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EPR and optical spectroscopy of SrF_2 doped with Yb^{3+}

M.L. Falin[a,*], K.I. Gerasimov[a], A.M. Leushin[b], H. Bill[c], D. Lovy[c], T. Sanadze[d]

[a]Zavoisky Physical-Technical Institute, 420029 Kazan, Russia
[b]Kazan State University, 420008 Kazan, Russia
[c]Group PCB, University of Geneva, 1211 Geneva 4, Switzerland
[d]Tbilisi State University, 380028 Tbilisi, Georgia

Abstract

Results of EPR and optical spectroscopic investigation of the trigonal paramagnetic Yb^{3+} ion in SrF_2 ('oxygen' paramagnetic center — T_2) are presented. The energy level scheme of the center is determined from its optical spectra and the parameters of the crystal field potential are calculated. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is known that depending on the conditions of crystal synthesis, the Yb^{3+} ion in a CaF_2 single crystal forms up to 13 paramagnetic centers (PC) with different symmetry [1]. The Yb^{3+} ion in this matrix has been extensively studied by EPR, ENDOR and optical spectroscopy (including Zeeman spectroscopy). Yet, considerable discrepancies in the interpretation of the optical absorption and luminescence spectra of the PCs still remain, and the Stark structures of these centers are not unambiguously identified. Systematic optical data for Yb^{3+} in crystals of the homologous series MeF_2 (Me=Sr, Pb, Ba) are practically absent. In comparison with the CaF_2 lattice, a considerable decrease in the number of PCs with different symmetries is observed in these latter systems and the study of their optical spectra may thus enable an unambiguous identification of some of them. As-grown crystals of SrF_2 and BaF_2 show two Yb^{3+} PCs: a cubic one (non-local compensation of the excess positive charge) and a trigonal one [1]. In the latter case, the excess positive charge is compensated by an additional fluorine ion located in the center of the normally empty cube next to Yb^{3+} along a C_3-axis (this is the so-called 'fluorine' trigonal PC — T_4). By special thermal treatment (hydrolysis) these PCs may be partially transformed into a trigonal 'oxygen' PC (T_2), where the oxygen ion substitutes one of the fluorine ions in the nearest cubic environment of Yb^{3+} [5]. Thus the number of different PCs in SrF_2 and BaF_2 crystals may be increased to three. This process is controllable providing additional means for identification of the spectral lines. The structural models have been experimentally established, by the radiofrequency discrete saturation method (analogous to ENDOR) [2–4]. In the PbF_2 host, only one cubic PC is usually observed [1], although there is a report that a trigonal PC may also exist [6].

In view of these facts, we chose to study those systems which show a minimum number of PCs. This paper presents EPR and optical spectroscopy results on the T_2 center formed by the Yb^{3+} ion in SrF_2. Data from preliminary optical experiments on BaF_2:Yb^{3+} were published in an earlier paper [7].

2. Experimental results and discussion

SrF_2:Yb crystals were grown by the Bridgman method in graphite crucibles in a fluorine atmosphere. Some crystals were subsequently hydrolyzed during several hours according to the method described [8]. EPR experiments were carried out on an X-band spectrometer at 4.2, 77 K. Optical spectra were recorded at $T=2$, 300 K on a home built multifunctional computerized spectrometer [7]. A cooled photomultiplier formed the detector, and the light from a xenon lamp dispersed by a monochromator was used as an excitation source. The luminescence and excitation spectra were recorded by time delayed (stroboscopic) detection.

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*Corresponding author. Fax: +7-8432-765-075.
E-mail address: falin@kfti.knc.ru (M.L. Falin).

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The as-grown single crystal SrF_2:Yb^{3+} showed EPR of only two PCs with different symmetries: the cubic one (g=3.438 [5]) and the T_4 center ($g_{\parallel}$=2.804, $g_{\perp}$=3.743 [5]). After hydrolysis, the T_2 center ($g_{\parallel}$=1.345, $g_{\perp}$=4.420 [5]) was observed.

The luminescence and excitation spectra of SrF_2:Yb^{3+} are shown in Figs. 1 and 2. They were obtained before and after hydrolysis and for different temperatures with different concentrations of Yb. As seen in these figures, the number of observed optical transitions exceeds the number expected for the cubic and trigonal PCs. The transitions which correspond to the Yb^{3+} T_2 center are labeled by arrows. The analysis of the spectra showed that the emission lines labeled 1, 2, 3, 4 in Fig. 1(a,c) were due to transitions from the lower Stark level of the excited multiplet $^2F_{5/2}$ to the four Stark components of the ground multiplet $^2F_{7/2}$ of the Yb^{3+}. The spectral components labeled 4, 5 and 6 in the excitation spectrum in Fig. 2(a) corresponded to transitions from the lower level of the multiplet $^2F_{7/2}$ to the three Stark components of $^2F_{5/2}$. Comparison of the luminescence and excitation spectra showed that line 4 was an electronic transition between the same energy levels in emission as well as in absorption. The labeling of the spectral lines given in Figs. 1 and 2 corresponds to the labeling of the transitions in the energy level diagram of Yb^{3+} (see insert in Fig. 1). The spectra of Figs. 1 and 2 exhibit a series of other lines in addition to the zero-phonon transitions, which we used to construct the energy levels diagram for the T_2 center. There are probably phonon sidebands of purely electronic transitions.

The electronic configuration of the free Yb^{3+} ion is $4f^{13}$ with a $^2F_{7/2}$ ground level and a $^2F_{5/2}$ excited level. The trigonal crystal field of C_{3v}-symmetry of the oxygen-center lifts the degeneracies of these terms into four and three Kramers's doublets, respectively. Energy levels and wave functions were determined by diagonalizing the Hamiltonian $H=H_{so}+H_{cf}(C_{3v})$ of Yb^{3+} ion where $H_{so}=-\xi(\mathbf{SL})$ is the spin–orbit contribution and $H_{cf}(C_{3v})=B_2^0V_2^0+B_4^0V_4^0+B_4^3V_4^3+B_6^0V_6^0+B_6^3V_6^3+B_6^6V_6^6$, is the crystal-field term, in Stevens' notation. In these expressions, ξ is the spin–orbit coupling parameter, and **S** and **L** are the spin and orbit momentum operator, respectively; B_k^q are crystal-field parameters, and V_k^q are standard harmonic polynomials [9]. The ground doublet wave functions were used to calculate values for $g_{\parallel}$ and $g_{\perp}$. Then, eight experimental data (two g-values and six energy differences) were fitted by a least-squares procedure (similar to the program in Ref. [10]) to determine the spin–orbit and crystal-field parameters. The results of the best fit are given in Tables 1 and 2. The experimental energy level scheme and the values of

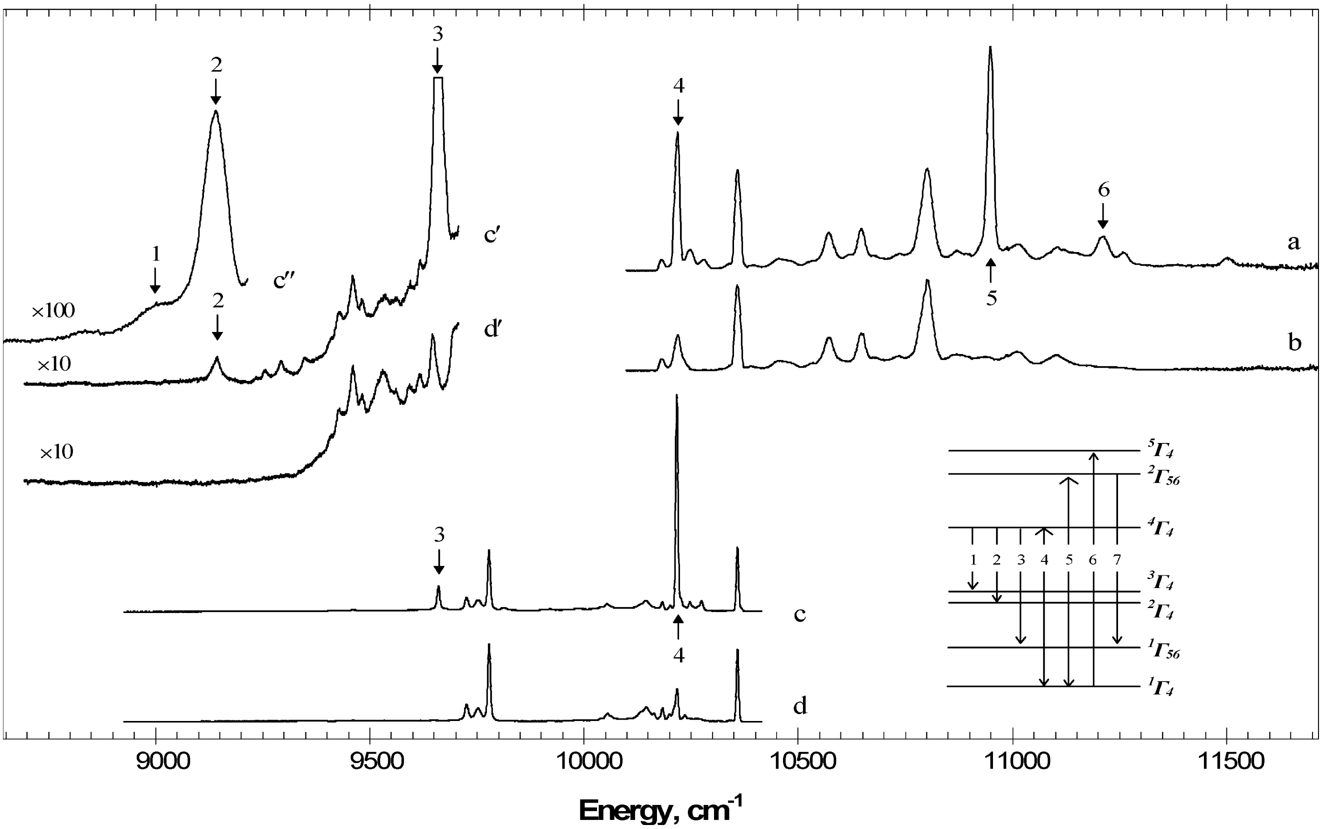

Fig. 1. Excitation (a, b) and luminescence (c, d, c′, c″, d′) spectra of Yb^{3+} in SrF_2 (c=0.05%) at T=2 K before (b, d, d′) and after (a, c, c′, c″) hydrolysis. c, d, c′, d′ — high resolution; a, b, c″ — low resolution. Optical lines corresponding to the T_2 center are marked by arrows. The insert shows the energy level scheme of the T_2 Yb^{3+} center in SrF_2. The arrows indicate transitions observed in optical spectra, shown here and in Fig. 2.

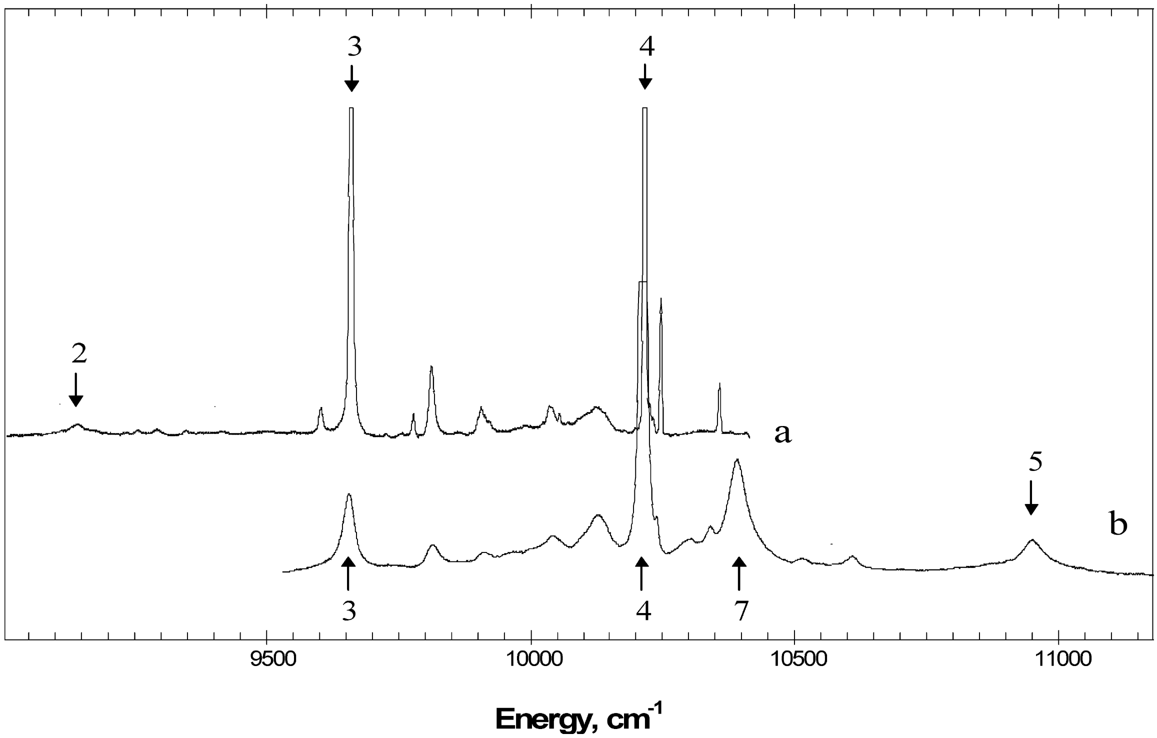

Fig. 2. Luminescence spectra of Yb^{3+} in SrF_2 ($c=0.01\%$) after hydrolysis at $T=2$ K (a) and $T=300$ K (b). Optical lines corresponding to the T_2 center are marked by arrows. Numbering of spectral lines corresponds to the numbering of transitions in the insert of Fig. 1.

Table 1
Energy levels (cm^{-1}) and g-factors of Yb^{3+} (T_2) in MeF_2[a]

J	Symmetry properties and g-factors of energy levels	Experiment SrF_2	Theory SrF_2	Theory CaF_2 [11]	Theory CaF_2
5/2	$^5\Gamma_4$	11 212	11 227	11 421	11 423
	$^2\Gamma_{56}$	10 949	10 949	10 995[b]	10 989
	$^4\Gamma_4$	10 216	10 200	10 268[b]	10 253
7/2	$^3\Gamma_4$	1228	1228	1276	1264
	$^2\Gamma_4$	1073	1073	1128	1119
	$^1\Gamma_{56}$	556	556	390	386
	$^1\Gamma_4$	0	0	0	0
	$g_\parallel$ ($^1\Gamma_4$)	$\lvert 1.345 \rvert$ [5]	1.380	$\lvert 1.421 \rvert$ [12][b]	1.421
	$g_\perp$ ($^1\Gamma_4$)	$\lvert 4.420 \rvert$ [5]	-4.340	$\lvert 4.389 \rvert$ [12][b]	-4.379

[b] Experimental values.
[a] The results for CaF_2 [11] are given for comparison.

the g-factors are correctly reproduced with an r.m.s. deviation of the energy level positions not exceeding 9 cm^{-1}. For comparison, Table 1 gives theoretical energy levels and Table 2 the corresponding crystal-field parameters of the T_2 Yb^{3+} center in CaF_2 [11]. By using the energy levels and the experimental g-values as the initial eight input parameters for the fitting process for this system, we obtained iteratively new theoretical energy levels, g-values (row 6, Table 1) and crystal-field parameters (line 4, Table 2), which are in close correspondence

Table 2
Crystal field and spin–orbital interaction parameters (cm^{-1}) of Yb^{3+} (T_2) in MeF_2

Crystal	ξ	B_2^0	B_4^0	B_4^3	B_6^0	B_6^3	B_6^6
SrF_2	2871.6	737	211	5036	-5.6	246	1177
CaF_2 [11]	2909.1	1351	440	9338	-130	-1750	1361
CaF_2	2906.7	911	175	5049	-55	-268	677

with the crystal-field parameters of the T_2 center in SrF_2 crystal.

3. Conclusion

Optical spectra of the trigonal T_2 Yb^{3+} center in SrF_2 were interpreted and with their aid, the energy level scheme of the studied center determined. The total crystal field potential was obtained for the first time enabling the interpretation of the optical spectra of other paramagnetic centers formed by Yb^{3+} in homologous fluorite crystals.

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