

OPTICAL  $\text{Er}^{3+}$  CENTERS IN CUBIC CRYSTALS OF THE FLUORITE TYPE

Yu. K. VORON'KO, A. A. KAMINSKIĬ, and V. V. OSIKO

P. N. Lebedev Physics Institute, Academy of Sciences, U.S.S.R.; Crystallography Institute, Academy of Sciences, U.S.S.R.

Submitted to JETP editor July 21, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) 50, 15-22 (January, 1966)

The spectral regularities of  $\text{CaF}_2\text{-Er}^{3+}$  crystals (Type I) are analyzed by the concentration series method<sup>[9]</sup> and the selective excitation method<sup>[8]</sup> in a concentration range from 0.003 to 2.0 weight % of  $\text{ErF}_3$  and temperatures between 300 and 4.2° K. It is found that the erbium ions introduced into the crystal are distributed among several centers which differ with respect to their structure. The results obtained are compared with EPR data. The effect of yttrium fluoride on the distribution of  $\text{Er}^{3+}$  is studied.

## INTRODUCTION

RECENTLY there has been renewed interest shown in fluorite crystals activated with rare-earth ions ( $\text{TR}^{2+}$ ,  $\text{TR}^{3+}$ ). This is because of their use in lasers. As has already been noted by Feofilov<sup>[1]</sup> and other authors<sup>[2, 3]</sup> fluorite crystals containing rare-earth elements as impurities are complex systems containing a collection of optical centers, the relative number of which depends on technological characteristics, the concentration of rare-earth ions, and the concentration of certain other impurities. As a result, the optical spectra of  $\text{TR}^{3+}$  in  $\text{CaF}_2$  are a superposition of the spectra of different types of centers with their individual Stark structures. In order to study the character of the distribution of  $\text{TR}^{3+}$  over centers of different structure and estimate the concentration of these centers, it is necessary to analyze the optical spectra and separate out from them the lines belonging to each of these centers. As our spectral investigations of  $\text{CaF}_2\text{-Nd}^{3+}$  crystals<sup>[3]</sup> and the investigation of Porto and Yariv<sup>[4]</sup> on  $\text{CaF}_2\text{-U}^{3+}$  have shown, the centers differ in their capabilities for laser action. Therefore, by studying the distribution of an active impurity among centers of different structure, we have the opportunity, by changing the conditions of crystal growth and adding specific impurities, to obtain crystals with the best properties for laser action.

The symmetry of the crystalline electric field of different centers of  $\text{Er}^{3+}$  in  $\text{CaF}_2$  was studied by EPR by Ranon and Low.<sup>[5]</sup> They discovered five different kinds of symmetry: cubic, two tetragonal types, and two trigonal types. However, there is no information in<sup>[5]</sup> about the technology

of the crystals investigated, which makes the comparison of these data with the results obtained by other authors<sup>[6, 7]</sup> difficult.

The EPR spectrum of  $\text{CaF}_2\text{-Er}^{3+}$  crystals (Type I)<sup>[1]</sup> was investigated in a paper by one of the present authors.<sup>[6]</sup> It was shown that tetragonal symmetry of the surroundings of the erbium ion is the most characteristic for this type of crystal. The investigations also demonstrated the existence of EPR spectra different from tetragonal, the intensity of which, however, was considerably weaker for the concentrations of erbium studied.

Pollack<sup>[7]</sup> has considered the optical spectra of  $\text{CaF}_2\text{-Er}^{3+}$  crystals in some detail. He investigated the absorption, luminescence, and excitation spectra in the spectral region 0.12 to 1.7  $\mu$  at temperatures 300, 77, and 4.2° K. As the concentration of  $\text{Er}^{3+}$  was changed, a redistribution of the luminescence intensity among groups of lines corresponding to transitions between levels with different J was noted. The Stark structure of the spectra within each of these groups was not investigated.

In one of our previous papers<sup>[8]</sup> we showed the possibility of analyzing the Stark structure of  $\text{TR}^{3+}$  spectra in  $\text{CaF}_2$  by the method of selective excitation in the case of  $\text{CaF}_2\text{-Er}^{3+}$ . It was found that in the investigated groups of absorption ( ${}^4\text{I}_{15/2} \rightarrow {}^2\text{H}_{11/2}$ ) and luminescence ( ${}^4\text{S}_{3/2} \rightarrow {}^4\text{I}_{15/2}$ ), lines are present which belong to at least three different types of optical centers.

The goal of the present paper was to study, with the aid of methods we previously derived—the concentration series method<sup>[9]</sup> and the method of se-

<sup>1)</sup>In<sup>[6]</sup> these crystals were called Type II.

lective excitation,<sup>[8]</sup> the character of the distribution of erbium ions among the centers of different structure and to construct the energy level diagram for each of them.

### CRYSTALS FOR THE INVESTIGATION

The concentration series of  $\text{CaF}_2\text{-Er}^{3+}$  crystals (Type I) was prepared by lowering the crucible in a measured fluoridizing atmosphere, the composition of which guaranteed the removal of contaminating oxides. The erbium concentration was varied within the limits 0.003 to 2 weight% (as  $\text{ErF}_3$ ). Fluorite crystals with the additions 0.03%  $\text{ErF}_3$  + 2%  $\text{YF}_3$  and 0.4%  $\text{ErF}_3$  + 0.5%  $\text{YF}_3$  were also grown in order to investigate the effect of yttrium impurity on the distribution of  $\text{Er}^{3+}$  ions over the different optical centers. A detailed description of the technology of fluorite crystal (Type I) growth and the control of impurity concentration is given in [3, 10].

### ABSORPTION, LUMINESCENCE, AND EXCITATION SPECTRA

**Absorption spectra.** The absorption spectra of the crystals were recorded at  $T = 300^\circ\text{K}$  with an SP-700 instrument in the wavelength interval 0.185–2.5  $\mu$  (Fig. 1). A detailed investigation of the absorption spectra of the  $\text{CaF}_2\text{-Er}^{3+}$  crystals was carried out on the  ${}^4\text{I}_{15/2} \rightarrow {}^4\text{F}_{5/2}$  (447.0  $\text{m}\mu$ ),  ${}^4\text{I}_{15/2} \rightarrow {}^2\text{H}_{11/2}$  (525.0  $\text{m}\mu$ ), and  ${}^4\text{I}_{15/2} \rightarrow {}^4\text{S}_{3/2}$  (539.0  $\text{m}\mu$ ) groups in instruments of high resolving power at 77 and 4.2° K. The absorption spectra at 4.2° K were photographed in a DFS-13. The absorption spectra at 77° K were recorded in a DFS-12 diffraction spectrometer. The experimental arrange-

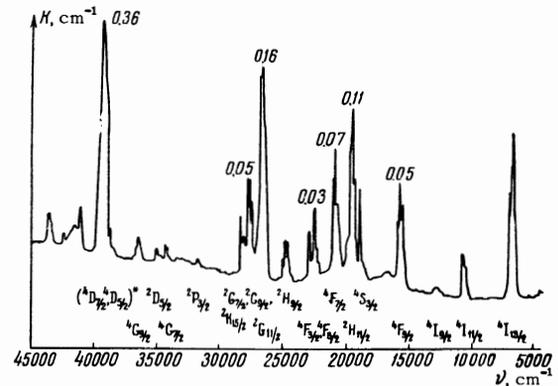


FIG. 1. Absorption spectrum of a  $\text{CaF}_2\text{-Er}^{3+}$  (0.3%) crystal at 300°K.

ment and method of measurement were similar to those described in [3].

The Stark structure of the absorption spectrum can be analyzed by using any of the other groups. The investigated groups with small value of  $J$  were chosen, however, because of their analytical simplicity (a small value of  $J$  corresponds to a small number of Stark components). Figure 2 shows the concentration series of absorption curves for  $\text{CaF}_2\text{-Er}^{3+}$ . As can be seen, as the  $\text{Er}^{3+}$  concentration increases, the structure of the investigated groups changes significantly: the number of lines increases and their intensity is redistributed. In going from the spectra obtained at 77° K to those taken at 4.2° K, the total number of lines within each group decreases.

**Luminescence spectrum.** As is known from Pollack's work,<sup>[7]</sup> when excited in the 250- $\text{m}\mu$  band the luminescence spectrum of  $\text{CaF}_2\text{-Er}^{3+}$  takes up the entire visible and the near infrared regions. In our work, the excitation was carried

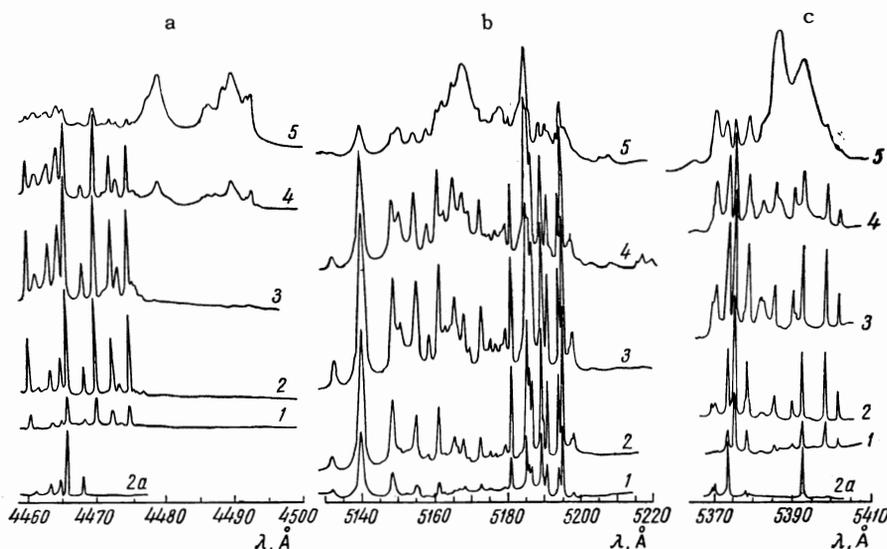


FIG. 2. Absorption spectra of  $\text{CaF}_2\text{-Er}^{3+}$  crystals at 77°K: a – for the transition  ${}^4\text{I}_{15/2} \rightarrow {}^4\text{F}_{5/2}$ , b –  ${}^4\text{I}_{15/2} \rightarrow {}^2\text{H}_{11/2}$ , c –  ${}^4\text{I}_{15/2} \rightarrow {}^4\text{S}_{3/2}$ . Concentration of  $\text{Er}^{3+}$  (in weight %): curve 1 – 0.01; 2 – 0.03; 3 – 0.1; 4 – 0.3; 5 – 1. Spectrum 2a – concentration 0.03%,  $T = 4.2^\circ\text{K}$ .

out at longer wavelengths, and so the luminescence spectrum was located in the region of wavelengths greater than  $520 \text{ m}\mu$ . Only the band near  $540 \text{ m}\mu$ , which corresponds to the transition  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ , was analyzed in detail, since it is structurally the most simple and is located in a convenient spectral region. The spectra were recorded with a DFS-12 spectrometer at 300 and  $77^\circ \text{K}$ . The method of measurement was the same as in [3]. The concentration series of luminescence spectra are shown in Fig. 3. The characteristic feature of these spectra, as in the case of the absorption spectra considered above, is their clearly expressed concentration dependence.

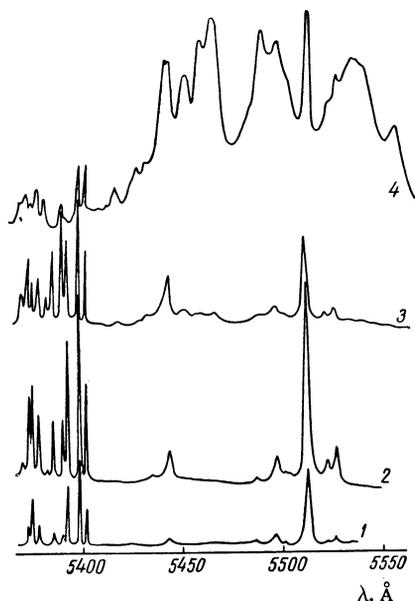


FIG. 3. Luminescence spectrum of  $\text{CaF}_2 - \text{Er}^{3+}$  crystals at  $77^\circ \text{K}$ . Transition  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ . Concentration of  $\text{Er}^{3+}$  (in weight %): curve 1 - 0.003; 2 - 0.03; 3 - 0.3; 4 - 2.

In [8] we gave the development of the luminescence spectrum of the transition  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$  with respect to the wavelengths of the lines of the exciting group  ${}^4I_{15/2} \rightarrow {}^2H_{11/2}$  for a crystal of

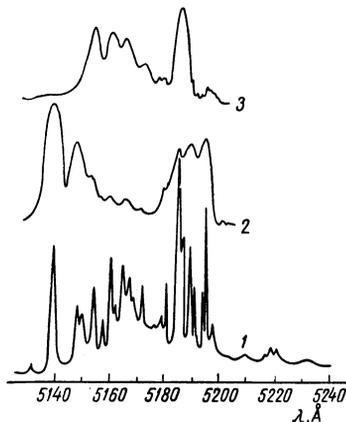


FIG. 4. Absorption and excitation spectra of a  $\text{CaF}_2 - \text{Er}^{3+}$  (0.3%) crystal at  $77^\circ \text{K}$ : 1 - absorption spectrum of the group  ${}^4I_{15/2} \rightarrow {}^2H_{11/2}$ , in which the excitation was carried out; 2 - microphotogram of the luminescence line of the L spectrum in the group  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ ; 3 - microphotogram of the luminescence line of the M spectrum in the group  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ .

$\text{CaF}_2 - \text{Er}^{3+}$  (0.3%). Additional treatment of these results has enabled us to obtain the excitation spectra for the individual luminescence lines in the group  ${}^4S_{3/2} \rightarrow {}^4I_{15/2}$ . These spectra are given in Fig. 4.

Figure 5 shows the absorption and luminescence spectra of the  $\text{CaF}_2 - \text{Er}^{3+}$ ,  $\text{Y}^{3+}$  crystals, recorded with a DFS-12 at  $77^\circ \text{K}$ . By comparing the spectra 5-3 and 5-6 with the spectra 5-1, 5-2, 5-4, and 5-5, it is seen that the introduction of yttrium impurity into the initial  $\text{CaF}_2 - \text{Er}^{3+}$  crystals does not evoke the appearance of new lines. There is only a redistribution of the intensities of the lines that were present in the crystals without yttrium.

## DISCUSSION OF THE RESULTS

The term scheme for the  $\text{Er}^{3+}$  ion (electronic configuration  $4f^{11}$ ) is well known. [11] The experimental position of these terms for the  $\text{Er}^{3+}$  ion in  $\text{CaF}_2$  was determined by Pollack. [7] However, the Stark structure of each of these terms has not as

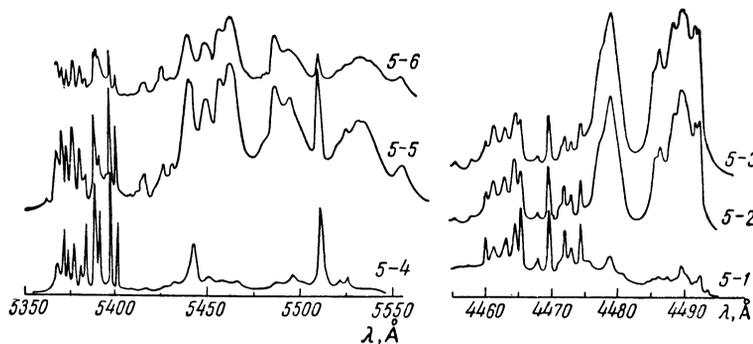


FIG. 5. Absorption and luminescence spectra of  $\text{CaF}_2 - \text{Er}^{3+}$  and  $\text{CaF}_2 - \text{Er}^{3+}, \text{Y}^{3+}$  crystals at  $77^\circ \text{K}$ : 5-1 - absorption of a  $\text{CaF}_2 - \text{Er}^{3+}$  (0.3%) crystal; 5-2 - absorption spectrum of a  $\text{CaF}_2 - \text{Er}^{3+}$  (1%) crystal; 5-3 - absorption spectrum of a  $\text{CaF}_2 - \text{Er}^{3+}$  (0.4%),  $\text{Y}^{3+}$  (0.5%) crystal; 5-4 - luminescence spectrum of a  $\text{CaF}_2 - \text{Er}^{3+}$  (0.3%) crystal; 5-5 - luminescence spectrum of a  $\text{CaF}_2 - \text{Er}^{3+}$  (1.0%) crystal; 5-6 - luminescence spectrum of a  $\text{CaF}_2 - \text{Er}^{3+}$  (0.4%),  $\text{Y}^{3+}$  (0.5%) crystal.

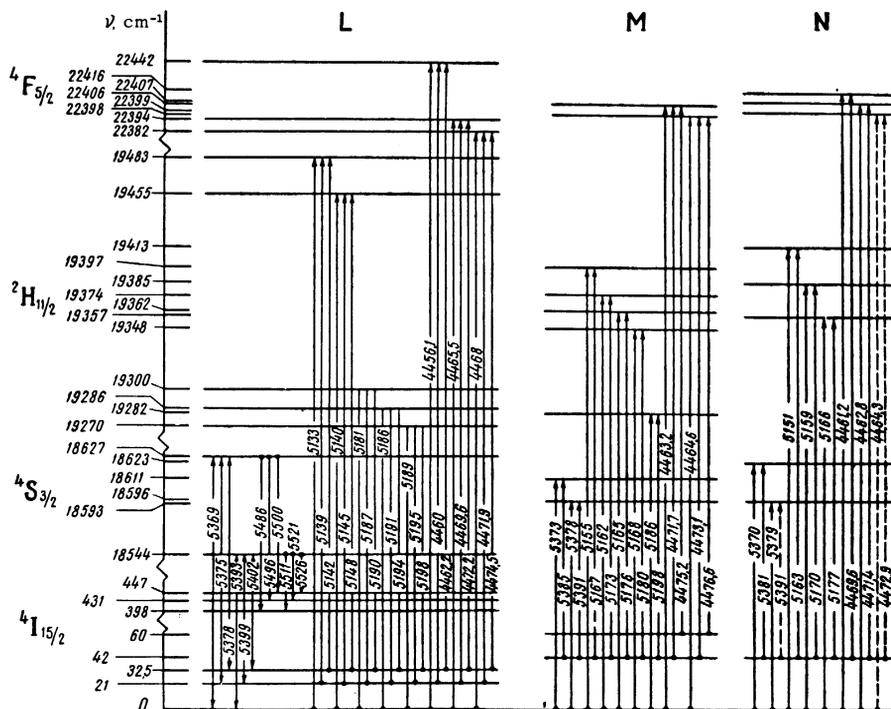


FIG. 6. Energy-level diagrams for  $\text{Er}^{3+}$  in  $\text{CaF}_2$  (Type I) for three types of centers.

yet been deciphered. The attempt undertaken in [7] to interpret the structure of the group  $4I_{15/2} \rightarrow 4S_{3/2}$  as electron-vibrational appears unconvincing, since the author did not take into account the multiplicity of optical  $\text{Er}^{3+}$  centers in fluorite crystals.

The recently developed ideas about the existence in  $\text{CaF}_2\text{-TR}^{3+}$  of several kinds of optical centers and methods for isolating the spectral lines belonging to these centers<sup>[1-3, 5, 12]</sup> have facilitated the analysis of the Stark structure in the individual groups of the absorption and luminescence spectra of  $\text{CaF}_2\text{-Er}^{3+}$  (type I) crystals. In accordance with the concentration-series method, the dependence of the absorption coefficient on  $\text{Er}^{3+}$  concentration was constructed for the lines of the spectra of Fig. 2. According to the character of the change in absorption coefficient the curves were divided into four families (L, M, N, P), which correspond to the different types of optical centers.<sup>2)</sup> Further, the lines corresponding to transitions from the lowest Stark components were determined from the change in the form of the spectra in going from nitrogen to helium temperature. Additional information about the identification of lines in the group  $4I_{15/2} \rightarrow 2H_{11/2}$  with one optical center or other was obtained with the aid of the excitation spectra.

Figure 4 shows the entire absorption spectra of a crystal of  $\text{CaF}_2\text{-Er}^{3+}$  (0.3%) in the group  $4I_{15/2} \rightarrow 2H_{11/2}$ , as well as microphotograms of the excitation spectra of the individual lines belonging to the L and M centers. It is clearly seen from the figure that the lines of the L spectrum are in the 5132–5148 and 5181–5197 Å regions, whereas the principal lines of the M spectrum are in the 5151–5186 Å region. The position of the higher components of the ground state  $4I_{15/2}$  for the L center was determined from the luminescence spectra. The question as to which of the two components of the upper level  $4S_{3/2}$  pertains to which luminescence line was resolved by comparing the spectra at 300 and 77° K.

It should be mentioned that all the methods used for identification of the spectral lines, by supplementing and checking one another, gave consistent results.

On the basis of these results, we constructed energy-level diagrams for each of the centers L, M, and N (Fig. 6). The accuracy of determining the positions of the levels differed somewhat for the different groups and averaged  $\pm 1.5 \text{ cm}^{-1}$ . It is seen that the first excited component of the ground state  $4I_{15/2}$  for the L centers stands at  $21 \text{ cm}^{-1}$  and the second at  $32.5 \text{ cm}^{-1}$  from the unexcited one; for the M centers these numbers are 43 and  $60 \text{ cm}^{-1}$ , respectively. In the N system, only one Stark component is found above the ground level ( $42 \text{ cm}^{-1}$ ). Higher components of the  $4I_{15/2}$  level

<sup>2)</sup>Henceforth, both these systems of lines and the optical centers to which they belong will be symbolized by the same letter.

for centers of type L stand at 398, 431, and 446  $\text{cm}^{-1}$  from the ground component. The splitting of the  $^4\text{S}_{3/2}$  level is respectively 83, 16, and 32  $\text{cm}^{-1}$  for the L, M, and N centers.

In the EPR investigation of  $\text{CaF}_2\text{-Er}^{3+}$  crystals<sup>[6]</sup> it was determined that the two closest excited sublevels of the  $^4\text{I}_{15/2}$  ground state for the centers of tetragonal symmetry were at 21 and 32  $\text{cm}^{-1}$  from the bottom sublevel, which agrees well with the splitting of this same level for the L centers. It follows from this that the L centers are the centers of tetragonal symmetry. The centers of types M, N, and P that show up with higher  $\text{Er}^{3+}$  concentration are more complicated. By analogy with the corresponding  $\text{Nd}^{3+}$  centers<sup>[3]</sup> and according to a theoretical calculation by one of the authors,<sup>[12]</sup> the M centers most likely have rhombohedral symmetry. The N centers evidently have an even more complex structure.

Returning to Fig. 2, it can be seen that the system of lines emerging at relatively high (0.1 to 0.3 weight %)  $\text{Er}^{3+}$  concentrations (the P system) grows rapidly and has already become the predominant one at  $\text{Er}^{3+}$  concentrations of the order of 1 weight %. This system is particularly clearly manifested in the group  $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{5/2}$ , where there is no interference from absorption lines of the L, M, and N systems. It should be mentioned that even at helium temperature this system contains considerably more lines than predicted by theory. A detailed analysis by the concentration-series method is impossible in this case owing to the large line widths. Hence the lines of this system belong, evidently, to several types of optical centers arising at a high  $\text{Er}^{3+}$  concentration.

In the investigations of the optical properties of  $\text{CaF}_2\text{-Nd}^{3+}$  crystals described in<sup>[13]</sup> it was found that the introduction into these crystals of even insignificant amounts of yttrium (0.03%) leads to a redistribution of the intensities of the individual lines and to the appearance of new ones, not observed in the spectra of  $\text{CaF}_2\text{-Nd}^{3+}$  crystals. In the present work, the effect of adding yttrium fluoride on the optical spectra of  $\text{CaF}_2\text{-Er}^{3+}$  was analyzed in a very similar fashion. It was found thereby that the observed regularities differ markedly from those observed for  $\text{CaF}_2\text{-Nd}^{3+}$ ,  $\text{Y}^{3+}$ . These regularities can be formulated in the following way:

1. No new lines that are not present in the spectra of  $\text{CaF}_2\text{-Er}^{3+}$  appear either in the absorption spectra or in the luminescence spectra of  $\text{CaF}_2\text{-Er}^{3+}$ ,  $\text{Y}^{3+}$  crystals.
2. In the optical spectra of  $\text{CaF}_2\text{-Nd}^{3+}$ ,  $\text{Y}^{3+}$  and  $\text{CaF}_2\text{-Er}^{3+}$ ,  $\text{Y}^{3+}$  a similar dependence is found for

the lines belonging to the tetragonal centers: the intensity of the luminescence lines and the magnitude of the absorption coefficients slowly decrease with increasing yttrium concentration. The absorption and luminescence lines of the more complex centers behave differently with the introduction of yttrium impurity. In  $\text{CaF}_2\text{-Er}^{3+}$ ,  $\text{Y}^{3+}$  crystals the M and N lines decrease somewhat more rapidly than the L lines; however, their magnitude remains significant even at relatively high (about 2 weight %) yttrium concentrations. The N lines in  $\text{CaF}_2\text{-Nd}^{3+}$ ,  $\text{Y}^{3+}$ , on the other hand, disappear completely at yttrium concentrations of 0.03 weight %, and the M lines become negligibly small at a concentration of about 1 weight %.

3. The distribution of intensity of the lines within the groups in the spectra of fluorite with a small concentration of  $\text{Er}^{3+}$  and a considerable amount of yttrium (about 1–2 weight %) is the same as in  $\text{CaF}_2$  crystals with a high (about 1–2 weight %) erbium concentration. In such spectra the lines of the P system are predominant. The ratio of the absorption coefficients of some of the strongest lines of this system for  $\text{CaF}_2\text{-Er}^{3+}$  and  $\text{CaF}_2\text{-Er}^{3+}$ ,  $\text{Y}^{3+}$  crystals with the same total impurity concentration of erbium and yttrium is of the order of magnitude of the ratio of the  $\text{Er}^{3+}$  concentrations:

$$K(\text{CaF}_2 - \text{Er}(1\%)) / K(\text{CaF}_2 - \text{Er}(0.4\%))$$

$$- \text{Y}(0.5\%) \approx 2.25,$$

$$K(\text{CaF}_2 - \text{Er}(2\%)) / K(\text{CaF}_2 - \text{Er}(0.03\%))$$

$$- \text{Y}(2\%) \approx 30.$$

Just as in  $\text{CaF}_2\text{-Nd}^{3+}$  crystals,<sup>[13]</sup> the introduction of  $\text{YF}_3$  into  $\text{CaF}_2\text{-Er}^{3+}$  crystals shifts the equilibrium of the centers toward the formation of more complex associates. In the presence of considerable amounts of yttrium the overwhelming majority of erbium ions enters into the compositions of complex optical centers formed by erbium and yttrium ions. This is what causes the appearance of the P centers even at small  $\text{Er}^{3+}$  concentrations (about 0.03%). The identical behavior of the change in intensity of the lines of the L centers for  $\text{CaF}_2\text{-Er}^{3+}$  and  $\text{CaF}_2\text{-Nd}^{3+}$  also finds its explanation. Actually, the L centers are tetragonal, and the  $\text{Y}^{3+}$  ions do not enter into them; their change in concentration is due only to the equilibrium shift.

The change in the optical spectra of  $\text{CaF}_2\text{-Nd}^{3+}$  crystals with the introduction of yttrium is evidence that the energy levels of  $\text{Nd}^{3+}$  in the complex centers formed by neodymium and yttrium ions differ from the levels of centers of the same structure containing only  $\text{Nd}^{3+}$  ions. In  $\text{CaF}_2\text{-Er}^{3+}$  crys-

tals, on the other hand, replacement of  $\text{Er}^{3+}$  by  $\text{Y}^{3+}$  in the complex centers does not alter the positions of the energy levels of the erbium ions that remain in the composition of this center. One gets the impression that the erbium ions in the complex centers "don't care" what ion is next door— $\text{Er}^{3+}$  or  $\text{Y}^{3+}$ ; only the symmetry of the centers is of importance to them.

The authors thank V. B. Aleksandrov for helping with the experiments and S. P. Afanas'ev for helping with the crystal growing.

<sup>1</sup>P. P. Feofilov, Proceedings of the 5th Luminescence Conference, Tartu, 1956, p. 3.

<sup>2</sup>V. V. Osiko, in Rost kristallov (Crystal Growth), 5, Izd. AN SSSR, 1965.

<sup>3</sup>Yu. K. Voron'ko, A. A. Kaminskiĭ, and V. V. Osiko, JETP 49, 420 (1965), Soviet Phys. JETP 22, 295 (1966).

<sup>4</sup>S. P. S. Porto and A. Yariv, Quantum Electronics, 3d International Congress, Columbia Univ. Press, New York, 1964, p. 717.

<sup>5</sup>U. Ranon and W. Low, Phys. Rev. 132, 1609 (1963).

<sup>6</sup>Yu. K. Voron'ko, G. M. Zverev, B. B. Meshkov, and A. I. Smirnov, FTT 6, 2799 (1964), Soviet Phys. Solid State 6, 2225 (1965).

<sup>7</sup>S. A. Pollack, J. Chem. Phys. 40, 2751 (1964).

<sup>8</sup>Yu. K. Voron'ko, A. A. Kaminskiĭ, V. V. Osiko, and A. M. Prokhorov, JETP Letters 1, No. 4, 33 (1965), transl. 1, 120 (1965).

<sup>9</sup>Yu. K. Voron'ko, A. A. Kaminskiĭ, and V. V. Osiko, JETP 49, 724 (1965), Soviet Phys. JETP 22, 501 (1966).

<sup>10</sup>Yu. K. Voron'ko, V. V. Osiko, V. T. Udovenchik, and M. M. Fursikov, FTT 7, 267 (1965), Soviet Phys. Solid State 7, 204 (1965).

<sup>11</sup>M. A. El'yashevich, Spektry redkikh zemel' (Rare-earth Spectra), Gostekhizdat, 1953.

<sup>12</sup>V. V. Osiko, FTT 7, 1294 (1965), Soviet Phys. Solid State 7, 1047 (1965).

<sup>13</sup>Kh. S. Bagdasarov, Yu. K. Voron'ko, L. V. Krotova, A. A. Kaminskiĭ, and V. V. Osiko, Phys. Stat. Sol. 12, 905 (1965).

Translated by L. M. Matarrese