Absorption and Luminescence Spectra and Energy Levels of Nd3+ and Er3+ Ions in LiNbO3 Crystals

ARTICLE *in* PHYSICA STATUS SOLIDI (A) · SEPTEMBER 1970

Impact Factor: 1.21 · DOI: 10.1002/pssa.19700030141

phys. stat. sol. (a) 3, K37 (1970)

Subject classification: 20.1 and 20.3; 13.4; 22.8.1

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Absorption and Luminescence Spectra and Energy Levels of Nd^{3+} and Er^{3+} Ions in $LiNbO_3$ Crystals

By

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Dedicated to Prof. Dr. Dr. h.c. P. GÖRLICH,
on the occasion of his 65th birthday

We studied $LiNbO_3$ crystals activated by Nd^{3+} and Er^{3+} ions. The object of study was twofold: namely, to analyze the activator centers formed in this crystal and to obtain fuller information on the scheme of ionic levels. Lithium metaniobate crystallizes in the trigonal system and contains the spatial group C_{3v}^6 -R3C; Li^{1+} and Nb^{5+} occupy the equivalent rhombohedral vacancies with local C_3 symmetry (1). On analysing optical spectra we find that some lines have a distinct two-component structure, which is practically independent of the activator concentration. Fig. 1 shows the nonpolarized absorption and luminescence spectra in the axial direction of a $LiNbO_3 - Nd^{3+}$ crystal for activator concentrations 0.003 and 5.0 wt% (to the initial charge).[1] From this figure it is evident that the two-component lines are distinctly observed in the low-temperature spectra associated with the transitions $^4I_{9/2} \rightarrow {}^2P_{1/2}$, $^4I_{9/2} \rightarrow {}^4F_{3/2}$, and $^4F_{3/2} \rightarrow {}^4I_{11/2}$. Such a bifurcation is observed also on the lines of other groups with inter-component interval not exceeding 10 cm^{-1}. On increasing the activator concentration new lines appear in absorption spectra, and their intensities steeply rise, for instance, in our example these are the lines a and c (transition $^4I_{9/2} \rightarrow {}^2P_{1/2}$) and b (transition $^4I_{9/2} \rightarrow {}^4F_{3/2}$). Besides, this figure shows the concentration plots of absorption coefficients of these new lines, and for the sake of comparison, similar plots are also shown for some of the lines which can be recorded at any arbitrary activator concentration. The plots corresponding to the lines a, b, c and 1, 2, 3 form two families of curves with different concentration dependences. The luminescence spectra did not

1) According to (2) the distribution coefficient of Nd^{3+} ions in $LiNbO_3$ crystals is < 0.1.

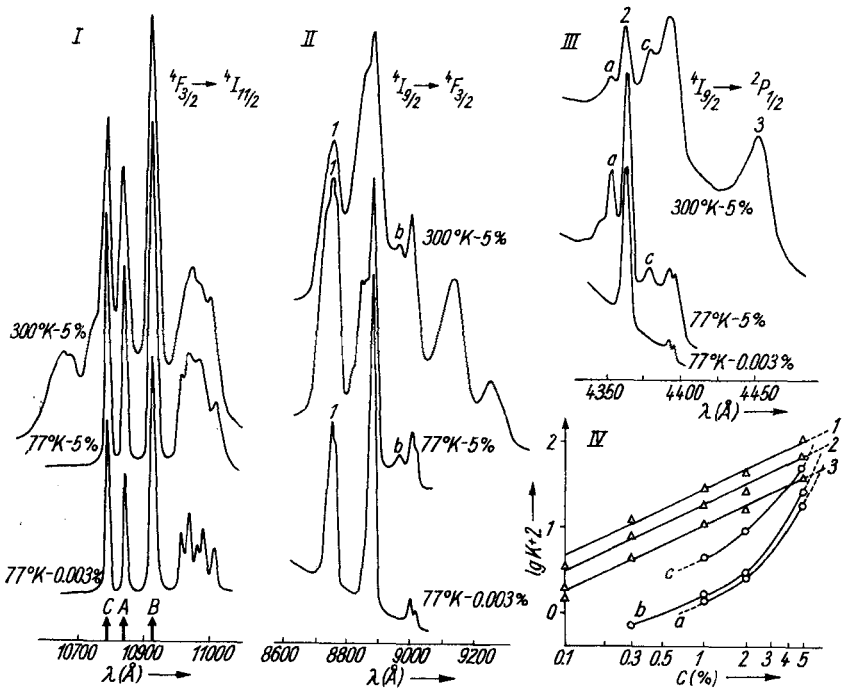

Fig. 1. Non-polarized absorption and luminescence spectra of Nd^{3+} ions in $LiNbO_3$ crystals for activator concentrations of 0.003 and 5.0 wt% (to the initial charge) at 77 and 300 °K: I - transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$, II - transition $^4I_{9/2} \rightarrow {}^4F_{3/2}$, III - transition $^4I_{9/2} \rightarrow {}^2P_{1/2}$, IV - concentration dependence of absorption coefficients for the lines a, b, c and 1, 2, 3

exhibit any new lines within the concentration range used in the experiments. This is evident from Fig. 1 which presents the luminescence spectra associated with the transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$. From general crystallochemical considerations, we can presuppose that on entering the $LiNbO_3$ lattice, the Nd^{3+} ions are capable of replacing both Li^{1+}, as well as Nb^{5+} ions in the equivalent vacancies (C_3). When both Li and Nb are replaced simultaneously, there arises the question of compensating the excess charge caused by the nonisovalency between Nd^{3+} and Li^{1+} or Nb^{5+} ions. In such a case, the activator in $LiNbO_3$ crystals will be formed by two structurally similar centers. We assumed that the bifurcation of the spectral lines is due to

Table 1

Terms	Energy levels of Nd^{3+} ions in $LiNbO_3$ at 77 °K (cm^{-1})	Number		ΔE (cm^{-1})
		Theor.	Exp.	
$^4I_{9/2}$	0, 156, 170, 440, 486	5	5	486
$^4I_{11/2}$	1987, 2033, 2107, 2190, 2228, 2263	6	6	276
$^4I_{13/2}$	3918, 3973, 4035, 4118, 4140, 4184, 4211	7	7	293
$^4I_{15/2}$	5777, 5916, 6005, 6087, 6105, 6217, 6290, 6449	8	8	672
$^4F_{3/2}$	11250, 11409	2	2	159
$^4F_{5/2}$, $^2H_{9/2}$	12133*, 12291, 12396, 12421, 12449, 12463, 12574, 12692*	8	8	559*
$^4F_{7/2}$, $^4S_{3/2}$	13199, 13291, 13398*, 13437	6	4	238*
$^4F_{9/2}$	14498, 14567, 14620, 14664, 14685	5	5	187
$^2H_{11/2}$	15748, 15803, 15873, 15888, 15911, 15926	6	6	178
$^4G_{5/2}$	16753, 16852, 16909	3	3	156
$(^4G, {}^2G)_{7/2}$	16949*, 17071, 17135, 17176	4	4	227*
$(^4G, {}^2G)_{7/2}$	18719, 18786, 18836	4	3	117*
$^4G_{9/2}$	19135, 19260, 19331	5	3	196*
$^2G_{9/2}$	20682, 20764, 20799, 20868, 20938	5	5	256
$^4G_{11/2}$ + $^2K_{15/2}$ + $^2(P, D)_{3/2}$	20973, 21022, 21039, 21213, 21372, 21631, 21696	14	7	723*
$^2P_{1/2}$	22914	1	1	-
$^2D_{5/2}$	23348, 23554, 23608	3	3	260
$^2(P, D)_{3/2}$	25745, 25882	2	2	137
$^4D_{3/2}$	27365, 27469	2	2	104
$^2D_{1/2}$	28031	1	1	-

Note: Energy levels and ΔE values indicated by asterisks require more accurate definition.

this phenomenon. Two such structurally similar centers were observed in paper (3) at low activator concentrations in the EPR studies of Nd^{3+} ions in $LiNbO_3$ crystals.

Table 2

Terms	Energy levels of Er^{3+} ions in $LiNbO_3$ at 77 $^{o}K(cm^{-1})$	Number		ΔE (cm^{-1})
		Theor.	Exp.	
$^4I_{15/2}$	0, 63, 132, 156*, 182, 278, 353, 414	8	8	414
$^4I_{13/2}$	6524, 6586, 6611, 6631, 6759, 6778, 6804	7	7	280
$^4I_{11/2}$	10207, 10260*, 10270, 10303, 10316, 10338	6	6	131
$^4I_{9/2}$	12381, 12410, 12453, 12603, 12612	5	5	231
$^4F_{9/2}$	15151, 15174*, 15255, 15344	5	4	193*
$^4S_{3/2}$	18265, 18354	2	2	89
$^2H_{11/2}$	19043*, 19061*, 19152*, 19177*, 19188*, 19199*	6	6	156*
$^4F_{7/2}$	20370, 20407*, 20538, 20557	4	4	187
$^4F_{5/2}$	22060, 22124, 22136	3	3	76
$^4F_{3/2}$	22395, 22526	2	2	131
$^2H_{9/2}$	24371*, 24417, 24444, 24500, 24594	5	5	223*
$^4G_{11/2}$	26185*, 26197, 26300, 26349, 26380, 26398	6	6	213*

Note: Energy levels and ΔE values indicated by asterisks require more accurate definition.

In analyzing the spectra and in constructing a scheme for the crystalline splitting of levels, we regarded these almost similar activator centers as one "quasi-center". The energy levels of Nd^{3+} ions in $LiNbO_3$ crystals at 77 ^{o}K are shown in Table 1. The experiments on the absorption, luminescence and stimulated emission of $LiNbO_3 - Nd^{3+}$ made it possible to determine with great reliability the position of the ^4I_J multiplet terms, whose crystalline splitting is shown in Fig. 2. The dotted arrows indicate the transitions corresponding to the faint lines in the absorption spectra. As regards the new lines appearing at high concentrations, we can attribute them to paired or more complex associates with respect to the nature of the concentration dependence of their absorption coefficients. Analogous phenomena were observed with $LiNbO_3$ crystals activated by Er^{3+} ions. An analysis of the

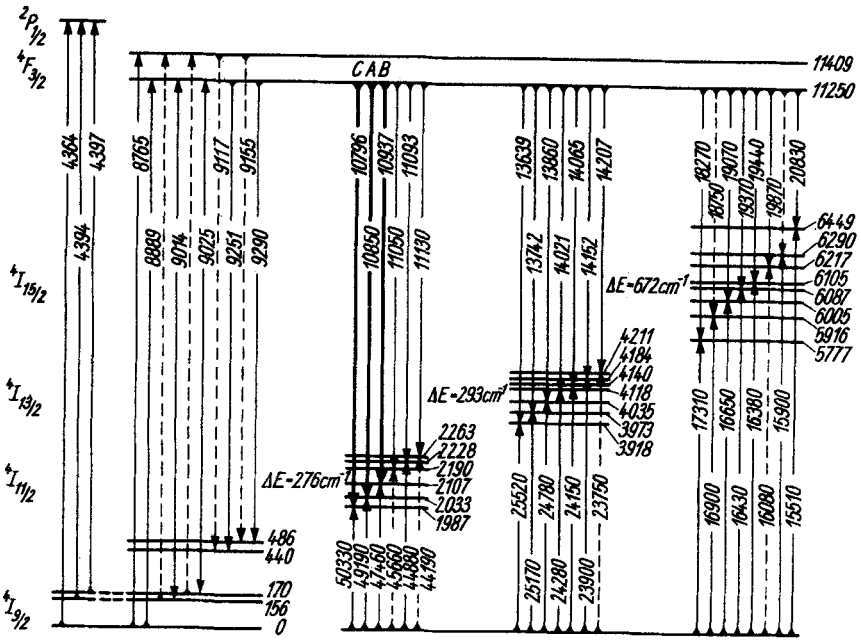

Fig. 2. The scheme of crystalline splitting of terms $^2P_{1/2}$, $^4F_{3/2}$, and ^4I_J of Nd^{3+} ions in $LiNbO_3$ crystals at 77 °K. The position of levels are given in cm^{-1}, and the transition between them in Å. The stimulated transitions A, B, and C are denoted by thick arrows

optical spectra gave the exact position of levels of all those terms, transitions between which were observed in the transparent band of the crystal (0.35 to 5.5 μm). These results are shown in Table 2. Fig. 3 shows a scheme for the energy levels of Er^{3+} ions in $LiNbO_3$ which are directly associated with the observed luminescence.

Thus, at low concentrations of activator ions (Nd^{3+}, Er^{3+}) in $LiNbO_3$ crystal, two structurally similar centers are formed which are associated with equiprobable substitutions of Li^{1+} and Nb^{5+} ions. At higher admixture concentrations in $LiNbO_3$, paired or more complex associates are formed.

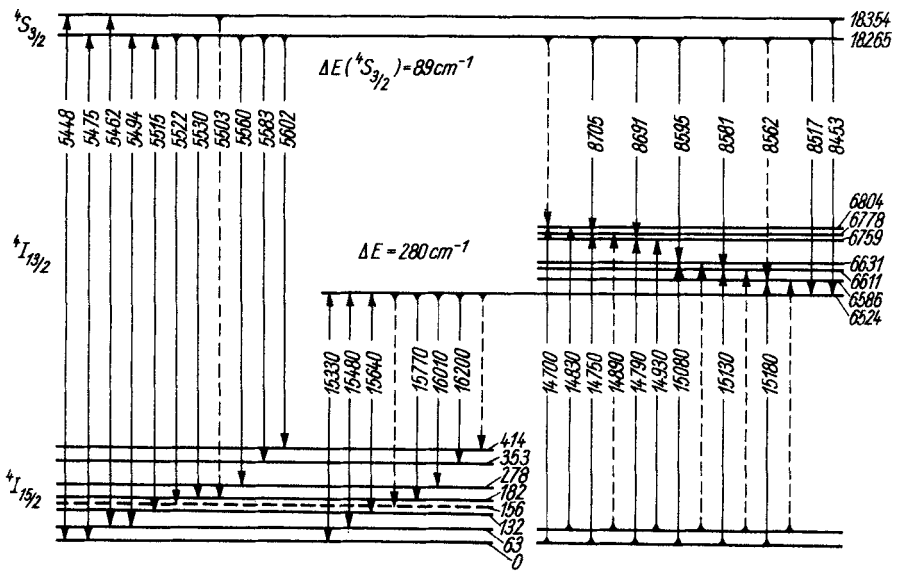

Fig. 3. The scheme of crystalline splitting of levels of terms $^4S_{3/2}$, $^4I_{13/2}$, and $^4I_{15/2}$ of Er^{3+} ions in $LiNbO_3$ crystal at 77 °K. The position of levels is given in cm^{-1}, whereas the transitions between them in Å

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(Received July 31, 1970)