an effective field resulting from the invariant of the fourth degree in γ and $\mathbf{m}$ in the thermodynamic potential that describes the magnetic properties of the crystal. Knowing the values of the magnetic susceptibilities for $FeCl_2$, we can determine the values of the effective field $H_E = (140 \pm 10)$ kOe, where $2H_e = BL_0$.

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1) B. P. Konstantinov Leningrad Institute of Nuclear Physics, Academy of Sciences, USSR.

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Kinetics of population and decay of highly excited states of TR^{3+} ions under conditions of strong incoherent interaction in the intermediate states

A. A. Glushko, V. V. Osiko, Yu. P. Timofeev, and I. A. Shcherbakov

P. N. Lebedev Physics Institute, USSR Academy of Sciences

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The possible mechanisms of population of highly excited states of erbium ions by IR excitation into the absorption band of ytterbium ions is analyzed. The time dependences of the populations of these states following pulsed excitation are theoretically obtained for these mechanisms in a large temperature interval. The time evolutions of the populations of the highly excited states of erbium are measured in the dynamic range of variation of the radiation intensity, which reaches three orders of magnitude when they are excited into the ytterbium absorption band in polycrystalline $Y_{1-x-y}Yb_xEr_yOCl$ samples. All the intermediate levels that participate in the population of the highly excited states of erbium are selectively excited and their population and depletion kinetics are measured. The population mechanisms of these excited states are identified and switching from one mechanism to another in the course of time is observed. The theoretical and experimental results are in agreement. It is shown that a regime of strongly incoherent interaction in the low excited states of erbium and ytterbium is realized in the $Y_{0.87}Yb_{0.1}Er_{0.02}OCl$ system. The complicated time evolutions of the populations of the highly excited states of erbium are described by characteristic times that are determined by the regime of strong incoherent interaction of the erbium and ytterbium in low excited states.

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INTRODUCTION

The discovery of the interaction of trivalent ions of rare-earth elements (TR^{3+}) in excited states[1,2] is to a considerable degree the result of the use of kinetic methods to investigate the excitation-energy transformation in condensed media.[3] To distinguish between the mechanisms of interaction between the impurity system and the radiation, which brings about anti-Stokes radiation, many criteria were subsequently developed, based on an analysis of the optical spectra and of the dependences of the intensity on the impurity-particle concentration and on the excitation density.[1,2] It was reliably established as a result that in most cases the process of population of the highly excited states of TR^{3+} ions in condensed media is collective and proceeds via many stages. The branched structure of the states of the TR^{3+} ions, in conjunction with multistage character of the process, leads to an extraordinary variety of mechanisms whereby the highly excited states of these ions are populated. In many cases it remained unclear which of the TR^{3+} ion levels participate in the population of the highly excited states from which the anti-Stokes radiation is observed, and which stages of the nonradiative energy transfer limit the process of population of these states in each concrete case. These questions are closely related to the more general unsolved problem of the influence of the crystalline host on the effectiveness of the anti-Stokes energy conversion in systems with rare-earth activators. It is well known that by virtue of the good screening of the $4f$ electrons the multiplet energies and the Einstein coefficients of the intermultiplet transitions of the TR^{3+} ions vary little on going from one matrix to another. It is also known, however, that in various hosts, for the same interactions of the TR^{3+} ion pairs, different excited states are populated with different effectiveness.[4-6] The crystal lattice determines the probability of the electron-phonon interaction and the Stark structure of the multiplets. This can strongly influence in turn each stage of the successive energy transfers. To understand on which of the stages the influence of the host on the population of the excited states is decisive, we must determine the contribution of each stage to the observed anti-Stokes radiation, taking it into account that the interaction of the impurity ions is collective in all stages. It was recently established that the temporal population evolutions due to the interation of TR^{3+} ions that are mainly in excited states are in general not described by simple experimental relations.[7] A precise analysis of these relations yields extensive information on the mechanisms of nonradiative energy transfer. It is natural to assume that interactions of TR^{3+} ions in excited states should lead in the general case to non-exponential population time evolutions that reflect the contributions of different stages of the nonradiative energy transfer. There are practically no published experimental data on this subject, and the employed kinetic methods did not make it possible to analyze the decay curves of highly excited TR^{3+} states following anti-Stokes excitation in a sufficiently wide dynamic range of radiation intensity.

The task of the present paper is to study the time evolutions of the populations of the excited states of Er^{3+} ions following anti-Stokes excitation via Yb^{3+} ions, wherein the time of registration of the anti-Stokes radiation exceeds greatly the characteristic lifetimes of all the excited states. Other tasks are to determine the contributions of various mechanisms to the population of the excited levels, and an investigation of the influence of interactions in intermediate states on the kinetics of the anti-Stokes radiation.

INVESTIGATED OBJECTS AND EXPERIMENTAL PROCEDURE

We investigated a group of polycrystals $Y_{1-x-y}Yb_xEr_yOCl$ with $x=0$, 1, 3, and 10 and $y=0$, 1, 3, and 10 at.%. Upon excitation into the Yb^{3+} absorption bands, the Er^{3+} ions in the YOCl crystals emit primarily in the red region of the spectrum. The Yb^{3+} ion was selectively excited by the first harmonic of a neodymium-garnet laser ($\lambda_{exc}=1.06$ μm) or by a gallium-arsenide semiconductor laser ($\lambda_{exc}=0.906$ μm). The exciting-pulse duration was 15 and 100 nsec in the first and second cases, respectively. The Er^{3+} ion ($^2H_{11/2}$ level) was selectively excited by the second harmonic of the garnet laser ($\lambda_{exc}=0.53$ μm). The spectral instruments used were the DFS-12 spectrometer and MDR-2 monochromator. The radiation receivers were FÉU-62 or FÉU-14B photomultipliers or photoresistors based on PbS. In the former case the time resolution was not worse than 5 μsec, and in the latter not worse than 200 μsec. The radiation was time scanned by an EMG-1546 or S1-15 oscilloscope. The procedure developed made it possible to investigate the kinetics of the anti-Stokes radiation in an intensity dynamic range as large as three orders of magnitude.

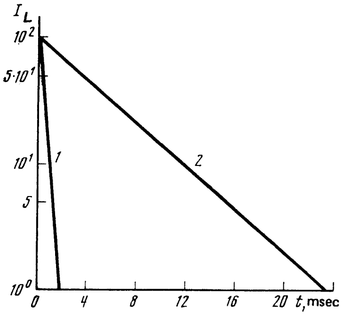

FIG. 1. Decay curves of excited $^2F_{5/2}$ states of ytterbium ions (1) and $^4I_{13/2}$ states of erbium ions (2).

EXPERIMENTAL RESULTS

Figure 1 shows the decay curves of the excited state $^2F_{5/2}$ of the Yb^{3+} ion. The kinetics of the Yb^{3+} emission turned out to be exponential with a damping constant 400 μsec for all three Yb^{3+} concentrations (1, 3, and 10 at.%). Figure 1 shows also the exponential decay curves of the $^4I_{13/2}$ state of the Er^{3+} ions under Stokes excitation ($\lambda_{exc}=0.53$ μm). The decay constant was 5 msec. Figure 2 shows the decay of the $^4I_{11/2}$ level of Ef^{3+} ions following Stokes excitation. The decay is exponential with constants 2 and 2.6 msec and 300 and 77 K, respectively. The deactivation of the states $^2F_{3/2}$ and Yb^{3+} and $^4I_{11/2}$ and $^4I_{13/2}$ of Er^{3+}, shown in Figs. 1 and 2, is due to intracenter relaxation processes.

Figure 3 shows the decay curves of the states $^4S_{3/2}$ and $^4F_{9/2}$ of the erbium ions under Stokes excitation. In contrast to the states $^4I_{11/2}$ and $^4I_{13/2}$ of the Er^{3+} ions, these states are subject to cross relaxation via the low-lying erbium level, and the emission from the $^4S_{3/2}$ and

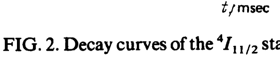

FIG. 2. Decay curves of the $^4I_{11/2}$ state of erbium ions: 1—$T=300$ K; 2—$T=77$ K.

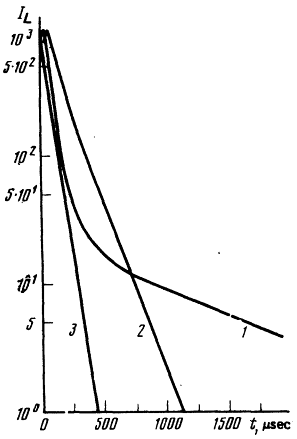

FIG. 3. Decay curves of states $^4F_{9/2}$(1,2) and $^4S_{3/2}$(3) of the erbium ion: 1,3 — $T = 300$ K; 2—$T = 77$ K.

$^4F_{9/2}$ levels is subject to concentration quenching. This is precisely the cause of the deviation of the decay from exponential during the initial stage of the process for the state $^4S_{3/2}$ (Fig. 3). In the course of time the curve becomes exponential with a constant 65 μsec. An even more complicated time evolution is experienced by the population of the $^4F_{9/2}$ state (Fig. 3). The maximum of the population is reached 25 μsec after the excitation pulse, followed by a rapid decrease with a characteristic time 60 μsec, which slows down in the subsequent stages of the process to a characteristic time 1.2 μsec. At 77 K, however, no slow relaxation process is observed, and the characteristic decay time turns out to be 140 μsec (Fig. 3).

The foregoing experimental results pertain to singly activated systems. These data are needed for the interpretation of the results on anti-Stokes emission of erbium ions excited via ytterbium ions. The experimental decay curves of a doubly activated system are shown in Fig. 4. The coactivation of the erbium ions by the ytterbium ions has led to equalization of the lifetime τ of the states $^2F_{5/2}$ and the Yb^{3+} ions and $^4I_{11/2}$ of the Er^{3+} ions. The time τ of the state $^2F_{5/2}$ of the ytterbium ions has increased from 400 to 440 μsec, while τ of the state $^4I_{11/2}$ of the erbium ions decreased correspondingly from 2 msec to 440 μsec. This effect is independent of which of the interacting ions is subjected to selective excitation. The decay kinetics of highly excited states of erbium ions that are anti-Stokes excited via ytterbium ions changed substantially (Fig. 4) in comparison with the kinetics observed in Stokes excitation of the same states of the erbium ions (Fig. 3). The maxima of the populations have shifted towards longer times, while the characteristic times of the population growth and falloff increased, the latter acquiring a substantial dispersion. Thus, for the system $Y_{0,87}Yb_{0,1}Er_{0,03}OCl$ the maximum of the population of the $^4F_{9/2}$ state shifted to 80 μsec as against the 25 μsec for Stokes excitation, a fact likewise accompanied by an increase of the growth time.

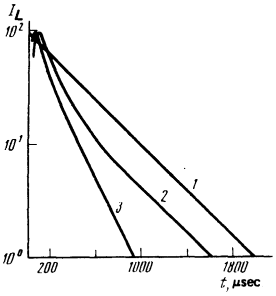

FIG. 4. Decay curves of excited states of ytterbium and erbium ions in the doubly activated system $Y_{0.87}Yb_{0.1}Er_{00.1}OCl$: 1—states $^2F_{5/2}$ Yb^{3+} and $^4I_{11/2}$ Er^{3+}; 2—state $^4F_{9/2}$ Er^{3+}; 3—state $^4S_{3/2}$ Er^{3+}.

On their initial sections, the decay curves are characterized by a smooth increase of the characteristic decay times to their asymptotic values, which set in at the later stages of the process, at 400 and 210 μsec for the states $^4F_{9/2}$ and $^4S_{3/2}$ respectively.

ANALYSIS OF POSSIBLE MECHANISMS OF POPULATION OF HIGHLY EXCITED STATES OF ERBIUM IN ANTI-STOKES EXCITATION VIA YTTERBIUM IONS

By now we can regard as firmly established the mechanism whereby the state $^4S_{3/2}$ of the erbium ion is populated upon excitation via ytterbium ions,[8-10] leading to emission in the green region of the spectrum (Fig. 5). During the first stage of the process, the ytterbium ion excited into the $^2F_{5/2}$ state transfers its energy to the $^4I_{11/2}$ level of the erbium ion. The second stage of the transfer is the result of the interaction between the erbium ions in the $^4I_{11/2}$ state and the ytterbium ion in the excited $^2F_{5/2}$ state. Excitation by the Yb^{3+} ions participating in the subsequent transfer stages can be the results of either the energy migration over the Yb^{3+} ions or of the action of an external source. The energy transfer excites the state $^4F_{7/2}$ of the erbium ion,

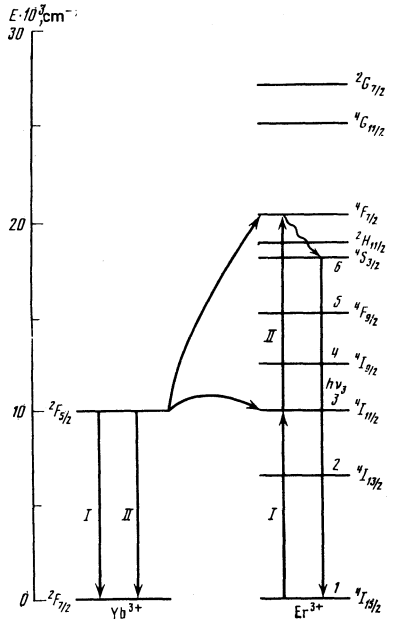

FIG. 5. Level schemes of Yb^{3+} and Er^{3+} (showing only the levels tht participate in the onset of anti-Stokes radiation). The numbers I and II designate the stages of successive energy transfer when green radiation is produced. Wavy arrow—nonradiative relaxation.

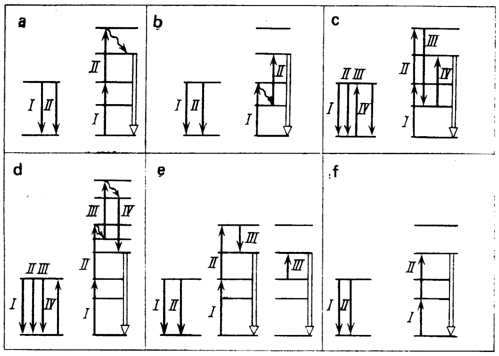

FIG. 6. Schemes of possible mechanisms of the population of the $^4F_{9/2}$ state of the erbium ion. The Roman numbers designate the stages of the successive energy transfer (double arrow– the $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transition with emission of red photon).

which undergo a rapid intracenter relaxation that determines the irreversibility of the second act of the transfer, into the state $^4S_{3/2}$. The unequivocal establishment of this mechanism is due to the use of kinetic methods to investigate the population of the $^4S_{3/2}$ state.[9-10]

The situation is much more complicated with the mechanism that populates the $^4F_{9/2}$ state of the erbium ion. Six possible mechanisms are discussed in the literature (Fig. 6).[2] In five of them, the first transfer stage is identical with the one just considered, i. e., it is determined by the interaction between the ytterbium ions in the state $^2F_{5/2}$ and the erbium ions in the ground state $^4I_{15/2}$ (Fig. 6, a–e). We discuss briefly the differences in the succeeding transfer stages.

1. The first mechanism[11,12] is similar to the mechanism that populates the $^4S_{3/2}$ state, but it is assumed that the erbium ion goes over non-radiatively, by virtue of the electron-phonon interaction, from the $^4S_{3/2}$ to the $^4F_{9/2}$ state, followed by emission of a red photon (Fig. 6a).

2. The second mechanism[13] presupposes that the first transfer act is followed by intracenter relaxation of the erbium ion form the $^4I_{11/2}$ state to the $^4I_{13/2}$ state. The $^4F_{9/2}$ level of the erbium ion is populated as a result of the interaction between the Yb^{3+} ions in the $^2F_{5/2}$ state with the erbium ions in the $^4I_{13/2}$ state (Fig. 6b).

3. The third mechanism consists of four energy-transfer stages.[14,15] The first two transfer stages are identical with those of the first mechanism. These are followed by the interaction of the ytterbium ions in the ground state $^2F_{7/2}$ with the erbium ions in the state $^4S_{3/2}$; this interaction populates the level $^4I_{13/2}$ of the erbium ions. The last and fourth transfer stage is identical with the second stage of the second mechanism, i. e., interaction of Yb^{3+} ions in the $^2F_{5/2}$ state with erbium ions in the $^4I_{13/2}$ state, and leads to population of the $^4F_{9/2}$ state (Fig. 6c).

4. The fourth mechanism proceeds likewise in four stages.[16,17] In contains in their entirety the two stages of the mechanism that populates the $^4S_{3/2}$ state and leads to the onset of the green emission. The first stage is the interaction of ytterbium ions in the $^2F_{5/2}$ state and erbium ions in the $^4S_{3/2}$ state, as a result of which the erbium ions are excited to the $^2G_{7/2}$ state, followed by intracenter relaxation into the $^4G_{11/2}$ state. The last and fourth transfer act is due to the interaction of the ytterbium atoms in the ground state and erbium ions in the state $^4G_{11/2}$, which leads to excitation of the ytterbium ions to the $^2F_{3/2}$ level and of erbium ions to the $^4F_{9/2}$ level (Fig. 6d).

5. The fifth mechanism allows for an interation of erbium ions in excited states[18] in addition to the interaction of the ytterbium and erbium ions in excited states. The population of the $^4F_{7/2}$ state proceeds via the mechanism that produces the green emission. On the other hand the third energy transfer act is due to the interaction of the erbium ions in the states $^4F_{7/2}$ and $^4I_{11/2}$, and leads to population of the $^4F_{9/2}$ states in both erbium ions (Fig. 6e).

6. The sixth mechanism differs from all the preceding ones in that the first act of energy transfer[19] is supposed to be an essentially nonresonant interaction of the ytterbium ions in the $^2F_{5/2}$ state with the erbium ions in the $^4I_{15/2}$ state, leading to population of the $^4I_{13/2}$ state of the erbium ions. The second transfer act leads to population of the $^4F_{9/2}$ state via interaction between the ytterbium ions in the $^2F_{5/2}$ state with the erbium ions in the $^4I_{13/2}$ state, in analogy with the second mechanism (Fig. 6f).

We shall not discuss in detail the advantages and shortcomings of each of the considered mechanisms. We note only that the much more complicated description of the population of the highly excited states of the erbium ions in the last four mechanisms compared with the first two is justified to some degree. This is due to the need for explaining the experimentally observed dependences of the intensity of the emission from the $^4F_{9/2}$ level of the erbium ions on the intensity of the exciting IR radiation in certain hosts.

The first two mechanisms should lead to a quadratic dependence. Experiment, however, has shown for some hosts a cubic dependence,[16,17] which follows from the third and fourth mechanisms, as well as a sublinear dependence[18] that is implied in the fifth mechanism. We note also that the only methods used to distinguish between the mechanisms that populate the $^4F_{9/2}$ state were based on stationary excitation, and no use was made of the most informative kinetic methods. An exception is Ref. 14, in which the kinetics of the emission from the $^4F_{9/2}$ level of the erbium ion in an La_2O_2S host was attributed to the third mechanism. No alternate mechanisms were considered, however.

As will be shown below, our analysis of the kinetic equations for the description of the population of the $^4F_{9/2}$ state of the erbium ions under IR excitation, and the comparison with the obtained experimental data, make it possible to identify uniquely the mechanism whereby the highly excited states of the erbium ion are populated.

We have solved the standard kinetic equations.[9,10,14] We shall not specify at first the concrete mechanism whereby the excitation reaches the radiative states of the erbium ions following the IR excitation. We then obtain automatically for the populations of the levels $^4F_{9/2}$ and $^4S_{3/2}$

$$n_5(t)=A_1e^{-a_5^*t}\left[\int\Phi_5e^{a_5^*t}\,dt+A_2\right], \tag{1}$$

$$n_6(t)=B_1e^{-a_6^*t}\left[\int\Phi_6e^{a_6^*t}\,dt+B_2\right], \tag{2}$$

where A_1, A_2, B_1, and B_2 are constants that do not depend on the time; a_5^* and a_6^* are the probabilities of the deactivation of the states $^4F_{9/2}$ and $^4S_{3/2}$ of the erbium ions, respectively, Stokes-excited in the presence of ytterbium ions; Φ_5 and Φ_6 are the respective population functions of the erbium-ion states $^4F_{9/2}$ and $^4S_{3/2}$ determined by the concrete mechanisms that populate these states in anti-Stokes excitations, i.e., Φ_5 and Φ_6 are determined entirely by the populations of the levels that participate in the intermediate stages of energy summation.

Using for the linearization of the complete system of kinetic equation the standard assumptions, it is easy to obtain analytic solutions for n_5 and n_6 for all the mechanisms considered above, except the fifth, and this is what we did. The obtained expressions, however, are cumbersome and do permit comparison of theory with experiment. It is more useful to consider one limiting case of interaction of ytterbium and erbium in the respective intermediate states $^2F_{5/2}$ and $^4I_{11/2}$, namely the case of a strong incoherent interaction, defined by the condition

$$\overleftarrow{P}_1N_0,\ \overrightarrow{P}_1n_0\gg A_2,\ a_3, \tag{3}$$

where P_1 is the constant of energy transfer between the $^2F_{5/2}$ level of the ytterbium ion and the $^4I_{11/2}$ level of the erbium ion (the arrow indicates the transfer direction); N_0 and n_0 are the concentrations of the ytterbium and erbium ions, respectively; A_2 is the probability of the deactivation of the $^2F_{5/2}$ of the ytterbium ion; a_3 is the probability of deactivation of the $^4I_{11/2}$ state of the erbium ion.

As shown in Refs. 9, 20, and 21, if the energy-donor system has in the absence of interaction a lifetime τ_1, and the energy acceptor system has a lifetime τ_2, then if condition (3) is satisfied both systems will emit with a single lifetime τ_{av} which in our notation can be written in the form

$$\tau_{\mathrm{av}}=\frac{\overleftarrow{P}_1N_0+\overrightarrow{P}_1n_0}{A_2\overleftarrow{P}_1N_0+a_3\overrightarrow{P}_1n_0}. \tag{4}$$

We then obtain for the population of the $^4S_{3/2}$ state of the erbium ion when excited in ytterbium ions in accord with the described mechanism

$$n_6(t)=\frac{N_{20}{}^2\overleftarrow{P}_1N_0\overrightarrow{P}_1n_0\overrightarrow{P}_2}{(\overleftarrow{P}_1N_0+\overrightarrow{P}_1n_0)^2(a_6^*-2\tau_{\mathrm{av}}^{-1})}\left(e^{-2t/\tau_{\mathrm{av}}}-e^{-a_6^*t}\right), \tag{5}$$

where N_{20} is the population of the $^2F_{5/2}$ state of the Yb^{3+} ion after the end of the action of the exciting pulse; $\overrightarrow{P}_2$ is the constant of energy transfer from the $^2F_{5/2}$ level of the Yb^{3+} ion to the $^4S_{3/2}$ level of the Er^{3+} ion, which is already in the state $^4I_{11/2}$. Similar expressions were obtained in Refs. 9 and 14.

We write down the expressions obtained by us for the populations of the $^4F_{9/2}$ state of the erbium ion for the various population mechanisms considered above (Fig. 6).

The first mechanism (Fig. 6a):

$$n_5(t)=\frac{N_{20}{}^2\overleftarrow{P}_1N_0\overrightarrow{P}_1n_0\overrightarrow{P}_2w_{65}}{(\overleftarrow{P}_1N_0+\overrightarrow{P}_1n_0)^2(a_6^*-2\tau_{\mathrm{av}}^{-1})}\left\{\frac{1}{a_5^*-2\tau_{\mathrm{cp}}^{-1}}e^{-2t/\tau_{\mathrm{av}}}-\frac{1}{a_5^*-a_6^*}e^{-a_6^*t}-\left(\frac{1}{a_5^*-2\tau_{\mathrm{av}}^{-1}}-\frac{1}{a_5^*-a_6^*}\right)e^{-a_5^*t}\right\}, \tag{6}$$

where w_{65} is the probability of relaxation from the state $^4S_{3/2}$ to the state $^4F_{9/2}$.

The second mechanism (Fig. 6b):

$$n_5(t)=\frac{N_{20}{}^2\overleftarrow{P}_1N_0\overrightarrow{P}_1n_0w_{32}\overrightarrow{P}_3}{(\overleftarrow{P}_1N_0+\overrightarrow{P}_1n_0)^2(\tau_{\mathrm{av}}^{-1}-a_2)}\left\{\frac{1}{a_5^*-a_2-\tau_{\mathrm{av}}^{-1}}e^{-(a_2+\tau_{\mathrm{av}}^{-1})t}-\frac{1}{a_5^*-2\tau_{\mathrm{av}}^{-1}}e^{-2t/\tau_{\mathrm{av}}}+\left(\frac{\tau_{\mathrm{av}}^{-1}-a_2}{(a_5^*-a_2-\tau_{\mathrm{av}}^{-1})(a_5^*-2\tau_{\mathrm{av}}^{-1})}\right)e^{-a_5^*t}\right\}, \tag{7}$$

where w_{32} is the probability of relaxation from the state $^4I_{11/2}$ to the state $^4I_{13/2}$; $\overrightarrow{P}_3$ is the constant of energy transfer from the level $^2F_{3/2}$ of the Yb^{3+} ion to the $^4F_{9/2}$ level of the Er^{3+} ion, which is already in the $^4I_{15/2}$ state; a_2 is the probability of deactivation of the $^4I_{13/2}$ state of the erbium ion.

Third mechanism (Fig. 6c):

$$n_5(t)=\frac{N_{20}{}^3(\overleftarrow{P}_1N_0)^2\overrightarrow{P}_1n_0\overrightarrow{P}_2\overleftarrow{P}_5N_0\overrightarrow{P}_3}{(\overleftarrow{P}_1N_0+\overrightarrow{P}_1n_0)^3(a_6^*-2\tau_{\mathrm{av}}^{-1})}\left\{\left(\frac{1}{2\tau_{\mathrm{av}}^{-1}-a_2}-\frac{1}{a_6^*-a_2}\right)\frac{1}{a_5^*-\tau_{\mathrm{av}}^{-1}-a_2}e^{-(a_2+\tau_{\mathrm{av}}^{-1})t}-\frac{(a_5^*-3\tau_{\mathrm{av}}^{-1})^{-1}}{2\tau_{\mathrm{av}}^{-1}-a_2}e^{-3t/\tau_{\mathrm{av}}}+\frac{(a_6^*-a_2)^{-1}}{a_5^*-a_6^*-\tau_{\mathrm{av}}^{-1}}e^{-(a_6+\tau_{\mathrm{av}}^{-1})t}-[\ldots]e^{-a_5^*t}\right\}, \tag{8}$$

where $\overleftarrow{P}_5$ is the constant of energy transfer from the $^4S_{3/2}$ level of the erbium ion to the $^4I_{13/2}$ level of the erbium ion, and the ytterbium ion goes over at that time from the ground to the excited state. Here and elsewhere [. . .] stands for the sum of the coefficients of all the preceding exponentials.

Fourth mechanism (Fig. 6d):

$$n_5(t)=\frac{N_{20}{}^3(\overleftarrow{P}_1N_0)^2\overrightarrow{P}_1n_0\overrightarrow{P}_2\overrightarrow{P}_4\overleftarrow{P}_4N_0}{(\overleftarrow{P}_1N_0+\overrightarrow{P}_1n_0)^3(a_6^*-2\tau_{\mathrm{av}}^{-1})}\left\{\frac{(a_5^*-3\tau_{\mathrm{av}}^{-1})}{a_7^*-3\tau_{\mathrm{av}}^{-1}}e^{-3t/\tau_{\mathrm{av}}}-\frac{(a_5^*-a_6^*-\tau_{\mathrm{av}}^{-1})^{-1}}{a_7^*-a_6^*-\tau_{\mathrm{av}}^{-1}}e^{-(a_6^*+\tau_{\mathrm{av}}^{-1})t}\left[\frac{a_5^*-a_7^*}{a_7^*-3\tau_{\mathrm{av}}^{-1}}-\frac{a_5^*-a_7^*}{a_7^*-a_6^*-\tau_{\mathrm{av}}^{-1}}\right]e^{-a_7^*t}-[\ldots]e^{-a_5^*t}\right\}, \tag{9}$$

where $\overrightarrow{P}_4$ is the constant of energy transfer to the $^4G_{7/2}$ level of the Er^{3+} ion as a result of summation of the energies of the states $^2F_{5/2}$ of Yb^{3+} and $^4S_{3/2}$ of Er^{3+}; $\overleftarrow{P}_4$ is the constant of the reverse transfer of energy from the level $^4G_{11/2}$ to the levels $^4F_{9/2}$ of Er^{3+} and $^2F_{5/2}$ of Yb^{3+}; a^* is the probability of deactivation of the $^4G_{11/2}$ state following Stokes excitation in the presence of Yb^{3+}.

Sixth mechanism (Fig. 6f):

$$n_5(t)=\frac{N_{20}{}^2(\overleftarrow{P}_1N_0)^2\overrightarrow{P}_3\overrightarrow{P}_6n_0}{(\overleftarrow{P}_1N_0+\overrightarrow{P}_1n_0)^2(\tau_{\mathrm{av}}^{-1}-a_2)}\left\{\frac{1}{a_5^*-a_2-\tau_{\mathrm{av}}^{-1}}e^{-(a_2+\tau_{\mathrm{av}}^{-1})t}-\frac{1}{a_5^*-2\tau_{\mathrm{av}}^{-1}}e^{-2t/\tau_{\mathrm{av}}}+\left(\frac{\tau_{\mathrm{av}}^{-1}-a_2}{(a_5^*-a_2-\tau_{\mathrm{av}}^{-1})(a_5^*-2\tau_{\mathrm{av}}^{-1})}\right)e^{-a_5^*t}\right\}, \tag{10}$$

where $\overrightarrow{P}_6$ is the constant of the direct nonresonant energy transfer from the level $^2F_{5/2}$ of Yb^{3+} to the level $^4I_{13/2}$ of Er^{3+}.

ANALYSIS OF EXPERIMENTAL RESULTS

The analysis of the mechanisms of population of the high-lying excited states of erbium ion following IR excitation via ytterbium ions shows that an investigation of the kinetics of the populations of these states permits an unambiguous interpretation of the mechanisms of their population. The experimental results show that in the case of the $Y_{0.87}Yb_{0.1}Er_{0.03}OCl$ system there is realized a case of strong incoherent interaction in the intermediate states. Indeed, the states $^2F_{5/2}$ of the ytterbium ions and $^4I_{11/2}$ of erbium ions emit with the same lifetime, 440 μsec, regardless of which of these ions is excited. When account is taken of the fact that $\vec{P}_1$ and $\bar{P}_1$ are different, owing to the presence of an energy gap in the energies of the transitions $^2F_{7/2} \to {}^2F_{5/2}$ of the Yb ions and $^4I_{15/2} \to {}^4I_{11/2}$ of the Er^{3+} ions,[22] satisfaction of the condition (3) should yield for τ_{av} a value, calculated from (4), of 450 μsec, in agreement with experiment. Accordingly, the observed evolution of the population of the state $^4S_{3/2}$ is well described by expression (5) (Fig. 4). We note that in Ref. 9 agreement was obtained between the calculated and experimental curves in the later stages of the damping for the $LaF_3 - Yb^{3+} - Er^{3+}$ crystal, whereas in Ref. 11 the agreement was in the region of the maximum of the population for the $La_2O_2S - Yb^{3+} - Er^{3+}$ system. The reasons are the single mechanism of populating the $^4S_{3/2}$ state and the realization of the regime of strong incoherent interaction.

The strong incoherent interaction determines also the rate of population of the $^4I_{13/2}$ state of the erbium ion when excited via ytterbium ions (Fig. 7). An analysis of this figure shows that in this case the increase of the population of the $^4I_{13/2}$ state takes place in a time $\sim\tau_{av}$, whereas in the case of excitation into high-lying erbium level this time is much shorter, a fact apparently determined by the rates of the transitions from the upper states to this level.

Figure 8 shows the time evolutions of the populations of the $^4F_{9/2}$ state of the erbium ion *IR*—excited via ytterbium ions for two possible population mechanisms, described by Eqs. (6) and (7), curve 1 of Fig. 8 is experimental. It is seen that the experimentally observed asymptotic behavior in the later stages of the decay process can be described within the framework of the second mechanism. However, a complete description of the experimental curve can be obtained only by combining the curves corresponding to different mechanisms; furthermore, analysis shows that there is only one combination, namely a combination of curves 2 and 3.

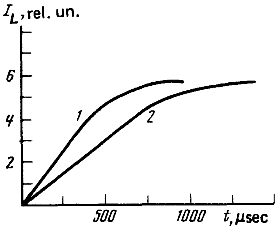

FIG. 7. Kinetics of population of the state $^4I_{13/2}$ in the systems $Y_{0.97}Er_{0.03}OCl$ (λ_{exc} 0.53 μm) (1) II $Y_{0.87}Yb_{0.1}Er_{0.03} \cdot OCl$ ($\lambda_{exc} = 1.06$ μm (2), λ_{exc} is the excitation wavelength.

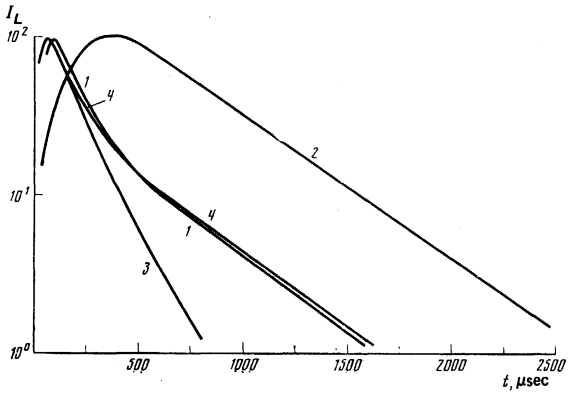

FIG. 8. Time evolution of the populations of the $^4F_{9/2}$ state of erbium: 1—experiment; 2 and 3—theoretical curves plotted in accord with Eqs. (6) and (7), respectively; 4—superposition of curves 1 and 3, taken with statistical weight 8:1.

Thus, the experimentally observed curve of the time evolution of the population of the $^4F_{9/2}$ state is well described by a combination of curves 1 and 3; the ratio of the excitation fluxes to this level in accord with the first and second mechanisms is 8 : 1 at the initial of time.1) At 300–400 μsec after the end of the excitation pulse, however, these fluxes become equal, and the second flux predominated during the later stages. This means that at the initial instant the $^4F_{9/2}$ level is populated by relaxation from the $^4S_{3/2}$ level, the relaxation rate being $(\frac{1}{2}\tau_{av})^{-1}$, while the $^4I_{13/2}$ level, with a population rate τ_{av}^{-1}, is note yet populated. Population of the $^4I_{13/2}$ level after the lapse of a time $\sim\tau_{av}$ switches over the channel through which the $^4F_{9/2}$ state is populated. In fact, by that time the $^4S_{3/2}$ level has become depleted and, accordingly, no longer feeds the $^4F_{9/2}$ state, the excitation of which now becomes excited on account of summation of the energies of the $^2F_{5/2}$ state of the ytterbium ions and the $^4I_{13/2}$ state of the erbium ions, at a rate τ_{av}^{-1}.

The experimentally observed flareup of radiation from the $^4F_{9/2}$ level, with a time constant 35 μsec, is determined by the lifetime of this state under Stokes excitation in the presence of ytterbium ions, as follows from (6). That the chosen combination of mechanisms for the description of the time evolutions of the population of the $^4F_{9/2}$ state erbium ions IR-excited into the ytterbium absorption band is correct, is confirmed also by the fact that, unlike the others, these two mechanisms yield a quadratic dependence of the radiation intensity on the exciting IR radiation in the stationary regime, as was indeed observed in experiment.[23] Our experiments on stationary excitations have confirmed this result. Attention should be called to the fact that the case of strong incoherent interaction is realized in not all hosts, even at high activator concentration. This is attested to by the result of Ref. 24 as well as by our preliminary measurements of the kinetics of the anti-Stokes radiation in the $(Y_{0.84}Yb_{0.1}Er_{0.06})_2O_2S)$ system.

We note in conclusion that the time evolutions of the populations of the low excited states influence the time evolution of the high-lying excited states of erbium even in a singly activated system. In fact, when the YOCl : Er^{3+} system is excited into the $^4S_{3/2}$ state (Fig. 3), multiphonon relaxation populates the $^4F_{9/2}$ level, from which luminescence with the proper lifetime begins. At the same time, all the remaining low-lying levels of erbium begin to be populated. This is due both the intracenter process and to cross relaxation processes. Therefore, after some time interval, the $^4F_{9/2}$ level starts to be populated not on account of relaxation from above, but on account of summation of the energies of two erbium ions, one of which is in the state $^4I_{11/2}$ and the other in the state $^4I_{13/2}$. The damping constant that will be observed at the later stages of the decay of the $^4F_{9/2}$ level is determined by the sum of the probabilities of the deactivation of the levels $^4I_{11/2}$ ($\tau = 2$ msec) and $^4I_{13/2}$ ($\tau = 5$ msec), yielding a value 1.4 msec. This is in good agreement with experiment.

1) It is appropriate to note that this result does not contradict the data of Ref. 6, inasmuch as under stationary excitation this relation does not hold and the second mechanism predominates.

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Relaxation currents in solids

V. K. Malinovskiĭ and B. I. Sturman

Institute of Automation and Electrometry, Siberian Division, USSR Academy of Sciences

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It is shown that in a crystal possessing a polar direction any process of relaxation to thermodyanmic equilibrium should be accompanied by a current. Unlike the currents connected with polarization direction ($\mathbf{j} = \dot{\mathbf{P}}$), relaxation currents do not destroy the existing charge separation but lead to the appearance and to maintenance of this separation. The nonuniformity that causes the charge separation can cause also electrization of the crystal for a prolonged time. Concrete models are considered, in which the disequilibrium of the crystal is attributed to an excess concentration of point defects. The question of activation of relaxation currents by light is considered.

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1. INTRODUCTION

The results of research into the photogalvanic effect in crystals that have no symmetry centers,[1,2] which has been intensively pursued in the past 4–5 years, point to the existence of a new class of transport phenomena. Namely, fluxes of charges, particles, and other physical quantities can exist in media without symmetry centers even in the absence of macroscopic inhomogeneities or external field. For these fluxes to exist it suffices only that there be no complete thermodynamic equilibrium in the medium. Thus, in the case of the photogalvanic effect a disequilibrium of the electron subsystem and a direct electric current are maintained by uniform illumination.

The disequilibrium of the medium need not necessarily be due to an external action. Even the presence of all types of defects (point, line, or volume) takes the medium quite far from thermodynamic equilibrium. The relaxation time of this disequilibrium obeys as a rule the activation law. Even at room temperatures, it can be quite long-on the order of months and years. Thus, a real crystal (as well as an amorphous medium) constitutes a highly unbalanced system that relaxes very slowly to equilibrium. It can be stated that in a medium