

Spectroscopic Manifestations of Local Crystal Distortions in Excited 4f States in Crystals of Huntite Structure¹

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Abstract—Optical absorption spectra of YbAl₃(BO₃)₄, TmAl₃(BO₃)₄ and TbFe₃(BO₃)₄ trigonal crystals have been studied in temperature range 2–300 K. Temperature behavior of absorption lines parameters has shown, that during some *f–f* transitions the local environment of rare earth ions undergo distortions, which are absent in the ground state.

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Crystal structure directly depends on electronic structure of atoms composed the crystal. Electronically excited atom is, actually, another atom, and, consequently, the local environment of the excited atom can change. Spectroscopic manifestations of such local distortions in different crystals were earlier observed in Ref. [1–3]. Present work is devoted to study of the similar phenomena in crystals TmAl₃(BO₃)₄, YbAl₃(BO₃)₄, and TbFe₃(BO₃)₄, when *f–f* transitions take place. Symmetry of the huntite structure ferroborate is sensitive to electronic structure of rare earth atoms. So, temperature of transition to lower symmetry increases with the increase of number of 4f electrons in rare earth (RE) ion. Therefore, we can expect modification of the RE ion local environment during *f–f* transitions at least in the ferroborate. The *f–f* transitions are allowed only due to odd distortions of the environment. Therefore, their properties are the sensitive tool for detection of the local distortions.

There are few criteria, which testify to the phenomenon under discussion: 1—larger number of observed absorption lines than that followed from the local symmetry of the 4f ion position in the ground state; 2—different temperature dependences of intensities of the same *f–f* transition in π and σ polarizations and (or) deviation of these dependences from those followed only from the thermal population of the ground state crystal field splitting sublevels; 3—abrupt change or another singularities of some spectroscopic characteristics of *f–f* transitions at temperature, when there are no corresponding changes in the ground state. We shall consider manifestations of these criteria in turn.

1st Case. TmAl₃(BO₃)₄ crystal at room temperature has *R*32 space symmetry and local symmetry *D*₃ of the Tm³⁺ ion positions. Heat capacity temperature dependence shown in Fig. 1 testifies that there are no phase transitions in the ground electronic state down to 2 K. We have studied absorption spectra of *f–f* transitions in TmAl₃(BO₃)₄ crystal in temperature range 1.8–293 K [4]. In Fig. 2 the σ -polarized absorption spectra at two temperatures in the region of ³H₆ → ³F₃ transition are presented. Some of absorption lines are not observed in σ -polarization, but they are observed in π -polarization. Overall, at the lowest temperature, there are 14 lines, whose intensity does not increase with the temperature rising. Consequently, these are transitions from the lowest crystal field sublevel. Lines in the region of 14450 cm⁻¹ (Fig. 2) are due to transitions

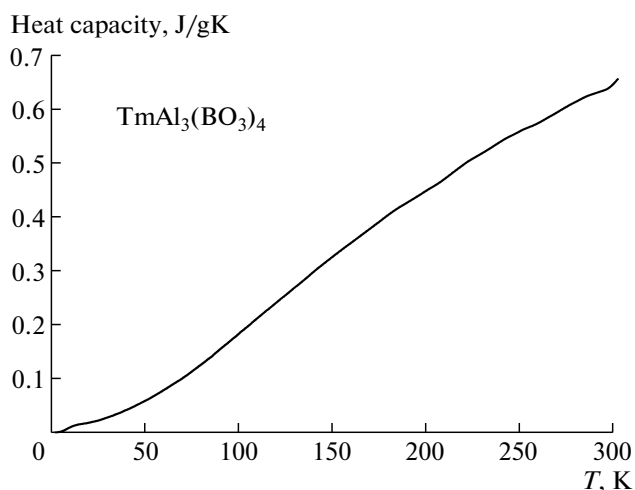


Fig. 1. Heat capacity of TmAl₃(BO₃)₄.

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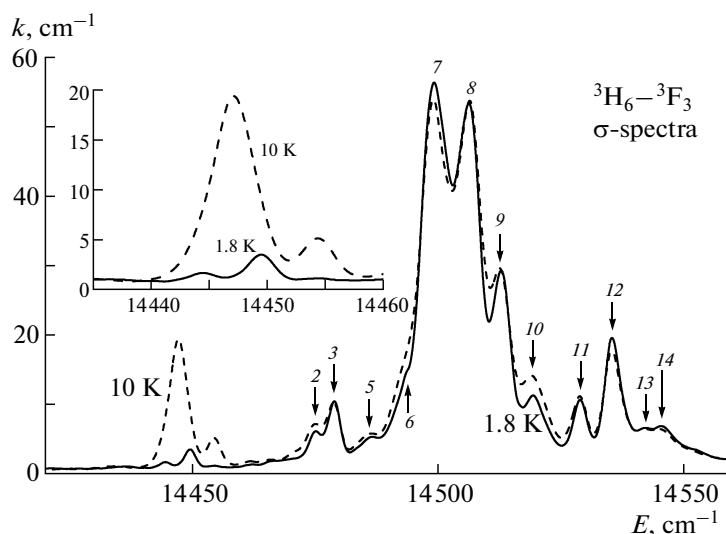


Fig. 2. Absorption spectra of $\text{TmAl}_3(\text{BO}_3)_4$.

from the level close to the lowest one. Its energy is $\sim 17 \text{ cm}^{-1}$ [4]. It is possible to show [4], that these levels are the consequence of splitting of the Γ_5 cubic state in trigonal D_3 symmetry: $\Gamma_5 \in \gamma_1 + \gamma_3$. Excited state splits in D_3 symmetry in the following way: $J = 3$ (3F_3) $\in \gamma_1 + 2\gamma_2 + 2\gamma_3$. States γ_1 and γ_2 are singlets and γ_3 is doublet. With the help of selection rules of Table we obtain, that in D_3 symmetry 4 transitions should be from γ_1 state and 5 transitions from γ_3 state. This contradicts the above mentioned experimental results. In C_3 group (subgroup of D_3 group) doublets γ_3 split: $\gamma_3 \in \gamma_2 + \gamma_3$. Then, with the help of Table 1 in C_3 symmetry we obtain 14 transitions from the quasi doublet γ_3 (in D_3 notation) and 7 transitions from the γ_1 state. Thus, after compare with the experiment we conclude, that the lowest level is quasi doublet $\gamma_3 \in \gamma_2 + \gamma_3$ and that during the considered transition the local symmetry reduces (similar situation takes place also in some other absorption bands of $\text{TmAl}_3(\text{BO}_3)_4$). This statement does not obligatory means that the atoms really change their positions during the electron transition, but these positions are already not equilibrium ones for the excited state since interaction with ligands changes. The change of the positions (i. e. deviation from the adiabatic approximation) can also take place, but this is more actually

Selection rules of electric dipole transitions in different symmetries

	D_3			C_3		
	γ_1	γ_2	γ_3	γ_1	γ_2	γ_3
γ_1	—	π	σ	π	σ	σ
γ_2	π	—	σ	σ	σ	π
γ_3	σ	σ	π, σ	σ	π	σ

for luminescence [1]. Moreover, electron transition is not an instant event, but a process, which is going on during some time. According to the perturbation theory, electron transitions occur due to mixing of initial and final states by the time dependent perturbation caused by electromagnetic wave. Therefore, during electron transition, initial state and its interaction with the environment also change. Indeed, obtained above 14 transitions are possible only in assumption that not only in the excited state, but also in the ground one the equilibrium local symmetry decreases during electron transition.

2nd Case. Spectra of absorption bands $^3H_6 \rightarrow ^3H_5$, 3H_4 , 3F_3 , and 1G_4 in $\text{TmAl}_3(\text{BO}_3)_4$ were studied as a function of temperature in the range of 1.8–293 K. The spectra were decomposed to Gauss components, and temperature dependences of individual line intensities were obtained. If geometry of $4f$ ion local environment does not change during electron transition and does not depend on temperature, than quantum mechanical probability of $f-f$ transition should not change, and absorption line intensity should vary only according to the thermal population of the initial state. In this case temperature dependences of the line intensities in π - and σ -polarizations (if they are allowed) should be identical. For majority of absorption lines in $\text{TmAl}_3(\text{BO}_3)_4$ it is indeed so. However, some absorption lines reveal substantially different behavior in two polarizations (Fig. 3). This means that during corresponding $f-f$ transitions the Tm^{3+} ion local equilibrium environment is distorted and this distortion changes with temperature.

$f-f$ transition $^2F_{7/2} \rightarrow ^2F_{5/2}$ in $\text{YbAl}_3(\text{BO}_3)_4$ crystal presents one more example of the similar spectroscopic manifestation of the discussed phenomenon. Temperature dependence of heat capacity of this crystal is mainly identical to that of $\text{TmAl}_3(\text{BO}_3)_4$ and also

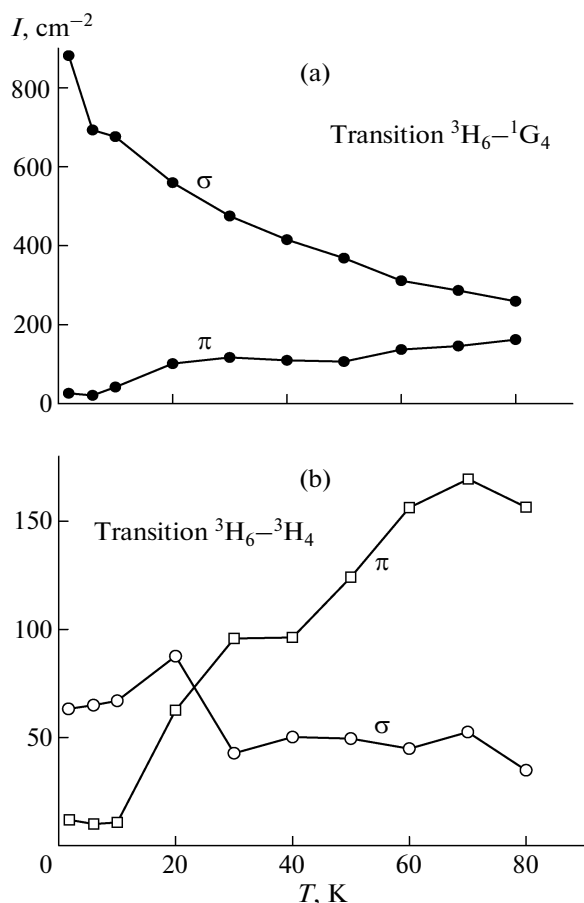


Fig. 3. Temperature dependences of the line intensities in two polarizations in spectra of $\text{TmAl}_3(\text{BO}_3)_4$: (a) at line 21316 cm^{-1} , (b) at line 12645 cm^{-1} .

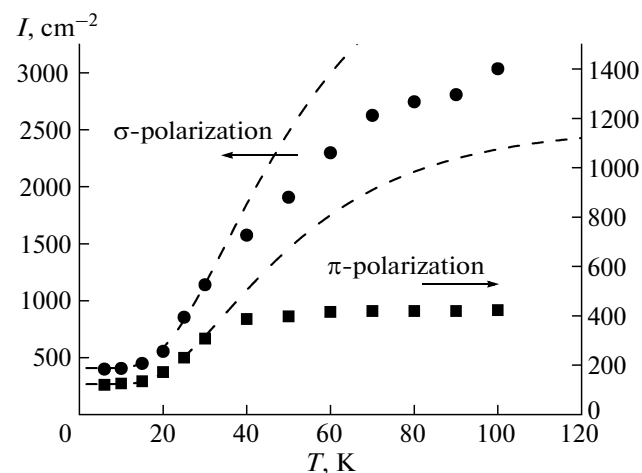


Fig. 4. Temperature dependences of the line 10187 cm^{-1} intensities in two polarizations in spectra of $\text{YbAl}_3(\text{BO}_3)_4$.

does not reveal singularities. We studied temperature dependence of the ${}^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition spectrum in π - and σ -polarizations and obtained temperature dependences of the line intensities [5]. Such dependences for one of lines are shown in Fig. 4. We have managed to find the ground state energy structure [5]. It permitted to calculate the line intensity temperature dependence (dash lines in Fig. 4) caused only by the thermal population of states. Experimental dependences (points) are different for π - and σ -polarizations and beginning from $T \sim 40\text{ K}$ they deviate from the theoretical ones (especially strong for π -polarization).

3rd Case. Crystal $\text{TbFe}_3(\text{BO}_3)_4$ at room temperature has the same symmetry as alumoborates have. A

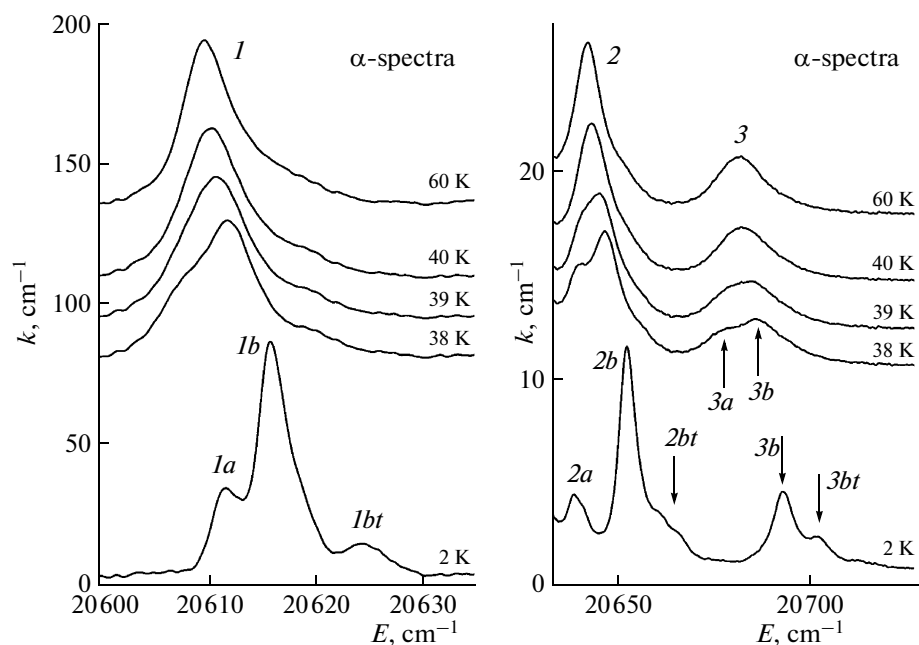


Fig. 5. Absorption spectra of $\text{TbFe}_3(\text{BO}_3)_4$.

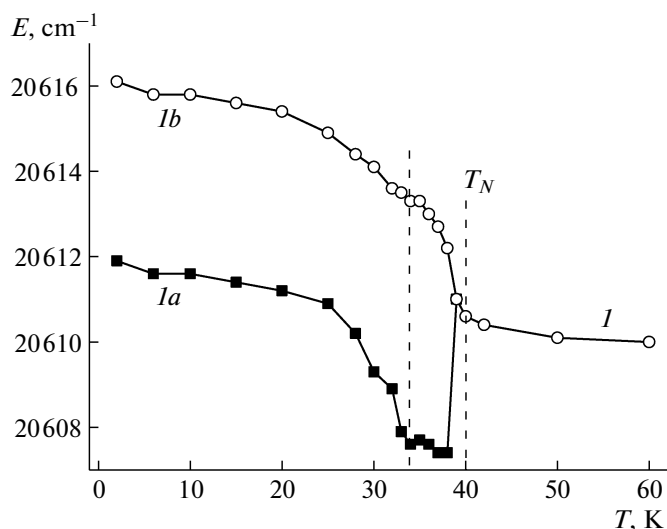


Fig. 6. Temperature behavior of line *I* position in $\text{TbFe}_3(\text{BO}_3)_4$ absorption spectrum.

structural phase transition to the $P3_121$ (D_3^4) phase was found in $\text{TbFe}_3(\text{BO}_3)_4$ at $T = 192$ K [6]. Correspondingly, the local symmetry of the Tb^{3+} environment reduces from D_3 to C_2 one. At $T_N = 40$ K, antiferromagnetic ordering of the Fe-sublattice with magnetic moments along the trigonal C_3 axis of the crystal arises [6]. Simultaneously, due to interaction with the Fe-sublattice, antiferromagnetic ordering appears also in Tb-sublattice with magnetic moments parallel to the same axis [6].

We have studied absorption spectra in the region of ${}^7F_6 \rightarrow {}^5D_4$ transition in Tb^{3+} ion (Fig. 5) depending on temperature (2–220 K) and on magnetic field (0–60 kOe). Here we are interested in temperature behavior of line positions. Splitting of all lines (besides No. 1) at $T < T_N$ and not far from T_N follow the temperature dependence of the Fe sublattice magnetization, while splitting of line *I* demonstrates abrupt change at temperature near T_N (Fig. 6). Such behavior of the line *I* position means that near the Neel temperature a local structural phase transition during electron transition *Ia* takes place. According above interpretation, it is not a real substantial displacement of atoms, but abrupt change of the equilibrium configuration of the local Tb^{3+} ion environment. A singularity in the local structure temperature behavior occurs also at $T \sim 34$ K (see Fig. 6).

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