A Spectroscopic Study of the $TbAl_3(BO_3)_4$ Crystal*

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This paper reports on the polarized absorption and fluorescence spectra of the $TbAl_3(BO_3)_4$ crystal. In order to obtain information on the energy levels and corresponding wavefunctions, a crystal field fitting has been performed in the framework of a descending symmetry model from D_{3h} to D_3.

Experimental

Crystallographic Structure

The Tb^{3+} ion is surrounded by a trigonal prism of six oxygens from six borate anions, the overall symmetry being lowered from D_{3h} to D_3 by a distortion angle $\Delta\varphi = 8.14°$. The crystals are elongated along the *c*-axis which is the C_3 axis of the trigonal prism [1].

Spectroscopic Measurements

Absorption spectra in the UV–Vis region were recorded at nitrogen and He temperature with a McPherson (1200 lines/mm) and a HR 1000 Jobin–Yvon (1200 lines/mm) monochromator. In the IR region use was made of a 600 lines/mm grating. Polarized absorption spectra were recorded with the electric radiation vector parallel (π-spectrum) and perpendicular (σ-spectrum) to the *c*-axis of the crystal.

The fluorescence spectra were excited by a Hg lamp or by a dye laser (Rhodamine 6G) pumped by a 4 W Argon laser. The fluorescence light was analysed with a Jarrel–Ash monochromator.

For low temperature measurements use was made of an Oxford cryostat.

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Results and Discussion

Assignment of the Transitions

The assignments of Figs. 1 and 2 giving the polarized absorption and fluorescence spectra have been deduced from the following considerations:

(i) Table I gives the polarization for the transitions expected in the near-infrared and involving the ground state $^7F_6$ and the excited states $^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$.

(ii) Both the absorption data and fluorescence data were combined and used as complementary to each other.

(iii) Some transitions have been simulated from the theoretical calculation discussed in the next section and compared with the experimental possibilities provided by the spectra.

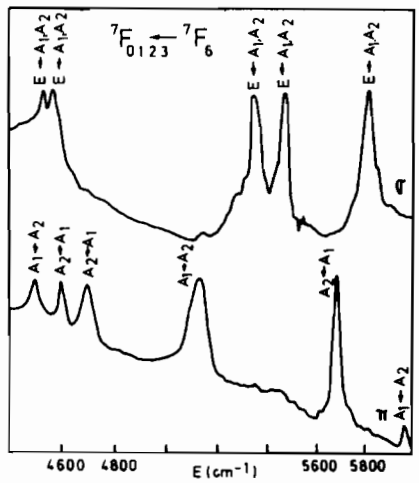

Fig. 1. Absorption spectrum of $TbAl_3(BO_3)_4$ in the near-infrared (transitions $^7F_6 \rightarrow {}^7F_{0,1,2,3}$).

TABLE Ia. Polarization Data for the Expected Transitions in the Near Infrared Involving the Transitions from the Ground State $^7F_6$ to the Excited States $^7F_{0,1,2,3}$[a]

$^7F_6$	A_1	A_2	E
$^7F_0$ (A_1)		π	σ
$^7F_1$ ($A_2 + E$)	$\pi + \sigma$	σ	$\sigma + (\pi + \sigma)$
$^7F_2$ ($A_1 + 2E$)	2σ	$\pi + 2\sigma$	$\sigma + 2(\pi + \sigma)$
$^7F_3$ ($A_1 + 2A_2 + 2E$)	$2\pi + 2\sigma$	$\pi + 2\sigma$	$\sigma + 2\sigma + 2(\pi + \sigma)$

[a]All transitions are considered as electric dipole. The existence of brackets means that the transitions take place at the same energy.

TABLE Ib. Compatibility Table Between D_{3h} and D_3

D_{3h}	A_1'	A_2'	A_1''	A_2''	E'	E''
D_3	A_1	A_2	A_1	A_2	E	E

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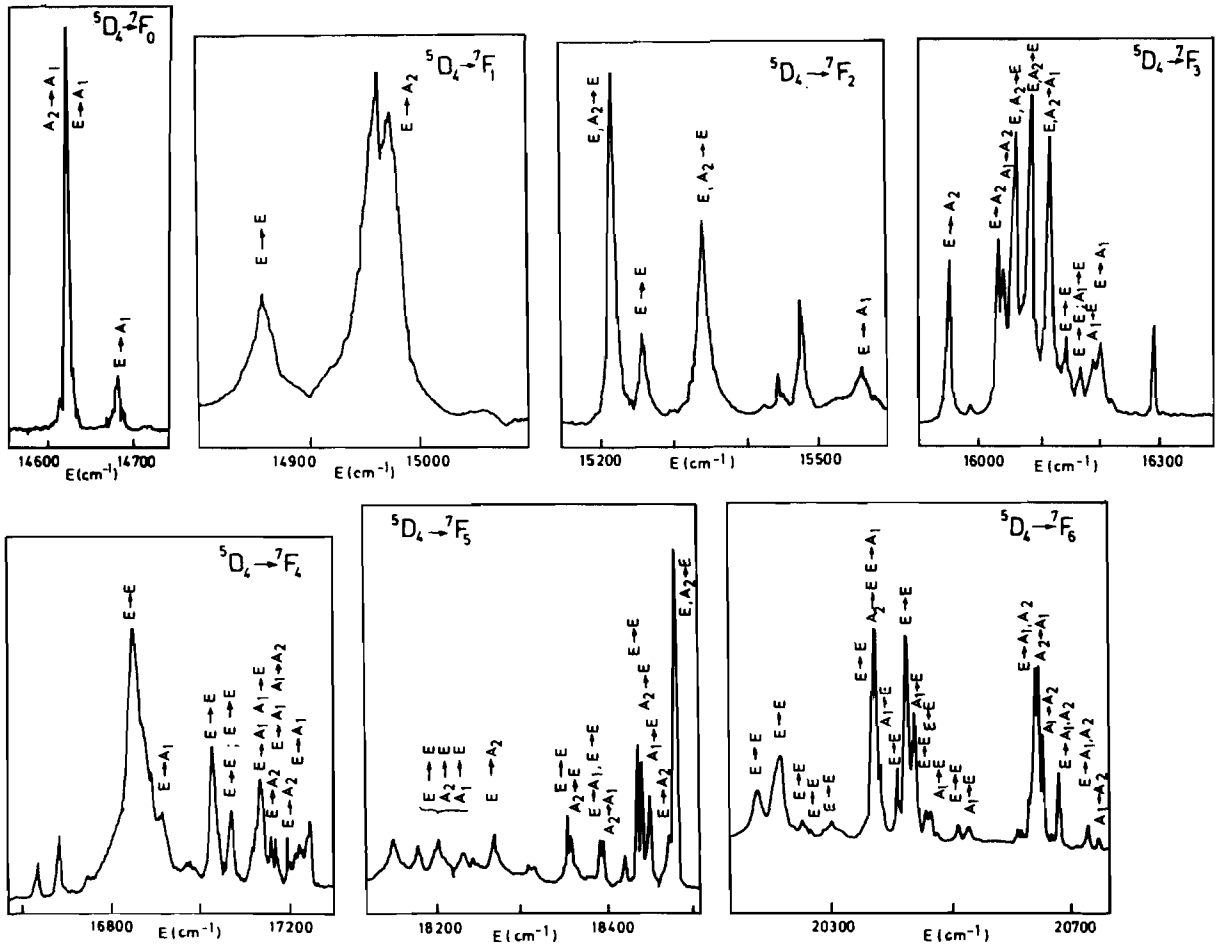

Fig. 2. Fluorescence spectra of $TbAl_3(BO_3)_4$ (transitions $^5D_4 \rightarrow {}^7F_{0,1,2,3,4,5,6}$).

Crystal Field Fitting

Starting with the Eu^{3+} free ion parameters previously published [2], we applied the method of descending symmetry [3] (D_{3h} to D_3) for the crystal field parametrization. The set of parameters is shown in Table II.

TABLE II. Free Ion and Crystal Field Parameters Calculated by the Procedure of Descending Symmetry

Free ion parameters (cm^{-1})	
$E^0 = 2917$	$\alpha = 20$
$E^1 = 5544$	$\beta = -640$
$E^2 = 24.8$	$\gamma = 1750$
$E^3 = 585$	$\xi = 1295$
D_3-parameters (cm^{-1})	
$B_0^2 = -554$	$B_0^6 = 256$
$B_0^4 = 1157$	$B_3^6 = 212$
$B_3^4 = 856$	$B_6^6 = -11$

Conclusions

As a result of the experimental spectra and the crystal field calculation a fairly complete energy diagram is proposed in Table III. With respect to the ground state, this diagram is slightly different from the earlier one presented by other authors [4]. The

TABLE III. Observed Energy Levels in $TbAl_3(BO_3)_4$

State	Irreducible representation	Energy (cm^{-1})	
		Calculated	Experimental
$^7F_6$	A_2, A_1	0	0
	E	217	210
	A_1	271	272
	E	275	275
	E	436	434
	E	472	472
$^7F_5$	E	2150	2144
	A_2	2157	2166

(continued)

TABLE III. *(continued)*

State	Irreducible representation	Energy (cm^{-1})	
		Calculated	Experimental
	E	2195	2190
	A_1	2237	2247
	E	2277	2287
	A_2	2393	2393
	E	2426	2443
$^7F_4$	A_2	3454	3448
	A_1	3479	3486
	E	3550	3548
	E	3593	3590
	A_1	3709	3723
	E	3775	3774
$^7F_3$	A_1	4525	4539
	E	4559	4542
	E	4585	4592
	A_2	4604	4623
	A_2	4691	4682
$^7F_2$	A_1	5425	5418
	E	5302	5307
	E	5144	5145
$^7F_1$	A_2	5672	5661
	E	5787	5793
$^7F_0$	A_1	5992	5993
$^5D_4$	E	20631	
	A_2	20634	
	A_1	20645	
	E	20670	
	E	20719	
	A_1	20746	

Number of levels: 30. σ: 9, 6.

function corresponding to the energy levels can be obtained on demand from the authors.

With regard to the crystal field parameters, one should note that the $B_6^6 \equiv 11$ cm^{-1} parameters is very small and does not support the comparison with the corresponding parameter $B_6^6 \equiv 860$ cm^{-1} derived for the Eu^{3+} ion. Other systems are analogous; reference can for example be made to the case of the $LaCl_3$ crystal doped with the Tb^{3+} and Eu^{3+} ion [5].

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