

Influence of crystal lattice on the population of high excited states of Er^{3+} ions under infrared excitation

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The influence of the base on the population of the Er^{3+} ion, $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ states due to nonradiative energy transfer from the Yb^{3+} ions under infrared excitation is considered. It is established that the change of the ratio of the populations of the states $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ of the Er^{3+} ion on going from one base to another can reach three orders of magnitude and is due to the change in the probability of the final act of summation of the energies of the $^2\text{F}_{5/2}$ state of the Yb^{3+} ion and the $^4\text{I}_{3/2}$ state of the Er^{3+} ion. The summation of the energies of these states takes place in the absence of resonance of the electronic intermultiplet transitions and with participation of the lattice phonons. The change of the probability of the summation of these states on going from one base to another is due to the change in the difference between the energies of the electronic intermultiplet transitions $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ of Yb^{3+} and $^4\text{I}_{13/2} \rightarrow ^4\text{F}_{9/2}$ of Er^{3+} , and also to the lattice phonon energy.

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Observation of visible radiation of trivalent rare-earth ions (TR^{3+}) excited by infrared photons^{1,2} has led to discovery of a large number of new physical phenomena,³⁻⁵ such as Raman absorption,⁶ Raman luminescence,^{7,8} cooperative luminescence sensitization,⁹ emission from virtual states,¹⁰ and others. Even the very first investigations led to the fundamental conclusions that these phenomena are based on the interaction of the impurity particles in the excited states, and that this interaction is collective.

A large group of these phenomena, named cooperative processes,³ was intensively investigated recently, but some fundamental questions still remain unanswered. In particular, the question of the influence of the base on the effectiveness of the ion-ion interactions that lead to infrared excitation of visible radiation remains unclear. It has been established quite definitely by now that the electron-phonon interaction plays a role in the processes of population and depletion of the excited states of TR^{3+} ions when they do not interact with one another. The nonradiative relaxation rate, due to the electron-phonon interaction is determined by the energy gap between the upper and lower states and by the phonon spectrum of the base.¹¹ Thus, for example, in $\text{LaCl}_3:\text{Nd}^{3+}$ crystals which have an anomalously "short" phonon spectrum, radiation is observed from many Nd^{3+} excited states¹² that are nonradiative in crystals having a more extended phonon spectrum.¹³ It is known on the other hand that glass matrices have a more extended phonon spectrum. Thus, for example, it was possible to develop rather effective laser based on the transition $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ ($\lambda \sim 3 \mu\text{m}$) of the Er^{3+} ion in crystals,^{14,15} whereas in glasses emission from the $^4\text{I}_{11/2}$ level was practically completely suppressed by nonradiative transitions due to the strong electron-phonon interaction.¹⁶

The foregoing considerations were used also to explain the effects of anti-Stokes radiation.^{5,17-19} However, an analysis of the known experimental results shows that the difference between the intensities of the emission from different states under anti-Stokes excitation cannot be explained within the framework of the

electron-phonon interaction model. Thus, for example, it was established recently²⁰ that cooperative processes take place quite effectively not only in crystals but also in glasses. There are also many experimental facts, discussed below, that confirm the arguments presented above. In this connection, the purpose of the present study was to ascertain the role of the base in the competition of the population of the various highly excited states of TR^{3+} ions under anti-Stokes excitation.

It is known the infrared radiation is transformed into visible light with maximum efficiency by interaction of Yb^{3+} and Er^{3+} ions.^{5,21,22} Furthermore, for example in YF_3 and NaYF_3 crystals under anti-Stokes excitation, the $^4\text{S}_{3/2}$ state of the Er^{3+} ion becomes effectively populated and this produces green emission with $\lambda \sim 0.55 \mu\text{m}$, whereas in YOCl and Y_2O_3 crystals the predominantly populated state is $^4\text{F}_{9/2}$ of the Er^{3+} ions, and the observed emission lies in the red region of the spectrum with $\lambda \sim 0.67 \mu\text{m}$ (Fig. 1).

It is appropriate to note here that the energies of the multiplets of TR^{3+} ions, by virtue of the good screening of the $4f$ shell, change only negligibly on going from one base to another. The mechanisms that populate the indicated states are the following.⁵ In both cases an external source was used to excite initially the state

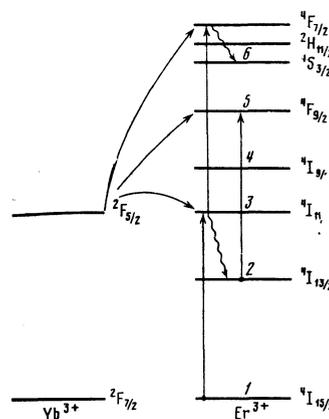


FIG. 1. Energy level schemes of the Yb^{3+} and Er^{3+} ions.

${}^2F_{5/2}$ of the Yb^{3+} ion ($\lambda \sim 1 \mu\text{m}$). As a result of the interaction of the Yb^{3+} ion in the ${}^2F_{5/2}$ state with the unexcited Er^{3+} ion (in the ${}^4I_{15/2}$ state), the Yb^{3+} ion turns out to be in the ground state ${}^2F_{7/2}$, and the Er^{3+} ion goes over into the excited state ${}^4I_{11/2}$. The population of the ${}^4S_{3/2}$ level is the result of the interaction of the Yb^{3+} and Er^{3+} ions that are respectively in the excited states ${}^2F_{5/2}$ and ${}^4I_{11/2}$. This second interaction returns the excited Yb^{3+} ion to be in the ground state, while the Er^{3+} ion goes over into the higher state ${}^4F_{7/2}$, rapid relaxation from which leads to population of the ${}^4S_{3/2}$ level. The observed radiation from this state lies in the green region of the spectrum with $\lambda \sim 0.55 \mu\text{m}$.

The ${}^4F_{9/2}$ level of the Er^{3+} ion can be populated by several methods. The most effective, however, is the following mechanism.⁵ The first transfer stage is analogous to the one considered above. Subsequently, however, the Er^{3+} ion excited to the ${}^4I_{11/2}$ level relaxes to the ${}^4I_{13/2}$ state and the second act of energy transfer is the result of the interaction of the Yb^{3+} in the ${}^2F_{5/2}$ state with the Er^{3+} ion in the ${}^4I_{13/2}$ state, as a result of which the ${}^4F_{9/2}$ level of the Er^{3+} ion is populated, and radiation from this level is observed in the red region of the spectrum, with $\lambda \sim 0.67 \mu\text{m}$.

The question is: why is the ${}^4S_{3/2}$ state more effectively populated in some systems and ${}^4F_{9/2}$ in others? The arguments presented above concerning the decisive role of the electron-phonon interaction as applied to the described concrete case seem at first glance plausible. The competition between the described mechanisms that populate the high excited states of Er^{3+} is determined by the rate of the multiphonon relaxation w_{32} on the ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition (see Fig. 1). It is known that the probability of multiphonon relaxation through an energy gap ΔE in the single-particle model is described by the expression¹¹

$$W(\Delta E) = W(0) \exp(-\alpha \Delta E), \quad (1)$$

where $W(0)$ is the asymptotic value of $W(\Delta E)$ as $\Delta E \rightarrow 0$.

The constant α is connected with the constant g of the electron-phonon interaction and with the energy $\hbar\omega$ of the phonon that participates in the relaxation process:

$$\alpha = \frac{1}{\hbar\omega} \left[\ln \left(\frac{N}{g(n+1)} \right) - 1 \right], \quad (2)$$

where $N = \Delta E / \hbar\omega$ is the number of phonons needed to overlap the energy gap, and $n = [\exp(\hbar\omega/kT) - 1]^{-1}$ is the occupation number of the phonon states of energy $\hbar\omega$ at the temperature T .

A relation of the type (1) is in sufficiently good agreement with the available experimental data.¹³ Since the energy gap between the states ${}^4I_{11/2}$ and ${}^4I_{13/2}$ of the Er^{3+} ion remains practically unchanged on going from one base to another, it follows that in the electron-phonon interaction model w_{32} is determined by the character of the phonon spectrum of the crystal. On the basis of the foregoing considerations, a simple empirical rule was formulated.¹⁷ If the end-point frequency of the phonons is less than 400 cm^{-1} , then the rate of the non-radiative relaxation from the ${}^4I_{11/2}$ level to the ${}^4I_{13/2}$ level is small, and the more probable is the first mechanism, which leads to the population of the state ${}^4S_{3/2}$

of the Er^{3+} ion. At a phonon endpoint frequency larger than 500 cm^{-1} , the probability w_{32} increases substantially, and the first mechanism turns out to be discriminated, since the state ${}^4I_{11/2}$ decays rapidly, populating the ${}^4I_{13/2}$ level, and the state ${}^4F_{9/2}$ of the Er^{3+} ion is excited more effectively.

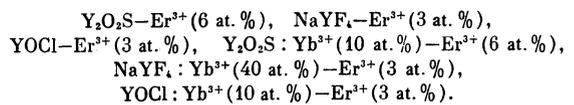
We shall show that the foregoing arguments cannot explain the totality of the observed experimental facts.

1. There are known experimental data that show that the ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition of the erbium ion in many bases that have an extended phonon spectrum is nonetheless radiative^{15,23} and in this case the population of the ${}^4I_{13/2}$ level through the ${}^4I_{11/2}$ level is not connected in any way with the effect of the electron-phonon interaction.

2. It is known that when Yb^{3+} ions in a $\text{Y}_2\text{O}_3\text{S}$ crystal activated with Yb^{3+} and Er^{3+} are excited, the state predominantly populated is ${}^4S_{3/2}$ of the Er^{3+} ions. On the other hand, the end-point frequency of the phonons in this crystal is 520 cm^{-1} , thus contradicting the empirical rule¹⁷ mentioned above.

3. Our experiments, which will be discussed below, have shown that the rate of relaxation from the ${}^4I_{11/2}$ level to the ${}^4I_{13/2}$ level of the Er^{3+} ions, in the case of selective excitation of the ${}^2F_{5/2}$ level ytterbium in various bases, changes by not more than 10 times, whereas the changes of the ratios of the intensities of the radiation from the levels ${}^4S_{3/2}$ and ${}^4F_{9/2}$ in the same bases reach three orders of magnitude.

We used in our experiments the following polycrystalline samples:



The relaxation rates of the states ${}^4S_{3/2}$, ${}^4F_{9/2}$, ${}^4I_{11/2}$, ${}^4I_{13/2}$ of the Er^{3+} ions were measured both in the absence and in the presence of Yb^{3+} ions under selective excitation of the state ${}^2H_{11/2}$ of the Er^{3+} ions. The rates of population of the state ${}^4I_{13/2}$ of the Er^{3+} ion in the doubly activated samples were measured under selective excitation of the ${}^2F_{5/2}$ level of the Yb^{3+} ion. Selective excitation in the measurement of the relaxation characteristics was effected with the aid of the fundamental frequency ($\lambda \sim 1.06 \mu\text{m}$) and the second harmonic ($0.53 \mu\text{m}$) of a garnet laser with neodymium, operating in a Q -switched pulsed-periodic regime. We measured the ratios of the intensities of the radiation from the levels ${}^4S_{3/2}$ and ${}^4F_{9/2}$ of the Er^{3+} ions in various bases under selective excitation via ytterbium ions, using a semiconductor gallium-arsenide laser ($\lambda \sim 906 \text{ nm}$). The necessary information on the positions and widths of the erbium and ytterbium levels in the various bases was obtained by investigating the absorption and luminescence spectra, using standard spectral apparatus.

Recognizing that the change of the ratios of the Einstein coefficients for transitions between different multiplets of Tr^{3+} ions changes little on going from one base to another,¹⁶⁻²⁴⁻²⁶ the ratio Q of the intensities of

the emission from the levels ${}^4S_{3/2}(I_6)$ and ${}^4F_{9/2}(I_5)$ can be represented in the following manner (Fig. 1):

$$Q = \frac{I_6}{I_5} = \frac{n_6 \eta_6 a_6}{n_5 \eta_5 a_5}, \quad (3)$$

where n_5 and n_6 , η_5 and η_6 , and a_5 and a_6 are the populations, quantum yields, and probabilities of the deactivation of the levels ${}^4F_{9/2}$ and ${}^4S_{3/2}$, respectively.

Solving the stationary kinetic equations for the populations n_5 and n_6 following the excitation of the states ${}^4S_{3/2}$ and ${}^4F_{9/2}$ via the Yb^{3+} ions in accord with the mechanisms considered above, making the standard assumption that the level of the IR excitation is weak (the concentration of the ions in the ground states is much higher than the concentration of the ions in the excited states), which ensures a linear dependence of the quantum yield of the anti-Stokes radiation on the excitation density, and substituting the results of this solution in (3), we get

$$Q = \frac{a_6 a_5 \eta_6 a_2 P_2}{a_5 a_6 \eta_5 w_{32} P_3} = R \frac{P_2}{P_3}, \quad (4)$$

where a_5^* and a_6^* are the probabilities of deactivation of the levels ${}^4F_{9/2}$ and ${}^4S_{3/2}$ of the Er^{3+} ions under Stokes excitation in the presence of Yb^{3+} ; a_2 is the probability of deactivation of the ${}^4I_{13/2}$ level of the Er^{3+} ions, w_{32} is the relaxation rate from the state ${}^4I_{11/2}$ to the level ${}^4I_{13/2}$; P_2 is the constant of the interaction of the Yb^{3+} and Er^{3+} ions in the states ${}^2F_{5/2}$ and ${}^4I_{11/2}$, respectively, and P_3 is the constant of the interaction of the Yb^{3+} and Er^{3+} ions in the respective states ${}^2F_{5/2}$ and ${}^4I_{13/2}$ (Fig. 1).

As already indicated, it was previously assumed^{5,17,18} that the change of the value of Q on going from one base to another is due mainly to the change of w_{32} . The methods described above were used to measure all the quantities that enter in (4), with the exception of the ratio P_2/P_3 . The values of a_2 , a_5 , a_6 , a_5^* and a_6^* were determined from the kinetics of the decays of the corresponding levels of the Er^{3+} ions (Fig. 1) when the latter were excited by the second harmonic of a neodymium garnet laser. The quantity w_{32} was measured with the Yb^{3+} ions excited by the fundamental frequency of the same laser, using both the luminescence buildup curve of the ${}^4I_{13/2}$ state, and the decay curve of the ${}^4I_{11/2}$ state. The results of these two methods agreed within the limits of the error of the measurement of w_{32} . The ratio η_6/η_5 were determined from measurements by the integrating-sphere method.²⁷ The quantity Q is relative and was measured as the ratio of the areas under the luminescence spectra of the Er^{3+} ions in the transitions ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ following the excitation of the ${}^2F_{5/2}$ state of the Yb^{3+} ions with a semiconductor laser. The results of the measurements are given in Table I. As already noted above, the change in the probability w_{32} in the investigated bases does not

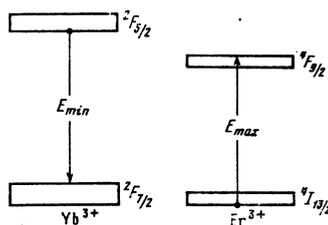


FIG. 2. Scheme of the final act of summing the energies of the states of ${}^2F_{3/2}$ of the Yb^{3+} ion and ${}^4I_{13/2}$ of the Er^{3+} ion.

exceed one order of magnitude, whereas the change of W reaches three orders of magnitude. It is also seen from the table that the value of the coefficient R changes by not more than a factor of 2. Thus, the results of the measurements show that the competition of the populations of the states ${}^4S_{3/2}$ and ${}^4F_{9/2}$ of the Er^{3+} ions when excited via the Yb^{3+} ions is determined by the ratio of the constants P_2/P_3 , and the change of this ratio in the investigated bases reaches three orders of magnitude (Table I).

It is of interest to determine which of the transfer constants undergoes such a considerable change on going from one base to another. An analysis of the optical spectra shows that the interaction of the Yb^{3+} and Er^{3+} ions in the states ${}^2F_{5/2}$ and ${}^4I_{11/2}$, which leads to population of the level ${}^4S_{3/2}$ via relaxation from the level ${}^4F_{7/2}$ (the constant P_2) takes place under conditions of good resonance of the electronic transitions which remains practically unchanged on going from one base to another. The situation is substantially different in the interaction of the ions Yb^{3+} and Er^{3+} in the states ${}^2F_{5/2}$ and ${}^4I_{13/2}$ (the constant P_3). No resonance of the electronic transitions is observed in this case, i.e., the process of the population of the ${}^4F_{9/2}$ state calls for participation of the lattice phonons, namely: the lattice must absorb a certain excess of energy, since the minimum energy of the electron intermultiplet transition ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ of the ion Yb^{3+} (E_{\min}) exceeds in all of the bases the maximum energy of the electronic intermultiplet transition ${}^4I_{13/2} \rightarrow {}^4F_{9/2}$ of the ion Er^{3+} (E_{\max}) by an amount ΔE , $\Delta E = E_{\min} - E_{\max}$ (Fig. 2).

It is important that in all the bases the value of ΔE exceeds kT . This circumstance ensures irreversibility of the last energy transfer act and, properly speaking, the very possibility of emission from the ${}^4F_{9/2}$ level. In the case of population of the ${}^4S_{3/2}$ state, the irreversibility of the last energy-transfer act is ensured by the nonradiative relaxation from the ${}^4F_{7/2}$ level via the ${}^2H_{11/2}$ into the state ${}^4S_{3/2}$. The energy gap between these states is also substantially larger than kT .

Quantitative information for the investigated bases, obtained from an analysis of the optical spectra, is given in Table II. This table lists also the published data for two bases: YF_2 and Y_3OCl_7 .¹⁹ The first of them emits in the green region of the spectrum, i.e., excitation through the Yb^{3+} ions populates predominantly the state ${}^4S_{3/2}$ of the erbium ion; the second emits in the red region of the spectrum, i.e., excitation through the Yb^{3+} populates in it predominantly the state ${}^4F_{9/2}$ of the Er^{3+} ion.

TABLE I.

Base	a_2^{-1} , msec	a_5^{-1} , μsec	a_6^{-1} , μsec	a_5^{*-1} , μsec	a_6^{*-1} , μsec	w_{32}^{-1} , μsec	η_6/η_5	Q	$R \cdot 10^2$	P_2/P_3
NaYF_4	12	170	100	330	600	2.9	0.7	20	18	$\sim 10^2$
YOC1	5	65	30	35	60	0.44	2.0	1/36	14	$\sim 2 \cdot 10^{-1}$
$\text{Y}_2\text{O}_3\text{S}$	2.85	50	20	80	100	1.3	0.9	2	20	~ 10

TABLE II.

	YF ₃	NaYF ₄	Y ₂ O ₂ S	Y ₃ OCl ₇	YOCl
E_{\min} , cm ⁻¹	9830	9960	9760	9520	9380
E_{\max} , cm ⁻¹	8940	8960	8830	8970	8760
ΔE , cm ⁻¹	890	1000	920	550	620
$\hbar\omega$, cm ⁻¹	375	350	520	600	620
N	~3	~3	~2	~1	~1
Emission color	green	green	{ red green	red	red

An estimate of the probability of ion-ion interaction with participation of lattice phonons can be obtained by using the theory developed by Miyakawa and Dexter.¹¹ This theory yields the following expression for the energy-transfer constant in the case of detuning ΔE of the electronic transitions from resonance:

$$P(\Delta E) = P(0) \exp(-\beta \Delta E), \quad (5)$$

where $P(0)$ is the asymptotic value of $P(\Delta E)$ as ΔE tends to zero;

$$\beta = \alpha - \gamma, \quad (6)$$

where

$$\gamma = \frac{1}{\hbar\omega} \ln \left(1 + \frac{g_b}{g_a} \right), \quad (7)$$

g_b and g_a are the constants of the electron-phonon interaction for the interacting ions. Thus, the parameters $P(0)$ and β characterize the effectiveness of the transfer of energy of the electron excitation with participation of phonons between Tr^{3+} ions.

In our concrete case the value of ΔE corresponds to the detuning from the resonance of the transition in ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ of the Yb^{3+} and the transition ${}^4I_{13/2} \rightarrow {}^4F_{9/2}$ of the Er^{3+} ion. The values of ΔE listed in Table II for $\text{Y}_2\text{O}_2\text{S}$, YOCl and NaYF_4 were measured by us, while those for YF_3 and Y_3OCl_7 were taken from Ref. 19. The results obtained by us and the available published data make it possible, using (5), to estimate the changes in the value of P_3 on going from YOCl to NaYF_4 , i.e., for bases in which, according to our data, the most effectively populated are respectively the states ${}^4F_{9/2}$ and ${}^4S_{3/2}$ of the Er^{3+} ions.

The values of β and $P(0)$ for YOCl are respectively 8×10^{-4} cm (Ref. 19) and 10^{-16} cm³/sec (Refs. 18 and 28), while ΔE amounts to 620 cm⁻¹ (Table II) leading to a value $P_3 = 6 \times 10^{-17}$ cm³ sec⁻¹. For the NaYF_4 base $\beta = 0.4 \times 10^{-2}$ cm,¹⁸ $P(0) = 10^{-17}$ cm³ sec⁻¹,^{18,28} and $\Delta E = 1000$ cm⁻¹ (Table II), so that in this case we get $P_3 = 2 \times 10^{-19}$ cm³ sec⁻¹. Thus, the change in the value of P_3 on going from YOCl , which radiates in the red region of the spectrum, to NaYF_4 , which radiates in the green region of the spectrum, is in satisfactory agreement with the experimentally measured ratios P_2/P_3 for the same bases, (Table II). This allows us to conclude that the predominant contribution to the competition of the population of the states ${}^4S_{3/2}$ and ${}^4F_{9/2}$ of the Er^{3+} when excited via the Yb^{3+} ions is made by P_3 . In other words, the ratio of the efficiencies of the population of the states ${}^4S_{3/2}$ and ${}^4F_{9/2}$ of the ions excited via the Yb^{3+} ions in different bases is determined by the change in the probability of the interaction of the Yb^{3+} ions in the ${}^2F_{5/2}$ with the Er^{3+} ions in the state ${}^4I_{13/2}$, which takes place with participation of the lattice

phonons.

We consider now the physical principles that lead to appreciable change of P_3 on going from one base to another. An analysis of expression (5) and (6) shows that the effectiveness of the ion-ion interaction with participation of phonons is determined by the ratio of the detuning from resonance of the interacting transitions and by the phonon energy $\hbar\omega$, i.e., it depends substantially on the number of phonons needed to cover the excess energy. In Table II are given the phonon energies for different bases. The data for the YF_3 , YOCl , Y_3OCl_7 , NaYF_4 lattices are taken from Ref. 19, in which the phonon energies were obtained from an analysis of the electron-vibrational spectra of the TR^{3+} ions in these bases. The phonon energy in the $\text{Y}_2\text{O}_2\text{S}$ lattice was taken by us from Ref. 23.

Table II gives also the phonon-multiplicity factors N for different bases, i.e., the number of phonons of energy $\hbar\omega$ needed to cover the energy deficit ΔE of the intermultiplet electronic transitions when Yb^{3+} ions in the state ${}^2F_{5/2}$ interact with Er^{3+} ions in the state ${}^4I_{13/2}$. The last line of the table indicates the predominant color of the emission of these bases. It is seen that the arguments advanced by us, namely that the base influences the competition between the population of the states ${}^4S_{3/2}$ and ${}^4F_{9/2}$ or the Er^{3+} ions upon excitation via Yb^{3+} ions by acting on the value of P_3 explains well the available experimental results on the wavelength of the anti-Stokes emission of various bases with Er^{3+} and Yb^{3+} . In fact, in the case when the ratio of the quantity $\Delta E = E_{\min} - E_{\max}$ to the lattice-phonon energy $\hbar\omega$ is maximal ($N \sim 3$), a sample with Yb^{3+} and Er^{3+} radiates predominantly in the green region of the spectrum. If ΔE and $\hbar\omega$ are approximately equal ($N \sim 1$), the constant P_3 increases substantially and the Er^{3+} ion radiates predominantly in the red region of the spectrum. In the intermediate case ($N \sim 2$) the intensities of the emission of the Er^{3+} ions in the red and green region of the spectrum are comparable.

It should be noted that an analysis of the theory of multiphonon relaxation and of the theory of ion-ion interaction with participation of lattice phonons reveals the common features of these two processes. Thus, the theory yields the analogous relations $P = f(\Delta E)$ (5) and $W = f(\Delta E)$ (1), the constants α and β in the arguments of the exponentials in (1) and (5) are also closely connected—see Eqs. (2), (6), and (7).

In our concrete case the energy gap between the states ${}^4I_{11/2}$ and ${}^4I_{13/2}$, which can be overcome as a result of electron-phonon interaction, turns out to be much larger (~ 3500 cm⁻¹) than the excess energy given up to the phonon reservoir in the case of interaction of Yb^{3+} ions in the ${}^2F_{5/2}$ state and Er^{3+} ions in the ${}^4I_{13/2}$ state ($\Delta E = 600\text{--}1000$ cm⁻¹). It is obvious here that the available changes in the energies of the phonons in different bases (see Table II) lead to much larger changes of P_3 than in the rate of multiphonon relaxation on the transition ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ of the Er^{3+} ions.

In addition, our investigations of the nature of the ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition in the Er^{3+} ion upon excitation

of the ${}^2F_{5/2}$ of the Yb^{3+} ion have shown that the ${}^4I_{11/2} \rightarrow {}^4I_{13/2}$ relaxation is not connected with the electron-phonon interaction; the rate of this relaxation is governed by the interaction of the ions Yb^{3+} and Er^{3+} in the states ${}^2F_{5/2}$, ${}^4I_{15/2}$ and ${}^2F_{7/2}$ and ${}^4I_{11/2}$ (Fig. 1).²⁹

Thus, the main conclusion of the present study, concerning the influence of the base on the ratio of the populations of the states ${}^4S_{3/2}$ and ${}^4F_{9/2}$ of Er^{3+} ions under stationary excitation of the ${}^2F_{5/2}$ of Yb^{3+} ions, can be formulated in the following manner. The influence of the base on the conversion of IR radiation into visible light consists of a strong (reaching three orders of magnitude) change in the probability of the final act of summing the energies of states ${}^2F_{5/2}$ Yb^{3+} and ${}^4I_{13/2}$ Er^{3+} on going from one base to the other. So considerable a change of the probability of energy summation in different bases is due to the change in the ratio of the energy difference between the electronic intermultiplet transitions ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ of the Yb^{3+} ions and ${}^4I_{13/2} \rightarrow {}^4F_{9/2}$ of the Er^{3+} ions, on the one hand, and the energy of the phonons of the given lattice on the other.

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