

Magneto-resonance properties of antiferromagnetic $\text{TbFe}_3(\text{BO}_3)_4$ at low temperatures

Cite as: Low Temp. Phys. **39**, 167 (2013); <https://doi.org/10.1063/1.4792134>
Published Online: 26 February 2013

V. A. Bedarev, M. I. Paschenko, M. I. Kobets, K. G. Dergachev, V. A. Paschenko, A. N. Bludov, E. N. Khatsko, S. L. Gnatchenko, L. N. Bezmaternykh, and V. L. Temerov



View Online



Export Citation



CrossMark

ARTICLES YOU MAY BE INTERESTED IN

Electrical resistivity of HTSC-normal metal interface

Low Temperature Physics **39**, 98 (2013); <https://doi.org/10.1063/1.4791769>

Electronic states of monatomic layers of alkali and rare earth metals adsorbed on graphene surfaces

Low Temperature Physics **39**, 172 (2013); <https://doi.org/10.1063/1.4791767>

Oscillating modes of a massive single vortex line in an anisotropic superconductor: The role of temperature

Low Temperature Physics **39**, 102 (2013); <https://doi.org/10.1063/1.4791771>

LOW TEMPERATURE TECHNIQUES
OPTICAL CAVITY PHYSICS
MITIGATING THERMAL
& VIBRATIONAL NOISE

[DOWNLOAD THE WHITE PAPER](#)

downloads.montanainstruments.com/optical_cavities

MONTANA INSTRUMENTS
COLD SCIENCE MADE SIMPLE



Magneto-resonance properties of antiferromagnetic $\text{TbFe}_3(\text{BO}_3)_4$ at low temperatures

V. A. Bedarev,^{a)} M. I. Paschenko, M. I. Kobets, K. G. Dergachev, V. A. Paschenko, A. N. Bludov, E. N. Khatsko, and S. L. Gnatchenko

B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine, pr. Lenina 47, Kharkov 61103, Ukraine

L. N. Bezmaternykh and V. L. Temerov

L.V. Kirensky Institute of Physics, Siberian Department of the Academy of Sciences, Krasnoyarsk 660036, Russia

(Submitted July 18, 2012; revised September 13, 2012)

Fiz. Nizk. Temp. **39**, 219–224 (February 2013)

The magnetic resonance and field dependence of magnetization were studied in a single crystal of $\text{TbFe}_3(\text{BO}_3)_4$ at temperatures from 2 to 13 K and frequencies from 18 to 142 GHz. Two pairs of lines with different intensities were found in the EPR spectrum. The found lines can be assigned to two types of centers: the Tb^{3+} ions which neighbor with the Bi and Mo growth impurities. The initial splitting of the lowest quasi-doublet of such Tb^{3+} ions by the crystal field and exchange field acting on the rare-earth ions from the iron sublattices were determined. The amount of these centers was estimated. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4792134>]

Introduction

A compound $\text{TbFe}_3(\text{BO}_3)_4$ belongs to a family of rare earth ferrobates, magnetoelectric properties of which are now being intensively investigated.^{1–4} The study of its crystal structure has shown that there is a structural phase transition at 192 K with the change of the space group from $R32$ to $P3_121$.⁵ At the temperature $T_N = 40$ K such a crystal becomes an easy-axis antiferromagnet. A subsystem of iron ions of the crystal orders antiferromagnetically. The magnetic moments of iron ions lie along the trigonal axis c .⁵ Terbium ions are in a paramagnetic state and magnetized by an effective field H_{eff} of the iron subsystem. The magnetic moments of terbium ions also lie along the c axis. If an external magnetic field is directed along the axis c , then the spin-reorientation phase transition of the first order is observed in the $\text{TbFe}_3(\text{BO}_3)_4$ crystal at temperatures below 40 K.⁵

Above the temperature of the structural phase transition the symmetry of positions of Tb^{3+} ions in terbium ferrobate is described by a trigonal point group D_3 . A crystal field of this symmetry splits the ground multiplet of Tb^{3+} ion in this crystal 7F_6 ($S = 3; L = 3; J = 6$) as follows:

$${}^7F_6 \rightarrow 3\Gamma_1 + 2\Gamma_2 + 4\Gamma_3.$$

Here, Γ_1 and Γ_2 are the non-degenerate representations, and Γ_3 is the two-fold degenerate representation. Below the temperature of the structural phase transition the symmetry of positions of Tb^{3+} ions lowers down to C_2 and the degeneracy is lifted. This leads to the appearance of 13 singlet levels in the ground multiplet 7F_6 of Tb^{3+} ion.

Studies of transmission spectra of the crystal $\text{TbFe}_3(\text{BO}_3)_4$ in the optical range suggests that the ground state of Tb^{3+} ion is two close singlets—a quasi-doublet which is split by the effective field of iron.^{6–8} The magnitude of this splitting at 2 K is about 32 cm^{-1} . According to experimental studies^{5,7} the magnetic moment of the ground state of Tb^{3+} ion is $(8.6 \pm 0.4) \mu_B$, and g -factor is 17.8 ± 0.2 .

In Refs. 7–9, the satellites around the main lines were observed in optical spectra. A distance between the satellites and the main lines varies from 5.8 cm^{-1} to 11.5 cm^{-1} for different lines. The appearance of the satellites is associated with f - f optical transitions in Tb^{3+} ions, located near defects caused by growth impurities of Bi and Mo ions, which change crystal-line and effective fields in the surrounding of Tb^{3+} ions.^{7,10,11}

Electron paramagnetic resonance (EPR) can provide new information about Tb^{3+} ions located in the vicinity of growth impurities. In addition, if initial splitting of quasi-doublets of these ions is much smaller than 32 cm^{-1} , it can affect the field dependence of magnetization at low temperatures. Therefore the aim of the present work is to study the influence of impurities on the energy structure of Tb^{3+} ions by means of magnetic and resonance techniques in a single crystal of $\text{TbFe}_3(\text{BO}_3)_4$.

Experimental procedure

A single crystal of $\text{TbFe}_3(\text{BO}_3)_4$ was grown from a flux based on bismuth trimolibdate $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. The crystal size reached 10–12 mm. A single-crystal plate with the area of $1.5 \times 1.5 \text{ mm}$ and the thickness of 0.11 mm was cut out from the crystal. The trigonal axis c was perpendicular to the plane of the plate. The field dependence of magnetization was measured using a SQUID magnetometer MPMS-XL5. The magnetic field was directed along the trigonal c axis of the crystal.

To perform the resonance studies in the frequency range 18–142 GHz, a spectrometer with direct amplification was used. The polarization of the microwave field was perpendicular to the trigonal axis c of the crystal. The static magnetic field was created by a superconducting solenoid and applied along the trigonal axis c to within 0.5 degrees.

Experimental results

Fig. 1 shows the EPR spectrum of the crystal $\text{TbFe}_3(\text{BO}_3)_4$ in a magnetic field $H \parallel c$ for the frequency $\nu = 72.13 \text{ GHz}$ at the temperature 4.2 K. In the figure it is seen that the spectrum has

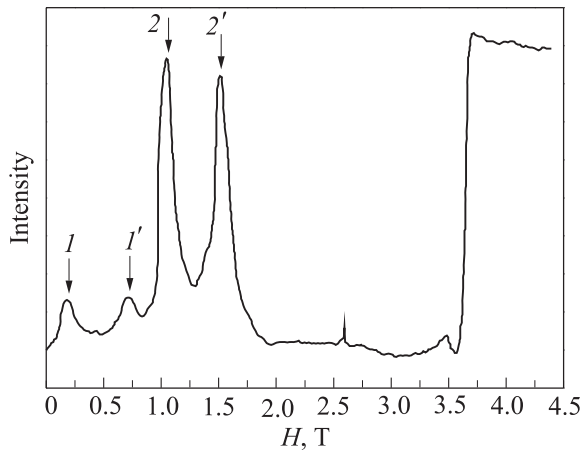


FIG. 1. The EPR spectrum of the crystal $\text{TbFe}_3(\text{BO}_3)_4$ in a magnetic field $H\parallel c$ at the frequency $\nu = 72.13$ GHz at the temperature 4.2 K.

two pairs of absorption lines: low-intensity lines I and I' and high-intensity lines 2 and $2'$. A step-like feature on the spectrum in a magnetic field $H = 3.6$ T corresponds to the spin-flop transition.⁵

Fig. 2 shows the absorption spectra in a magnetic field at different temperatures. It is seen that the change in temperature from 2 to 12.2 K does not shift resonance fields of the absorption lines. However, the change in frequency leads to their shift in the magnetic field, as illustrated in Fig. 3, which shows the absorption at frequencies from 42.36 to 77.94 GHz at the temperature 4.2 K. It is seen that a decrease

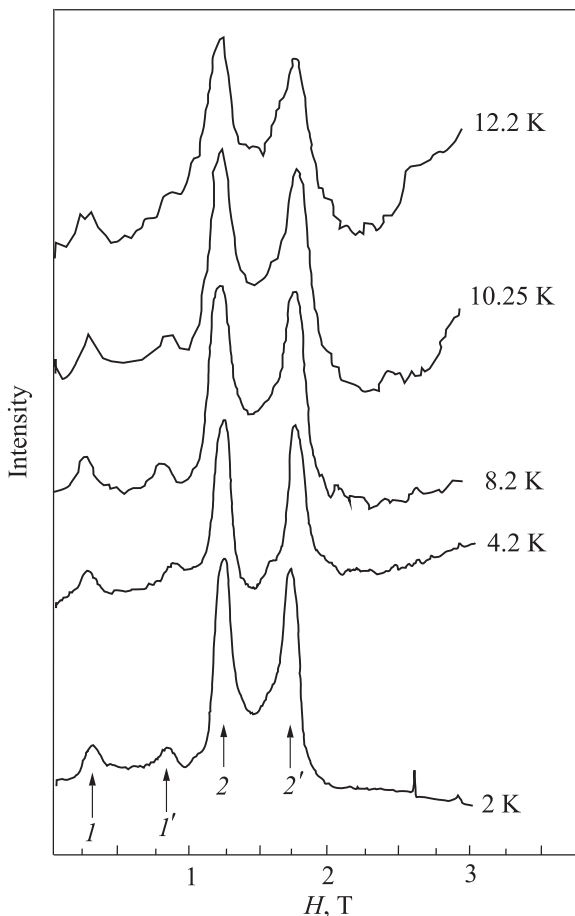


FIG. 2. The EPR spectra of the crystal $\text{TbFe}_3(\text{BO}_3)_4$ in a magnetic field $H\parallel c$ at the frequency $\nu = 72.13$ GHz for the temperatures from 2 to 12.2 K.

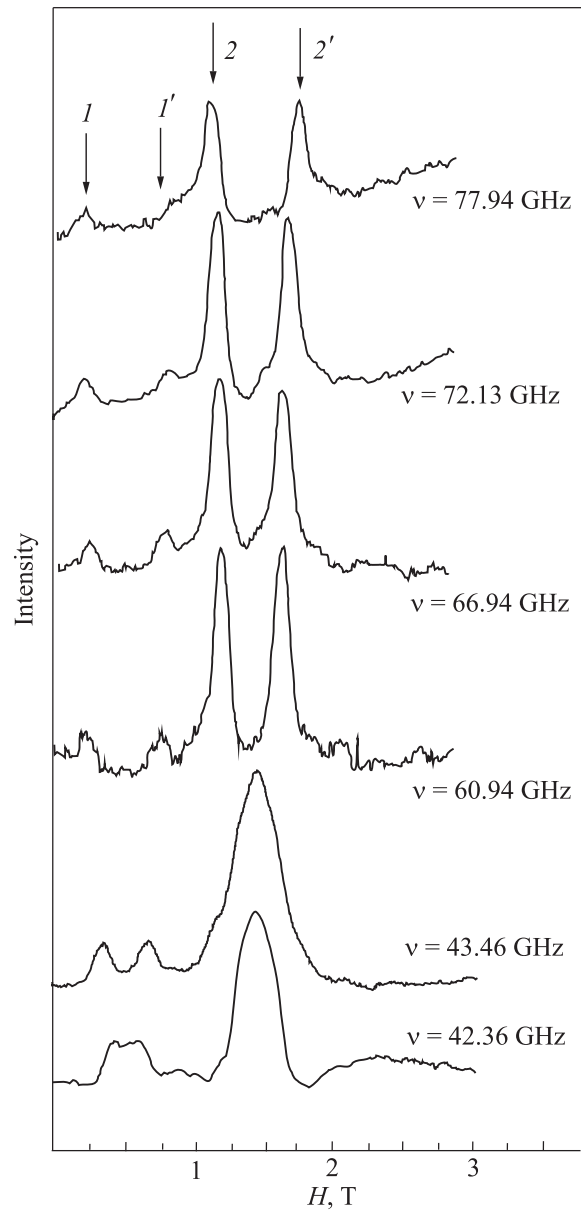


FIG. 3. The EPR spectra of the crystal $\text{TbFe}_3(\text{BO}_3)_4$ in a magnetic field $H\parallel c$ at the temperature 4.2 K for the frequencies from 42 to 78 GHz.

in frequency results in a convergence of the resonance lines. At the frequency $\nu = 42.36$ GHz in the high-intensity pair of absorption lines the 2 and $2'$ lines converge so that they are almost impossible to resolve, and one broad intensive line is observed in the spectrum. And at the frequency $\nu = 41$ GHz instead of the low-intensity lines I and I' in the EPR spectrum there is one broad low-intensity line.

Based on the experimental data, we constructed a frequency-field dependence $\nu(H)$ for the four absorption lines of the EPR spectrum of terbium ferroborate at the temperature $T = 4.2$ K, which is shown in Fig. 4. As seen in Fig. 4, the dependences I and 2 can be described by a linear law:

$$\nu(H) = \Delta_{1,2} - g_{1,2}\mu_B H. \tag{1}$$

Here, Δ_1 and Δ_2 are the initial splittings, $g_{1,2}$ are the effective g -factors, μ_B is the Bohr magneton. From the slope of the dependences $\nu(H)$ the effective g -factors for the lines I and 2 were determined, and appeared to be the same and equal to 16. An extrapolation of the dependences $\nu(H)$ to $H = 0$

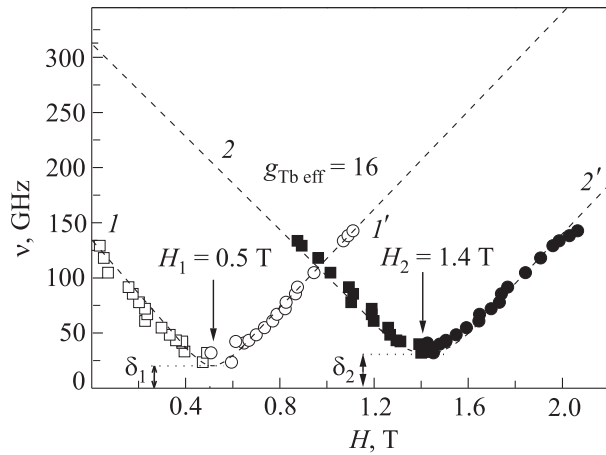


FIG. 4. The frequency-field dependences of the absorption lines of the EPR spectrum in the crystal $\text{TbFe}_3(\text{BO}_3)_4$ in a magnetic field $H\parallel c$ at the temperature 4.2 K.

gives the initial splitting for the first line $\Delta_1 = 134 \text{ GHz}$ (4.5 cm^{-1}) and for the second one $\Delta_2 = 313 \text{ GHz}$ (10.5 cm^{-1}).

From the frequency-field dependence it follows that in a magnetic field $H_1 = 0.5 \text{ T}$ the lines I and I' are merged, and in the higher magnetic field $H_2 = 1.4 \text{ T}$ the confluence of the lines 2 and $2'$ takes place. Moreover, this occurs not at zero frequency. At the frequency $\delta_1 = 19 \text{ GHz}$ ($\approx 0.6 \text{ cm}^{-1}$) the lines I and I' are merged; the lines 2 and $2'$ are merged at the frequency $\delta_2 = 29 \text{ GHz}$ ($\approx 1 \text{ cm}^{-1}$). The values of δ_1 and δ_2 were defined as intervals between zero and a line drawn through the experimental points of the frequency-field dependence by means of the least squares method.

It has been mentioned above that Tb^{3+} ions, which neighbor with growth impurities, can manifest themselves on a field dependence of magnetization of terbium ferroborate. Therefore, in this study the field dependence of magnetization was measured at 2 K in a magnetic field $H\parallel c$, shown in Fig. 5. A behavior of the field dependence of magnetization in fields up to 3 T is clearly nonlinear. Features that appear on the field dependence of magnetization in the form of non-linearity are more clearly visible on the field dependence of differential susceptibility, dM/dH , shown in the inset of Fig. 5. The distinct maxima are observed in fields 0.5 T

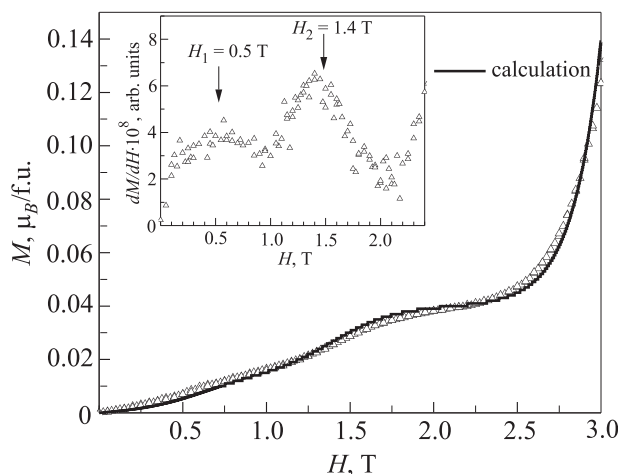


FIG. 5. The field dependence of magnetization $M(H)$ of the crystal $\text{TbFe}_3(\text{BO}_3)_4$ at $H\parallel c$ and $T = 2 \text{ K}$. Inset: the field dependence of differential magnetic susceptibility dM/dH in the crystal $\text{TbFe}_3(\text{BO}_3)_4$.

and 1.4 T in the differential susceptibility dM/dH . Note that the values of these fields identical to the fields H_1 and H_2 , at which the confluence of the lines is observed in the frequency-field dependence of the EPR spectra.

Discussion of the experimental results

The reason for the appearance of the two pairs of absorption lines in the EPR spectrum of a single crystal $\text{TbFe}_3(\text{BO}_3)_4$ may be the same as in the case of appearance of the above-mentioned satellites in the optical spectrum. The belonging of the found EPR lines to transitions in Tb^{3+} ions is evident by the effective g -factor which is close to 18. As already noted, for growing a crystal of terbium ferroborate the bismuth trimolibdate $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ is used. Apparently, the presence of Bi and Mo impurities nearby Tb^{3+} ions changes the crystal field and the effective field of the iron on Tb^{3+} ions. The presence of growth impurities in terbium ferroborate results in the appearance on Tb^{3+} ions of initial splittings of the quasi-doublets in the crystal field and the effective field of iron of the magnitude of 4.5 cm^{-1} and 10.5 cm^{-1} . In this case, the values of splitting of the quasi-doublets in the crystal field of these ions are $\delta_1 = 19 \text{ GHz}$ ($\approx 0.6 \text{ cm}^{-1}$) and $\delta_2 = 29 \text{ GHz}$ ($\approx 1 \text{ cm}^{-1}$). Assuming that the energy spectra of such terbium ions are the same, except for the initial splitting, we denote the terbium ions with the initial splitting of 32 cm^{-1} as Tb_0^{3+} , and with the splitting of 4.5 cm^{-1} and 10.5 cm^{-1} as Tb_1^{3+} and Tb_2^{3+} respectively.

The splitting of the quasi-doublet of Tb_1^{3+} ion in an external magnetic field H changes by the value $\sqrt{\delta_1^2 + g_{\text{eff}}^2 \mu_B^2 (H \pm H_{\text{eff}})^2}$, which takes into account that for oppositely directed magnetic moments of Tb^{3+} ions the fields H_{eff} are opposite. Fig. 6(a) shows schematically a behavior of levels of the quasi-doublet of Tb_1^{3+} ion with the initial splitting Δ_1 in the case when an external magnetic field is opposite to the local effective magnetic field of iron. As the magnetic field increases the levels A and B of the quasi-doublet Tb_1^{3+} are converged to a value δ_1 in the magnetic field H_1 . A further increase in the magnetic field leads to the fact that these levels begin to diverge. In the region of maximum convergence of the levels, a maximum of differential magnetic susceptibility dM/dH is observed in the field H_1 . In Tb_2^{3+} ion with the initial splitting Δ_2 there is a larger than in Tb_1^{3+} minimal energy gap δ_2 between the levels A and B of the quasi-doublet, which is achieved in the higher magnetic field H_2 (Fig. 6(b)). In this magnetic field there is also a maximum on the differential susceptibility dM/dH .

The value of the g -factor of Tb_1^{3+} and Tb_2^{3+} ions is close to 18, and this indicates that the main contribution to wave functions of the levels of their quasi-doublets is made by the states with $M_J^Z = \pm 6$. As mentioned above, the local symmetry of Tb_0^{3+} ion is C_2 . And for Tb_1^{3+} and Tb_2^{3+} ions, due to the presence of impurities in their surroundings, the local symmetry may be even lower. Due to the low local symmetry it can be assumed that in addition to the states with $M_J^Z = \pm 6$, the states with smaller M_J^Z also contribute in wave functions of the ground and excited levels of the quasi-doublets. If there is such a mixture of the states with different M_J^Z , then between these levels there are possible transitions, for which the selection

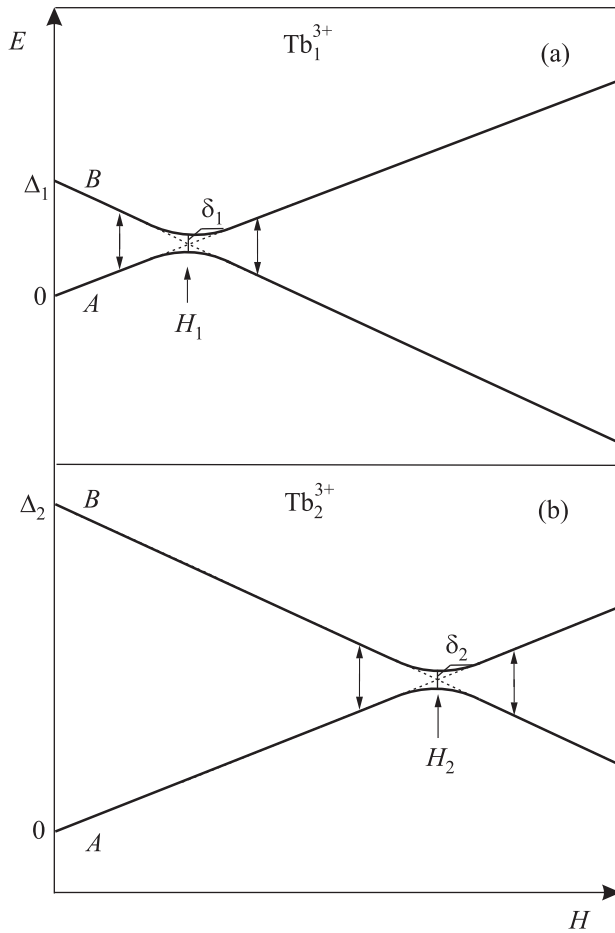


FIG. 6. The energy levels of the lowest quasi-doublet of Tb_1^{3+} ion (a) and Tb_2^{3+} ion (b) in a magnetic field in the crystal $TbFe_3(BO_3)_4$. The arrows indicate the EPR transitions.

rules $\Delta M_J^Z = \pm 1$ is valid. Because of this the EPR is experimentally observed in terbium ferroborate.

As follows from the experimental data, the position of the absorption lines in a magnetic field is almost not changed with increasing temperature from 2 to 12.2 K. The reason for this may be in a weak change in this temperature range of the effective field of iron, acting on Tb^{3+} ion.⁵ The initial splitting Δ_1 and Δ_2 is mainly due to influence of this field, so the position of energy levels vary also slightly. Thanks to that the absorption lines do almost not move in the magnetic field with increasing temperature.

In order to estimate the amount of impurities n_1 and n_2 , we use the field dependence of magnetization. As is known, at low temperatures the contribution to the magnetization of terbium ferroborate is mainly made by the subsystem of terbium ions, compared to which the contribution of the iron subsystem is negligible.⁴ The magnetization of this subsystem, in turn, consists of the magnetization M_{Tb0} created by Tb_0^{3+} ions, as well as the magnetizations M_{Tb1} and M_{Tb2} , created by Tb_1^{3+} and Tb_2^{3+} ions, respectively. Thus, the magnetization of terbium ferroborate $M(H)$ can be expressed by the sum,

$$M(H) = M_{Tb0} + M_{Tb1} + M_{Tb2}. \quad (2)$$

The magnetization of the subsystem of terbium ions with taking into account the magnetic moments of the two

sublattices, one of which is co-directional with the magnetic field, and the other is opposite to it, will be determined by the following equation:^{2,4}

$$M_i(H) = \frac{n_i g_{eff i} \mu_B}{4} \cdot \left[\text{th} \left(\frac{g_{eff i} \mu_B (H + H_{eff i})}{2kT} \right) + \text{th} \left(\frac{g_{eff i} \mu_B (H - H_{eff i})}{2kT} \right) \right], \quad (3)$$

where $i=0,1,2$; $g_{eff i}$ is the effective g -factor of the ground quasi-doublet of terbium ion, μ_B is the Bohr magneton, n_i is the number of terbium ions per one formula unit. As mentioned above, for the Tb_0^{3+} ions $g_{eff 0} = 17.8$, and for the Tb_1^{3+} and Tb_2^{3+} ions the effective g -factors $g_{eff 1}$ and $g_{eff 2}$ are equal to 16. From $g_{eff i}$ and the magnitude of splitting of the quasi-doublet Δ_i , it is easy to calculate $H_{eff i}$ using the formula $H_{eff i} = \Delta_i / g_{eff i} \mu_B$. The result is effective exchange fields acting on the Tb_0^{3+} , Tb_1^{3+} , Tb_2^{3+} ions, which are equal to $H_{eff 0} = 3.7$ T, $H_{eff 1} = 0.6$ T and $H_{eff 2} = 1.4$ T, respectively. Now knowing $H_{eff i}$ and taking into account Eqs. (2) and (3), one can calculate the field dependence of magnetization at 2 K. In the calculations the number of terbium ions, $Tb_0^{3+} - n_0$, $Tb_1^{3+} - n_1$ and $Tb_2^{3+} - n_2$ was varied. As seen in Fig. 5, the calculated dependence (solid line) fits well to the experimental field dependence of the magnetization. It should be noted that in this calculation a splitting of the quasi-doublet for all terbium ions by the crystal field was not taken into account. The values n_0 , n_1 and n_2 were determined from the best agreement between the experimental and the calculated field dependences. This agreement is achieved when $n_0 = 0.9949$, $n_1 = 1.8 \times 10^{-3}$, $n_2 = 3.3 \times 10^{-3}$ per one formula unit.

Conclusions

Two pairs of absorption lines, low-intensity and high-intensity, are observed at the temperatures from 2 K to 12.2 K and the frequency $\nu = 72.13$ GHz in the EPR spectra of the $TbFe_3(BO_3)_4$ crystal, measured in a magnetic field $H \parallel c$. In the investigated temperature range, the resonance fields of the absorption lines do not depend on temperature. A decrease of the frequency leads to a pairwise convergence of the lines, and instead of two low-intensity and two high-intensity lines only one line in each pair is observed in the magnetic fields $H_1 = 0.5$ T and $H_2 = 1.4$ T respectively.

The field dependence of magnetization of the crystal $TbFe_3(BO_3)_4$, measured at the temperature 2 K and $H \parallel c$, is nonlinear, and in the differential magnetic susceptibility dM/dH there are two broad maxima in the fields $H_1 = 0.5$ T and $H_2 = 1.4$ T.

The lines found in the ESR spectrum of terbium ferroborate may be associated with two types of centers: the Tb^{3+} ions, in the surrounding of which there are presumably the bismuth and molybdenum growth impurities. The initial splittings of the lowest quasi-doublets of such Tb^{3+} ions were found to be $\delta_1 = 0.6 \text{ cm}^{-1}$, $\delta_2 = 1 \text{ cm}^{-1}$ in the crystal field, and $\Delta_1 = 4.5 \text{ cm}^{-1}$ and $\Delta_2 = 10.5 \text{ cm}^{-1}$ in the effective field of iron. The amount of both types of centers was estimated to be $n_1 = 1.8 \times 10^{-3}$, $n_2 = 3.3 \times 10^{-3}$ per one formula unit.

The authors thank V. I. Fomin for fruitful discussions and important remarks.

^{a)}Email: bedarev@ilt.kharkov.ua

- ¹A. K. Zvezdin, S. S. Krotov, A. M. Kadomtseva, G. P. Vorob'ev, Yu. F. Popov, A. P. Pyatakov, L. N. Bezmaternykh, and E. N. Popova, *Pis'ma Zh. Eksp. Teor. Fiz.* **81**, 335 (2005).
- ²A. K. Zvezdin, G. P. Vorob'ev, A. M. Kadomtseva, Yu. F. Popov, A. P. Pyatakov, L. N. Bezmaternykh, A. V. Kuvardin, and E. N. Popova, *Pis'ma Zh. Eksp. Teor. Fiz.* **83**, 600 (2006).
- ³A. M. Kadomtseva, Yu. F. Popov, G. P. Vorob'ev, A. P. Pyatakov, S. S. Krotov, K. I. Kamilov, V. Yu. Ivanov, A. A. Mukhin, A. K. Zvezdin, A. M. Kuzmenko, L. N. Bezmaternykh, I. A. Gudim, and V. L. Temerov, *Fiz. Nizk. Temp.* **36**, 640 (2010) [*Low Temp. Phys.* **36**, 511 (2010)].
- ⁴V. A. Bedarev, M. I. Paschenko, A. N. Bludov, S. L. Gnatchenko, L. N. Bezmaternykh, and V. L. Temerov, *Fiz. Nizk. Temp.* **37**, 598 (2011) [*Low Temp. Phys.* **37**, 476 (2011)].

- ⁵C. Ritter, A. Bulaev, A. Vorotynov, G. Petrakovskii, D. Velikanov, V. Temerov, and I. Gudim, *J. Phys.: Condens. Matter* **19**, 196227 (2007).
- ⁶M. N. Popova, E. P. Chukalina, T. N. Stanislavchuk, and L. N. Bezmaternykh, *Izv. RAN Ser. Fiz.* **70**, 1652 (2006).
- ⁷M. N. Popova, T. N. Stanislavchuk, B. Z. Malkin, and L. N. Bezmaternykh, *J. Phys.: Condens. Matter* **24**, 196002 (2012).
- ⁸V. Malakhovskii, S. L. Gnatchenko, I. S. Kachur, V. G. Piryatinskaya, A. L. Sukhachev, and V. L. Temerov, *Eur. Phys. J. B* **80**, 1 (2011).
- ⁹A. V. Malakhovskii, S. L. Gnatchenko, I. S. Kachur, V. G. Piryatinskaya, A. L. Sukhachev, and V. L. Temerov, *Bull. Russ. Acad. Sci.: Phys.* **74**, 721 (2010).
- ¹⁰M. N. Popova, K. N. Boldyrev, P. O. Petit, B. Viana, and L. N. Bezmaternykh, *J. Phys.: Condens. Matter* **20**, 455210 (2008).
- ¹¹K. Boldyrev, M. Popova, L. Bezmaternykh, and M. Bettinelli, *Quantum Electron.* **41**, 120 (2011).

Translated by A. Sidorenko