SPECTRAL INVESTIGATION OF THE STIMULATED RADIATION OF Nd^{3+} *IN* CaF_2

A. A. KAMINSKIĬ, L. S. KORNIENKO, and A. M. PROKHOROV

Nuclear Physics Institute, Moscow State University

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The experimental results are given of a spectral investigation of the transition ${}^4F_{3/2} \to {}^4I_{11/2}$ of the Nd^{3+} ion in CaF_2, in the temperature range from 300 to 15°K. The results of a study of the electron paramagnetic resonance are compared with those of the stimulated radiation study. The wavelengths of five new generation lines are reported.

THE stimulated radiation of the transition ${}^4F_{3/2} \to {}^4I_{11/2}$ of the Nd^{3+} ion in CaF_2 has been detected both at 77°K,[1] and at room temperature.[2] In all cases, only one generation line has been observed.

The present paper reports the experimental results of a spectral investigation of the stimulated radiation of the transition ${}^4F_{3/2} \to {}^4I_{11/2}$ of the Nd^{3+} ion in CaF_2, in the temperature range from 300 to 15°K. The generation was investigated in crystals which had a Nd^{3+} ion concentration ranging from 0.02 to 0.7%, and were grown from the melt in a fluorinating atmosphere by the method involving lowering of a crucible. Below 100°K, five new generation lines, lying between the limits 10 448 and 10 650 Å, were detected.

1. EXPERIMENTAL APPARATUS

A cylindrical illuminating system, having an elliptical cross section and with a pulse-discharge xenon lamp (type IFP-800) placed along one of its focal axes, was used in the experiments. This system was surrounded by a tubular filter of ZhS-16 glass, which cut off the ultraviolet part of radiation of the lamp up to 480 mμ. To cool the filter and the lamp, and also to remove the infrared radiation not needed for the excitation of the generator, tap water circulated between the filter and the lamp. A tubular double-walled glass cryostat, along which the working crystal was placed, was located along the other focal axis. One end of the cryostat was connected to an evacuated Dewar flask containing liquid helium. It was possible to cool the working crystal to approximately 10°K by evaporation of the liquid helium. This was achieved by heating an evaporator (a glass-coated resistance of the PO type) placed in the Dewar flask, and by regulating the passage of helium vapor through the cryostat. Above 77°K, the Dewar flask was filled with liquid nitrogen. The optical efficiency of the illuminating system with the filter, water, and the tubular cryostat amounted to about 0.15.

Preliminary experiments showed that, in the absence of a yellow glass filter, the application of intense light pulses from the lamp to the crystal gave rise to a gradual increase of the excitation threshold and finally complete stoppage of the generation. Thus, for example, the generation observed at room temperatures in samples containing about 0.7% neodymium, stopped after 500—700 flashes of energy of the order of 800 J. At lower neodymium concentrations, the generation stopped after a larger number of flashes.

The use of a light filter, which removed the ultraviolet part of the exciting radiation, made it possible to avoid this harmful effect.

The spectrum was recorded with a DFS-13 spectrograph, having a grating with 1200 lines/mm, whose long-wave range was extended to 1.07 μ. The dispersion of the spectrograph in the region of 1.05 μ was about 1.6 Å/mm. The spectrum was photographed on a film (type I-1070) with a maximum threshold sensitivity of 1.8 standard (GOST) units. The wavelength was measured to within ± 0.1 Å.

In the determination of the threshold values of the electrical energy consumed by the lamp, the stimulated radiation was detected by means of a photomultiplier with an oxygen-cesium photocathode, whose signal was applied to a pulse oscillograph. To record the threshold energy values for various generation lines, the photomultiplier was placed in the exit focal plane of the DFS-13. The time constant of the system recording the time dependence of the radiation was $\approx 10^{-7}$ sec.

Crystal No.	Lines	Generation line wavelengths (Å) and wave numbers (cm^{-1})				
		300° K	140° K	90° K	77° K	50—15° K
2	*A*	10461 (9559)	10457.7 (9562.3)	10457.6 (9562.4)	10457.1 (9562.9)	10457.0 (9563.0)
	B				10466.8 (9554.0)	10466.8 (9554.0)
3	*C*				10447.8 (9571.4)	10447.8 (9571.4)
	A	10461 (9559)	10457.3 (9562.7)	10456.8 (9563.2)	10456.6 (9563.3)	10456.6 (9563.3)
	B			10466.6 (9554.2)	10466.5 (9554.3)	10466.5 (9554.3)
	F					10480.6 (9541.4)
	D					10507.3 (9517.2)
	E					10650.1 (9389.6)
4	*C*			10448.3 (9570.9)		10448.2 (9571.0)
	A	10461 (9559)		10457.0 (9562.9)		10457.0 (9563.0)
	B			10466.8 (9554.0)		10466.7 (9554.1)
	F					10480.9 (9541.2)
	D			10507.6 (9516.9)		10507.5 (9517.0)
	E					10650.3 (9389.4)
5	*C*			10448.2 (9571.0)		10448.2 (9571.0)
	A	10461 (9559)	10457.5 (9562.5)	10457.0 (9563.0)		10456.9 (9563.1)
	B			10466.7 (9554.1)		10466.6 (9554.2)
	F					10480.8 (9541.3)
	D					10507.9 (9516.6)
	E					10650.1 (9389.6)
6	*C*				10448.8 (9570.5)	
	A	10461 (9559)	10457.4 (9562.6)		10457.2 (9562.8)	
	B				10466.8 (9554.0)	

2. EXPERIMENTAL RESULTS

The investigations were carried out on crystals 75 mm long and 6.5 mm in diameter, whose cylindrical surface was polished. The parallelism of the ends was poor and on the average was in error by 1′ for all the crystals. The optical resonator consisted of 13-layer dielectric mirrors, deposited on the crystal ends, and having a reflection coefficient of ≈ 99% (≈ 0.6% transmission) at a wavelength of 1.05 μ. All the crystals used had very good optical homogeneity. Some of the properties of the crystals are listed below.

Crystal No.	1	2	3	4	5	6
Concentration of Nd^{3+} ions, at.%	0.02	0.07	0.35	0.41	0.62	0.70
Threshold values[1)] of electrical energy at 300°K, J	–	370	310	300	330	400
Lifetime of excited level at 300°K, msec	1.0	1.1	1.4	1.5	1.5	1.5

At 300°K, all the crystals, except those having about 0.02% Nd^{3+}, exhibited only one generation line at a wavelength of 10,461 Å (9559 cm^{-1}). Cooling led to the appearance of other lines, whose positions are listed in the main table. Latin capital letters denote the generation lines in increasing order of their excitation threshold.

An investigation of the electron paramagnetic resonance (EPR) spectrum of the investigated crystals showed that some of the Nd^{3+} ions were in a crystal electric field of tetragonal symmetry, and some in a field of orthorhombic symmetry.[3] The tetragonal spectrum predominated in the crystals containing 0.02—0.07% Nd^{3+}. When the concentration was increased to 1%, the intensity of the orthorhombic spectrum increased compared with the tetragonal spectrum, approximately as the square of the Nd^{3+} concentration. Thus, at a Nd^{3+} concentration of about 0.07%, the intensity of the orthorhombic EPR spectrum amounted to several per cent of the tetragonal spectrum intensity, but at a concentration of ≈ 0.4% the orthorhombic spectrum intensity rose to 30%. From these data, we may conclude that in crystals containing less than 0.1% Nd^{3+} the majority of the Nd^{3+} ions is in an environment of tetragonal symmetry, but in crystals containing more than 0.1% Nd^{3+} there are some ions which are also in an environment of orthorhombic symmetry. Optical investigations of the absorption and luminescence spectra also confirmed the presence of two different types of environmental symmetry for Nd^{3+} ions.

Generation frequencies. It is evident from the table that in crystals in which ions have mainly a tetragonal environment, only two lines (A and B) are observed, separated by 9 cm^{-1}. In crystals containing ions of both types, there are, apart from the lines A and B, also four new lines, which may be assumed to be due to ions with an orthorhombic environment.

1)Values of the threshold generation energy refer to the illumination system used.

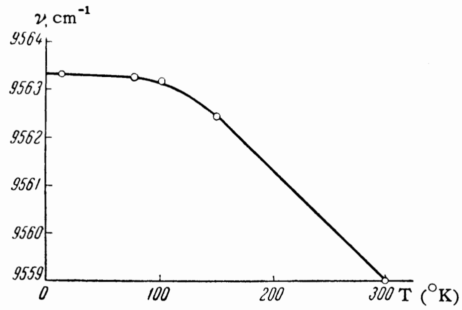

FIG. 1. Temperature dependence of the wavelength of the generation line A.

We had two crystals for each concentration of ions. A study of these crystals showed that the positions of the generation lines coincided, within the experimental error, for each pair of crystals. Figure 1 shows the measured wavelengths of the generation line A plotted as a function of temperature. It is evident that below 50°K the wavelength remains practically constant. This indicates that below 50°K the thermal deformation of the lattice becomes negligibly small and does not affect the parameters of the resonator and the positions of the energy levels. Figure 2 shows the radiation lines for two crystals, with an indication of the wavelengths, threshold energies and working temperature.

Generation line widths. Figure 3 illustrates, for two temperatures, the dependence of the width of the generation line A on the Nd^{3+} concentration. As the concentration was increased from 0.07 to 0.7%, the line width increased by a factor of approximately 2.5. Figure 4 shows the width of the generation lines belonging to ions with different environmental symmetries as a function of the working temperature. The widths could be measured only for the strongest lines with low excitation thresholds. It is seen that the lines belonging to ions with a tetragonal environment (A and B) become narrower on cooling and have their minimum width in the 70—80°K region. Further cooling gradually broadens the A line and its excitation threshold begins to increase. This is evidently associated with the change from stimulated radiation to luminescence, since at temperatures below 18°K the A line radiation has not been recorded. The B line width remains practically constant. The C line, associated with ions having an orthorhombic environment, becomes narrower and narrower on cooling in the investigated range of temperatures and the excitation threshold decreases proportionally. Thus, in the crystals with Nd^{3+} concentration of about 0.62% the C line width at 28°K is ≈ 0.07 cm^{-1}. All the measurements of the line widths were carried out with an accuracy of $\pm 30\%$ under the nom-

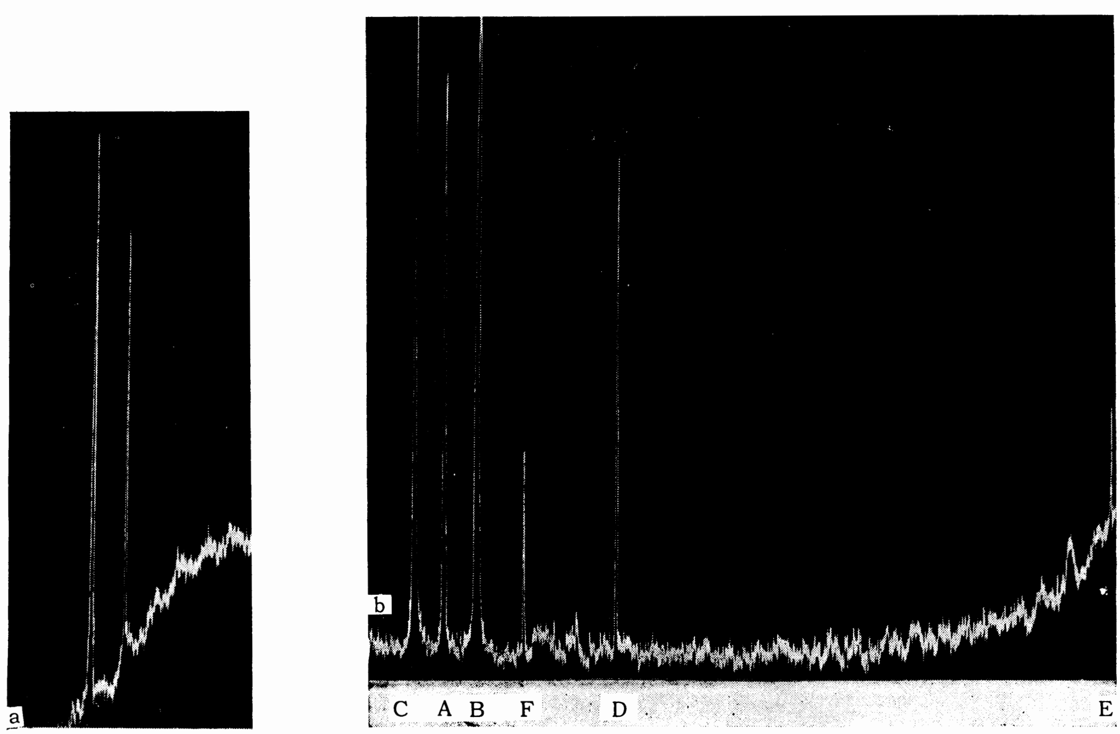

FIG. 2. Stimulated radiation spectra at 50°K: a) crystal with 0.07% Nd^{3+}, line A at $\lambda = 10\,457.0$ Å, 60 J; line B at $\lambda = 10\,466.8$ Å, 176 J; b) crystal with 0.62% Nd^{3+}, line A at $\lambda = 10\,456.9$ Å, 70 J; line B at $\lambda = 10\,466.6$ Å, 160 J; line C at $\lambda = 10\,448.2$ Å, 240 J; line D at $\lambda = 10\,507.9$ Å, 870 J; line E at $\lambda = 10\,650.1$ Å, 1100 J; line F at $\lambda = 10\,480.8$ Å, 1350 J.

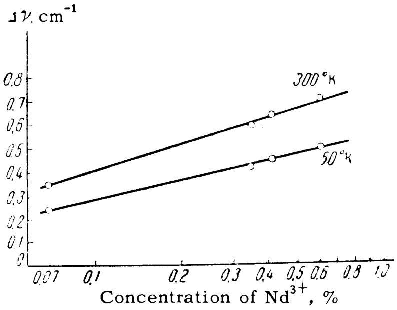

FIG. 3. Concentration dependence of the A generation line width.

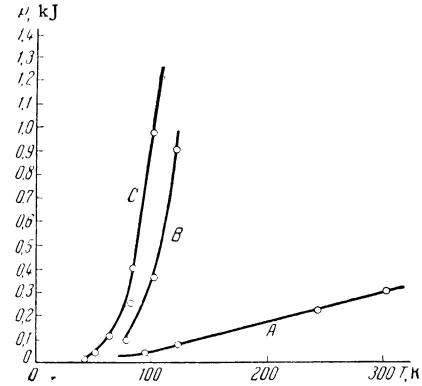

FIG. 5. Temperature dependence of the excitation threshold of the generation lines of a crystal containing 0.41% Nd^{3+}.

inal conditions of the power supply to the IFP-800 lamp.

Threshold excitation energies. All the listed values of the threshold energies were measured in the illumination system described above and having an efficiency of about 0.15. For the A line at 300°K, the values of the threshold excitation energies are listed at the beginning of Sec. 2. The crystals with Nd^{3+} concentration of about 0.4% had minimum threshold at this temperature. Figure 5 shows the temperature dependence of the excitation threshold for some of the generation lines of crystals containing about 0.4% Nd^{3+}. It is evident that the B and C lines have a threshold approximately 7–12 times greater than the A line at about 80°K. At 40°K, the threshold of the D line amounts to 300 J, of the E line 380 J, and of the F line about 500 J. We shall mention for the sake of comparison that the excitation threshold of the C line at 40°K does not exceed 15 J.

Time dependence of the generation. The duration and the time dependence of the generation were measured from oscillograms of a pulse oscillograph whose horizontal scan was calibrated with respect to time. Figure 6 shows oscillograms of the radiation pulses for three lines. For the A line (Fig. 6b), a characteristic generation spike was observed, the total duration of the pulse depending on the energy supplied to the lamp. Thus, for example, at 90°K with the energy three times greater than the threshold value, the total duration amounted to about 400 μsec, with the individual spikes having an average duration of ≈ 10 μsec. The nature of the pulse of the B and C lines (Figs. 6c and 6d) differed somewhat from the radiation pulse of the A line. The generation pulse obviously did not have these little spikes. With an increase in temperature or a reduction in the excitation energy, each of these

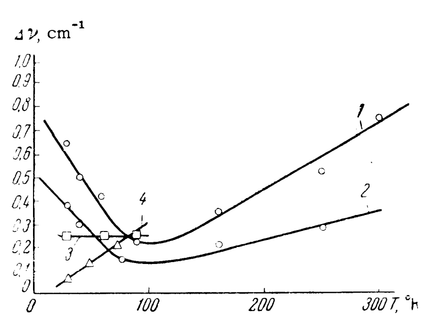

FIG. 4. Temperature dependence of the radiation line widths of crystals containing 0.07 and 0.62% Nd^{3+}: 1) line A, 0.62% Nd^{3+}; 2) line A, 0.07% Nd^{3+}; 3) line B, 0.62% Nd^{3+}; 4) line C, 0.62% Nd^{3+}.

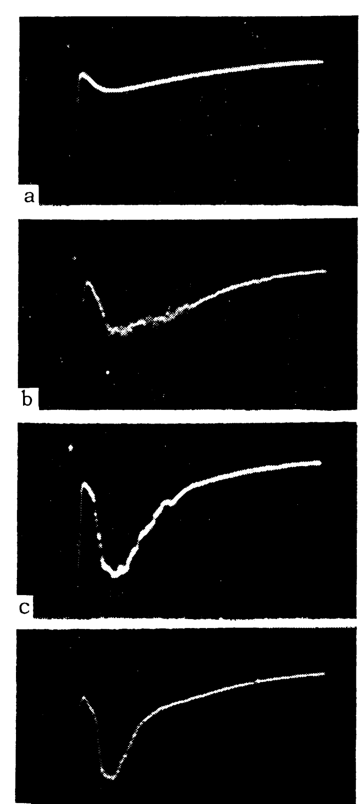

FIG. 6. Time dependence of the generation lines of a crystal containing 0.41% Nd^{3+}: a) no generation; b) generation of line A; c) generation of line B; d) generation of line C.

pulses decreased in amplitude and shifted to the right with respect to the excitation pulse. The figure shows the generation of the B and C lines when the threshold energy was exceeded by a factor of 1.5. In both cases, the duration of the radiation amounted to about 200 μsec at 90°K. The time resolution of the recording system was, as mentioned earlier, $\approx 10^{-7}$ sec. The nature of the time dependence of other lines could not be investigated in detail because of their high excitation thresholds.

3. DISCUSSION OF THE EXPERIMENTAL RESULTS

The stimulated radiation is due to transitions between the Stark components of the levels $^4F_{3/2}$ and $^4I_{11/2}$, separated by approximately 12 000 cm^{-1}. In tetragonal and orthorhombic symmetry fields, the upper level $^4F_{3/2}$ splits into two components, and the lower level $^4I_{11/2}$ into six.[4] Consideration of the dependence of the behavior of individual generation lines on the Nd^{3+} ion concentration and working temperature allows one to make some suggestions about the Stark components between which the stimulated transitions take place.

Orthorhombic environmental symmetry. The generation lines C, D, E, and F appear only in crystals with Nd^{3+} concentrations from 0.35% up. With cooling, their intensity increases and the threshold decreases. We may assume that in this case the stimulated transitions take place from the lower component of the $^4F_{3/2}$ level.

Tetragonal environmental symmetry. This case occurs both in crystals with low Nd^{3+} content and in crystals with a mixed spectrum. The A line intensity decreases gradually with cooling, and below 18°K the radiation practically disappears. The A line begins to broaden rapidly when there is cooling to below 70—80°K, and it is then recorded only at very high excitation energies. Such behavior may be explained by the fact that the generation takes place from the upper component of $^4F_{3/2}$, separated by approximately 40—70 cm^{-1} from the lower component. The B line appears at liquid nitrogen temperatures. Its threshold decreases with cooling, but the width remains practically constant. This corresponds to the generation from the lower component of $^4F_{3/2}$ (cf. the main table and Fig. 2).

The positions of the remaining components and the separations between them may be determined from the luminescence and absorption spectra, recorded using high-resolution instruments.

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[1] L. F. Johnson, J. Appl. Phys. 38, 756 (1962).

[2] Kaminskiĭ, Kornienko, Makarenko, Prokhorov, and Fursikov, JETP **46**, 386 (1964), Soviet Phys. JETP **19**, 262 (1964).

[3] Kask, Kornienko, and Fakir, FTT **6**, 549 (1964), Soviet Phys. Solid State **6**, 430 (1964).

[4] M. A. El'yashevich, Spektry redkikh zemel' (Spectra of Rare Earths), Gostekhizdat, 1963.

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