AN ANALYSIS OF THE STARK STRUCTURE OF TR^{3+} *ION SPECTRA BY A LASER SPECTROSCOPY METHOD*

A. A. KAMINSKIĬ

Crystallography Institute, USSR Academy of Sciences

Submitted July 16, 1968

Zh. Eksp. Teor. Fiz. 56, 83–87 (January, 1969)

A new method for the analysis of the Stark structure of trivalent rare-earth ion spectra is described, in which lasers with combined active media are employed.

A new method is proposed for the precision analysis of the Stark structure of TR^{3+} ion spectra in various crystal matrices; the method is based on a spectroscopic investigation of stimulated transitions in lasers with combined active media.[1]

The first stage in the spectroscopic investigations of crystals activated with TR^{3+} ions is an analysis of the Stark structure of their spectra and the construction of a detailed energy level scheme. This stage becomes more important if the TR^{3+} ions are distributed in the matrix in the form of centers with various structures and the medium itself is laser-active. The method of equivalent operators, developed by Stevens, Elliott, and Judd[2] is currently widely used in theoretical calculations of the levels of TR^{3+} ions in various crystals. In spite of the approximate nature of this method, it requires the knowledge of the exact values of the crystal field parameters B_n^m, particularly in the case of optical centers which have small absolute values of the term splitting. Investigations have shown that it is best to determine B_n^m from the experimentally measured splitting of terms of the main multiplet, which usually satisfies well the Russell–Saunders coupling.[3] The experimental aspects of these problems are normally solved by standard spectroscopic methods, including studies of low-temperature absorption and luminescence spectra. Unfortunately, high accuracy cannot always be achieved in such methods. The errors are particularly large in the determinations of the positions of the Stark components of the lower terms, transitions between which correspond to the infrared range.

In that respect, the proposed method is more accurate because for some ions (Nd^{3+}) it does not require low temperatures and, which is most important, it uses stimulated transitions which are almost always due to transitions between lower terms in TR^{3+} ions.[4] We shall explain this method using, as an example, an analysis of the splitting of the $^4F_{3/2}$ and $^4I_{11/2}$ terms of Nd^{3+} ions, which are directly related to stimulated transitions in YVO$_4$, CaWO$_4$, Y$_3$Al$_5$O$_{12}$, and LaF$_3$ crystals.

YVO$_4$-Nd^{3+} crystals. The spectroscopic and laser properties of yttrium orthovanadate containing Nd^{3+} ions are described in[5]. At 300° K, a laser based on YVO$_4$-Nd^{3+} ($\sim$1 wt.%) emits two wavelengths:[1)] λ_e = 10 641 Å (9398 cm^{-1}), known as line A, and λ_e = 10 664 Å (9377 cm^{-1}) which is known as line B. Figure 1 shows the luminescence spectrum of a YVO$_4$-Nd^{3+} crystal, corresponding to the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$, observed at 300° K using a DFS-12 spectrometer, as well as the crystal splitting scheme of the terms $^4F_{3/2}$ and $^4I_{11/2}$. A laser with a combined active medium, consisting of YVO$_4$-Nd^{3+} + CaF$_2$-YF$_3$-Nd^{3+}, exhibits two new stimulated transitions: transition C at λ_e = 10 625 Å (9412 cm^{-1}) and transition D at λ_e = 10 648 Å (9391 cm^{-1}). It is evident from Fig. 1 that these transi-

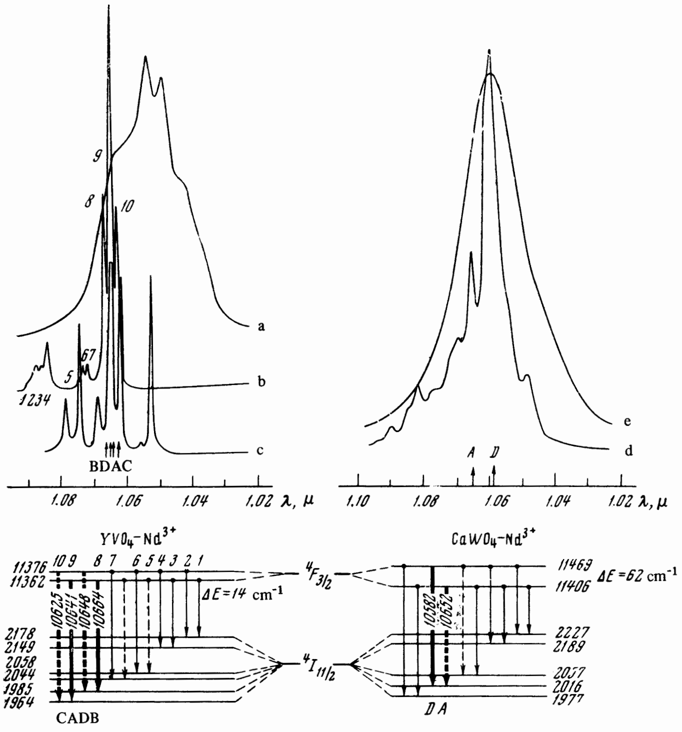


FIG. 1. Unpolarized luminescence spectra ($^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition, T = 300°K) of the following Nd^{3+}-doped crystals: a) CaF$_2$-YF$_3$; b) YVO$_4$; c) Y$_3$Al$_5$O$_{12}$; d) CaWO$_4$; e) neodymium glass LGS-1; the crystal splitting schemes of the $^4F_{3/2}$and $^4I_{11/2}$ terms of Nd^{3+} ions in YVO$_4$ and CaWO$_4$ crystals are given below the spectra. The positions of the levels are given in cm^{-1} and the wavelength of transitions between them are given in Å. Thick arrows denote stimulated transitions (dashed arrows are used to indicate newly discovered transitions).

[1)] The spectral composition of the emitted radiation depends on the mutual orientation of the optical and geometrical axes of a crystal.

tions couple the 1964 and 1985 cm^{-1} components of the $^4I_{11/2}$ term with the R_2 level of the $^4F_{3/2}$ term (11 376 cm^{-1}). The observed stimulated transitions have made it possible to double check and to obtain a more accurate value of the splitting of the $^4F_{3/2}$ term, which is found to be $\Delta E = 14 \pm 0.2$ cm^{-1}. It must be mentioned that transition D (10 648 Å) does not appear in the luminescence spectrum at 300°K. A laser with a combined active medium, consisting of YVO_4-Nd^{3+} + $Y_3Al_5O_{12}$-Nd^{3+} emits, at 300°K, only one line A. All the laser spectra considered so far are shown in Figs. 2a—2e.

$CaWO_4$-Nd^{3+} crystals. The fullest information on the spectroscopic and laser properties of scheelite containing Nd^{3+} ions are given in[6]. At 300°K, a $CaWO_4$-Nd^{3+} laser with the zeroth orientation of the c axis generates line D at a wavelength of 10 582 Å (9450 cm^{-1}) with the π polarization. This line couples the R_2 level (11 469 cm^{-1}) and the 2016 cm^{-1} component of the $^4I_{11/2}$ term (cf. Fig. 1). A laser with a combined active medium, consisting of $CaWO_4$-Nd^{3+} + LGS-1 (neodymium glass), emits two lines: D and A. Line A, which has the σ polarization, is usually present in the laser spectrum when the c axis is perpendicular to the geometrical axis. In our case, the radiation emitted at a wavelength 10 652 Å (9388 cm^{-1}) was not polarized. The obtained spectra are shown in Figs. 2f—2h.

$Y_3Al_5O_{12}$-Nd^{3+} crystals.[7] At 300°K, a garnet laser with Nd^{3+} ions emits line A at a wavelength 10 641 Å (9398 cm^{-1}). Lasers with combined active media, consisting of $Y_3Al_5O_{12}$-Nd^{3+} + α-$NaCaYF_6$-Nd^{3+} and $Y_3Al_5O_{12}$-Nd^{3+} + inorganic liquid $POCl_3$ with Nd^{3+} ions, emit two new stimulated transitions B and C at λ_e = 10 615 Å (9421 cm^{-1}) and 10 521 Å (9505 cm^{-1}). It is evident from Fig. 3 that these two new transitions couple the 2004 cm^{-1} component ($^4I_{11/2}$) with the R_1 and R_2 levels of the $^4F_{3/2}$ term. On the basis of these results, we conclude that $\Delta E(^4F_{3/2})$ is 84 ± 0.3 cm^{-1}. The stimulated radiation spectra of these two lasers are shown in Figs. 2i—2l.

LaF_3-Nd^{3+} crystals.[8] At 300°K, a laser based on tysonite containing Nd^{3+} ions emits two wavelengths (cf. Footnote 1): line A at 10 407 Å (9609 cm^{-1}) and line B at 10 633 Å (9405 cm^{-1}). The luminescence spectrum ($^4F_{3/2} \rightarrow {}^4I_{11/2}$) and the crystal splitting scheme of LaF_3-Nd^3 are shown in Fig. 4. We can see that the luminescence spectrum at 300°K cannot be used to determine all the positions of the Stark components of the term $^4I_{11/2}$. However, using a laser with a combined active medium and the high-temperature laser spectroscopy method,[9] we find three new stimulated transitions which give more information about the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition than the standard spectroscopic method. At

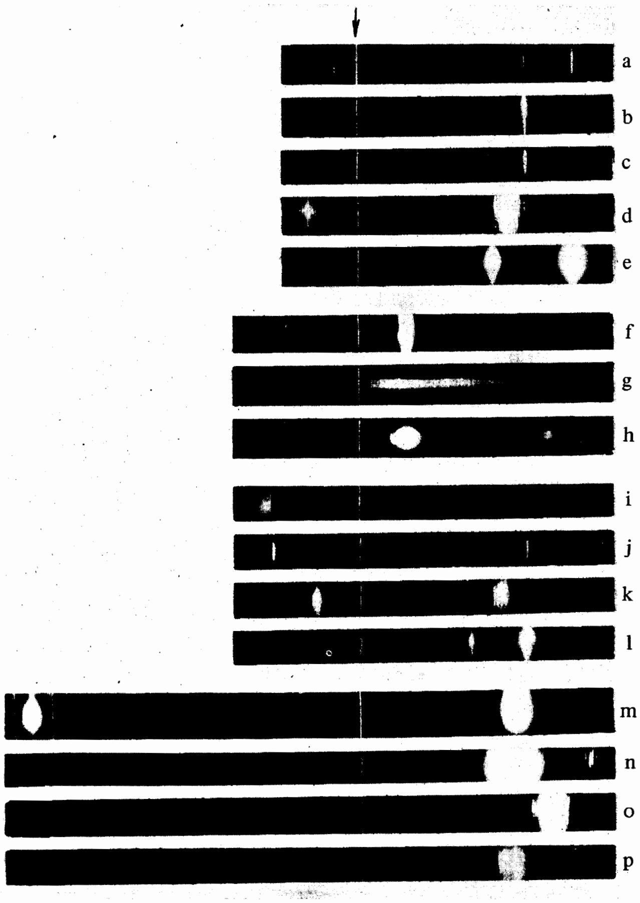
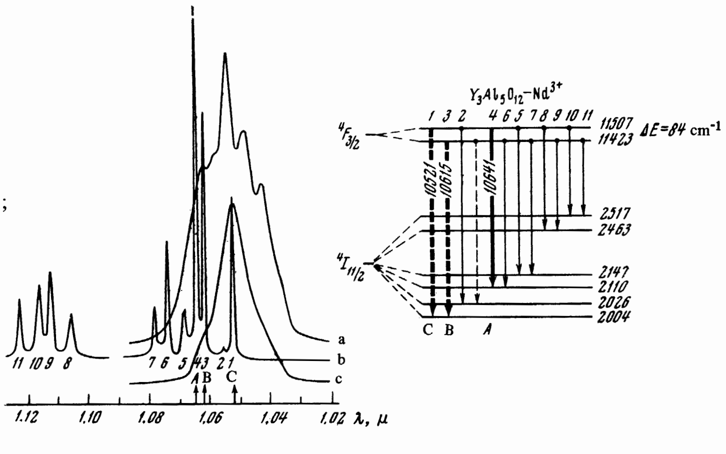


FIG. 2. Laser spectra of: a) YVO_4-Nd^{3+}; b) $Y_3Al_5O_{12}$-Nd^{3+}; c) YVO_4-Nd^{3+}+ $Y_5Al_5O_{12}$-Nd^{3+}; d) CaF_2-YF_3-Nd^{3+}; e) YVO_4-Nd^{3+} + CaF_2-YF_3-Nd^{3+}; f) $CaWO_4$-Nd^{3+}; g) LGS-1; h) $CaWO_4$-Nd^{3+} + LSG-1; i) $POCl_2$-Nd^{3+}; j) $Y_3Al_5O_{12}$-Nd^{3+} + $POCl_2$-Nd^{3+}; k) α-$NaCaYF_6$-Nd^{3+}; l) $Y_3Al_5O_{12}$-Nd^{3+} + α-$NaCaYF_6$-Nd^{3+}; m) LaF_3-Nd^{3+}; n) LaF_3-Nd^{3+} + α-$NaCaYF_6$-Nd^{3+}; o) α-$NaCaClF_6$-Nd^{3+}; p) LaF_3-Nd^{3+} + α-$NaCaClF_6$-Nd^{3+}. The arrow indicates a reference line at λ = 10,561.5 Å·

FIG. 3. Unpolarized luminescence spectra ($^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition, t = 300°K) of the following Nd^{3+}-doped crystals: a) α-$NaCaYF_6$; b) $Y_3Al_5O_{12}$; c) inorganic liquid $POCl_3$; the crystal splitting scheme of the $^4F_{3/2}$ and $^4I_{11/2}$ terms of Nd^{3+} ions in $Y_3Al_5O_{12}$ is given alongside the luminescence spectra. The notation is the same as in figure 1.



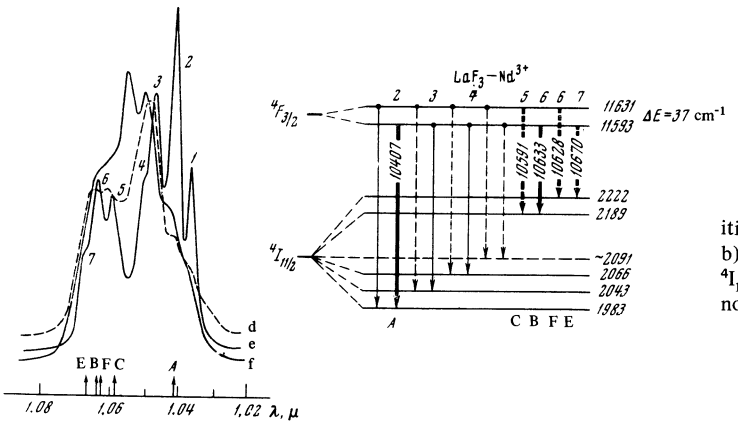


FIG. 4. Unpolarized luminescence spectra ($^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition, T = 300°K of the following Nd^{3+}-doped crystals : a) $NaCaCeF_6$; b) LaF_3 ; c) CaF_2 -YF_3 ; the crystal splitting scheme of the $^4F_{3/2}$ and $^4I_{11/2}$ terms of Nd^{3+} ions in LaF_3 is given alongside the spectra. The notation is the same as in Fig. 1.

360°K, line C appears at λ_e = 10 591 Å (9442 cm^{-1}), which couples the R_2 level (11 630 cm^{-1}) with the 2189 cm^{-1} component of the $^4I_{11/2}$ term. A laser with a combined active medium, consisting of LaF_3-Nd^{3+} + α-$NaCaCeF_6$-Nd^{3+} crystals, can be used to generate a fourth line F at λ_e = 10 628 Å (9409 cm^{-1}). This stimulated transition is coupled to the R_2 level and the highest component of the $^4I_{11/2}$ term (2222 cm^{-1}). It must be mentioned that transition 6 (Fig. 4) cannot be determined from the luminescence spectrum at 300°K. Finally, a laser with a combined active medium, consisting of LaF_3-Nd^{3+} + CaF_2-YF_3-Nd^{3+}, produces also line E at λ_e = 10 670 Å (9372 cm^{-1}). Analysis of the stimulated C—F transitions gives $\Delta E(^4F_{3/2}) = 37 \pm 0.3$ cm^{-1}, which is an order of magnitude more accurate than the results obtained from investigations of luminescence and absorption. The laser emission spectra are shown in Figs. 2m—2p.

Thus, it follows from our paper that the laser spectroscopy method, in which lasers with a combined active medium are employed, extends considerably the experimental possibilities of investigating the Stark structure of the spectra of TR^{3+} ions in crystals. Using this method, we can determine the level positions more accurately (even at 300°K) than by the standard spectroscopic methods. In some cases, the laser spectroscopy method provides new information (LaF_3, YVO_4 with Nd^{3+} ions).

---

[1] A. A. Kaminskiĭ, ZhETF Pis. Red. 7, 260 (1968) [JETP Lett. 7, 201 (1968)]; Dokl. Akad. Nauk SSSR **180**, 59 (1968) [Sov. Phys.-Dokl. **13**, 413 (1968)].

[2] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952); R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953); B. R. Judd, Proc. Roy. Soc. (London) **A227**, 552 (1955).

[3] L. Ya. Shekun, Opt. Spektrosk. **22**, 776 (1967).

[4] A. A. Kaminskiĭ and V. V. Osiko, Izv. Akad. Nauk SSSR, Neorgan. Mat. **1**, 2049 (1965); **3**, 417 (1967).

[5] A. A. Kaminskiĭ, G. A. Bogomolova, and L. Li, Izv. Akad. Nauk SSSR, Neorgan. Mat. (in press); Kh. S. Bagdasarov, A. A. Kaminskiĭ, V. S. Krylov, and V. I. Popov, Phys. Status Solidi **27**, K1 (1968).

[6] L. F. Johnson, J. Appl. Phys. **34**, 897 (1963); L. F. Johnson and R. A. Thomas, Phys. Rev. **131**, 2038 (1963); Ya. É. Kariss, A. M. Morozov, and P. P. Feofilov, Opt. Spektrosk. **17**, 887 (1964).

[7] J. A. Koningstein, J. Chem. Phys. **44**, 3957 (1966); A. A. Kaminskiĭ, Zh. Eksp. Teor. Fiz. **51**, 49 (1966) [Sov. Phys.-JETP **24**, 33 (1967)].

[8] H. H. Caspers, H. E. Rast, and R. A. Buchanan, J. Chem. Phys. **42**, 3214 (1965); M. V. Dmitruk and A. A. Kaminskiĭ, Zh. Eksp. Teor. Fiz. **53**, 874 (1967) [Sov. Phys.-JETP **26**, 531 (1968)].

[9] A. A. Kaminskiĭ, ZhETF Pis. Red. **6**, 615 (1967) [JETP Lett. **6**, 115 (1967)]; Zh. Eksp. Teor. Fiz. **54**, 727 (1968) [Sov. Phys.-JETP **27**, 388 (1968)].

Translated by A. Tybulewicz
11