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INVESTIGATION OF THE INTERACTION OF Nd^{3+} *IONS IN* CaF_2, SrF_2, *AND* BaF_2 *CRYSTALS (TYPE I)*

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The mechanism of the interaction of Nd^{3+} ions and the nature of concentration quenching in CaF_2, SrF_2, and BaF_2 crystals were investigated. The concentration dependences of the absorption and luminescence spectra were obtained at 300, 77, and 4.2° K in a wide range of Nd^{3+} concentrations (0.01–30 wt.%). The concentration dependences of the relative quantum yield were plotted and the lifetimes of the excited states of various Nd^{3+} ion centers were measured. A scheme of crystal splitting of some Nd^{3+} levels in SrF_2 was deduced for centers of the tetragonal symmetry.

INTRODUCTION

THE optical properties of Nd^{3+} ions in CaF_2, SrF_2, and BaF_2 crystals have already been investigated several times. These investigations are, to a considerable degree, related to the use of these materials in lasers.[1] The fullest information on the optical and EPR spectra of the Nd^{3+} ion is available for the CaF_2 lattice.[2-5] in[5], the method of concentration series was used to distinguish, in the total optical spectrum, the spectra representing various types of tetragonal and two types of orthorhombic optical center, an energy level scheme for these types of center has been deduced taking into account their Stark splitting, and the Nd^{3+} centers participating in stimulated emission have been identified. Elsewhere,[6] the results are given of an investigation of the nature of the concentration quenching in fluorite crystals with Nd^{3+} impurities, as well as of measurements of the relative quantum yield η and the radiative lifetime τ_{rad} of the tetragonal centers and two types of orthorhombic centers as a function of the activator concentration in a crystal.

Kariss, Tolstoĭ, and Feofilov[7] carried out spectroscopic investigations of MeF_2 (Me = Ca, Sr, Ba) crystals activated with Nd^{3+}; they obtained empirical schemes for the crystal splitting of the lower terms of the Nd^{3+} ion in CaF_2 (type I and II spectra) and SrF_2 (type II spectra)[1)]; the lifetime of the excited state of $^4F_{3/2}$ level of the Nd^{3+} ion in CaF_2 was determined.

The EPR spectra of $SrF_2:Nd^{3+}$ crystals were investigated by Bleaney et al.[9] and by Kask and Kornienko.[10] They showed that, in these crystals, the Nd^{3+} ion is in fields of the tetragonal and orthorhombic symmetries. Shekun[11] gave a table of the EPR data, which indicate that the tetragonal optical Nd^{3+} centers exist in the lattices of CaF_2 and SrF_2. No Nd^{3+} centers of any type have yet been observed in BaF_2.

It must be mentioned that all these investigations were carried out using relatively low activator concentrations. Only in one case[5] has the concentration of Nd^{3+} in the investigated crystals reached 2 wt.%.

The purpose of our investigation was to study the absorption and luminescence spectra, as well as the concentration dependences of the lifetime of the excited state of the Nd^{3+} ion in SrF_2 and BaF_2 crystals in a wide range of Nd^{3+} concentrations (0.01–30 wt.%) in order to obtain information on the interaction of Nd^{3+} ions and on the quenching processes.

APPARATUS AND EXPERIMENTAL METHOD

The absorption spectra were recorded at 300, 77, and 4.2°K using a DFS-12 diffraction spectrometer. At the spectrometer output, we used an FÉU-22 photomultiplier in the measurement of the absorption in groups corresponding to transitions from the ground level $^4I_{9/2}$ to the Stark components of the levels $^4F_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^4S_{3/2}$, $^2G_{7/2}$, $^4G_{5/2}$; an FÉU-17 photomultiplier was used in the measurement of the absorption corresponding to $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transitions. The absorption spectra corresponding to transitions from the ground level $^4I_{9/2}$ to the Stark components of the $^4I_{15/2}$ level at room and liquid nitrogen temperatures were obtained using an SF-8 spectrophotometer and a DFS-12 diffraction spectrometer, adapted for recording spectra in the infrared region. A PGS-2 spectrograph was used for simultaneous photographic recording of the absorption spectra at liquid helium and nitrogen temperatures.

The luminescence of Nd^{3+} at 77 and 4.2°K was investigated in the region of 1.05 μ, corresponding to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition. The luminescence was excited with an elliptical cylindrical light source fitted with a K-14 water-cooled tungsten incandescent lamp.

To calculate the dependence of the relative quantum yield of the luminescence from the concentration of Nd^{3+}, we used the luminescence and absorption spectra of $SrF_2:Nd^{3+}$ crystals containing 0.1–5 wt.% Nd^{3+}, and of $BaF_2:Nd^{3+}$ crystals containing 0.3–30 wt.% Nd^{3+}. To ensure that the absorption and luminescence results were comparable, our measurements were carried out on the same crystals, which all had the same length (30 mm). The luminescence was excited at one end of a crystal by the radiation of the incandescent lamp. This ensured that the geometrical conditions during the experiments were exactly reproducible. Two filters were placed between the lamp

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[1)] The designations of the types of crystal follow Feofilov.[8]

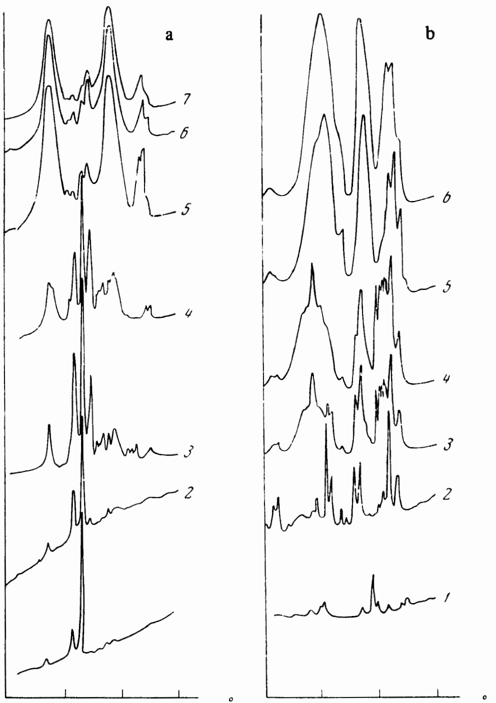

FIG. 1. Absorption spectra of $SrF_2:Nd^{3+}$ (a) and $BaF_2:Nd^{3+}$ (b) crystals at 77°K for the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition, as a function of the Nd^{3+} concentration (in wt.%): a – 1) 0.1; 2) 0.1; 3) 0.3; 4) 1; 5) 2; 6) 5; 7) 10; b – 1) 0.1; 2)0.3; 3) 1; 4) 2; 5)5; 6) 10.

and the Dewar flask containing a crystal: a water-cooled SZS-14 filter, which transmitted in the wavelength range 3000–10 000 Å, and an OS-12-filter, which transmitted wavelengths longer than 5200 Å. Thus, the luminescence was excited in the absorption bands of Nd^{3+} corresponding to the transitions $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^4S_{3/2}$, $^2G_{7/2}$, $^4G_{5/2}$. These transitions were the only ones whose contribution to the absorption was included in the calculation of the concentration dependence of the relative quantum yield because a control absorption spectrum, obtained using the SF-8 diffraction spectrometer, indicated that the absorption corresponding to the transitions $^4I_{9/2} \rightarrow {}^4F_{9/2}$, $^2H_{11/2}$ (the radiation frequencies corresponding to these transitions were passed by the OS-12 filter) was negligibly weak and because allowance for the spectral distribution of the excitation source reduced the contribution of these two transitions even further. To check the reproducibility of the luminescence spectra, after each measurement we recorded a control spectrum of a crystal containing 0.3 wt.% Nd^{3+}. The scatter of the values of the integral (total) luminescence, obtained using this control crystal, did not exceed 5%.

To measure τ_{rad}, the luminescence of the $SrF_2:Nd^{3+}$ and $BaF_2:Nd^{3+}$ crystals was excited with pulses from an IFP-800 xenon lamp in an elliptical source. The duration of the pulse produced by this lamp was 50 μsec. An SZS-14 filter placed between the lamp and the crystal. Single lines, representing a particular type of Nd^{3+} centers, were selected from the luminescence spectrum using the DFS-12 diffraction spectrometer. To obtain time displays of the luminescence, the photomultiplier signal was applied to an S-1-15 oscillograph. The measurements of τ_{rad} were carried out at 77°K.

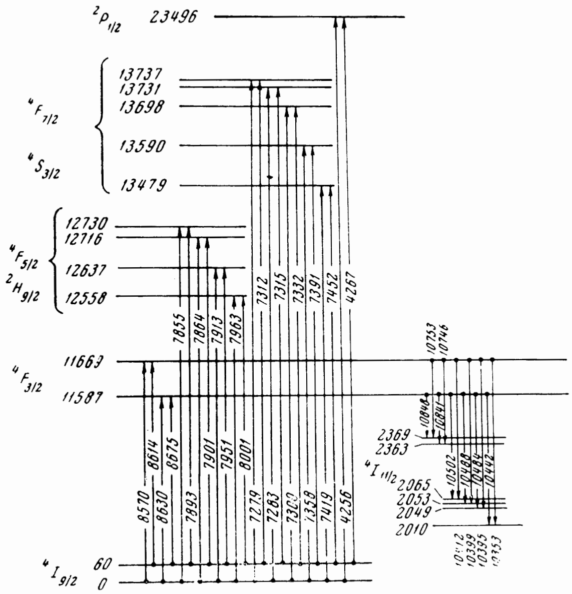

FIG. 2. Energy level scheme of the Nd^{3+} tetragonal centers in SrF_2.

EXPERIMENTAL RESULTS

Absorption and luminescence spectra of Nd^{3+} in the SrF_2 lattice. The absorption spectra of $SrF_2:Nd^{3+}$ crystals, like those of Nd^{3+}-activated fluorite crystals, consisted of a series of narrow lines, whose number and relative intensities depended on the activator concentration. Using the method of concentration series, the temperature dependences of the absorption and luminescence, and the method of constant differences, we were able to distinguish the lines of centers which were dominant at Nd^{3+} concentrations of 0.01–0.1 wt.% (Fig. 1a) and to plot for these centers a scheme of the energy levels $^4I_{9/2}$, $^4I_{11/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^4S_{3/2}$, $^2P_{1/2}$ allowing for their Stark splitting (Fig. 2). By analogy with the results reported in[5], we called these centers L type centers. We found that the splitting of the $^4F_{3/2}$ level for L type centers was 82 cm^{-1}, which was in agreement with the results of Kariss, Tolstoĭ, and Feofilov.[7]

The position of the first excited component of the $^4I_{9/2}$ level, obtained from analysis of the concentration and temperature dependences of the absorption corresponding to the transitions shown in the scheme of Fig. 2, was 60 cm^{-1} (the accuracy of the determination of the level positions was ± 2 cm^{-1}).

Analysis of the luminescence spectra established the positions of all six split components of the $^4I_{11/2}$ level. The positions of three components (2010, 2065, and 2369 cm^{-1}) coincided, within the limits of the experimental error, with the results of Kariss, Tolstoĭ, and Feofilov.[7] The component at 2283 cm^{-1}, reported in[7], was not observed by us.

The suggested scheme of the energy levels of the Nd^{3+} ion in the SrF_2 lattice, modified to allow for the

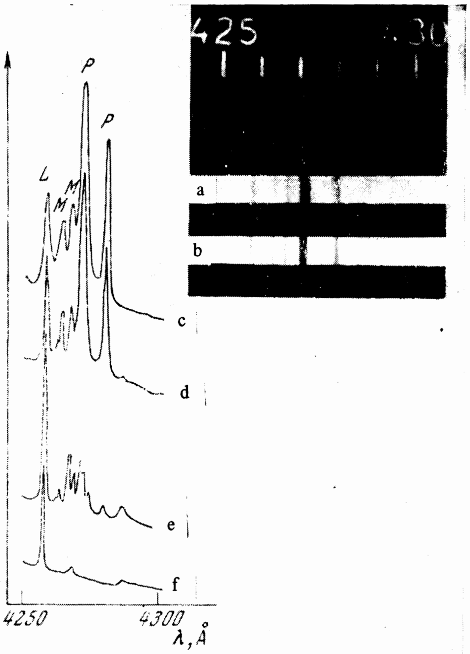

FIG. 3. Absorption spectra of $SrF_2:Nd^{3+}$ crystals for the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition as a function of the Nd^{3+} concentration (in wt.%) and temperature (in °K): a) 5%, 77°; b) 5%, 4.2°; c) 5%, 77°; d) 2%, 77°; e) 0.8%, 77°; f) 0.1%, 77°.

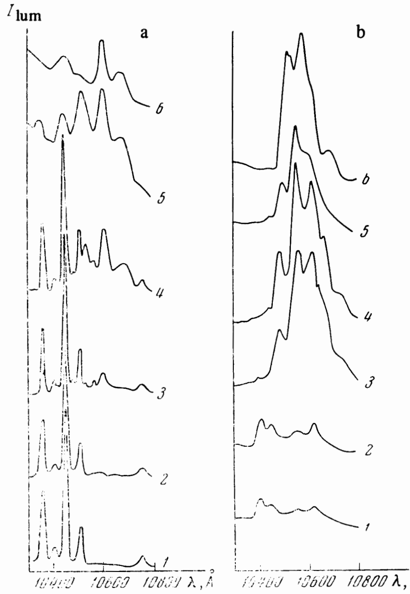

FIG. 4. Luminescence spectra of $SrF_2:Nd^{3+}$ (a) and BaF_2Nd^{3+} (b) crystals for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition as a function of the Nd^{3+} concentration (in wt.%) and the temperature (in °K): a – 1) 0.1%, 77°; 2) 0.3%, 77°; 3) 1%, 77°; 4) 2%, 77°; 5) 5%, 77°; 6) 5%, 4.2°; b – 1) 0.3%, 77°; 2) 1%, 77°; 3) 5%, 77°; 4) 10%, 77°; 5) 30%, 77°; 6) 5%, 4.2°.

crystal-field splitting of the L type centers, was similar to the splitting scheme of Nd^{3+} in a field of tetragonal symmetry in fluorite, given in[5].

When the activator concentration was increased above 0.1 wt.%, the absorption spectra of $SrF_2:Nd^{3+}$ exhibited, like the spectra of Nd^{3+} in CaF_2, another series of lines (Fig. 1a). However, in contrast to fluorite, these lines appeared in the absorption spectra of $SrF_2:Nd^{3+}$ crystals at higher concentrations, they were wider, and weaker, all of which prevented us from carrying out a detailed analysis of the Stark structure.

When the concentration of Nd^{3+} was increased further, the absorption spectra of $SrF_2:Nd^{3+}$ exhibited another family of lines. A characteristic feature of these spectra was a relatively small number of wide bands (Fig. 3). At high activator concentrations (5 wt.%), the absorption spectra were not affected by cooling from liquid nitrogen to liquid helium temperature, which indicated that the absorption involved transitions from the lower component of the ground level $^4I_{9/2}$. The group of centers responsible for the appearance of these lines was designated the P type centers.

An investigation of the luminescence spectra (Fig. 4a), using the methods already mentioned, also made possible the identification of the lines corresponding to the L type centers. At an Nd^{3+} concentration of 0.3 wt.%, the luminescence spectra had a system of very weak lines which were evidently analogs of the M and N systems of lines in $CaF_2:Nd^{3+}$.[5] At activator concentrations from 1 wt.% upward, we observed broad lines of increasing intensity, which became dominant at 5 wt.% Nd^{3+} (Fig. 4a); this was not observed in the luminescence spectra of fluorite.

Absorption and Luminescence spectra of Nd^{3+} in the BaF_2 lattice. The Nd^{3+} absorption in BaF_2 at a concentration of 0.1 wt.% was much weaker than in CaF_2 and SrF_2 at the same concentration. Moreover, the absorption region corresponding to the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ transition had about ten weak lines at liquid nitrogen temperature (fig. 1b). When the activator concentration was increased to 0.3 wt.%, the number and intensities of the absorption lines corresponding to this transition increased considerably. When the Nd^{3+} concentration was raised to 2 wt.%, the absorption spectra were found to consist only of three broad bands with a complex structure, which were observed also, with some modifications, at 30% concentration of the activator (Fig. 1b). We were unable to resolve the total spectra into their components.

Figure 5 shows the concentration dependences of the absorption in $BaF_2:Nd^{3+}$ corresponding to the transition $^4I_{9/2} \rightarrow {}^2P_{1/2}$. It is evident from this figure that, as in the case of $SrF_2:Nd^{3+}$, the absorption spectrum in the case of high activator concentrations (5 wt.%) was not affected by cooling from liquid nitrogen to liquid helium temperature.

Figure 4b shows the luminescence spectra of $BaF_2:Nd^{3+}$. We could distinguish two groups of lines in these spectra. The first group consisted of two short-wavelength lines (they were observed at activator concentrations of 0.3–1 wt.% and disappeared completely from the luminescence spectrum at 5 wt.% Nd^{3+}); the second group consisted of long-wavelength lines, whose intensity was comparable with the short-wavelength lines at 0.3 wt.% Nd^{3+}, but at 5 wt.% the long-wavelength lines became dominant.

Concentration dependences of the luminescence, relative quantum yield, and lifetime of the excited

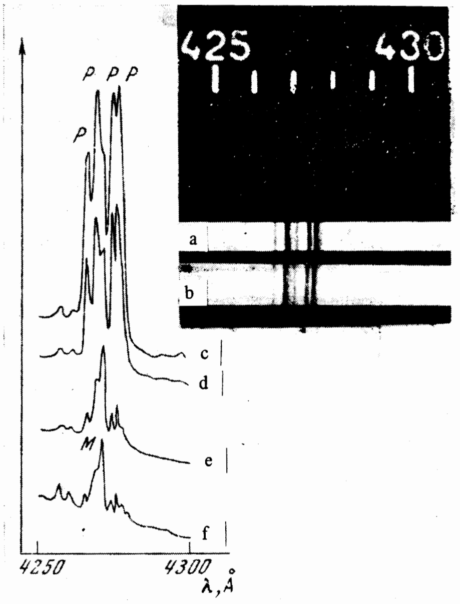

FIG. 5. Absorption spectra of $BaF_2:Nd^{3+}$ crystals for the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition as a function of the Nd^{3+} concentration (in wt.%) and temperature (in °K): a) 5%, 4.2°; b) 5%, 77°; c) 10%, 77°; d) 5%, 77°; e) 2%, 77°; f) 1%, 77°.

states of the Nd^{3+} ion in the SrF_2 and BaF_2 lattices. Figure 6 shows the concentration dependence of the relative quantum yield of the luminescence of Nd^{3+} in the SrF_2 and BaF_2 lattices. This dependence was calculated as the ratio of the total luminescence to the total absorption. In the case of $BaF_2:Nd^{3+}$, we found a maximum at an activator concentration of about 2.5 wt.%. At this activator concentration, the absorption and luminescence spectra consisted mainly of lines corresponding to the P type centers. The relative quantum yield of Nd^{3+} in the SrF_2 lattice did not exhibit such a maximum but the dependence became less strong at activator concentrations higher than 1 wt.%. Figure 7 shows the concentration dependences of the total Nd^{3+} luminescence in SrF_2 (curve a) as well as the separate concentration dependences for different centers (curves b and c).

Figure 8 shows the corresponding dependences for $BaF_2:Nd^{3+}$. At Nd^{3+} concentrations higher than 2 wt.%, we observed in practice only the P-center luminescence and curves a and c merged.

Figure 9 shows the values of τ_{rad} of the excited state of the $^4F_{3/2}$ level of the Nd^{3+} ion in the SrF_2 lattice as a function of the activator concentration. The lifetime of the excited state of $^4F_{3/2}$ for the L type Nd^{3+} centers, amounting to 1.2 msec, remained constant up to a concentration of 0.8 wt.% Nd^{3+} (curve a). When the activator concentration was increased above this value, a considerable fall of the lifetime was observed for the L type centers. For the other types of center active in the luminescence, τ_{rad} was considerably shorter and had a weak dependence on the concentration (curve b). At a concentration of 10 wt.% Nd^{3+}, the values of τ_{rad} for different centers became comparable.

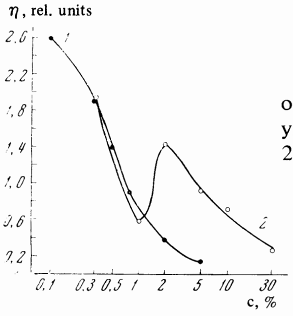

FIG. 6. Concentration dependences of the value of the relative quantum yield at T = 77°K: 1) $SrF_2:Nd^{3+}$; 2) $BaF_2:Nd^{3+}$.

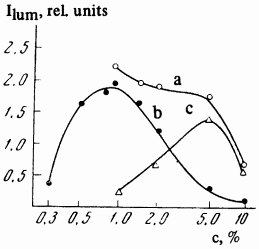

FIG. 7. Concentration dependences of the luminescence intensity of $SrF_2:Nd^{3+}$ at 77°K: a) total luminescence; b) luminescence of tetragonal centers; c) luminescence of P centers.

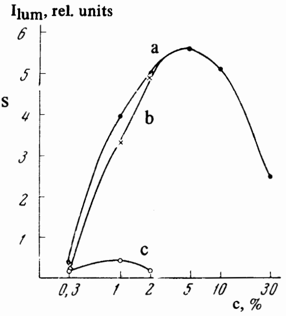

FIG. 8. Concentration dependences of the luminescence intensity of $BaF_2:Nd^{3+}$ crystals at 77°K: a) total luminescence; b) luminescence of L centers; c) luminescence of P centers.

The dependence of τ_{rad} on the activator concentration for $BaF_2:Nd^{3+}$ is shown in Fig. 10. The lifetime of the excited state of the Nd^{3+} ion in optical centers, observed at low concentrations and corresponding to the luminescence lines at 10 400 and 10 434 Å, was 8 msec (curve a). When the concentration of Nd^{3+} exceeded 1.5 wt.%, we observed a rapid fall of τ_{rad}. Comparison of Figs. 9a and 10a indicated that the lifetime of the excited state of the centers observed in BaF_2 at low Nd^{3+} concentrations was approximately seven times longer than that for the L centers in the SrF_2 lattice.

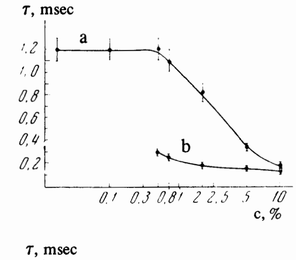

FIG. 9. Concentration dependences of the lifetime of the excited state of $^4F_{3/2}$ of the Nd^{3+} ion in SrF_2 at 77°K: a) for tetragonal centers; b) for P centers.

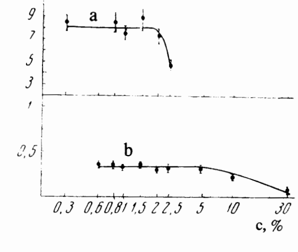

FIG. 10. Concentration dependences of the lifetime of the excited state of $^4F_{3/2}$ of the Nd^{3+} ion in BaF_2 at 77°K: a) for L centers: b) for P centers.

DISCUSSION OF RESULTS

Analysis of the absorption and luminescence spectra and of the concentration dependences of the radiative quantum yield and the excited state lifetimes of Nd^{3+} in SrF_2 and BaF_2 crystals shows that, as in fluorite, the optical properties are governed by several types of optical centers. In the first approximation, these centers can be divided into three groups, which we shall call the L, M, and P systems for all the investigated crystals. The absolute and relative numbers of centers in each group vary with the activator concentration and this is responsible for the changes observed in the optical spectra with the concentration and for the concentration dependences of the relative quantum yield and the excited state lifetimes of Nd^{3+} in the investigated crystals. The L type centers are responsible for the absorption and luminescence spectra of crystals with low activator concentrations (0.3–0.5 wt.%). According to the EPR data for $CaF_2:Nd^{3+}$[12] and $SrF_2:Nd^{3+}$, the L type centers in these crystals are tetragonal[2]. We have been unable to determine the symmetry of the L system of centers in $BaF_2:Nd^{3+}$ crystals.

The M type centers are active in the absorption spectra at activator concentrations of 0.3–2 wt.%. As demonstrated in[5], in fluorite crystals centers of this type have the orthorhombic symmetry. We have been unable to identify in SrF_2 and BaF_2 crystals the lines of centers analogous to the lines of the orthorhombic M and N centers in fluorite, or to determine the energy level scheme and the symmetry of these centers. This failure has been largely due to the considerable width of the spectral lines in the investigated crystals, which has prevented us from applying the method of concentration series[5] to the spectra of these crystals.

At still higher concentrations (>1 wt.%), the optical spectra of CaF_2, SrF_2, and BaF_2 crystals are governed by the P type centers. Strictly speaking the M and P type centers in SrF_2 and BaF_2 represent whole new systems of centers. Thus, Fig. 3 shows the concentration and temperature dependences of the absorption spectra for the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition in $SrF_2:Nd^{3+}$. We can see that, in the case of SrF_2, two lines belong to the P type centers, two lines to the M type centers, and one line to the L type centers; at high activator concentrations, the spectrum is not affected by cooling from liquid nitrogen to liquid helium temperature and therefore we cannot regard the long-wavelength components of the M and P series as excited. For the $^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition in $BaF_2:Nd^{3+}$ with high activator concentrations (5 wt.%), there are five lines of the P centers and one line of the M centers. Cooling from liquid nitrogen to liquid helium temperature again does not change the spectrum (Fig. 5). However, since no appreciable redistribution of intensities is observed between the lines of the various P centers in the absorption and luminescence spectra, we are justified in combining these centers into one P group. Comparison of the luminescence spectra of the P centers in SrF_2 at liquid nitrogen and liquid helium temperatures makes it possible to determine the splitting of the initial luminescence level $^4F_{3/2}$, which is found to be 90 cm^{-1} (Fig. 4a). The 10 473 Å line in the luminescence spectra of the P centers in BaF_2 is "frozen out" at liquid helium temperature. This line can represent an excited component either of the 10 541 Å line (in this case, the splitting of the $^4F_{3/2}$ level should be 62 cm^{-1}) or of the 10 603 Å line (in this case, the splitting of the level should be 117 cm^{-1}) (cf. Fig. 4b).

Our investigations show that the intensity and the quantum yield of the luminescence of Nd^{3+} vary from one matrix to another ($CaF_2 \rightarrow SrF_2 \rightarrow BaF_2$) and depend on the concentration of Nd^{3+} in each of these matrices. Moreover, the concentration dependences of the Nd^{3+} luminescence intensity and quantum yield in each of these matrices are different. In fact, the quenching of the Nd^{3+} luminescence in CaF_2 begins at a concentration of 0.5 wt.% and at 5 wt.% the luminescence of the P centers is no longer observed at 300 or 77°K, i.e., it is quenched completely.

It is evident from Fig. 7 that in SrF_2 crystals the maximum of the intensity of the total Nd^{3+} luminescence is observed at an activator concentration of 1 wt.%. This maximum is mainly due to the L type centers, although a small contribution to the total luminescence is made also by the P type centers. When the Nd^{3+} concentration is increased from 1 to 5 wt.%, the total luminescence decreases smoothly. Such a concentration dependence is due to a redistribution of the intensity of the luminescence of the L and P centers. Thus, at activator concentrations higher than 1 wt.% Nd^{3+}, the intensity of the luminescence of the L centers becomes weaker, while the intensity of the luminescence of the P centers increases and passes through a maximum at an Nd^{3+} concentration of 5 wt.%. However, the maximum intensity of the total luminescence is observed at 1 wt.% Nd^{3+}. This maximum is mainly due to the tetragonal centers. Completely different behavior is observed in the $BaF_2:Nd^{3+}$ system (Fig. 8). In this case, the total luminescence intensity at high activator concentration is many times higher than the total luminescence intensity at low concentrations. In this system, the luminescence of the L centers is extremely weak (curve b) and at concentrations higher than 2.5 wt.% this luminescence is not observed at all. The luminescence of the P centers has a maximum at an activator concentration of 5 wt.%, which is approximately three times higher than the maximum intensity of the Nd^{3+} luminescence in SrF_2 (Figs. 7 and 8). The luminescence of the M centers is practically absent in SrF_2 and BaF_2 crystals.

These experimental observations can be explained by the characteristic features of the energy level scheme of the Nd^{3+} ion. It is known that the luminescence of the Nd^{3+} ion starts from the $^4F_{3/2}$ level, which is separated by ~11 600 cm^{-1} from the ground level $^4I_{9/2}$. Between these two levels, there are levels of the ^4I multiplet, which are the final levels in the luminescence, and one of these levels ($^4I_{15/2}$) is separated by

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[2] The results of the measurements of the EPR spectra of the tetragonal centers in the $SrF_2:Nd^{3+}$ system were kindly supplied by N. E. Kask. According to these results, the first excited level of the tetragonal centers was separated by a gap of 50 ± 10 cm^{-1}, which was in agreement with our results for the L type centers (Fig. 2).

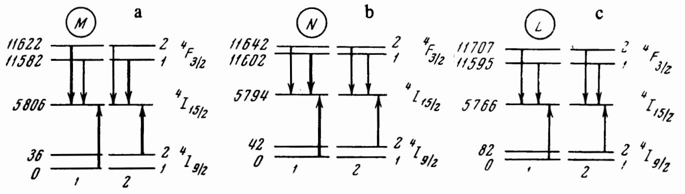

FIG. 11. Energy level scheme illustrating the possibility of resonant energy transfer between Nd^{3+} ions in CaF$_2$. a) Orthorhombic M centers: $^4F^{(1)}_{3/2} \to {}^4I_{15/2} = 5776$ cm^{-1}, $^4F^{(2)}_{3/2} \to {}^4I_{15/2} = 5816$ cm^{-1}; $\Delta_1 = 40$ cm^{-1}, $\Delta_2 = 10$ cm^{-1} for $^4I^{(1)}_{9/2}$; $\Delta_1 = 6$ cm^{-1}, $\Delta_2 = 46$ cm^{-1} for $^4I^{(2)}_{9/2}$. b) Orthorhombic N centers: $^4F^{(1)}_{3/2} \to {}^4I_{15/2} = 5808$ cm^{-1}, $^4F^{(2)}_{3/2} \to {}^4I_{15/2} = 5848$ cm^{-1}; $\Delta_1 = 14$ cm^{-1}, $\Delta_2 = 54$ cm^{-1} for $^4I^{(1)}_{9/2}$; $\Delta_1 = 56$ cm^{-1}, $\Delta_2 = 96$ cm^{-1} for $^4I^{(2)}_{9/2}$. c) Tetragonal L centers: $^4F^{(1)}_{3/2} \to {}^4I_{15/2} = 5829$ cm^{-1}, $^4F^{(2)}_{3/2} \to {}^4I_{15/2} = 5941$ cm^{-1}; $\Delta_1 = 63$ cm^{-1}, $\Delta_2 = 175$ cm^{-1} for $^4I^{(1)}_{9/2}$; $\Delta_1 = 145$ cm^{-1}, $\Delta_2 = 257$ cm^{-1} for $^4I^{(2)}_{9/2}$.

~5800 cm^{-1} from the ground state. Thus, in principle, we can have a resonant energy transfer from the $^4F_{3/2}$ level of one ion to the $^4I_{15/2}$ level of another ion, followed by nonradiative energy relaxation to the lattice (the $^4I_{15/2}$ level is nonradiative[12-14]). However, the positions of the $^4I_{15/2}$ and $^4F_{3/2}$ levels of the Nd^{3+} ion depend on the crystal matrix and on the nature of the center in which this ion is found. Very important contribution is also made by the broadening of the levels taking part in the cross relaxation, which is governed by the temperature and the vibration spectrum of the lattice. The conditions for the multipole energy transfer depend on these factors and thus they affect the magnitude and the nature of the luminescence quenching.

A detailed analysis of the energy level schemes of Nd^{3+} in CaF$_2$, SrF$_2$, and BaF$_2$ crystals yields the following results.

Figure 11 shows the scheme of the $^4F_{3/2}$ and $^4I_{15/2}$ levels of Nd^{3+} in CaF$_2$ with allowance for their Stark splitting. It is evident from this figure that in the case of the tetragonal centers there is no resonance. However, there is a fairly considerable overlap of transitions in the orthorhombic M and N centers which, combined with the minimum distances between Nd^{3+} ions in paired centers, should result in effective quenching. In fact, experiments reported in[6] show that the quantum yield of the luminescence of the paired orthorhombic M and N centers is two orders of magnitude lower and the lifetime of the excited state is approximately an order of magnitude shorter than that for single tetragonal centers.

Figure 12a shows schematically the resonant overlap of the frequencies of the transition $^4I_{9/2} \to {}^4F_{3/2}$ with doubled frequency of the transition $^4I_{9/2} \to {}^4I_{15/2}$ of the P centers in CaF$_2$: Nd^{3+} crystals. The shaded rectangles in Fig. 12b show that part of the spectrum of the $^4I_{9/2} \to {}^4I_{15/2}$ transition which takes part in the resonance. We can see that in the case of CaF$_2$: Nd^{3+}, an effective resonance is observed. In full agreement with this prediction, experiments show the absence of the Nd^{3+} luminescence in CaF$_2$ at high activator concentrations. The processes observed in SrF$_2$: Nd^{3+} and BaF$_2$: Nd^{3+} crystals at low activator concentrations are similar to the processes taking place in CaF$_2$: Nd^{3+} crystals. We observe weak quenching in the single L centers and strong quenching in the M centers. However, at high activator concentrations, the situation is different. It is evident from Figs. 12c and 12d that the degree of overlap of the frequencies of the transition $^4I_{9/2} \to {}^4F_{3/2}$ with doubled frequency of the transition $^4I_{9/2} \to {}^4I_{15/2}$ for the P centers in SrF$_2$ is considerably less than in fluorite. The overlap is even less in BaF$_2$: Nd^{3+} (Figs. 12e and 12f). This explains the slow decrease of the total luminescence intensity and the considerable intensity of the luminescence of the P centers in SrF$_2$ at high activator concentrations (5 wt.%) and the strong luminescence of the P centers in BaF$_2$ even at 30 wt.% Nd^{3+}. At room temperature, the resonance of the P centers in BaF$_2$ takes place easily because of the appearance of new excited lines in the long-wavelength part of the absorption spectrum ($^4I_{9/2} \to {}^4I_{15/2}$) and the luminescence of the P centers is not observed.

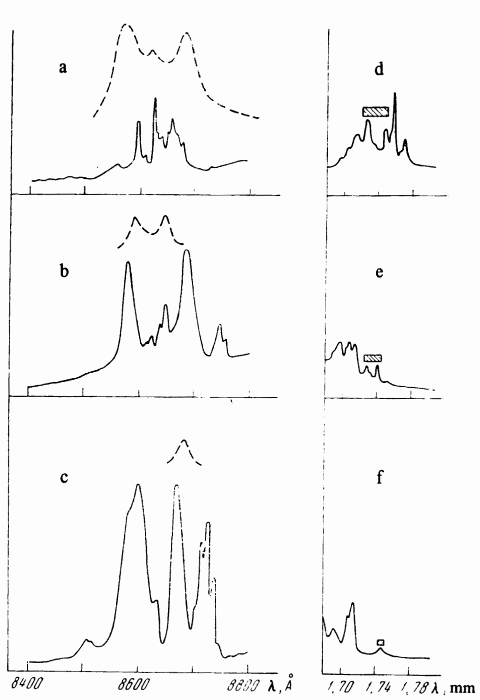

FIG. 12. Resonance of the $^4F_{3/2} \to {}^4I_{15/2}$ and $^4I_{15/2}$ Nd^{3+} transitions in CaF$_2$, SrF$_2$, and BaF$_2$ crystals. a) Absorption spectrum of CaF$_2$:Nd^{3+} at 77°K; Nd^{3+} concentration, 5 wt.%; $^4I_{9/2} \to {}^4F_{3/2}$ transition; line profiles corresponding to the doubled frequencies of the $^4I_{9/2} \to {}^4I_{15/2}$ transition are shown dashed. b) Absorption spectrum of CaF$_2$:Nd^{3+} at 77°K; Nd^{3+} concentration, 5 wt.%; $^4I_{9/2} \to {}^4I_{15/2}$ transition; the shaded rectangle shows a region taking part in resonance. c), d) The same results as in (a) and (b) but for SrF$_2$:Nd^{3+}; e), f) the same results as in (a) and (b) but for BaF$_2$:Nd^{3+}.

We must mention that the formula for the resonant interaction includes, according to[13], an integral of the type

$$\int \frac{f_1(E)F_2(E)}{E^n}\,dE,$$

where n = 6 in the dipole-dipole interaction case and n = 8 for the dipole-quadrupole interaction. In our case, the function $f_1(E)$ is understood to represent the luminescence corresponding to the $^4F_{3/2} \to {}^4I_{15/2}$ transition and the function $F_2(E)$ represents the absorption corresponding to the $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transition. However, because the $^4F_{3/2} \rightarrow {}^4I_{15/2}$ luminescence spectrum has not been investigated by us, we have considered resonance of the $^4I_{9/2} \rightarrow {}^4F_{3/2}$ absorption and the doubled frequencies of the $^4I_{9/2} \rightarrow {}^4I_{15/2}$ absorption. Such a change in the integrand is fully justified since there are practically no Stokes losses in our case.

The reported results allow one to explain completely the nature of the concentration dependences obtained for the optical spectra, the lifetimes, and the relative quantum yield of Nd^{3+} in CaF_2, SrF_2, and BaF_2. At low Nd^{3+} concentrations in the investigated crystals, single centers predominate and the absolute number of these centers is small, while the quantum yield of the luminescence is high. Centers of this type show practically no interaction with each other or with other centers because they are separated by considerable distances, which corresponds to the linear parts of the curves $\tau_{\mathrm{rad}}(c)$. At intermediate activator concentrations (0.3–1.5 wt.%), the M centers begin to play an important role. These centers have a low quantum yield and a short lifetime. Strong quenching in the M centers is responsible for the fall of the relative quantum yield since the M centers make a considerable contribution to the absorption but practically no contribution to the luminescence. In CaF_2 crystals, the luminescence is completely quenched in the P centers. However, in $SrF_2:Nd^{3+}$ crystals the P-center luminescence is not completely quenched. The degree of quenching of the luminescence of the P centers in BaF_2 crystals is even less. The maximum in the $\eta(c)$ curve of $BaF_2:Nd^{3+}$ at an activator concentration of ~2.5 wt.% is due to a reduction in the relative concentration of the nonluminescent M centers and an increase in the number of the luminescent P centers. Moreover, we must mention that a considerable fall of τ_{rad} of the L centers is observed exactly in the region of the rapid rise of the relative concentration of the P centers (~1 wt.% for SrF_2 and ~2 wt.% for BaF_2). This indicates that energy transfer takes place from the L to the P centers.

It is worth noting also the observation that the lifetime of the excited state of Nd^{3+} in the L centers in BaF_2 is approximately seven times longer than for the L centers in CaF_2 and SrF_2 (cf. Figs. 9a and 10a, as well as Fig. 2 in[6]). The reduction in the transition probability and the increase in the excited state lifetime may be due to the larger lattice constant of BaF_2 or the change in the nature of chemical binding because of the stronger polarization.

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