



Spectroscopic study of the magnetic ordering in $\text{SmFe}_3(\text{BO}_3)_4$

E.P. Chukalina^{a,*}, M.N. Popova^a, L.N. Bezmaternykh^b, I.A. Gudim^b

^a Institute of Spectroscopy, RAS, 5, Fizicheskaya str., 142190 Troitsk, Moscow region, Russia

^b L.V. Kirensky Institute of Physics, Siberian Branch of RAS, 660036 Krasnoyarsk, Russia

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ABSTRACT

$\text{SmFe}_3(\text{BO}_3)_4$ belongs to the family of rare-earth $\text{RFe}_3(\text{BO}_3)_4$ multiferroics. We present the first measurements of the optical spectra of $\text{SmFe}_3(\text{BO}_3)_4$ (on single crystals) and report the data on the crystal-field levels and their symmetries for the ground multiplet ${}^6\text{H}_{5/2}$ [0 (Γ_4), 135 (Γ_{56}), and 220 (Γ_4) cm^{-1}] and on the ground-state exchange splitting (13.2 cm^{-1} at 1.7 K), important to interpret the magnetic, magnetolectric, and thermodynamic properties of this compound. The observed exchange splitting of the Sm^{3+} Kramers doublets manifests the magnetic ordering in $\text{SmFe}_3(\text{BO}_3)_4$ at 32 ± 1 K. From a comparison of the temperature-dependent spectra of the Sm^{3+} ion in $\text{SmFe}_3(\text{BO}_3)_4$ and in Nd–Gd mixed iron borate where the magnetic spin reorientation has been found earlier, we suggest the easy-plane arrangement of the Fe spins in $\text{SmFe}_3(\text{BO}_3)_4$. The samarium iron borate preserves the $\text{R}32$ (D_3^7) crystal structure at all the investigated temperatures (down to 1.7 K).

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1. Introduction

The rare-earth (RE) iron borates $\text{RFe}_3(\text{BO}_3)_4$ (R = lanthanoid or yttrium) crystallize in the huntite-type non-centrosymmetric trigonal structure with D_3^7 space group (see, e.g., Ref. [1] and references therein). The main feature of the structure of these compounds is magnetic helicoidal chains of the FeO_6 octahedra running along the c -axis. The R^{3+} ions reside between the chains in single D_3 symmetry positions. The crystals of iron borates with magnetic R^{3+} ions have two interacting magnetic subsystems (Fe^{3+} and R^{3+}) which leads to interesting magnetic properties. Not long ago, multiferroic features of some of the RE iron borates have been shown in the studies of magnetoelectric properties [2–5], this opens new fields in optoelectronic applications of these compounds.

At present, most of the compounds from the family $\text{RFe}_3(\text{BO}_3)_4$ have been investigated. Magnetic and specific heat measurements, optical and Raman spectroscopy, X-ray and neutron scattering experiments on powder samples and oriented single crystals of $\text{RFe}_3(\text{BO}_3)_4$ have shown that the compounds with the R^{3+} ions having smaller than Sm^{3+} ionic radii undergo a structural phase transition from the high-temperature D_3^7 structure into the low-temperature D_3^4 one [1,6,7] (a single position for the R^{3+} ion survives at this structural phase transition but its symmetry lowers from D_3 to C_2 [1]) and that all the $\text{RFe}_3(\text{BO}_3)_4$ compounds order magnetically at the temperature of about 30–40 K (see, e.g., Ref. [8] and references therein). In our earlier works [9–11], the type of the

magnetic structure of the iron subsystem in the magnetically ordered phase of $\text{RFe}_3(\text{BO}_3)_4$ (R = Y, Tb–Er) has been determined by the method of erbium spectroscopic probe. Later, our conclusions have been confirmed by neutron scattering experiments and/or magnetic measurements [12–14]. As for $\text{SmFe}_3(\text{BO}_3)_4$, only magnetic susceptibility and specific heat studies on powder samples are known [6]. According to these data, antiferromagnetic ordering of $\text{SmFe}_3(\text{BO}_3)_4$ occurs at about 33 K.

In the present communication, we report on the first investigation of the $\text{SmFe}_3(\text{BO}_3)_4$ single crystals by the spectroscopic method.

2. Experiment

$\text{SmFe}_3(\text{BO}_3)_4$ single crystals have been grown using the bismuth trimolibdate $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ based flux, 80% mass ($\text{Bi}_2\text{Mo}_3\text{O}_{12} + 2\text{B}_2\text{O}_3 + 0.6\text{Sm}_2\text{O}_3$) + 20% mass $\text{SmFe}_3(\text{BO}_3)_4$. The temperature and hydrodynamical conditions have been chosen as described in Ref. [15], growth rates did not exceed 0.5 mm/day. Isometric crystals 10–12 mm in size were homogeneously transparent and green in color. It is known that the green color of iron borates is due to a broad absorption band of Fe^{3+} in the red spectral region [16,17]. Besides, most of the optical f – f transitions in Sm^{3+} are very strong. Because of these circumstances, we need very thin samples to register successfully spectral lines of the Sm^{3+} ion in the whole spectral region. Oriented samples of 0.1–0.3 mm thickness were prepared for optical measurements.

Optical absorption spectra in the spectral region 1500–25 000 cm^{-1} at a resolution up to 0.1 cm^{-1} were registered using a Fourier-transform spectrometer Bruker IFS 125HR with a Si

* Corresponding author.

E-mail address: echukalina@isan.troitsk.ru (E.P. Chukalina).

detector or a liquid-nitrogen-cooled InSb detector. The sample was either in a closed-cycle optical cryostat or in a helium-vapour optical cryostat at a variable (1.7–300 K) temperature stabilized within ± 0.05 K. We used unpolarized light propagating along the c -axis of the crystal ($\mathbf{k} \parallel c$, $\mathbf{E}, \mathbf{H} \perp c$ – α -polarization) and linearly polarized light incident perpendicular to the c -axis ($\mathbf{k} \perp c$, $\mathbf{E} \parallel c$ – π -polarization, $\mathbf{E} \perp c$ – σ -polarization).

3. Results and discussion

The absorption spectrum of Sm^{3+} in $\text{SmFe}_3(\text{BO}_3)_4$ consists of narrow spectral lines corresponding to the f - f transitions within the inner $4f^5$ electronic shell of Sm^{3+} , well shielded by the outer filled $5p$ and $5s$ shells. An energy level of the Sm^{3+} ion with the total momentum \mathbf{J} is split into $(\mathbf{J} + 1/2)$ Kramers doublets by the crystal field (CF) of any symmetry lower than a cubic one. Wave functions of Kramers doublets transform according to the Γ_4 or Γ_{56} irreducible representations of the D_3 point symmetry group in the case of the D_3^7 crystal structure and according to the single Γ_{34} irreducible representation of the C_2 group in the case of the D_3^4 crystal structure. While the C_2 symmetry results in optical transitions allowed for all the polarization geometries, the D_3 one selects particular polarizations depending on the symmetry of the wave functions involved into a particular transition (see, e.g., Table II in Ref. [18]), specifically, the $\Gamma_{56} \rightarrow \Gamma_{56}$ transitions are strictly forbidden in the α -polarization. Analysis of our broadband polarized temperature-dependent absorption spectra of Sm^{3+} unambiguously reveals the D_3^7 crystal structure for $\text{SmFe}_3(\text{BO}_3)_4$ in the whole temperature range, at least down to 1.7 K, and the following Stark structure of the ${}^6\text{H}_{5/2}$ ground multiplet: 0 (Γ_4), 135 (Γ_{56}), and 220 (Γ_4) cm^{-1} . Detailed information on the Stark structure of the excited multiplets will be presented in a forthcoming publication.

The Kramers ion is a sensitive probe of the magnetic ordering in a crystal, because the magnetic field is the only perturbation that can lift the Kramers degeneracy. Fig. 1(a) shows the line IA (see Fig. 1(b) for notations) of the ${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{1/2,3/2}$, ${}^6\text{H}_{15/2}$ transition in $\text{SmFe}_3(\text{BO}_3)_4$ at several temperatures below 50 K. With decreasing the temperature, the line IA splits into several components that gradually narrow with further decreasing the temperature. The observed splitting of the spectral line manifests appearance of the internal magnetic field (“exchange field”) due to the establishment of the magnetic order in the sample. The spectral line splits into four components, as shown in the scheme of Fig. 1(b). Two of them freeze out with decreasing the temperature, due to depopulation of the upper component of the split ground Kramers doublet. The temperature dependences of the ground-state splitting $\Delta_0(T)$ and of the linewidth $\delta\nu(T)$ are shown in Fig. 2. The value of the ground-state splitting at low temperature equals 13.2 cm^{-1} . The point of inflection in the $\Delta_0(T)$ dependence corresponds to the temperature of long-range magnetic ordering T_N , while the “tail” of the residual splitting for $T > T_N$ is due to short-range magnetic order [19]. This residual splitting manifests itself as an excess line broadening relative to the phonon-assisted broadening. The latter one was subtracted from the total linewidth and this difference was taken as a line splitting due to short-range order. The spectroscopic data hence demonstrate that the magnetic ordering occurs as a second order phase transition at $T_N = 32 \pm 1$ K.

Inset of Fig. 2 compares the temperature dependence of the ground-state splitting, $\Delta_0(T)$, and the temperature variation of the magnetic moment of the Fe^{3+} ions in the easy-plane magnet $\text{YFe}_3(\text{BO}_3)_4$ at $T < T_N$, M_{Fe} , obtained from the neutron scattering data [14]. One can clearly see that the splitting $\Delta_0(T)$ is proportional to M_{Fe} . This is because the “exchange field” is, mainly, due to the Sm–Fe exchange interaction, the Sm–Sm one being negligi-

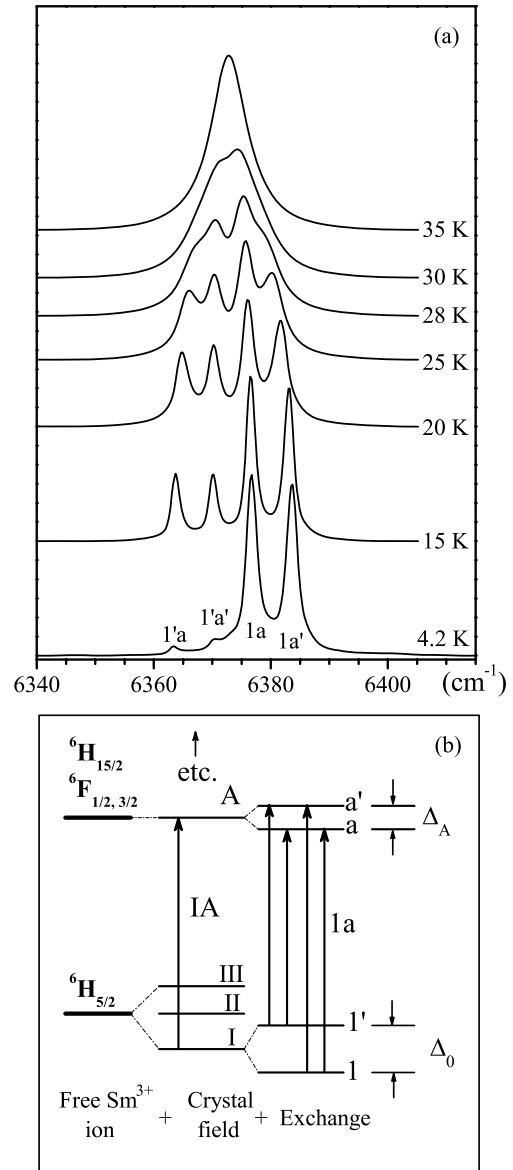


Fig. 1. The line IA of the ${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{1/2,3/2}$, ${}^6\text{H}_{15/2}$ transition of Sm^{3+} in $\text{SmFe}_3(\text{BO}_3)_4$ at different temperatures (a) and the scheme of splitting of the Sm^{3+} Kramers doublets, due to the crystal-field and Sm–Fe exchange interactions (b).

ble [18]. Thus, the Sm^{3+} ion probes the magnetic ordering within the iron magnetic subsystem of $\text{SmFe}_3(\text{BO}_3)_4$.

To answer the question about the magnetic structure of $\text{SmFe}_3(\text{BO}_3)_4$ at temperatures $T < T_N$, we compared the exchange splitting of the Sm^{3+} line IA (${}^6\text{H}_{5/2} \rightarrow {}^6\text{F}_{1/2,3/2}$, ${}^6\text{H}_{15/2}$) in $\text{SmFe}_3(\text{BO}_3)_4$ and in $\text{Nd}_{0.25}\text{Gd}_{0.75}\text{Fe}_3(\text{BO}_3)_4$ where samarium was present as a trace impurity at the level ~ 2.6 ppm. In the Nd–Gd mixed compound, the spin-reorientation phase transition from the easy-plane to the easy-axis magnetic structure at $T_R \sim 6.5$ K has been observed earlier [20]. The Sm^{3+} spectrum in the magnetically ordered $\text{SmFe}_3(\text{BO}_3)_4$ is similar to the Sm^{3+} spectrum in the easy-plane (but not the easy-axis) magnetic phase of $\text{Nd}_{0.25}\text{Gd}_{0.75}\text{Fe}_3(\text{BO}_3)_4:\text{Sm}^{3+}$. Thus, the magnetic structure of the ordered Fe subsystem in $\text{SmFe}_3(\text{BO}_3)_4$ is of the easy-plane type.

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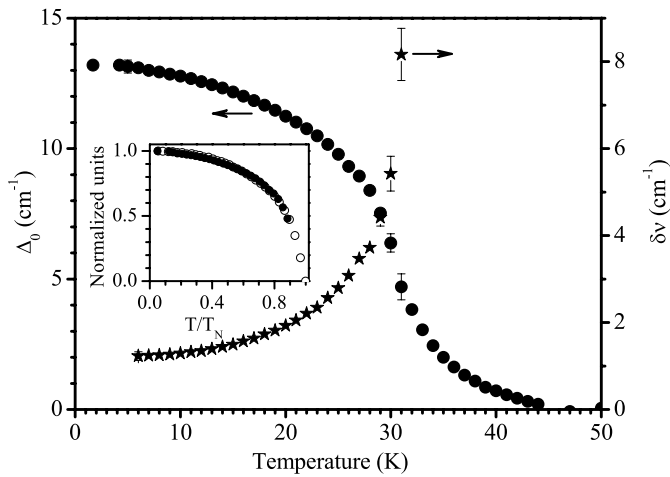


Fig. 2. Temperature dependence of the ground-state splitting Δ_0 (circles) and of the linewidth $\delta\nu$ (stars) for $\text{SmFe}_3(\text{BO}_3)_4$. Inset shows the normalized ground-state splitting $\Delta_0(T)/\Delta_0(1.7 \text{ K})$, $\Delta_0(1.7 \text{ K}) = 13.2 \text{ cm}^{-1}$ (circles) and the normalized spontaneous iron magnetic moment in $\text{YFe}_3(\text{BO}_3)_4$, $M_{\text{Fe}}(T)/M_{\text{Fe}}(2 \text{ K})$, $M_{\text{Fe}}(2 \text{ K}) = 4.24\mu_B$, measured by the neutron scattering [14] (open circles) as functions of the normalized temperature T/T_N .

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