Magnetization and specific heat of TbFe$_3$(BO$_3$)$_4$: Experiment and crystal-field calculations

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We have studied the thermodynamic properties of single-crystalline TbFe$_3$(BO$_3$)$_4$. Magnetization measurements have been carried out as a function of magnetic field (up to 50 T) and temperature up to 350 K with the magnetic field both parallel and perpendicular to the trigonal c-axis of the crystal. The specific heat has been measured in the temperature range 2-300 K with a magnetic field up to 9 T applied parallel to the c-axis. The data indicate a structural phase transition at 192 K and antiferromagnetic spin ordering at $T_N \approx 40$ K. A Schottky anomaly is present in the specific heat data around 20 K, arising due to two low-lying energy levels of the Tb$^{3+}$ ions being split by f-d coupling. Below $T_N$ magnetic fields parallel to the c-axis drive a spin-flop phase transition, which is associated with a large magnetization jump. The highly anisotropic character of the magnetic susceptibility is ascribed mainly to the Ising-like behavior of the Tb$^{3+}$ ions in the trigonal crystal field. We describe our results in the framework of an unified approach which is based on mean-field approximation and crystal-field calculations.

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I. INTRODUCTION

The family of ferroborates with the general formula RF$_3$(BO$_3$)$_4$ (R is a rare-earth ion or Y) attracts considerable attention since its members exhibit a wide variety of phase transitions. They possess magnetic structures which change as a function of temperature, external magnetic field and substitutions in the rare-earth subsystem. It was recently discovered that RF$_3$(BO$_3$)$_4$, (R = Gd, Nd) exhibits multiferroic features, i.e. the coexistence of elastic, magnetic and electric order parameters. The various ordering phenomena and their interaction cause anomalies in the dielectric permeability, electric polarization and magnetostriction, both spontaneous and field-induced. Our study aims to elucidate this interplay for the ferroborate TbFe$_3$(BO$_3$)$_4$, in which both the rare-earth ions and the Fe-ions form a magnetic subsystem.

The crystal structure of TbFe$_3$(BO$_3$)$_4$ at high temperatures is trigonal and belongs to the space group $D_3^4$ (R32). The main elements of the structure are spiral chains of edge-sharing FeO$_6$ octahedra running along the c-axis. The rare-earth ions are coordinated by triangular RO$_6$ prisms which are isolated from each other since they are separated by regular BO$_3$ triangles and have no common oxygen ions. Both the BO$_3$ triangles and RO$_6$ prisms connect three FeO$_6$ chains. There are no direct Fe-O-Fe links within the same c-plane and the shortest interchain exchange paths are therefore given by Fe-O-R-O-Fe and Fe-O-B-O-Fe, while the Fe-O Fe-exchange paths within the chains are much shorter (see Fig. 1). In the case of GdFe$_3$(BO$_3$)$_4$, the room temperature structure was found to be transformed to the $D_3^4$ (P3$_1$2$_1$) space group at $T_S = 156$ K. Below $T_S$, two non-equivalent Fe sites are present, which give rise to both a stretched and compressed modification of the FeO$_6$ spiral chains.

In GdFe$_3$(BO$_3$)$_4$, the presence of different magnetic sublattices causes several magnetic transitions below $T_S$, which are associated with antiferromagnetic spin ordering of the Fe-sublattice ($T_N \approx 37$ K) and a spin reorientation at $T_{SR} \approx 9$ K. In addition, strong magnetostrictive and magnetoelastic effects below $T_{SR}$ are associated with a spin reorientation which occurs in external magnetic fields with $B||c$.

In this paper, we report on the thermodynamic properties of TbFe$_3$(BO$_3$)$_4$. Our data on TbFe$_3$(BO$_3$)$_4$ show a spin-flop phase transition, which is driven by magnetic fields $B||c$. This transition is associated with a large jump of the magnetization. The highly anisotropic magnetic susceptibility is ascribed mainly to the Ising-like behavior of the Tb$^{3+}$ ions in the trigonal crystal field. Our experimental data are analyzed in the context of the unified approach which is based on mean-field approximation and crystal-field calculations. The spin-flop
FIG. 1: The crystal structure of RFe$_3$(BO$_3$)$_4$. The spiral chains formed by FeO$_6$ octahedra along c-axis (the shortest Fe-O-Fe exchange) are represented by the chains of shadowed areas.

The spin-flop transition is apparently accompanied by magnetoelastic effects. Magnetoelastic effects might therefore be associated with the spin-flop transition, leading TbFe$_3$(BO$_3$)$_4$ to be a candidate for a multiferroic compound.

II. EXPERIMENT

The single crystals of TbFe$_3$(BO$_3$)$_4$ were grown using a Bi$_2$Mo$_3$O$_{12}$-based flux. The seeds were obtained by spontaneous nucleation from the same flux. Single crystals were green in color and had a good optical quality. The orientation of the crystals was performed by x-ray diffraction. All magnetic measurements were performed with the external magnetic field either parallel or perpendicular to the c-axis of the crystal. The AC-susceptibility at 1000 Hz and DC-susceptibility were measured in magnetic fields of 0.001 T and 0.1 T, respectively, in the temperature range 1.8-350 K using a Quantum Design Physical Property Measurement System (PPMS). The magnetization $M(B)$ was measured between 4.2 and 120 K in fields up to 15 T with a vibrating sample magnetometer (VSM). The field sweep rate was approximately 0.2 T/min. In addition to this, a pulsed field magnetometer was used for magnetization measurements up to 50 T. Here, the total pulse duration amounted to 0.05 s. The temperature dependence of the specific heat was measured in the temperature range 1.8-300 K and in magnetic fields up to 9 T with a PPMS calorimeter.

FIG. 2: Specific heat in zero magnetic field (a) and magnetization at $B = 0.1$ T (b) of TbFe$_3$(BO$_3$)$_4$. The inset (c) highlights the Schottky anomaly of $C_p/T$ at $T \sim 20$ K. $T_S$ and $T_N$ label the (presumably) structural phase transition and the onset of antiferromagnetic spin ordering in the Fe sublattice, respectively.

III. EXPERIMENTAL RESULTS

TbFe$_3$(BO$_3$)$_4$ exhibits two phase transitions below room temperature, as is illustrated by the specific heat and magnetization data in Fig. 2. By comparison with GdFe$_3$(BO$_3$)$_4$, the first order phase transition at $T_S = 192$ K is tentatively attributed to a structural symmetry reduction to the low symmetric P3$_1$2$_1$1-phase. Actually, the data exhibit several first order anomalies of the specific heat in the vicinity of $T_S$ which are probably related to structural changes. The origin of these anomalies can not be clarified by our present study which focuses on the magnetic properties of TbFe$_3$(BO$_3$)$_4$. The structural phase transition is associated with an entropy jump of $\Delta S \approx 1.9$ J/mol K. At $T_N = 40$ K, the onset of antiferromagnetic spin order in the iron subsystem is demonstrated by a sharp jump in the specific heat and a kink
in the magnetization. We observe a specific heat jump of \( \Delta C_p \approx 59.4 J/mol K \). This result agrees with the jump \( \Delta C_p \) which is predicted from the mean field theory for the antiferromagnetic spin ordering of the \( S = 5/2 \) Fe-sublattice:

\[
\Delta C_p = \frac{5S(S + 1)}{S^2 + (S + 1)^2} R = 59 J/mol K, 
\]

with \( R \) being the gas constant. The entire spin entropy of the Fe\(^{3+} \) subsystem appears to develop only below \( T_N \). The Fe\(^{3+} \) subsystem must therefore be considered as a classical 3D antiferromagnet, since short range spin correlations at significantly higher temperatures which would be present if the Fe\(^{3+} \) chains were able to form quasi one-dimensional magnets are clearly absent. An analysis of the specific heat data\(^{10} \) indeed confirms that the magnetic ordering only occurs in the Fe subsystem while the Tb subsystem is polarized by the Fe subsystem.

In contrast to the anomalies due to the structural and magnetic phase transitions at \( T_S \) and \( T_N \), respectively, the Schottky anomaly in the specific heat at \( \sim 20 \text{K} \) reveals the temperature-driven population of the ground state of the Tb\(^{3+} \) ions split in the magnetic field of the Fe subsystem. No spin reorientation (similar to the one seen in GdFe\(_3\)(BO\(_3\))\(_4 \) ferrobate) was observed at low temperatures in zero magnetic field.

\[\text{FIG. 3: Magnetization, at } T = 4.2 \text{K, for the magnetic field applied to the } c \text{- and } a \text{-axis, respectively. Data obtained in a quasi-static field (VSM) are shown in (a) whereas (b) displays pulsed magnetic field data (see text).}\]

Depending on their direction, external magnetic fields can have a drastic effect on the magnetic properties of TbFe\(_3\)(BO\(_3\))\(_4 \). As shown in Fig. 3 for applied magnetic fields parallel to the \( a \)-axis there is a linear field dependence of the magnetization at \( 4.2 \text{K} \). The data imply \( \chi_a = 0.14 \mu_B/T \text{ f.u.} \). In contrast, applying a magnetic field along the easy magnetic axis, i.e. the trigonal \( c \)-axis, causes a sharp jump in the magnetization at \( B_c(4.2 \text{K}) \sim 3.5 \text{T} \). Here, the magnetic field drives a first order transition. We demonstrate further below that the main feature of this transition is a spin-flop of the AFM ordered Fe\(^{3+} \) spins which is accompanied by the orientation of magnetic moments of the Tb\(^{3+} \) subsystem along the external magnetic field. The strongly discontinuous character of the transition is illustrated also by the pulsed field data in Fig. 3(b). In the pulsed field \( (\partial B/\partial t \sim 5000 \text{T/s}) \) the hysteresis at the spin-flop transition is one order of magnitude larger than in the quasi-static measurement \( (\partial B/\partial t \sim 10^{-3} \text{T/s}) \) shown in Fig. 3(a), due to the relaxation processes and magnetocaloric effect. At high magnetic fields \( B > B_c \), the data show a linear \( M(B) \) curve with \( \chi_c = 0.13 \mu_B/T \text{ f.u.} \) being slightly smaller than \( \chi_a \).

The magnetization data in Fig. 3 show a strong anisotropy. It is reasonable (and will be shown in Sec. IV in a detailed analysis) to attribute this anisotropy to the highly anisotropic Tb\(^{3+} \) magnetic moments, which are subject to the staggered field of the antiferromagnetically ordered Fe spins. The discussion hence must not only address the two subsystems of Fe and Tb moments, of which the Fe system divides in the two sublattices below \( T_N \), but also the Tb subsystem must be discussed in terms of two sublattices since it is polarized by the indirect exchange interaction with the iron subsystem.

The field dependences of the magnetization at 4.2 K shown in Fig. 3 reveals two anisotropy features: (1) A sharp increase of the magnetic moment \( \sim 9 \mu_B \) evolves at the critical field \( B_C \). (2) The linear contribution to \( M(B||c) \) only exists above \( B_C \). If the extra moment (1) is neglected, the linear part of \( M(B||c) \) is a straight line through the origin which is very similar to \( M(B||a) \). Such behaviour (2) is typical for an uniaxial antiferromagnet magnetized along the easy axis.

Upon heating (see Fig. 4), the spin-flop transition shifts to higher temperatures and vanishes above \( T_N \), but it remains clearly visible in the entire antiferromagnetically spin ordered phase. However, the magnetization jump reduces in value and becomes less sharp as it is shifted towards higher fields. For fields larger than \( B_C \) as well as for \( T > T_N \) the magnetization curves become nonlinear.

Below \( T_N \) and for fields \( B||c < B_C \), the staggered field of the Fe spins polarizes the terbium subsystem due to \( f-d \) interactions yielding two Tb sublattices with the magnetic moments oriented oppositely and along the \( c \)-axis. For \( B||c \) the effective field acting on the terbium sublattice which magnetic moment opposes the applied field is decreased as the applied field increases and this magnetic moment tends to diminish. This is a factor determining the character of the magnetization at 4.2 K prior to the phase transition, since at low temperatures the longitudinal susceptibility of the iron subsystem is very small. At \( B_C \) the staggered field acting on the Tb\(^{3+} \) magnetic moments vanishes as the magnetic moments of Fe\(^{3+} \) ions become oriented nearly perpendicular to them. As a re-
The magnetic moments of Tb$^{3+}$ ions align with the external magnetic field reaching the saturation value of about 9 $\mu_B$ at low temperatures.

In the spin-flop phase both terbium sublattices have magnetic moments directed along the field $B/|c|$ and the magnetic moments of iron sublattices bend towards the field direction. This part of the magnetization curve allows us to estimate the transverse susceptibility of the iron subsystem: $\chi_{\perp}^{Fe} \approx \chi_c = 0.13 \mu_B/T$ f.u. The observation of $\chi_a > \chi_c$ suggests a small contribution from the Tb subsystem for $B/|a|$. At higher temperatures, as shown in Fig. 4, the magnetization curves gradually become less sharp. In the initial collinear phase the iron subsystem begins to contribute to the magnetization as longitudinal susceptibility grows with increasing temperature, thus stabilizing the initial phase.

The magnetic phase diagram, constructed from data and from specific heat measurements in magnetic fields, is presented in Fig. 5. The difference in phase boundaries shown by open and full symbols accounts for the hysteretic phenomena and finite slope of $M(B)$ curves at the spin-flop transition. This diagram shows that magnetic fields parallel to the $c$-axis slightly suppress the antiferromagnetic spin ordering temperature of the Fe sublattice. In contrast, the critical field of the spin-flop transition increases upon heating.

**IV. THEORY**

The magnetic properties of terbium ferroborate are governed by both magnetic subsystems interacting with each other. As already mentioned above, the crystal structure of rare-earth ferroborates suggests that the main feature of their magnetic structure is formed by the helical iron chains along the $c$-axis. However, our experimental data provide no evidence for quasi-1D magnetic properties, which indicates significant interactions between the chains. Moreover, the experimental magnetization curves and phase diagram have the form which is typical for 3D uniaxial antiferromagnets. This fact provides reason enough to consider the magnetic structure of the Fe subsystem as that of inaxial aitiferromagnet with two sublattices magnetic moments of which are equal in the absence of field. The interactions hierarchy in the system is such that it stabilizes the orientations of Fe and Tb magnetic moments along the trigonal axis. Indeed, the strongest interaction in the compound is the crystal field (the splitting of the ground multiplet comprises about 400–500 cm$^{-1}$, the energy interval between the ground quasi-doublet and the nearest excited states is of the order of 200 cm$^{-1}$), and the non-Kramers Tb$^{3+}$ ion in the trigonal crystal field acquires a huge anisotropy ($g_c \sim 18$, $g_a \sim 0$) and becomes an Ising ion with the preferred orientation of magnetic moment along the trigonal axis. Interaction comparable in value with the crystal field is absent in the system, therefore there is no source of any other orientation of Tb magnetic moments. And so there are grounds to suggest a collinear arrangement of magnetic moments in TbFe$_3$(BO$_3$)$_4$. We note however that only neutron diffraction studies on an 11B-enriched compound can unambiguously resolve the magnetic structure under discussion.

In the following section we model the magnetic properties of TbFe$_3$(BO$_3$)$_4$ using molecular field theory. Within this approximation the total Hamiltonian, which comprises the Hamiltonians of the iron and the terbium sub-
systems as well as the one considering the Tb-Fe interaction, can be expressed as a sum of single-particle Hamiltonians. In the presence of an external magnetic field \( B \), the effective Hamiltonians of the Tb/Fe ion of the \( i \)-th sublattice (\( i=1 \) and 2) can be written as:

\[
\mathcal{H}_i(Tb) = \mathcal{H}_i^{CF} - g_J \mu_B J_i \left[ B + B_{mi}(Tb) \right],
\]

\[
\mathcal{H}_i(Fe) = -g_S \mu_B S_i \left[ B + B_{mi}(Fe) \right],
\]

where \( g_J \) is the Landé factor and \( J_i \) is the angular momentum operator of the rare-earth ion; \( g_S = 2 \) is the g-factor and \( S_i \) is the spin momentum operator of the Fe ion; \( B_{mi}(Tb/Fe) \) are the molecular fields acting on the Tb or Fe ion in the \( i \)-th sublattice. The crystal-field Hamiltonian \( \mathcal{H}_{CF} \) is governed by the symmetry of the local environment of the rare-earth ion.

As explained in Sec. [11] from the analogy to the structural phase transition at 156 K in GdFe\(_3\)(BO\(_3\))\(_4\) we suppose that the specific heat anomaly at \( T_S = 192 \) K reflects a crystal symmetry reduction from the trigonal space group R\(_3\)2 to the trigonal group P3\(_1\)2\(_1\). This implies that the local symmetry of the Tb\(^{3+}\) ion is reduced from \( D_3 \) to \( D_3 \) at \( T > T_S \) to \( C_2 \) at \( T < T_S \). Nevertheless (as will be discussed below) a simpler Hamiltonian of \( D_3 \) symmetry is sufficient for describing the low-temperature magnetic properties of TbFe\(_3\)(BO\(_3\))\(_4\), since the available crystal-field parameters of isostructural compounds give rise to two closely-spaced (with a splitting less than 2-3 cm\(^{-1}\)) singlets as a low-lying state of the ground multiplet. These singlets are responsible for the Ising-like behavior of this non-Kramers ion in both the paramagnetic and the ordered phases.

In order to describe the thermodynamic properties of rare-earth compounds we only need to consider the ground multiplet. In terms of the equivalent operators \( O^m_n \) the crystal field Hamiltonian \( \mathcal{H}_{CF} \) reads as following:

\[
\mathcal{H}_{CF} = \alpha_J B_0^0 O_0^0 + \beta_J (B_2^0 O_2^0 + B_3^1 O_3^1) + \gamma_J (B_0^0 O_0^0 + B_2^3 O_2^3 + B_6^6 O_6^6),
\]

where \( B_n^m \) are the crystal-field parameters for the \( D_3 \) symmetry, \( \alpha_J, \beta_J \) and \( \gamma_J \) are the Stevens coefficients. The former are unknown for the Tb\(^{3+}\) ion in TbFe\(_3\)(BO\(_3\))\(_4\). However, our results depend only weakly on the actual crystal-field parameters since the magnetic properties of TbFe\(_3\)(BO\(_3\))\(_4\) are essentially controlled by the magnetic behavior of the iron subsystem and by the Ising character of the non-Kramers Tb\(^{3+}\) ion in the crystal field of the trigonal symmetry. We hence could not determine the crystal-field parameters from the experimental data. Instead, we have used the crystal-field parameters of the isostructural compounds, in particular the rare-earth aluminoborates (see e.g. Ref. [17]) and refined these using the data for crystal-field splitting of Nd\(^{3+}\) in NdFe\(_3\)(BO\(_3\))\(_4\).[18]

We have written the expressions for the molecular fields acting on the Tb and Fe ions from the \( i \)-th sublattice on the basis of the interactions hierarchy and magnetic structure of TbFe\(_3\)(BO\(_3\))\(_4\). A detailed analysis of the interactions which was performed for the low temperature phase of GdFe\(_3\)(BO\(_3\))\(_4\) in Ref. [12] also seems to be quite applicable to TbFe\(_3\)(BO\(_3\))\(_4\). According to this analysis, a rare-earth ion does not interact with iron ions from the same c-plane but interacts antiferromagnetically with iron ions from the neighboring planes, it is clearly shown in Fig.7b of Ref.12. The interaction between rare-earth ions can be neglected because the distances between them are larger than 6 Å and no reasonably superexchange path could be introduced. Consequently, none of the ferroborates demonstrates an intrinsic ordering in the rare-earth subsystem. The molecular fields \( B_{mi}(Tb) \) and \( B_{mi}(Fe) \) can therefore be written as

\[
B_{mi}(Tb) = \lambda_{fd} M_i,
\]

\[
B_{mi}(Fe) = \lambda M_j + \lambda_{fd} m_i, \quad j = 1 \text{ or } 2, \quad j \neq i,
\]

where \( \lambda_{fd} < 0 \) and \( \lambda < 0 \) are the molecular constants of the Tb-Fe and Fe-Fe antiferromagnetic interactions. The magnetic moments \( M_i \) and \( m_i \) of the \( i \)-th iron and terbium sublattices are defined as

\[
M_i = 3g_S \mu_B \langle S_i \rangle \quad \text{and} \quad m_i = g_J \mu_B \langle J_i \rangle.
\]

The thermodynamic potential of the system (per formula unit) has the following form:

\[
\Phi(T, B) = \frac{1}{2} \left[ -k_B T \sum_{i=1}^{2} \ln Z_i(Tb) + \sum_{i=1}^{2} g_J \mu_B \langle J_i \rangle B_{mi}(Tb) \right.
\]

\[
-3k_B T \sum_{i=1}^{2} \ln Z_i(Fe) + \frac{1}{2} \left[ 3g_S \mu_B \langle S_i \rangle B_{mi}(Fe) \right],
\]

with the partition functions

\[
Z_i(Tb/Fe) = \sum_{n} \exp \left[ -\frac{E_{mi}(Tb/Fe)}{k_B T} \right],
\]

where \( E_{mi}(Tb/Fe) \) are the eigenvalues of corresponding Hamiltonians (Eqs.2 and 3). To find the magnetic moments of the Tb and Fe subsystems Eqs.7 in the mean-field approximation one has to solve the self-consistent problem of deducing their values and orientations on the basis of Hamiltonians Eqs. 2 and 3 while considering the condition of the minimum of the thermodynamic potential (Eq. 8) for a given temperature and field. The right part of equation for \( M_i \) is the relevant Brillouin
function, as it should be in the case of an equidistant spectrum which is typical for the Fe$^{3+}$ ion with an orbital singlet as a ground state (S-ion). Substituting the magnetic moments for particular phases into the thermodynamic potential (Eq. 8), we obtain the energies of the phases and find the critical fields for the phase transitions from the condition of their equality. The magnetization of the compound (per formula unit) is given by:

$$M = \frac{1}{2} \sum_{i=1}^{2} (M_i + m_i).$$  (10)

Both magnetic subsystems contribute to the initial magnetic susceptibility of terbium ferroborate:

$$\chi_i = \chi_i^{Fe} + \chi_i^{Tb}, \ i = \parallel \ or \ \perp . \ (11)$$

In the paramagnetic range, where the interaction between iron and terbium subsystems can be neglected, the magnetic susceptibility of the Tb subsystem can be calculated with the help of the well-known Van Vleck formula on the basis of the crystal-field Hamiltonian Eq. 4. For the ordered phase at $T < T_N$ as well as for the paramagnetic phase, the initial magnetic susceptibilities of the compound can easily be found from the initial linear parts of the magnetization curve $M(B)$ calculated for the field along and perpendicular to the trigonal axis.

The contribution of the Tb$^{3+}$ subsystem to the heat capacity of the TbFe$_3$(BO$_3$)$_4$ compound can be calculated with the help of the usual expression (per rare-earth ion, i.e. per formula unit):

$$C_{Tb} = k_B \frac{\langle E^2 \rangle - \langle E \rangle^2}{(k_B T)^2}. \ (12)$$

The thermal averages were calculated for the spectrum of Tb$^{3+}$ ion formed by the crystal field and by interactions with the iron subsystem and an external magnetic field.

V. COMPARISON OF EXPERIMENTAL DATA AND THEORETICAL CALCULATIONS

A. Magnetization

In order to carry out a quantitative analysis of the magnetization curves for TbFe$_3$(BO$_3$)$_4$ in accordance with the approach presented in the previous section, the magnetizations in the collinear and flop phases were calculated in the mean-field approximation and the critical fields of the phase transitions $B_C$ were found from the equality of their thermodynamic potentials. In Fig. 6 the experimental and calculated magnetization curves are displayed for several temperatures.

The analysis of the magnetization curve at 4.2 K provides a possibility to determine some parameters of the compound. The f-d interaction parameter $\lambda_{fd} = -0.253 T/\mu_B$ was calculated by fitting the initial part of the magnetization curve at 4.2 K with the help of the usual expression (per rare-earth ion, i.e. per formula unit):

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The thermal averages were calculated for the spectrum of Tb$^{3+}$ ion formed by the crystal field and by interactions with the iron subsystem and an external magnetic field.
the exchange parameter for the collinear phase is taken equal to this value then the calculated phase transition critical field exceeds the experimentally observed value and a similar relation between experimental and calculated critical fields takes place for all temperatures. On the other hand, if one takes the exchange parameter in the collinear phase to be \( \sim 1\% \) less than that in the flop phase, the energy of the collinear phase increases slightly, the critical field decreases and its calculated value is in a good agreement with the experimental one (see Fig. 5). The difference between the values of the exchange parameter \( \lambda \) for two phases could be explained by the presence of the magnetoelastic effects accompanying the field-induced phase transition. In support of this hypothesis, it is known that, in GdFe\(_3\)(BO\(_3\))\(_4\) with the \( S \)-ion Gd\(^{3+}\), the field-induced phase transition in the low-temperature phase \((T < 10 \text{K})\) results in a magnetostriction jump of the order of \(2 \times 10^{-5}\). In TbFe\(_3\)(BO\(_3\))\(_4\) the highly anisotropic terbium ion should give a much more essential contribution to the magnetostriction at the field-induced spin-flop transition than the \( S \)-ion Gd\(^{3+}\). Indeed, calculations of the multipole moments \( Q_{nm} = a_n \langle O_{nm} \rangle \) of the Tb\(^{3+}\) ion in TbFe\(_3\)(BO\(_3\))\(_4\) (which provide an information on the rare-earth contribution to the magnetostriction\(^{20}\)) have shown that their changes at the spin-flop phase transition are very significant.

To analyze the temperature evolution of the magnetization we have to take into account the exchange between the Fe chains which is responsible for the three-dimensional ordering. This value of \( \lambda \) enters the Brillouin function in Eq.7, the well-known explicit form of which is not given for the sake of brevity. It was chosen from the best agreement between experimental and calculated magnetization curves for all temperatures as \( \lambda_2 = -2T/\mu_B \). The \( B - T \) phase diagram for the spin-flop transition (see Fig. 7) demonstrates a good agreement between the calculated and experimental data. We emphasize that quantitative description of the magnetization isotherms of TbFe\(_3\)(BO\(_3\))\(_4\) in the mean-field approximation requires an introduction of two exchange parameters characterizing Fe-Fe antiferromagnetic interaction, \( \lambda_1 \) and \( \lambda_2 \). The \( \lambda_1 \) enters Eq. 8 for the energy and determines the critical field of the spin-flop transition \( B_C \) and the transverse susceptibility of the iron subsystem in the flop phase. The \( \lambda_2 \) determines the magnitude of iron magnetic moments \( M_i \) for specific temperature and field as well as the Neel temperature. The necessity of introducing two exchange parameters is a consequence of the chain structure of the ferroborate when considered in the mean-field approximation. The intrachain exchange interactions are described by \( \lambda_1 \), whereas the interchain exchange interactions (which are responsible for the three-dimensional magnetic order) are described by \( \lambda_2 \). Our experimental data and the results of our theoretical analysis indicate that these two quantities are of the same order of magnitude.

B. AC magnetic susceptibility

As has already been discussed above, the strong anisotropy of the magnetic susceptibility is caused by the contribution of the Tb\(^{3+}\) ion with its Ising character of magnetic behavior. The \( \chi(T) \) dependencies have been calculated using parameters of TbFe\(_3\)(BO\(_3\))\(_4\) derived from the analysis of the magnetization isotherms. However, as one can see in Fig. 3 the experimentally obtained and calculated \( \chi_\parallel(T) \) curves differ substantially. The non-zero susceptibility \( \chi_\parallel \) at very low temperatures and a growth of \( \chi_\perp \) upon increasing the temperature up to \( T_K \) could be ascribed to a misorientation of the sample by a few degrees with respect to the crystallographic axis. In fact, the inclusion of a misorientation by 3° with respect to the basal plane leads to a significantly better agreement between the calculated and experimental data. The variation of the crystal-field parameters within reasonable limits does not result in any significant changes in the description of the \( \chi(T) \) dependencies; the agreement between experimental and calculated curves remains roughly the same.

A distinctive convexity of the experimental \( \chi_\parallel(T) \) curve in the temperature range 30-35 K is associated with a Schottky-type anomaly, i.e. with the change of occupation of two low-lying terbium singlets. This anomaly can also be observed in the calculated curves, especially in the susceptibility of the Tb subsystem. The calculated Neel temperature is higher than the corresponding experimental value but this is an usual feature of the mean-field theory.
C. Heat capacity

In the following, the specific heat and the effect of the magnetic field will be analyzed in terms of our approximation. The experimental specific heat data in magnetic fields $B = 0$ and $3\, \text{T}$ along the $c$-axis are presented in $C/T$ vs. $T$ coordinates in Fig. 9a. As one can see, the magnetic field shifts the Schottky anomaly to lower temperatures, specifically for $C(T)$ from $\sim 20\, \text{K}$ at $B = 0$ to $\sim 5\, \text{K}$ at $B = 3\, \text{T}$. The anomaly at around $5\, \text{K}$ is particularly evident since in this temperature range both the phonon and magnetic contributions are small.

The calculated temperature dependencies of the Tb contribution to the specific heat are presented in Fig. 9b. The calculated $C_{\text{Tb}}(T)$ for $B = 0$ demonstrates the Schottky anomaly around $20\, \text{K}$. As has already been mentioned above, the anomaly is caused by the occupation of the singlet level separated from the ground singlet by the temperature-dependent splitting due to the Tb-Fe interaction (Fig. 10).

Our analysis in Fig. 9b suggests that the Tb contribution to the specific heat is different for the two Tb sublattices if an external magnetic field is applied along the $c$-axis. For the terbium sublattice with magnetic moments opposed to the field direction, the Schottky anomaly shifts to lower temperatures. This is easy to understand because an increase of the magnetic field leads to a decrease of the energy gap between two singlets (see Fig. 10). It means that an external field demagnetizes this terbium sublattice. For the other terbium sublattice, however, the energy gap between the two singlets increases, the increased external field magnetizes the sublattice and the Schottky anomaly moves to higher temperatures. We emphasize the agreement between the experimental and numerical data which confirms that the description of Tb-Fe coupling in $\text{TbFe}_3(\text{BO}_3)_4$ provided in this work is appropriate.

VI. CONCLUSIONS

Our measurements of the specific heat and the magnetization and the theoretical description of the experimental data provide a detailed understanding of the thermodynamical properties of $\text{TbFe}_3(\text{BO}_3)_4$. Our unified approach describes the presence of the spin-flop transition for magnetic fields applied parallel to the trigonal
c-axis and the related magnetization jump below $T_N$. Microscopically, the highly anisotropic magnetization data have been attributed to the Ising character of the Tb$^{3+}$ ion in the trigonal crystal field. In addition, the presence of a Schottky anomaly in the specific heat data around 20 K and its shift as a function of the applied magnetic field have been explained as the Tb contribution to specific heat in terms of two low-lying energy levels of the Tb$^{3+}$ ions being split by f-d coupling.

In particular, our approximation considers the exchange interaction of the Fe-subsystem as well as the coupling between Fe- and Tb-subsystems. The $f-d$ coupling parameter has been determined and its value is in good agreement with available spectroscopic data. The antiferromagnetic exchange interaction in the iron subsystem has been described with the help of two parameters. The parameter $\lambda_1$ is responsible for bending the iron magnetic moments in the flop phase, which occurs against the intrachain exchange, and determines the spin-flop transition field; the parameter $\lambda_2$ is connected with the interchain exchange interaction responsible for the three-dimensional ordering, it controls the Neel temperature and magnitudes of the iron magnetic moments for specific temperatures and fields. The relation $|\lambda_1| > |\lambda_2|$ is naturally fulfilled because the Fe-O-Fe exchange paths within the chains are much shorter than the interchain exchange paths. The appearance of two exchange parameters is a special feature of consideration of magnetic properties of the compound with chain structure in the framework of the mean-field approximation, which is known to be of limited validity for description of magnetic lattices of lowered dimensionality. A substantial influence of the magnetoelastic effects which accompany the field-induced phase transition on the value of the molecular parameter responsible for bending the iron magnetic moments in the flop phase has been found.

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