STIMULATED RADIATION FROM $Y_3Al_5O_{12}-Nd^{3+}$ *CRYSTALS*

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The stimulated radiation and absorption and luminescence spectra from neodynium-activated (Nd^{3+}) yttrium-aluminum garnet ($Y_3Al_5O_{12}$) have been studied. A level scheme for the $^4F_{3/2}$ and $^4I_{11/2}$ terms at 300 and 77° K is proposed and compared with the observed induced transitions. Lasers are described of the pulsed type, a quasicontinuous type with a pyrotechnic source of excitation, and also a continuous laser.

INTRODUCTION

THE first report of stimulated radiation from crystals of yttrium-aluminum garnet $Y_3Al_5O_{12}$ activated by Nd^{3+} ions (YAlG) was made by Geusic, Marcos, and Van Uitert.[1] They constructed both pulsed and continuous lasers from YAlG—Nd^{3+} crystals. Somewhat later, Kiss and Duncan[2] observed sensitization of the radiation of Nd^{3+} ions by Cr^{3+} ions in YAlG crystals, as the result of which they constructed a laser with better characteristics.

In the present paper we report studies of the absorption, luminescence, and stimulated radiation spectra of $Y_3Al_5O_{12}-Nd^{3+}$ crystals produced in the Crystallography Institute of the U.S.S.R. Academy of Sciences. On the basis of the data obtained we have constructed a diagram of the Nd^{3+} levels participating in the laser action. In the paper we describe a pulsed laser, a quasicontinuous laser using a pyrotechnic source of excitation, and a continuous laser.

CRYSTALS USED FOR THE STUDIES

The YAlG—Nd^{3+} crystals used were grown from solution in a melt of PbO and PbF_2[3,4] and from the melt. Neodymium oxide was added to the melt in quantities from 0.2 to 2.0 wt.%. It was established that the Nd^{3+} enters into the crystal only partially, in the isomorphic replacement of yttrium ions. The neodymium concentration in the grown crystals was measured with an x-ray microanalyzer.[1)] From the single crystals produced, specimens were prepared for investigation. For the experiments on laser action we used cylindrical rods of circular (2–5 mm diameter) or square (2.5 × 2.5 mm) cross section and 5–35 mm long. The end faces of the crystals were plane-parallel to better than 15″. The optical quality of the crystals was satisfactory. In some samples of YAlG, in addition to neodymium, we introduced chromium (Cr_2O_3). According to the Linde catalog[5] the garnet crystals have the following characteristics:

refractive index:	1.83 (1.815[6])
density:	4.2 g/cm^3
melting point:	1970° C
hardness: (Mohs scale)	8.5
heat capacity:	0.14 cal/g-deg
thermal expansion coefficient:	9.3×10^{-6} deg^{-1}
thermal conductivity:	0.03 cal/deg-cm-sec

OPTICAL PROPERTIES OF YAlG—Nd^{3+} CRYSTALS

The spectroscopic properties of YAlG—Nd^{3+} crystals have been studied by Koningstein and Geusic[7] and by Feofilov and co-workers.[8] The American authors proposed a scheme for the crystal splitting of certain terms and have given a theoretical interpretation of this scheme. It was assumed that the crystal electric field surrounding the Nd^{3+} ion is tetragonal. Feofilov et al.[8] have used the results of a study of the infrared luminescence of the Nd^{3+} ion in $Y_3Al_5O_{12}$ to construct a scheme of Stark levels of all of the terms of the ground multiplet ^4I and the $^4F_{3/2}$ term. The data of these two studies differ somewhat, particularly in the structure of the $^4I_{13/2}$ terms and in the splitting of the $^4F_{3/2}$ term. Koningstein and Geusic[7] find the splitting of the $^4F_{3/2}$ term at 300° K

[1)]The measurements were made by V. P. Lider.

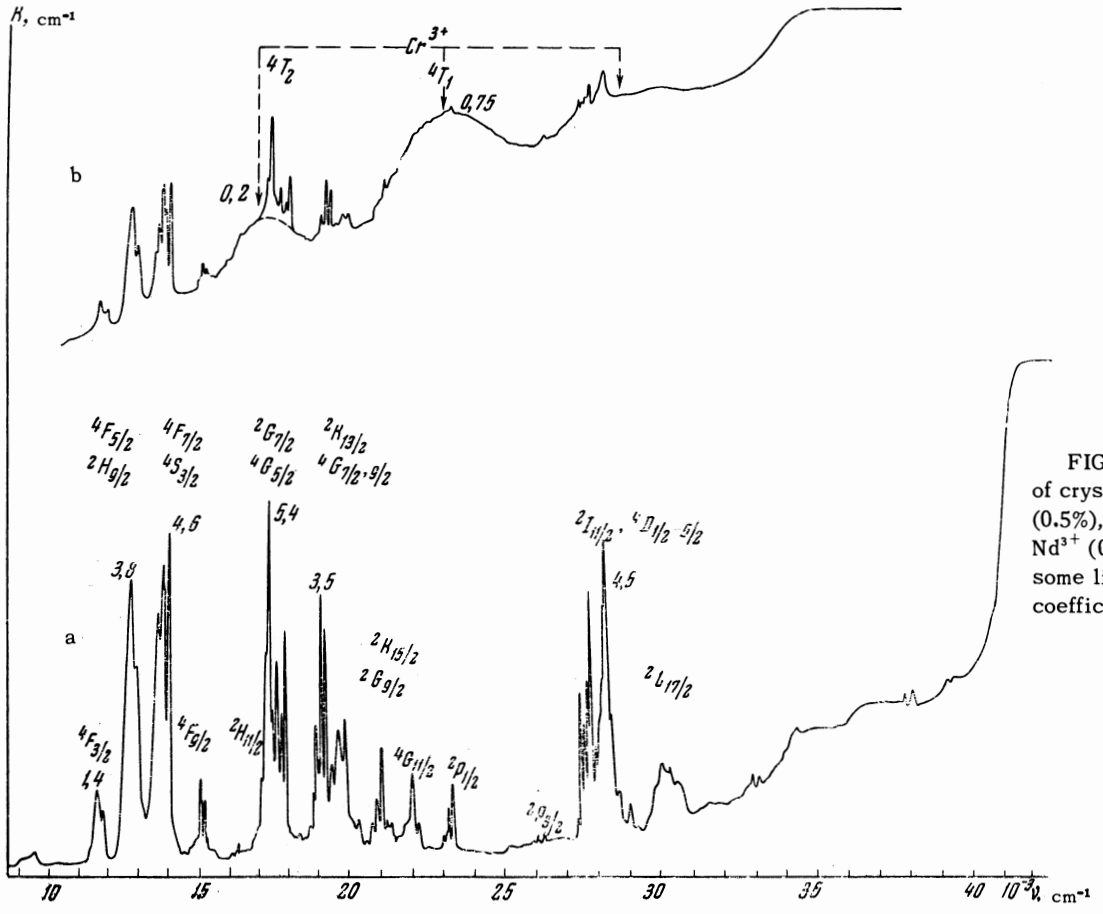

FIG. 1. Absorption spectra of crystals: a—of $Y_3Al_5O_{12}$—Nd^{3+} (0.5%), b—$Y_3Al_5O_{12}$—Cr^{3+} (0.2%)—Nd^{3+} (0.2%); T = 300°K. For some lines the peak absorption coefficients are shown.

to be 88 cm^{-1} and Feofilov et al.[8] report a value of 84^{-1}.

Our spectroscopic studies of the stimulated radiation have shown that laser action occurs in YAlG—Nd^{3+} crystals at a wavelength of 10 612 Å (9423 cm^{-1}) at 77° K and at 10 641 Å (9398 cm^{-1}) at room temperature. In comparing the results obtained with the data of the studies cited above[7, 8] we observed a certain discrepancy: the stimulated transitions observed are not included in the level schemes presented. The purpose of the spectroscopic studies described was to improve the accuracy of the results discussed above[7, 8] and to obtain the appropriate characteristics of YALG—Nd^{3+} and YAlG—Cr^{3+}—Nd^{3+} crystals, which are extremely important in the study of lasers.

Absorption spectra.

The broad-range absorption spectra of YAlG crystals was studied in a SP-700 spectrophotometer at 77 and 300° K over the frequency range 9000–42 000 cm^{-1}. Figure 1a shows the absorption spectrum obtained at 300° K from a YAlG crystal containing about 0.5% of Nd^{3+}, grown from solution in a melt. Values of the peak absorption coefficients have been placed over some of the characteristic lines. It can be seen that the most intense bands lie in the region 12 000–20 000 cm^{-1}.

In contrast to the absorption spectrum of $CaWO_4$—Nd^{3+} crystals, which have been used to make lasers with extremely low excitation thresholds,[9] a redistribution of the intensities of the principal bands occurs in the absorption spectrum of the YAlG—Nd^{3+} crystal. Thus, crystals of scheelite with Nd^{3+} have a strong absorption at a wavelength of ~5800 Å ($^2G_{7/2}$ and $^4G_{5/2}$) which considerably exceeds the absorption in the other bands. In garnet crystals the infrared bands ($^4F_{5/2}$, $^2H_{9/2}$, $^4F_{7/2}$, $^4S_{3/2}$) are the most intense. This fact provides the possibility of efficient use of an incandescent tungsten lamp for excitation of a laser,[1] and also of successfully using selective sources of infrared radiation (semiconductor lasers).

In this connection, in order to match the wavelengths emitted by semiconductor lasers with the spectrum of a YAlG—Nd^{3+} crystal, we have shown in Fig. 2 the detailed Stark structure of the infrared absorption bands corresponding to transitions from the ground level $^4I_{3/2}$ to the components of the terms $^4F_{3/2}$ (11 450 cm^{-1}), $^4F_{5/2}$, $^2H_{9/2}$

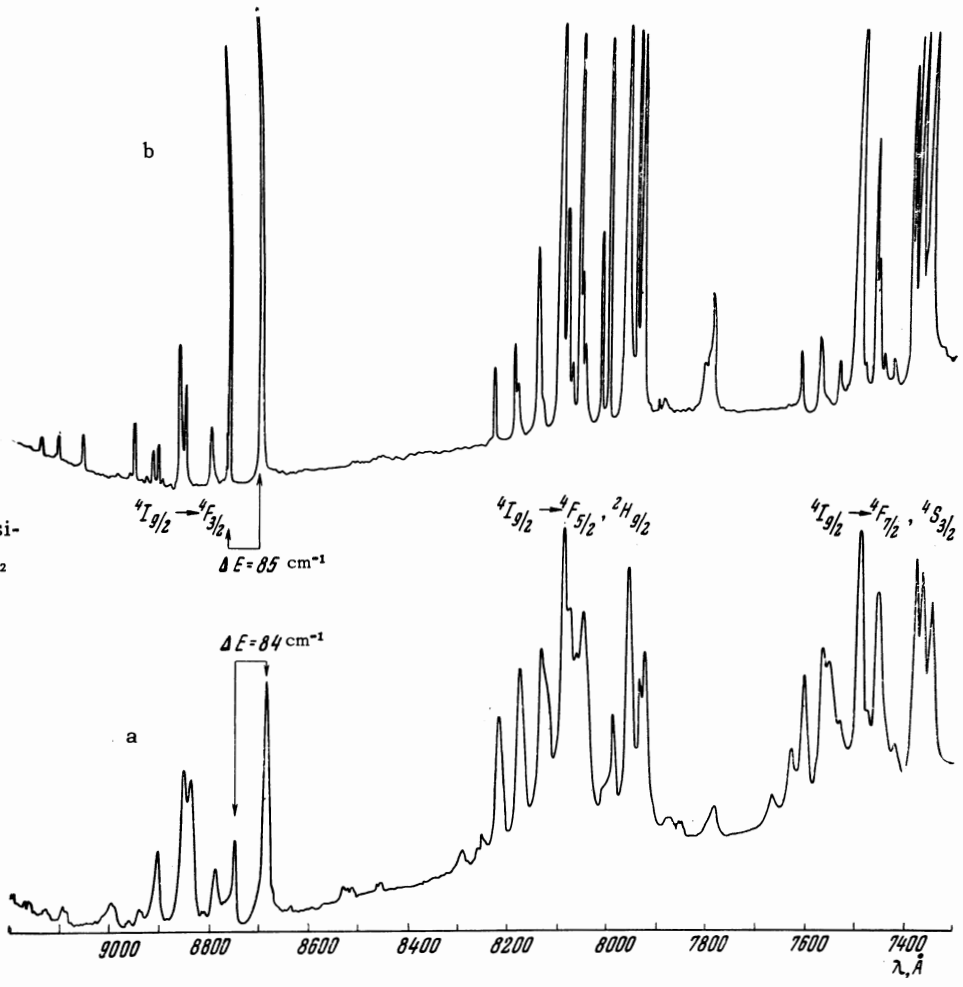

FIG. 2. Absorption spectra of a crystal of $Y_3Al_5O_{12}$—Nd^{3+}(0.5%); transitions $^4I_{9/2} \rightarrow {}^4F_{3/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$ and $^4I_{9/2} \rightarrow {}^4F_{7/2}$, $^4S_{3/2}$. Spectrum a—at 300°K, b—at 77°K.

(12 600 cm^{-1}), and $^4F_{7/2}$, $^4S_{3/2}$ (13 500 cm^{-1}). The spectra were obtained in a DFS-12 diffraction spectrometer with a 600 line/mm grating at temperatures of 77 and 300° K by the method described by Voron'ko et al.[10] We have listed in Table I the peak absorption coefficients of the individual Stark components for a YAlG specimen with a Nd^{3+} concentration of about 0.5%. It can be seen that with reduction of the temperature the absorption coefficients of some lines (transitions from the ground level) increase sharply.

A detailed study of the structure of the $^4F_{3/2}$ term also was made in a DFS-13 diffraction spectrograph (1200 line/mm grating) with a dispersion of ~1.6 Å/mm. According to our measurements, the value of the splitting of the $^4F_{3/2}$ term is 85 cm^{-1} at 77° K and 84 cm^{-1} at room temperature (the splitting values are given with an accuracy of ±0.5 cm^{-1}), which is very close to the value given by Feofilov et al.[8]

In addition to the principal lines, which are due to transitions from the ground level, components are observed in the spectra which correspond to transitions from excited levels of the $^4I_{9/2}$ term. This is most easily seen in the groups $^4I_{9/2} \rightarrow {}^4F_{3/2}$ and $^4I_{9/2} \rightarrow {}^2P_{1/2}$ (Fig. 3). At room temperature the splitting of the lowest components of the $^4I_{9/2}$ term is respectively 133, 201, and 307 cm^{-1}, and at 77° K, 134, 202, and 310 cm^{-1}.

In order to improve the operating characteristics of crystalline lasers, doubly activated media have recently come into use. In particular, Cr^{3+} ions have been introduced in YAlG—Nd^{3+} crystals as a sensitizing additive. As we have mentioned above, Kiss and Duncan[2] have described a laser using YAlG—Cr^{3+}—Nd^{3+} crystals and have discussed the mechanism of energy transfer from the Cr^{3+} ions to the radiating Nd^{3+} ions. Figure 1b shows the absorption spectrum of a YAlG—Cr^{3+}—Nd^{3+} obtained at 300° K in the SP-700 spectrophotometer. The concentrations of neodymium and chromium were ~0.2%. As can be seen, the combined spectrum is a superposition of the two spectra. Cr^{3+} ions in YAlG have two broad, intense bands $^4T_1$ (23 000 cm^{-1}) and $^4T_2$ (17 000 cm^{-1}), which give the crystal a greenish coloration. Doubly activated YAlG crystals utilize the radiation from the excitation lamp more efficiently.

Table I

λ, Å (ν, cm⁻¹)	ΔE, cm⁻¹	K, cm⁻¹	λ, Å (ν, cm⁻¹)	K, cm⁻¹
$^4I_{9/2} \rightarrow {}^4F_{3/2}$; T = 77° K			$^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$; T = 77° K	
9137 (10944)		0,15	8198 (12198)	0,37
9103 (10985)		0,16	8175 (12232)	0,54
9051 (11048)		0,17	8170 (12240)	0,29
8946 (11178)		0,35	8129 (12302)	1,2
8907 (11227)		0,2	8086 (12367)	20,5
8901 (11235)		0,17	8071 (12390)	1,5
8853 (11295)		0,6	8060 (12407)	0,37
8840 (11312)	202	0,5	8046 (12428)	10,0
8787 (11380)	134 + 202 = 336	0,3	8042 (12435)	—
8750 (11429)		5	8036 (12444)	—
8685 (11514)		12	8001 (12498)	1,3
$^4I_{9/2} \rightarrow {}^4F_{3/2}$: T = 300° K			7986 (12522)	6,6
9002 (11107)		0,1	7949 (12580)	16,7
8911 (11222)		0,37	7930 (12610)	7,5
—		—	7919 (12628)	7,4
8857 (11290)		0,8	$^4I_{9/2} \rightarrow {}^4F_{7/2}, {}^4S_{3/2}$; T = 77° K	
8844 (11306)	133	0,74	7782 (12850)	0,7
8792 (11374)	201	0,27	7598 (13161)	0,33
8754 (11423)	133 + 201 = 334	0,37	7560 (13227)	0,4
8690 (11507)		1,4	7519 (13300)	0,23
			7483 (13364)	19,0
			7465 (13396)	—
			7446 (13430)	2,3
			7440 (13441)	0,86
			7426 (13466)	0,18
			7406 (13503)	0,17
			7373 (13563)	4,5
			7368 (13572)	10,5
			7355 (13596)	11,6
			7335 (13633)	9,2

Luminescence spectra

The complete luminescence spectrum corresponding to transitions from levels of the $^4F_{3/2}$ term to components of the ^4I ground multiplet (0.85—2.2μ) was studied by means of an IKS-12 infrared spectrometer whose detector utilized a PbS photoconductive cell and a synchronously phased detector. Figure 4 shows the luminescence spectrum of a YAlG—Nd^{3+} crystal, obtained at 300° K. As a result of the fact that the intensity of luminescence in the groups studied is different, the spectrum has been recorded with difference entrance slits and synchronous detector amplification. Figure 4 shows the relative slit widths and line intensities. As can be seen, the most intense luminescence corresponds to the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$.

A detailed study of the luminescence spectrum corresponding to the transition $^4F_{3/2} \rightarrow {}^4F_{11/2}$ was made with the DFS-12 diffraction spectrometer at 77 and 300° K. The spectra obtained are shown in Fig. 5. It can be seen that, as we go from room temperature to 77° K, a redistribution of the intensities of the individual components occurs, as well as a small displacement of all the lines in the short wavelength direction. The splitting of the $^4F_{3/2}$ term found in study of the absorption spectrum shows up well in the luminescence spectra. The wavelengths of the lines of the luminescence spectra of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition are given

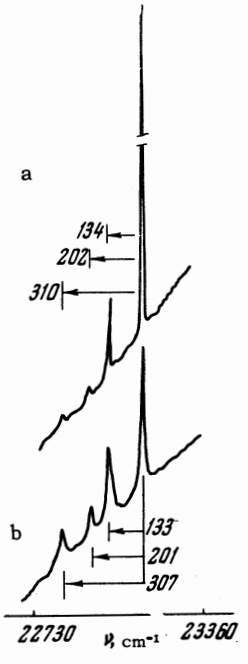

FIG. 3. Absorption spectra of a crystal of $Y_3Al_5O_{12}$–Nd^{3+}(0.5%); transition $^4I_{9/2} \rightarrow {}^2P_{1/2}$. Spectrum a—for 77°K, b—for 300°K.

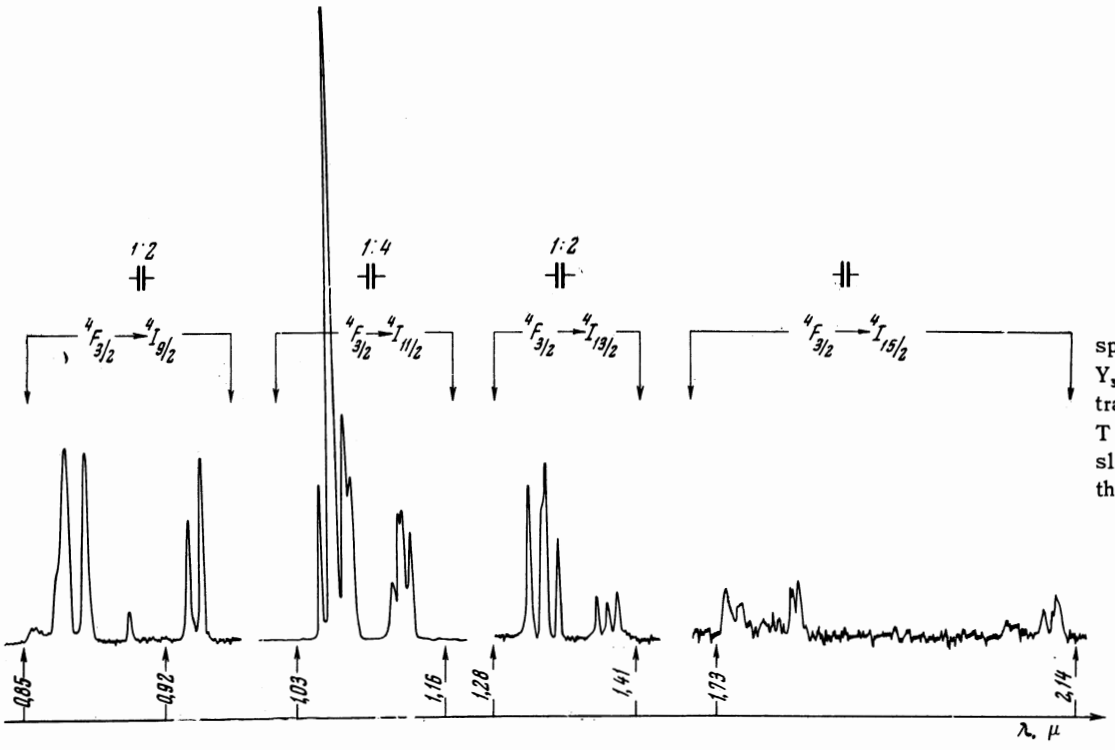

FIG. 4. Luminescence spectrum of crystal of $Y_3Al_5O_{12}$—Nd^{3+}(0.5%); transitions $^4F_{3/2} \rightarrow {}^4I_{9/2\text{-}15/2}$, T = 300°K (the relative slit widths are given at the top).

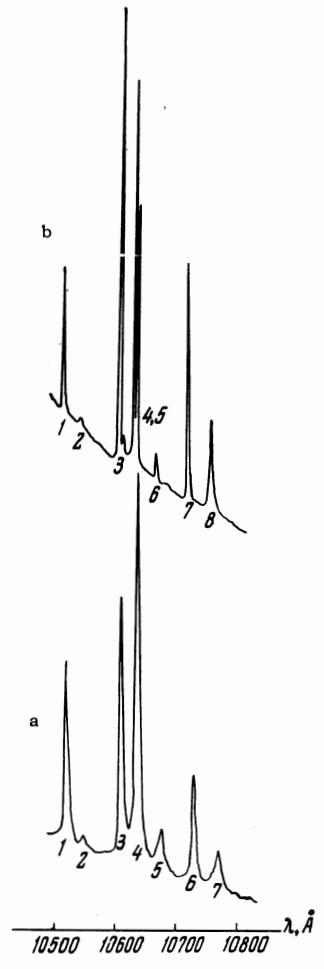

FIG. 5. Luminescence spectra of crystal of $Y_3Al_5O_{12}$—Nd^{3+}(0.5%); transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$. Spectrum a—for 300°K, b—for 77°K.

in Table II.

The widths of the luminescence lines for the most intense lines in which emission was detected are $\Delta\nu \approx 1$ cm^{-1} for $\lambda_e = 10\,612$ Å (77° K) and $\Delta\nu \approx 7.5$ cm^{-1} for $\lambda_e = 10\,641$ Å (300° K), the second case being the value for two lines which are not resolved at 300° K.

It should be noted that in the study of the detailed structure of the absorption and luminescence spectra with high concentrations of Nd^{3+}, new lines appear which are not included in the level scheme which has been determined. This fact apparently indicates that in garnet crystals with significant concentrations of Nd^{3+}, new optical centers begin to be formed with their own optical properties.

The lifetime of the $^4F_{3/2}$ excited state of the YAlG—Nd^{3+} crystal was measured with the technique described by Kaminskiĭ et al.[11] For crystals with an Nd^{3+} content of about 0.1% the lifetime

Table II

T = 300° K		T = 77° K	
λ, Å (ν, cm^{-1})	ΔE, cm^{-1}	λ, Å (ν, cm^{-1})	ΔE, cm^{-1}
10523 (9503)		10517 (9508)	
	84		85
10546 (9482)		10546 (9482)	
	84		85
10617 (9419)		10612 (9423)	
	84		85
10641 (9398)		10635 (9403)	
	84		85
10684 (9360)		10642 (9397)	
	84		85
10739 (9312)		10676 (9367)	
	84		85
10781 (9276)		10732 (9318)	
			85
		10774 (9282)	

τ at 300 and 77° K is approximately the same and equal to ~240 μsec; for specimens with Nd^{3+} concentrations of 0.5%, it is $\tau \approx 220$ μsec.

STIMULATED RADIATION

Pulsed operation

The laser employed a condenser of elliptical cross section with a luminous efficiency of ~0.5,[12] at one focus of which was placed a type IFP-800 pulsed xenon lamp. The lamp was surrounded by a tubular filter of ZhS-17 glass. Water flowed between the filter and the lamp. The working crystal was placed at the other focus. The optical resonator consisted of spherical mirrors with multilayer dielectric coverings, which were arranged confocally. The transmission of the mirrors at a wavelength of 1.06μ was ~0.7%. In studying the emission at 77° K, the crystal, with silver mirrors deposited on its end surfaces, was placed in a tube-shaped Dewar vessel. The radiation was detected through a liquid nitrogen layer ~40 mm thick.

The spectral composition of the stimulated radiation was studied in spectrographs of type DFS-13 (~1.6 Å/mm) and PGS-2 (~7 Å/mm). The spectrum was photographed on I-1070 film. The spectrum of iron in the third order was used as a standard. A hollow-cathode lamp was used.

At room temperature the emission wavelength of YAlG with an Nd^{3+} concentration of 0.5% is 10 641 Å (9398 cm^{-1}), which is 7 Å shorter than the wavelength given by the American authors.[1] At 77° K λ_e = 10 612 Å (9423 cm^{-1}). Figure 6 shows the emission spectra for the two temperatures.

The time characteristics of the radiation were investigated by means of a photomultiplier with an oxygen-cesium photocathode, the signal from which was fed to a pulse oscillograph. With an excitation energy three times the threshold value, the duration of the emission was ~300 μsec. The radiation is in spikes.

At room temperature, garnet rods 18 mm long and 2–4 mm in diameter began to emit at an excitation energy of 6 joules. In the absence of a yellow filter the threshold was reduced to 3 joules. It should be noted that the luminous column of the excitation lamp was more than four times longer than the crystal. The excitation threshold was reduced to 2 joules at 77° K.

Quasicontinuous operation

In the regime of long pulses considerably exceeding the lifetime of the excited state, we used as an excitation source a pyrotechnic lamp consisting of a quartz bulb inside which was mounted a plate of a compressed mixture of pyrotechnic composition. $KClO_4$ was used as an oxidizing agent and zirconium as a combustible. A detailed description of the pyrotechnic lamps used is given by Bodretsova et al.[13]

The experiments on laser operation were performed with crystals 5–18 mm long. In all cases an external resonator was used, similar to that described above. A crystal ~5 mm long began to emit with a weight of the pyrotechnic charge of ~10 mg (plate dimensions 8 × 2 × 0.5 mm). For a charge weight of ~100 mg the duration of the pulse emission was ~10 msec. This indicates that the emission is quasicontinuous, since the lifetime of the $^4F_{3/2}$ excited state of the Nd^{3+} ion in YAlG is 50 times shorter. Experiments with pyrotechnic excitation were performed only at 300° K.

Continuous operation

To obtain continuous radiation we used a YAlG crystal ~35 mm long and ~3 mm in diameter with an activator concentration of ~0.3%. An illumination chamber similar to that described by Kaminskiĭ et al.[9] was used as an excitation system. In our experiments only the yellow filter surrounding the working crystal was absent. As in the experiments described above, the optical resonator was produced by external spherical mirrors placed confocally. With the illumination system used, laser action at room temperature began at an input power of 4.5 kW to the lamp. With the same illumination system in the pulse regime of excitation the threshold was about 1 joule. The width of the emission line at 300° K was ~1 Å (~0.9 cm^{-1}).

The high excitation threshold in the continuous regime is explained, first, by the poor matching of the emission spectrum of the excitation source to the most intense absorption bands of the YAlG–Nd^{3+} crystal and, second, by the inadequate optical quality of the specimens and the non-optimum concen-

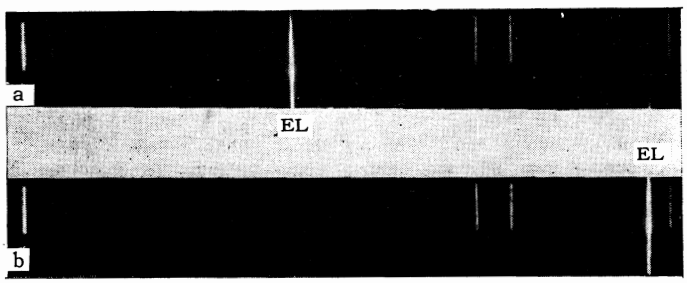

FIG. 6. Emission spectra of crystal of $Y_3Al_5O_{12}$–Nd^{3+} (0.5%): a–for 300°K, b–for 77°K. EL–emission lines.

tration of the activator.

CONCLUSION

On the basis of the results of studies made of the absorption, luminescence, and emission spectra, we have constructed a level scheme for 77 and 300° K for the Nd^{3+} $^4F_{3/2}$ and $^4I_{11/2}$ terms, which take part directly in the stimulated emission (Fig. 7). At room temperature the stimulated transition connects the upper level of the $^4F_{3/2}$ term and the 2110 cm^{-1} level of the $^4I_{11/2}$ term. At 77° K the emission corresponds to a transition from the lower level of the $^4F_{3/2}$ term to the 2006 cm^{-1} level ($^4I_{11/2}$). In Fig. 7 the stimulated transitions are indicated by the heavy arrows.

The results on the study of the optical centers of Nd^{3+} in $Y_3Al_5O_{12}$ crystals will be published in another paper.

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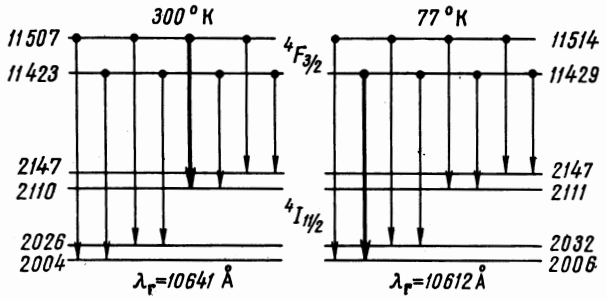

FIG. 7. Diagram of crystal splitting of $^4F_{3/2}$ and $^4I_{11/2}$ terms in a $Y_3Al_5O_{12}-Nd^{3+}$ crystal.

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