

INVESTIGATION OF THE  $\text{Nd}^{3+}$  OPTICAL CENTERS IN  $\text{CaF}_2\text{-Nd}^{3+}\text{-TR}^{3+}$  CRYSTALS (TYPE 1)

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The effect of  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$ , and  $\text{Lu}^{3+}$  impurities on the  $\text{Nd}^{3+}$  optical centers in fluorite crystals is investigated. The mechanism of the impurity effect and the structure of the optical centers of the investigated crystals are discussed.

As has been previously shown, rare-earth  $\text{TR}^{3+}$  ions are distributed in fluorite crystals ( $\text{CaF}_2$ ) over several types of centers of different structure.<sup>[1,2]</sup> Each type of center has its own set of energy levels, and correspondingly its characteristic absorption and luminescence spectrum.

Energy level schemes of three types of  $\text{Nd}^{3+}$  centers in  $\text{CaF}_2$ , provisionally denoted by L, M, and N, have been cited in<sup>[3]</sup>. A comparison with EPR data made it possible to associate the L centers with those of tetragonal symmetry, and the N and M centers with two centers of orthorhombic symmetry.

In<sup>[4]</sup> it was shown that the relative concentrations of the different types of centers depend on the general concentration of the  $\text{TR}^{3+}$  impurity and on the equilibrium temperature. In addition, the effect of an admixture of extraneous trivalent ions on the relative concentrations of certain  $\text{TR}^{3+}$  centers was noted. This effect was investigated experimentally in  $\text{CaF}_2\text{-Nd}^{3+}$ <sup>[5]</sup> and  $\text{CaF}_2\text{-Er}^{3+}$ <sup>[6]</sup> crystals into which yttrium fluoride,  $\text{YF}_3$ , was introduced as the "extraneous" impurity.

It turned out that in the presence of the  $\text{YF}_3$  impurity the intensities of the absorption lines of the L, M, and N spectra in  $\text{CaF}_2\text{-Nd}^{3+}$  crystals are redistributed, and systems of new lines appear in the spectra. In the spectra of  $\text{CaF}_2\text{-Er}^{3+}\text{-Y}^{3+}$  crystals, unlike those of  $\text{CaF}_2\text{-Nd}^{3+}$ , there occurs only a redistribution of intensities of the lines present in the spectra of  $\text{CaF}_2\text{-Er}^{3+}$  crystals.

The authors of<sup>[6]</sup> assume that  $\text{Y}^{3+}$  replaces the  $\text{TR}^{3+}$  in complex centers. The symmetry of the centers remains the same, but the energy levels of the  $\text{TR}^{3+}$  change. Thus, for example, the energy levels of  $\text{Nd}^{3+}$  in centers of  $\text{Nd-Y}$  composition differ from the corresponding  $\text{Nd}^{3+}$  levels in  $\text{Nd-Nd}$  centers; this leads to the appearance of systems of new lines. The absence of new lines in the absorption spectra of  $\text{Er}^{3+}$  in  $\text{CaF}_2\text{-Er}^{3+}\text{-Y}^{3+}$  crystals apparently indicates that the energy levels of  $\text{Er}^{3+}$  in complex  $\text{Er-Y}$  centers are close to those in  $\text{Er-Er}$  centers.

In this work we investigate the rules governing the effect of the  $\text{TR}^{3+}$  on the equilibrium of centers and the optical spectra of  $\text{Nd}^{3+}$  in fluorite crystals.

## THE INVESTIGATED CRYSTALS

$\text{CaF}_2\text{-Nd}^{3+}$  crystals with an admixture of other  $\text{TR}^{3+}$  were grown in a fluorinating atmosphere by a method presented in<sup>[7]</sup>. In all cases the concentration of  $\text{NdF}_3$  amounted to 0.1 wt. % and that of  $\text{TRF}_3$ —0.05 wt. %

$\text{CaF}_2\text{-NdF}_3 \cdot 0.1$  wt. % crystals served as a standard. All the crystals were synthesized under strictly the same conditions.

## ABSORPTION SPECTRA

The absorption spectra of the crystals were recorded at  $77^\circ\text{K}$  on a DFS-12 spectrometer and a PGS-2 spectrograph, and at  $4.2^\circ\text{K}$  on a PGS-2 spectrograph. Our main attention was given to the investigation of changes in the Stark structure of the group corresponding to the  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{3/2}$  transition ( $\lambda \approx 8600 \text{ \AA}$ ) which had previously been studied in detail in  $\text{CaF}_2\text{-Nd}^{3+}$  crystals.<sup>[3]</sup>

Absorption spectra were also obtained for the groups of lines corresponding to the transitions  ${}^4\text{I}_{9/2} \rightarrow {}^2\text{P}_{1/2}$  ( $\lambda \sim 4300 \text{ \AA}$ ), and  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{5/2}, {}^2\text{H}_{9/2}$  ( $\lambda \sim 8000 \text{ \AA}$ ).

Figure 1 shows the absorption of  $\text{Nd}^{3+}$  at  $77^\circ\text{K}$  corresponding to the  ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{3/2}$  transition in the presence of  $\text{TR}^{3+}$  impurities, the spectra being arranged in order of increasing atomic number of  $\text{TR}^{3+}$ .

It is seen that the  $\text{TR}^{3+}$  impurities lead to the appearance in the absorption of  $\text{Nd}^{3+}$  of lines located in a regular manner relative to the lines of the M and N centers. A redistribution of the intensities of the lines present in the  $\text{CaF}_2\text{-Nd}^{3+}$  spectra occurs in the case of

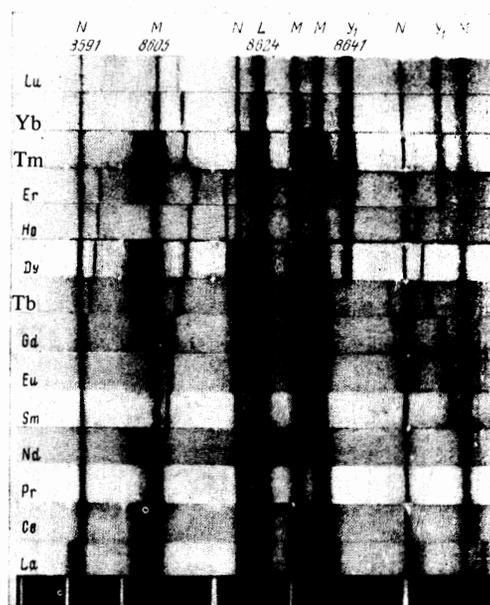


FIG. 1. Absorption spectra of  $\text{CaF}_2\text{-Nd}^{3+}\text{-TR}^{3+}$  crystals at  $77^\circ\text{K}$  ( ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{3/2}$  transition).

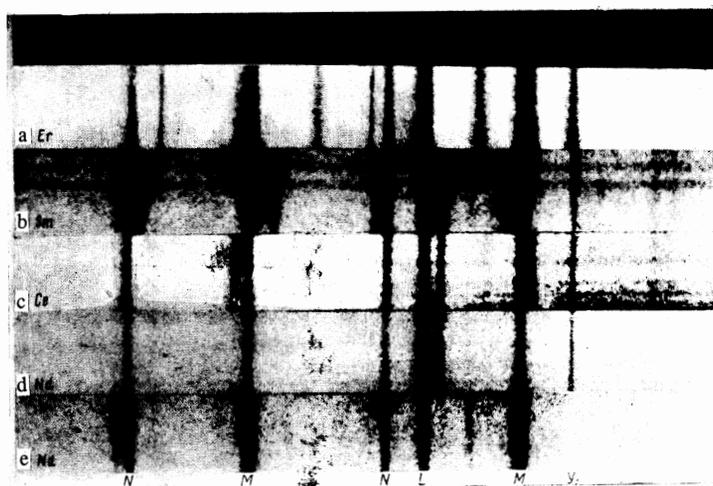


FIG. 2. Absorption spectra at 4.2°K ( $^4I_{9/2} \rightarrow ^4F_{3/2}$  transition) of CaF<sub>2</sub>-Nd<sup>3+</sup>-TR<sup>3+</sup> crystals (a, e) and of  $\gamma$  irradiated CaF<sub>2</sub>-Nd<sup>3+</sup>-TR<sup>3+</sup> crystals (b, c, and d).

CaF<sub>2</sub>-Nd<sup>3+</sup>-Pr<sup>3+</sup>. Starting with Gd<sup>3+</sup> there appear in the absorption of Nd<sup>3+</sup> new lines at 8641 and 8658 Å whose position does not change on going over to Tb<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, Yb<sup>3+</sup>, and Lu<sup>3+</sup>; their intensity increases from Gd<sup>3+</sup> to Lu<sup>3+</sup>.

On going over to spectra obtained at 4.2°K the described picture is even more pronounced.

The effect of  $\gamma$  irradiation on the spectra of some TR<sup>3+</sup> in CaF<sub>2</sub> has been communicated previously.<sup>[6]</sup> The effect of TR<sup>3+</sup> impurities on the Nd<sup>3+</sup> - Nd<sup>2+</sup> transition in  $\gamma$  irradiation is known from<sup>[9]</sup>. In this work along with investigations of the CaF<sub>2</sub>-Nd<sup>3+</sup>-TR<sup>3+</sup> crystals, these crystals were also investigated after  $\gamma$  irradiation.

The absorption spectra of  $\gamma$ -irradiated CaF<sub>2</sub>-Nd<sup>3+</sup>-TR<sup>3+</sup> crystals (Fig. 2) constitute a superposition of CaF<sub>2</sub>-Nd<sup>3+</sup>-TR<sup>3+</sup> spectra and the spectra of  $\gamma$ -irradiated CaF<sub>2</sub>-Nd<sup>3+</sup> crystals. In  $\gamma$  irradiation the effect of the second impurity on the Nd<sup>3+</sup> spectra is only manifested in the intensity of certain lines. The spectra of  $\gamma$ -irradiated CaF<sub>2</sub>-Nd<sup>3+</sup> crystals are interesting because in these spectra there appear lines which coincide in their position and structure with lines in the absorption spectra of unirradiated CaF<sub>2</sub>-Nd<sup>3+</sup>-(Gd<sup>3+</sup>...Lu<sup>3+</sup>) crystals. In the  $^4I_{9/2} \rightarrow ^4F_{3/2}$  group such lines are those occurring at 8641 and 8658 Å.

## DISCUSSION OF THE RESULTS

Having considered the experimental data, we have reached the conclusion that in CaF<sub>2</sub>-Nd<sup>3+</sup>-TR<sup>3+</sup> crystals the Nd<sup>3+</sup> ions are replaced by other TR<sup>3+</sup> ions in the M and N centers. We shall denote centers which contain both Nd<sup>3+</sup> and TR<sup>3+</sup> by M' and N' respectively. Clearly, the magnitude of the splitting between the Nd<sup>3+</sup> levels in M and M' and N and N' centers depends on the similarity of the properties of the corresponding TR<sup>3+</sup> ion and those of Nd<sup>3+</sup>. Figure 3 shows the dependence of the

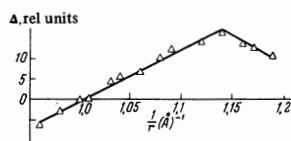


FIG. 3. Dependence of the magnitude of the splitting of the M and M' lines ( $\lambda_M = 8605$  Å) on the reciprocal of the ionic radius of TR<sup>3+</sup>.

magnitude of the splitting between the Nd<sup>3+</sup> levels in M and M' centers on the reciprocal of the ionic radius of the second impurity (the ionic radii follow the data of Zachariasen). It is clearly seen that the magnitude of the splitting increases linearly with increasing difference between the ionic radii. However, this dependence is destroyed on going over to Tm<sup>3+</sup>, Yb<sup>3+</sup>, and Lu<sup>3+</sup> ions. It follows that it is impossible to reduce the dependence of the splitting to a sole dependence on the principal properties of the ion—its charge and radius.

As is seen from Fig. 1, the lines of the M and N centers split in the presence of extraneous TR<sup>3+</sup> ions into two (or more) components, a fact which confirms the previously proposed model for the M and N centers as consisting of more than one Nd<sup>3+</sup> ion.

It has been established in<sup>[5]</sup> that the 8641 and 8658 Å lines belong to the same optical Y<sub>1</sub> center. It has also been shown<sup>[10]</sup> that these centers must be referred to centers with a simpler structure than that of the M and N centers. The unaltered position of these lines on going from one TR<sup>3+</sup> impurity to another indicates that they do not depend on the specific nature of the second impurity ion. Hence we concluded that the intensity of the lines of the Y<sub>1</sub> centers can serve as a measure of their concentration.

It follows from the results which we have obtained that not all TR<sup>3+</sup> ions form with Nd<sup>3+</sup> Y<sub>1</sub>-type centers to an equal extent. Thus the ions La<sup>3+</sup>, Ce<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, and Eu<sup>3+</sup> do not form such centers, while the probability of formation of Y<sub>1</sub> centers by the remaining ions increases with decreasing ionic radius of the second impurity. We relate the formation of Y<sub>1</sub> centers with the localization of TR<sup>3+</sup> ions possessing excess positive charge near the simpler Nd<sup>3+</sup> centers (in the second or third coordination sphere).

In view of the fact that the same lines (at 8441 and 8658 Å) appear in CaF<sub>2</sub>-Nd<sup>3+</sup> crystals after  $\gamma$  irradiation, we have assumed that in this case Y<sub>1</sub> centers are produced as a result of the localization of a hole near a simple Nd<sup>3+</sup> center.

It thus turns out that the appearance of excess positive charge in the second or third coordination sphere leads only to a change in the symmetry of the crystal field which is independent of the chemical nature of the charge carrier.

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