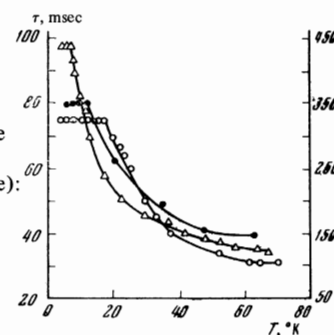

FIG. 6. Temperature dependence of τ in the following crystals : Δ — $LaF_3 : 8\% Nd^{3+}$ (right hand scale); ● — $Y_3Ga_5O_{12} : 6.6\% Nd^{3+}$; ○ — $Y_3Al_5O_{12} : 7\% Nd^{3+}$.

77 to 300°K (Fig. 3), a lengthening of the lifetime is observed, thus evidencing a deterioration of the energy transfer to the Tu^{3+} ions.

An equally effective transfer, strongly dependent on the temperature, was observed also in the case of Er^{3+} – Ho^{3+} (Fig. 3). A comparison of the $\tau(T)$ plots for both pairs (Fig. 3) shows them to be smaller. Thus, the change of the acceptor does not modify the temperature dependences of the energy transfer.

Moreover, the processes of concentration quenching of the luminescence of Er^{3+} from the level $^4I_{13/2}$ in YAG crystals have similar temperature dependences. Figure 4 shows the dependence of the lifetime on the erbium concentration at three temperatures. The quenching proceeds effectively at 77°K and weakly at 4.2°K. The $\tau(T)$ plot for the YAG crystal with 20% Er^{3+} is shown in Fig. 3. We see that for all the investigated systems the $\tau(T)$ plots are similar and are probably dependent by the interaction between the Er^{3+} ions in the YAG crystals.

2. Concentration Quenching of the Luminescence of Nd^{3+} Ions in YAG, YGG, and LaF_3 Crystals

The concentration quenching was investigated in a number of YAG crystals activated with 0.8, 1.2, 2.0, 4.2, and 7.0% Nd^{3+}. The dependence of the lifetime of the luminescence of Nd^{3+} ions from the $^4F_{3/2}$ level in these crystals on the concentration is shown in Fig. 5. We see that at low Nd^{3+} concentrations the lifetime does not depend on the temperature. However, starting with 2% concentration, the quenching weakens when the temperature drops from 77 to 4.2 °K. Thus, in the YAG crystal with 7% Nd^{3+}, the lifetime τ increases from 30 to 75 μsec on going over from nitrogen to helium temperature.

The concentration quenching of the luminescence of Nd^{3+} ions in YGG and LaF_3 crystals also weakens when the crystals are cooled to helium temperatures. The dependence of the lifetime on the temperature in the crystals YAG : 7% Nd^{3+}, YGG : 6.6% Nd^{3+}, and $LaF_3 : 8\%$ Nd^{3+} was investigated with continuous variation of the temperature from 4.2 to 77 °K (Fig. 6). The shortening of the luminescence lifetime of Nd^{3+} in these crystals begins at different temperatures: at 7°K in LaF_3, at 12°K in YGG, and at 16°K in YAG. The character of the curves (Fig. 6) is similar to the curves for crystals activated by Er^{3+} (see Fig. 3), but the start of the shortening of τ is shifted towards higher temperatures.

Thus, a weakening of the energy transfer or a concentration quenching of the luminescence takes place in all the investigated systems near helium temperatures.

DISCUSSION OF RESULTS

As shown in the preceding section, the temperature dependences of the energy transfer and of the concentration quenching of the luminescence in YAG crystals activated with Er^{3+}, $Er^{3+}-Tu^{3+}$, and $Er^{3+}-Ho^{3+}$ are all similar (see Fig. 3) and do not depend on the acceptor. Thus, the temperature variation of the transfer efficiency cannot be attributed to a change in the overlap of the spectra with changing temperature, since it has been shown that there is no such overlap in the case of the $Er^{3+}-Ho^{3+}$ pair.

The temperature dependences show that the increase of the energy transfer efficiency and the luminescence quenching as the temperature is increased from 2 to 77°K (Fig. 3) is connected with a temperature-dependent migration of the excitation energy along the Er^{3+} ions to the acceptor ions or to the quenching centers.

Since the experimentally observed luminescence atten-
uation curves of Er^{3+} in YAG crystals, in the case of
energy transfer and concentration quenching, were
singly-exponential, the average migration probability
($\overline{W}_M$) can be calculated from the relation

$$\frac{1}{\tau(T)} - \frac{1}{\tau_{exp}} = \frac{1}{\tau_M(T)} = \overline{W}_M(T) \qquad (1)$$

where $\tau(T)$ are the experimental dependences shown
in Fig. 3, and τ_{exp} is the lifetime measured at
$T \leq 4.2°K$ and does not depend on the temperature
(Fig. 3). The calculated probability $\overline{W}_M(T)$ is the
average migration probability of the excitation energy
over the Er^{3+} ions, with subsequent energy transfer
to the Tu^{3+} or Ho^{3+} ions.

The temperature dependence of the migration proba-
bility, obtained for systems with Er^{3+}, is shown in
Fig. 7. For three systems,

$$\overline{W}_M(T) \varpropto exp\left(-\Delta_1 / kT\right), \qquad (2)$$

where Δ_1 turned out to be equal to 12 cm^{-1} for the
$Er^{3+} - Tu^{3+}$ and $Er^{3+} - Ho^{3+}$ transfer and for the con-
centration quenching of the luminescence of Er^{3+}, cor-
responding to half the distance to the first excited
level of the ground state of the Er^{3+} ions in YAG
crystals (24 cm^{-1}).

In systems activated with Nd^{3+}, the temperature de-
pendences of $\tau(T)$ (Fig. 6) are caused also by migra-
tion over the Nd^{3+} ions towards the quenching centers
(apparently pairs of Nd^{3+} ions). The $\overline{W}_M(T)$ depend-
ence calculated from (1) turned out to be proportional
to $exp(-\Delta_1/kT)$, where Δ_1 corresponds approximately
to half the distance to the first excited state of the Nd^{3+}
ions in the indicated crystals. The calculated values of
Δ_1 for all the investigated systems and for the distance
to the first excited level of the term $^4I_{9/2}(Nd^{3+})$ and the
term $^4I_{15/2}(Er^{3+})$ are listed in the table. Thus, the im-
provement of the migration is directly connected with
the population of the first excited state in the investi-
gated systems.

At helium temperatures, the resonance lines of
transitions 3 − 1 (or 1 − 3), Fig. 8, of rare-earth ions
in crystals are inhomogeneously broadened. The widths
of these lines amount to[2] 1−5 cm^{-1}, and the homogene-
ous width, as shown by the EPR data, does not exceed
10^{-2} cm^{-1}. Therefore the efficiency of the process of
resonant transfer between the like ions remains small.
The nonresonant transfer (with emission of a phonon)
within the limits of the line width of the 3 − 1 transi-
tion, for low phonon frequencies (~ 1 cm^{-1}), is ineffec-
tive owing to the small density $\rho(\omega)$ of the phonon
states (in the Debye approximation, $\rho(\omega) \sim \omega^2 d\omega$,
where ω is the phonon frequency).

The probability W_{nt} of the elementary act of non-
resonant transfer between two impurity ions can be
written in the form

$$W_{nt} = (2\pi / \hbar)|M|^2\rho(\omega), \qquad (3)$$

FIG. 7. Temperature dependence
of W_M and YAG crystals activated
with 1% Er^{3+}, 0.2% Tu^{3+} (□), 1% Er^{3+},
0.5% Ho^{3+} (●), and 20% Er^{3+} (○).

System	Δ,cm^{-1}	Δ_1,cm^{-1}	Δ_1/Δ
$Y_3Al_5O_{12} : Er^{3+} : Tu^{3+}$	24 [4]	12±0.5	0.50
$Y_3Al_5O_{12} : Er^{3+} : Ho^{3+}$	24 [4]	12±0.5	0.50
$Y_3Al_5O_{12} : Er^{3+}$	24 [4]	12±0.5	0.50
$Y_3Al_5O_{12} : Nd^{3+}$	131 [7]	60±5.0	0.47
$Y_3Ga_5O_{12} : Nd^{3+}$	80 [8]	38±3.0	0.47
$LaF_3 : Nd^{3+}$	40 [9]	19±1.0	0.47
$SrMoO_4 : Nd^{3+}$	95	47±2.0	0.49
$NaLa(MoO_4)_2 : Nd^{3+}$	92 [10]	44±4.0	0.48

Here Δ is the distance to the first excited level of the ground state,
and Δ_1 is the experimentally obtained quantity.
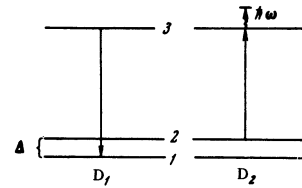
FIG. 8.

where M is the matrix element of the operator of
nonresonant interaction between these ions, which de-
pends weakly on ω; $\rho(\omega)$ is the density of the phonon
states. As follows from (3), the main dependence of
W_{nt} on ω is determined by the dependence of $\rho(\omega)$ on
the phonon frequency, and consequently W_{nt} is small
at low phonon frequencies. In this connection, the
migration is ineffective at helium temperatures, and
the energy transfer and luminescence quenching are
due only to the direct processes of interaction with the
acceptor or with the quenching center, which do not
depend on the temperature (see Fig. 3). With increas-
ing temperature, the efficiency of excitation migration
increases. This increase can be brought about by two
effects.

A. Increase of the homogeneous width of the level
1 (Fig. 8). With increasing temperature, the level 2
becomes populated as a result of the strong interaction
with the phonons, leading to a shortening of the lifetime
of the ions at the level 1, and consequently to an in-
crease of its homogeneous width $\delta\nu_1 \varpropto A_{21}e^{-\Delta/kT}$,
where A_{21} is the probability of the non-radiative
transition 2−1, and Δ is the distance between the
levels 1 and 2 (Fig. 8). This can lead to an improve-
ment in the overlap of the lines of neighboring ions
and to migration between them as a result of resonant
transfer.

B. When the temperature is increased, the level 2

[2]In particular, the width of the 0.875 μ resonance line of the Nd^{3+}
(0.5%) ions in YAG crystals at 4.2°K amounts to 2.5 ± 0.5 cm^{-1}. On go-
ing over to 77°K, the width of this line remains unchanged. This indicates
that the observed width is determined in the investigated temperature
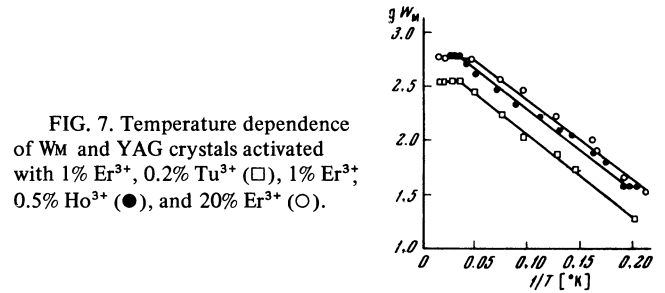interval by the inhomogeneous broadening.

becomes populated (Fig. 8), and nonresonant migration along the donor ions can take place: the ion D_1 goes over from the level 3 to level 1,[3], and the ion D_2 goes from level 2 to level 3, and a phonon with energy $\hbar\omega$ $= \hbar\omega_{31}^{D_1} - \hbar\omega_{23}^{D_2}$ is created. Since the probability of finding the ion D_2 in the state 2 is proportional to $e^{-\Delta/kT}$, the probability of the elementary act of non-resonant transfer is also proportional to this factor[4]. This process does not depend on the character of the line broadening, and its probability is much higher than that of processes of non-resonant transfer within the limits of the line width of the 3 – 1 transition (1—5 cm^{-1}), owing to the larger density of states $\rho(\omega)$ of the high-frequency phonons in expression (3).

To choose between the indicated effects, low-temperature experiments were performed on crystals with greatly differing resonance-line widths. We investigated the crystals $SrMoO_4$ and $NaLa(MoO_4)_2$, activated with Nd^{3+}, in which the widths of the resonance lines, connected with the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ are equal to ~ 3 cm^{-1} and ~ 15 cm^{-1}, respectively, at 77°K. The distances to the first excited level of the $^4I_{9/2}$ term were practically the same and amounted to, in our measurements, 95 cm^{-1} ($SrMoO_4$) and 92 cm^{-1} ($NaLa(MoO_4)_2$)[10]. If the main contribution to the improvement of the migration is made by resonance-interaction processes, then the lifetime τ should increase more rapidly for the $SrMoO_4$ crystals with increasing temperature. If the decisive role is played by the nonresonant interaction mechanism, then the $\tau(T)$ dependences should be the same for both crystals in the interval 4.2—77°K.

Figure 9 shows the temperature dependence of the luminescence lifetime of the Nd^{3+} ions at the level $^4F_{3/2}$ in the crystals $SrMoO_4$ and $NaLa(MoO_4)_2$. The curves turned out to be actually similar, and Δ_1 in both crystals were the same within the limits of the experimental error (see the table). Thus, a decisive role in the improvement of migration with increasing temperature to 77°K is played by the nonresonant processes in which the first excited level of the ground state of the donor ion takes part.

When the temperature is increased from 77 to 300°K, a lengthening of the lifetime of the Er^{3+} ions is observed in YAG crystals activated with $Er^{3+}-Tu^{3+}$ and $Er^{3+}-Ho^{3+}$ (Fig. 3), thus indicating a deterioration in the energy transfer to the Tu^{3+} and Ho^{3+} ions. Let us discuss the possible causes of the weakening of the transfer with increasing temperature.

One of them may be connected with the backward excitation-energy transfer from the Tu^{3+} and Ho^{3+} ions to the Er^{3+} ions. To check these assumptions, experiments were performed on monochromatic excitation of Ho^{3+} ions in YAG crystals with 1% Er^{3+} and 0.5% Ho^{3+} at 300°K. The excitation of the Ho^{3+} ions at the $^5I_6$ level with energy ~ 8500 cm^{-1} was produced by an incandescent lamp, from whose spectrum an interval ~ 150 Å was cut out with the aid of an interference filter. There is no absorption of Er^{3+} ions in YAG

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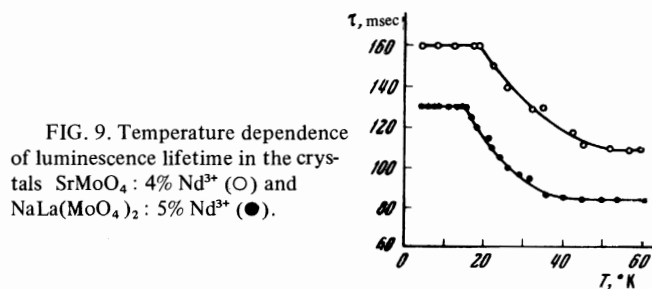[3] D_1 and D_2 are like ions.

[4] A similar temperature dependence for $\Delta \geqslant kT$ is possessed also by another transfer process such as $D_1 (3 \rightarrow 2)$, $D_2 (1 \rightarrow 3)$, absorption of a phonon $\hbar\omega$.

FIG. 9. Temperature dependence of luminescence lifetime in the crystals $SrMoO_4$: 4% Nd^{3+} (O) and $NaLa(MoO_4)_2$: 5% Nd^{3+} (●).

crystals in this section of the spectrum The luminescence spectrum in the region 1.6—2.2 μ was registered with the aid of a high-transmission monochromator (MDR-2).

In the presence of backward transfer from the Ho^{3+} ions to the Er^{3+} ions, luminescence of the Er^{3+} ions should be observed. We observed only an intense luminescence of Ho in the 2.1 μ region $^5I_7 \rightarrow {}^5I_8$ transition), and there was no luminescence of erbium in the 1.6 μ region. This experiment indicates that the backward transfer from the Ho^{3+} ions to the Er^{3+} is ineffective in the investigated crystals. An examination of Fig. 3 shows that in both pairs ($Er^{3+} - Tu^{3+}$ and $Er^{3+} - Ho^{3+}$) the $\tau(T)$ dependences of the Er^{3+} ions in the temperature interval 77—300°K are similar, and do not depend on the acceptor. Consequently, the increase of the lifetime of the Er^{3+} ions with increasing temperature cannot be attributed to the backward transfer.

The deterioration of the excitation-energy transfer from the Er^{3+} to the Tu^{3+} and Ho^{3+} ions at high temperatures may be connected with the ratio of the probability of migration over the Er^{3+} ions to the probability of the final act of interaction between the Er^{3+} ions and the Tu^{3+} and Ho^{3+} ions. With increasing temperature, the migration probability becomes larger than the probability of the final interaction, and the migration chains become much longer. The efficiency of the interaction with the acceptor (Tu^{3+}, Ho^{3+}) can then decrease.

To obtain the obtained experimental temperature dependence (2) of the probability $\overline{W}_M$ in the interval 4.2—77°K, a theoretical calculation was made of the average lifetime of the excited ions of the donor τ_{av} with allowance for the migration of the excitation energy. We considered a system of particles (donors and acceptors) uniformly distributed in an infinite volume. At the initial instant of time, the concentration of the excited ions of the donor per unit volume was $n(0)$. We determined the time variation of the number of excited donor ions. The number of excited particles can be decreased by the following processes: 1) radiative decay, 2) direct quenching interactions with the acceptor, 3) quenching due to migration of the excitation energy along the donor ions, with subsequent transfer of energy to the acceptor ions. The probability of radiative decay is independent of the temperature. We shall assume that the probability of the direct quenching interactions is also independent of the temperature. The total probability of these two processes is equal to $1/\tau_{exp}$. The quenching probability, which is connected with the diffusion of the excitation energy

to the acceptor ions and depends on the temperature, will be denoted by $W_M(T)$. Then in the case of the two-level system considered by us the equation for the time variation of the number of excited donor ions can be written in the form

$$\frac{dn}{dt} = -\left(\frac{1}{\tau_{exp}} + \overline{W}_M(T)\right). \tag{4}$$

Let us find an expression for $\overline{W}_M(T)$. When account is taken of the diffusion of the excitation energy of the crystal, the quenching probability is proportional to the "frequency of collision" of the excitation migrating along the crystal with the trap (acceptor ion). As a trap model we chose a sphere of radius R_0 surrounding the acceptor ion. Then the "frequency of collision" calculated in analogy with[11] is given by

$$\nu = 4\pi R_0 D n_0 (1 + R_0/\sqrt{\pi D t}), \tag{5}$$

where n_0 is the number of traps per unit volume, t is the time, D is the "coefficient of diffusion" of the excitation energy over the donor ions.

The "diffusion coefficient" D can be written in the form $D = \overline{r}^2/\tau_M$, where $\overline{r}$ is the average distance between the donor ions in the crystal and $1/\tau_M = W_M$ is the probability of the elementary act of energy transfer from one donor ion to another. When account is taken of the nonresonant character of the interaction, W_M is proportional to the population of level 2 (see Fig. 8), i.e., $W_M \infty e^{-\Delta/kT}$. Then the "diffusion coefficient" can be represented in the form

$$D = \overline{r}^2 W_M = D_0 e^{-\Delta/kT}. \tag{6}$$

The sought probability $\overline{W}_M(T)$ is then

$$\overline{W}_M(T) = P\nu. \tag{7}$$

(P is the probability that the excitation energy will be quenched by the "encounter" with the trap). Substituting (7) in (4) and solving (4), we obtain

$$n(t) = n(0) \exp\{-(\alpha t + 2\beta\sqrt{t})\}, \tag{8}$$

where

$$\alpha = 1/\tau_{exp} + 4\pi PR_0 n_0 D, \quad \beta = 4PR_0^2 n_0 \sqrt{\pi D}. \tag{9}$$

The obtained variation of the population (8) has a non-exponential character. As shown in[12], such a non-exponential law can be well approximated by an instantaneous initial drop followed by an exponential one. The average lifetime of the excited ions of the donor τ_{av} is determined by[5]

$$\tau_{av} = \left(\int_0^\infty n(t)dt\right)^{-1} \int_0^\infty tn(t)dt = \frac{1}{\alpha}\left(1 - \frac{\sqrt{\pi}}{2}q + \ldots\right), \tag{10}$$

where $q = \beta/\sqrt{\alpha}$. Substituting α and β in (10) and retaining the first two terms of the expansion, we get

$$\tau_{av} = \frac{\tau_{exp}}{1 + 4\pi PR_0 n_0 D\tau_{exp}}\left(1 - \frac{2\pi PR_0^2 n_0 \sqrt{D\tau_{exp}}}{\sqrt{1 + 4\pi PR_0 n_0 D\tau_{exp}}}\right). \tag{11}$$

In expression (11), τ_{exp} is the lifetime at helium temperature, when the migration processes are ineffective

for all the system considered by us.

Expression (11) can be simplified:

$$\tau_{av} = \tau_{exp}(1 - 2\pi PR_0^2 n_0 \sqrt{D_0\tau_{exp}} e^{-\Delta/2kT}). \tag{12}$$

This is valid if the term $4\pi PR_0 n_0 D\tau_{exp}$ in (11) is small compared with unity. Let us estimate the value of the diffusion coefficient $D = D_0 e^{-\Delta/kT}$ at which this requirement is satisfied for the system of YGG with Nd^{3+} (6.6 at.%). We put $P = 1/2$, $n_0 \approx 5 \times 10^{18}$ cm^{-3},[6] and $\Delta = 80$ cm^{-1}. The values $\tau_{exp} = 80$ μsec at $T = 4.2°$K and $\tau_{av} = 50$ μsec at $T = 35°$K are taken from experiment. For R_0 we chose the average distance between the activator ion, equal to ≈ 10Å. Then $D_0 \approx 10^{-8}$ cm^2/sec and the term $4\pi PR_0 n_0 D\tau_{exp}$ can actually be neglected compared with unity for temperatures to $40°$K. In the temperature interval $10-40°$K, the luminescence lifetimes of the Nd^{3+} ions, calculated by formula (12), are in good agreement with experiment.

Similar estimates, presented for other investigated systems, show that formula (12) is valid for YAG with $Er^{3+}-Tu^{3+}$, YAG with $Er^{3+}-Ho^{3+}$, and YAG with Er^{3+} to temperatures $10°$K, for LaF_3 with $Nd^{3+}-$ to $25°$K, and for YAG with $Nd^{3+}-$ to $50°$K.

Thus, the observed experimental dependence $\overline{W}_M \infty e^{-\Delta/2kT}$ follows directly from (12).

DEPENDENCE OF THE PROBABILITY OF NON-RESONANT TRANSFER ON THE PHONON FREQUENCY

As indicated in the preceding section, an interpretation of the temperature dependences of the transfer and concentration quenching in the region $2-77°$K is based on the assumption that the nonresonant transfer with emission of phonons having a frequency on the order of 100 cm^{-1} is much more effective than the nonresonant transfer with emission of low-frequency phonons ($1-5$ cm^{-1}). Interest attaches to direct experiments confirming this assumption.

The investigations were made on glasses activated with rare-earth ions, which contain, owing to the random distribution of the parameters of the crystal field within the limits of the line width, a set of centers that differ in energy. Monochromatic excitation within the limits of the line contour and subsequent observation of the luminescence signal make it possible to obtain information on the nonresonant processes.

The monochromatic-excitation experiments were performed on silicate glasses activated with Yd^{3+}. At low temperatures, the 0.974 μ resonance line of Yb, corresponding to the transition between the lower Stark components of the levels $^2F_{5/2}$ and $^2F_{7/2}$, practically does not overlap any other lines in the absorption and luminescence spectra[14], making it possible to carry out excitation within the contour of this line only. Its width at $4.2°$K is 60 cm^{-1}.

The luminescence was excited with an incandescent lamp, from the emission spectrum of which a spectral

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[5] An analogous expression for τ_{av} was obtained in [12] with account taken of the influence of the excitation-energy transfer on the average duration of the excited state in the case of immobile molecules.

[6] Assuming that the luminescence quenching of the Nd^{3+} ions in YAG occurs on paired centers, the trap concentration can be determined from statistical calculations (see, for example, [13]).
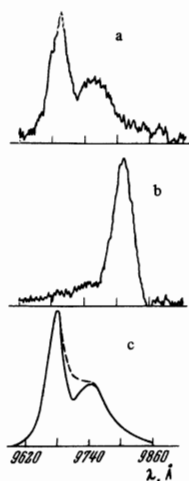
FIG. 10. Spectrum observed upon monochromatic excitation in the short-wave (a) and long-wave (b) edges of the resonance line of Yb^{3+} in silicate glass at 4.2°K; c — luminescence spectrum upon monochromatic excitation in the short-wave edge of the resonance line of Yb^{3+} in glass (solid line) and the summary radiation spectrum of the Yb^{3+} under non-monochromatic excitation at 4.2°K and of the scattered excitation at 4.2°K and of the scattered exciting light (dashed).

the summary spectrum of the radiation of the Yb^{3+} ions under non-monochromatic excitation and of the scattered exciting light. The dip on the solid curve near the peak of the scattered exciting light is connected with the ineffective transfer in which low-frequency phonons take part.

Thus, the results of our experiments demonstrate the important role of the non-resonant transfer processes, in which phonons take part at low temperatures, in media activated with rare-earth impurities.

interval of 15 cm^{-1} was separated by means of the high-transmission MDR-2 monochromator. The exciting light was focused on a sample placed in a helium Dewar. The luminescence light was registered with a DFS-12 spectrometer and an FÉU-22 photomultiplier. The photomultiplier signal was fed to an amplifier and an SD-1 synchronous detector. The spectral width of the DFS-12 slit was 15 cm^{-1}. The excitation was carried out successively in the short-wave and long-wave edges of the 0.974 μ resonance line of Yb, and the luminescence spectrum was then recorded.

Figure 10 shows the luminescence spectra of Yd^{3+} (5%) in silicate glass on the monochromatic excitation at 4.2°K. Upon excitation in the short-wave edge of the 0.974 μ line (Fig. 10a), luminescence in the Stokes region is observed besides the resonance luminescence and the scattered light (left-hand peak). Upon luminescence in the long-wave edge of the line (Fig. 10b), only the resonance luminescence and the scattered excited light are observed, and there is no luminescence in the anti-Stokes region. It is seen from an examination of Fig. 10a that effective energy transfer, together with phonon emission, takes place.

Figure 10c shows the experimentally observed luminescence spectrum of Yb^{3+} following monochromatic excitation (solid curve). The dashed line shows

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