

OPTICAL RELAXATION OF Ho^{3+} AND Er^{3+} IONS IN THE CaF_2 LATTICE (TYPE I) IN THE
VISIBLE WAVELENGTH REGION

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The concentration and temperature dependence of the optical relaxation of Ho^{3+} and Er^{3+} ions in CaF_2 crystals in the visible wavelength region have been studied. Lifetimes of the non-radiative transitions have been determined. An anomalous concentration dependence for the lifetime of the $^4\text{S}_{3/2}$ level of the Er^{3+} ion at low temperatures was detected.

INTRODUCTION

THE study of the kinetics of the processes taking place in fluorite-type crystals with an admixture of rare-earth ions in an excited state is of definite current interest in connection with the use of such crystals in lasers. Investigations of the lifetimes of excited states within a wide temperature range allows one to determine the probability of nonradiative transitions. In addition, the study of the temperature dependence of fluorescence quenching allows one to determine the optimum concentration of active ions for oscillation. Up until the present only such laser materials as ruby, CaF_2 with Dy^{2+} [1], CaF_2 (type I) [1], and CaWO_4 with Nd^{3+} [2] have been studied in detail from this point of view.

The object of the present investigation was to study the lifetimes of excited states of Ho^{3+} and Er^{3+} ions in CaF_2 crystals (type I) in the visible wavelength region. The reasons for this choice were, first, the fact that we had been recently studying the possibility of fabricating from these crystals a laser emitting in the visible, and, secondly, the similarity of the Ho^{3+} and Er^{3+} fluorescence spectra in CaF_2 . We have obtained oscillation for Ho^{3+} at 77°K at a wavelength 5512.2 Å [3], whereas for Er^{3+} we have not succeeded in detecting any oscillation in the yellow-green using the same excitation system.

Stimulated emission of Ho^{3+} and Er^{3+} in the IR region was obtained earlier in crystals of $\text{Ca}(\text{NbO}_3)_2$, CaWO_4 , and CaF_2 [4-8]. The values of the lifetimes of excited Er^{3+} states in CaF_2 — $^4\text{S}_{3/2}$ ($\lambda_{\text{center}} = 5450 \text{ Å}$) and $^4\text{F}_{9/2}$ ($\lambda_{\text{center}} = 6500 \text{ Å}$)—

are given by Pollack [9] for one particular concentration.

In the present work we have investigated the lifetimes of the excited states $^5\text{S}_2$ and $^5\text{F}_2$ in Ho^{3+} and $^4\text{S}_{3/2}$ and $^4\text{F}_{9/2}$ in Er^{3+} in CaF_2 crystals within the temperature range from 77°K to 300°K, with activator concentrations ranging from 0.01 to 2.0% by weight. The effect of nonradiative transitions upon the decrease of the lifetimes of excited states was analyzed and one possible cause for the failure to obtain oscillation in the yellow-green spectral region for Er^{3+} in CaF_2 crystals at 77°K is discussed.

DISCUSSION OF EXPERIMENTAL RESULTS

This investigation was carried out with CaF_2 crystals (type I) doped with Ho^{3+} and Er^{3+} and grown by the dipped crucible technique in a measured fluorinating atmosphere with activator concentration from 0.01 to 2.0% by weight. Cylindrical samples of various lengths with polished end faces and lateral surfaces were cut for study from crystals about 140 mm in length and 12 mm in diameter.

The tau-meter technique described earlier [2] was utilized for measuring the optical relaxation. The samples were excited by light flashes from a stroboscopic lamp (type ISSh-100-3). The length of the flashes was about 10 μsec with an energy of about 3 Joules. The fluorescence was detected with a multi-alkali photocathode photomultiplier mounted upon a type ZMR-3 monochromator. The photomultiplier signal was fed into an ENO-1 (C1-4) oscilloscope. Since the yellow-green and the red fluorescences of Ho^{3+} and Er^{3+} in CaF_2 have different τ and intensity, we carried out

¹ CaF_2 (type I) crystals contain no oxygen.

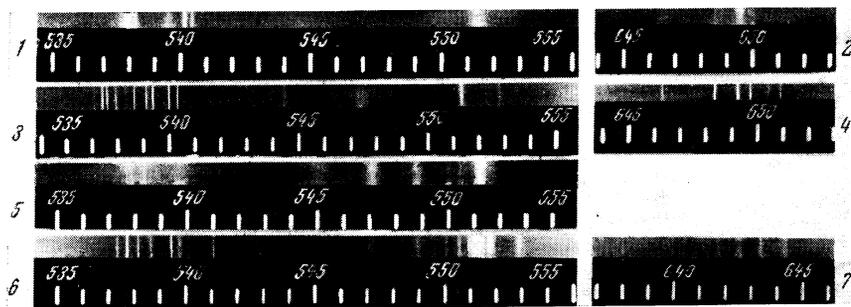


FIG. 1. Fluorescence spectra of Ho³⁺ and Er³⁺ ions in CaF₂ (type I): 1 – the ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition in Er³⁺ ions at 300°K, 2 – the ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition in Er³⁺ ions at 300°K, 3 – the ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition in Er³⁺ ions at 77°K, 4 – the ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition in Er³⁺ ions at 77°K, 5 – the ${}^5S_2 \rightarrow {}^5I_8$ transition in Ho³⁺ ions at 300°K, 6 – the ${}^5S_2 \rightarrow {}^5I_8$ transition in Ho³⁺ ions at 77°K, 7 – the ${}^5F_5 \rightarrow {}^5I_8$ transition in Ho³⁺ ions at 77°K.

individual excitations of the respective fluorescing levels. The time dependence of the fluorescence quenching was photographed from an oscilloscope screen whose sweep was calibrated by time markers. The precision of this measurement was $\pm 20 \mu\text{sec}$.

It is well known that Ho³⁺ and Er³⁺ ions in fluorite-type crystals fluoresce brightly in the yellow-green (5500 Å) and red (6500 Å) portions of the spectrum. These wavelengths correspond in Ho³⁺ to the transitions ${}^5S_2 \rightarrow {}^5I_8$ and ${}^5F_5 \rightarrow {}^5I_8$, and in Er³⁺ to the transitions ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ and ${}^4F_{9/2} \rightarrow {}^4I_{15/2}$. Figure 1 shows the fluorescence spectra of these ions in a CaF₂ crystal (type I) taken at 300 and 77°K with a PGS-2 instrument. As remarked above, stimulated emission was obtained with Ho³⁺ at 5512 Å.

CaF₂-Ho³⁺ crystals. Figure 2 shows a typical oscillogram of fluorescence quenching in a CaF₂ crystal with Ho³⁺ concentration about 0.1% at 77°K, for the transition ${}^5S_2 \rightarrow {}^5I_8$. It can be seen that the fluorescence quenching curve differs but little from exponential. Clearly, this can be well understood on the basis of the known fact that trivalent rare-earth ions are situated in the CaF₂ crystal at different structural centers. Each spectrum will possess its own characteristic excited-state lifetime. Thus, in Fig. 2 we show the quenching curve averaged over all spectra, i.e., the observed dependence is the sum of the quenching exponentials for the various spectra. Since the individual optical spectra of Ho³⁺ ions in CaF₂ (type I) have not as yet been identified, we shall consider subse-

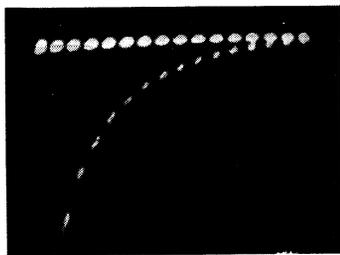


FIG. 2. Oscillogram of the quenching of fluorescence of a CaF₂ crystal containing about 0.1% Ho³⁺ at 77°K; transition ${}^5S_2 \rightarrow {}^5I_8$. Time markers are separated by 200 μsec .

quently only the summed lifetime. Figure 3 gives the dependence of the quenching lifetime of the fluorescence for the excited 5S_2 and 5F_5 levels at 300 and 77°K. From Fig. 3a it can be seen that on going from room temperature to that of liquid nitrogen, the lifetimes of the excited levels lengthen. This is because the probability of non-radiative transitions for a given ion at 300°K is comparable to the probabilities of spontaneous transitions. From the simple expression $1/\tau_{\Sigma} = 1/\tau_{\text{sp}} + 1/\tau_{\text{non}}$ we can determine the lifetime of nonradiative transitions for excited states. Graphs of the results of such calculations are given in Fig. 3,b for a CaF₂ crystal containing about 0.1% by weight of Ho³⁺ within a temperature range from 300° to 77°K.

Studies have shown that variation of the temperature below 100°K leads to practically no increase in the lifetime in the case of Nd³⁺ in CaF₂ and CaWO₄ [2] and Dy²⁺ in CaF₂ [1]. Therefore we have not measured the fluorescence quenching in our samples at temperatures lower than this.

CaF₂-Er³⁺ crystals. Unlike the case of Ho³⁺, the optical spectra of erbium ions in CaF₂ have been studied in detail [9]. Electron paramagnetic resonance (EPR) studies have shown [10] that the Er³⁺ ions in a CaF₂ (type I)²⁾ lattice are situated in fields of tetragonal, cubic, and trigonal symmetry. The strongest lines arise from ions with an environment of tetragonal symmetry.

As in the case of Ho³⁺, the quenching of fluorescence for CaF₂-Er³⁺ (type I) crystals differs little from the experimental result. Based upon the results of the EPR study of the spectrum, we can presume that the quenching curve in general is determined by the fluorescence of ions situated in a tetragonal environment. By investigating the concentration dependence of τ of the ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition (5500 Å) at low temperatures, it was found that the decrease in τ is smooth up to an Er³⁺ concentration of about 0.1%. With a further increase in the Er³⁺ content a sharp drop is ob-

²⁾CaF₂ - Er³⁺ (type I) corresponds to type II in [10].

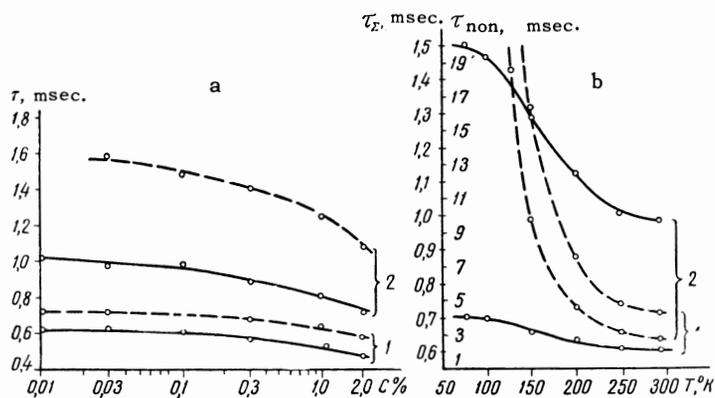


FIG. 3. a – concentration dependence of τ for Ho^{3+} ions in CaF_2 (1 – $^5\text{S}_2 \rightarrow ^5\text{I}_8$ transition, 2 – $^5\text{F}_5 \rightarrow ^5\text{I}_8$ transition, solid lines correspond to 300°K , dashed – 77°K); b – temperature dependence of τ_x (solid lines) and τ_{non} (dashed) for CaF_2 containing about 0.1% Ho^{3+} .

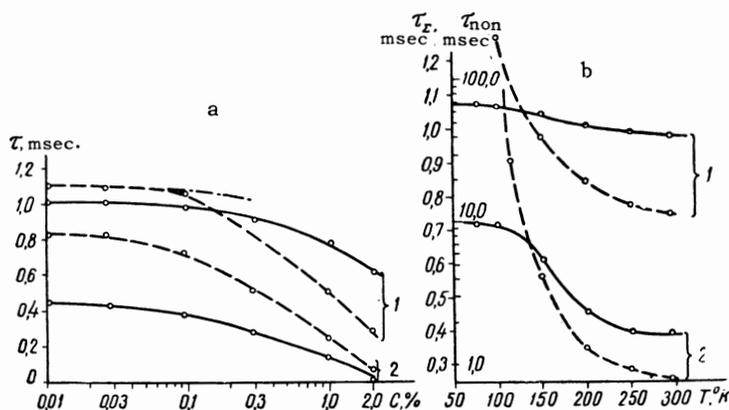


FIG. 4. a – concentration dependence of τ for Er^{3+} ions in CaF_2 (1 – $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition, 2 – $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition; solid lines correspond to 300°K , dashed – 77°K), b – temperature dependence of τ_x (solid line), τ_{non} (dashed line) for CaF_2 containing about 0.1% Er^{3+} .

served, differing from the ordinary concentration decrease in τ (dash-dot line in Fig. 4,a). For the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transition (6500 Å) and the $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transition at 300°K the decrease in τ is somewhat smoother. Figure 4,a shows the measured fluorescence quenching of Er^{3+} in CaF_2 (type I) as a function of concentration at 300 and 77°K . The reason for the odd behavior of the curve characterizing the variation of τ with concentration at 77°K is not clear.

Our spectroscopic investigations of Er^{3+} ions in CaF_2 (type I) have shown that with a sufficiently powerful excitation pulse it is possible to induce absorption from the metastable $^4\text{S}_{3/2}$ level to the $^4\text{G}_{9/2}$ level situated about $36,000\text{ cm}^{-1}$ above the ground level at a frequency corresponding to the most intense fluorescence line (5511 Å). The absorption spectrum of the $^4\text{G}_{9/2}$ level of Er^{3+} ions in CaF_2 (type I) at 77°K is shown in Fig. 5. On this figure the dashes denote the Stark component of the $^4\text{G}_{9/2}$ level, to which transitions from the $^4\text{S}_{3/2}$ level are possible at the frequency of the strongest fluorescence line (5511 Å).

This fact may explain the difficulty in producing stimulated emission in $\text{CaF}_2\text{-Er}^{3+}$ (Type I) at the brightest line, about 5511 Å. Despite this, we have set up an experiment to obtain oscillation at this wavelength. The experiment was quite similar to

that with which oscillation at a wavelength of about 5511 Å in $\text{CaF}_2\text{-Ho}^{3+}$ was detected. A crystal 75 mm in length and 6.5 mm in diameter with well polished confocal end faces, on which multilayer dielectric reflecting coatings were deposited, was placed in the illumination system described in [3]. We did not succeed in detecting any oscillation at 77°K . The maximum electrical energy supplied by the lamp was about 3000 Joules.

CONCLUSIONS

The results of this investigation of quenching times of Ho^{3+} and Er^{3+} fluorescence in CaF_2 (type I) crystals as a function of temperature and concentration allow us to draw the following conclusions.

1. Upon increase in the Ho^{3+} and Er^{3+} ion concentration in CaF_2 , the lifetimes of the excited states are reduced. As previously noted [2], the reason for this reduction is not completely clear.

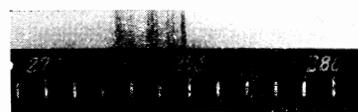


FIG. 5. Absorption spectrum of Er^{3+} ions in CaF_2 (type I) at 77°K – transition $^4\text{I}_{15/2} \rightarrow ^4\text{G}_{9/2}$.

It may be related to the distortion of the symmetry of the rare-earth ion environment, or it may be due to the most probable magnetic dipole-dipole interaction of the ions with one another.

2. At room temperature a major role is played by nonradiative transitions, markedly reducing the lifetimes of the spontaneous transitions. At 77°K the lifetimes of the excited levels are determined only by spontaneous transitions.

3. An anomalous concentration dependence for τ is exhibited by Er³⁺ in CaF₂ (type I) for the transition $^4S_{3/2} \rightarrow ^4I_{15/2}$ at 77°K.

4. The difficulty in obtaining stimulated emission in the illuminating system used at a wavelength of about 5511 Å for Er³⁺ ions in CaF₂ (type I) is related to the possible absorption from the metastable $^4S_{3/2}$ level to the $^4G_{9/2}$ level. Nonetheless, it is possible to obtain oscillation in the yellow-green portion of the spectrum, provided one uses the strong ultraviolet absorption band for excitation.

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¹Zolotov, Prokhorov, and Shipulo, JETP **49**, 720 (1965), Soviet Phys. JETP **22**, 498 (1966).

²Kaminskiĭ, Kornienko, and Prokhorov, JETP **48**, 1262 (1965), Soviet Phys. JETP **21**, 844 (1965).

³Voron'ko, Kaminskiĭ, Osiko, and Prokhorov, JETP Letters **1**, 5 (1965), transl. **1**, 3 (1965).

⁴L. F. Johnson, J. Appl. Phys. **34**, 897 (1963).

⁵Johnson, Boyd, and Nassau, Proc. IRE **50**, 87 (1962).

⁶Z. J. Kiss and R. C. Duncan, Jr. Proc. IRE **50**, 1531 (1962).

⁷Voron'ko, Zverev, and Prokhorov, JETP **48**, 1529 (1965), Soviet Phys. JETP **21**, 1023 (1965).

⁸Ballmann, Porto, and Yariv, J. Appl. Phys. **34**, 3155 (1963).

⁹S. A. Pollack, J. Chem. Phys. **40**, 2751 (1964).

¹⁰Voron'ko, Zverev, Meshkov, and Smirnov, FTT **6**, 2799 (1964), Soviet Phys. Solid State **6**, 2225 (1965).

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