

# IR active vibrations of a $\text{TbFe}_3(\text{BO}_3)_4$ crystal

Cite as: *Low Temp. Phys.* **36**, 638 (2010); <https://doi.org/10.1063/1.3479413>

Published Online: 15 September 2010

M. I. Pashchenko, V. A. Bedarev, V. I. Kut'ko, L. N. Besmaternykh, and V. L. Temerov



View Online



Export Citation

## ARTICLES YOU MAY BE INTERESTED IN

[IR spectroscopy of the low-frequency phonon spectrum of the  \$\text{TbFe}\_3\(\text{BO}\_3\)\_4\$  single-crystal](#)

*Low Temperature Physics* **40**, 1087 (2014); <https://doi.org/10.1063/1.4904002>

[Rotational magnetocaloric effect in  \$\text{TbAl}\_3\(\text{BO}\_3\)\_4\$](#)

*Low Temperature Physics* **43**, 631 (2017); <https://doi.org/10.1063/1.4985220>

[Rare-earth ferrobates  \$R\text{Fe}\_3\(\text{BO}\_3\)\_4\$](#)

*Low Temperature Physics* **32**, 735 (2006); <https://doi.org/10.1063/1.2219496>



MONTANA INSTRUMENTS

QUANTUM COMPUTING    SPINTRONICS : MOKE    DIAMOND NV CENTERS

CLICK HERE  
CRYOGENIC  
APPLICATION  
NOTES

[montanainstruments.com/Applications/Application-Notes/](http://montanainstruments.com/Applications/Application-Notes/)

COLD SCIENCE MADE SIMPLE

## QUANTUM EFFECTS IN SEMICONDUCTORS AND DIELECTRICS

### IR active vibrations of a $\text{TbFe}_3(\text{BO}_3)_4$ crystal

M. I. Pashchenko,<sup>a)</sup> V. A. Bedarev, and V. I. Kut'ko

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

L. N. Besmaternykh and V. L. Temerov

*L. V. Kirenskii Institute of Physics of the Siberian Branch of the Russian Academy of Sciences, Krasnoyarsk 660036, Russia*

(Submitted December 18, 2009)

Fiz. Nizk. Temp. **36**, 800–804 (July 2010)

The IR reflection spectra of a  $\text{TbFe}_3(\text{BO}_3)_4$  crystal are measured in the spectral range 200–2000  $\text{cm}^{-1}$  in  $E \perp c$  polarization at temperatures 10 and 300 K. The reflection spectrum so obtained is analyzed and its interpretation is given on the basis of the internal vibrations of the ionic complexes  $\text{BO}_3^{3-}$ ,  $\text{FeO}_6^{9-}$ , and  $\text{TbO}_6^{9-}$  of the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal. Davydov splitting on the internal vibrational modes at a structural phase transition, which is accompanied by multiplication of the unit cell, was not observed in the experimental spectral range. This is due to the localization of the vibrations of the ionic complexes  $\text{BO}_3^{3-}$ ,  $\text{FeO}_6^{9-}$ , and  $\text{TbO}_6^{9-}$  of the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal. © 2010 American Institute of Physics. [doi:10.1063/1.3479413]

### INTRODUCTION

Trigonal rare-earth borates with the general formula  $\text{RM}_3(\text{BO}_3)_4$ , where R is a rare-earth ion and  $M = \text{Al, Ga, Sc, Cr, and Fe}$ , are of interest as laser materials and materials which can be used in magneto-optical devices. The ferroborate family  $\text{RFe}_3(\text{BO}_3)_4$  is of interest due to the particulars of the formation of their magnetic structure, which is determined by the interaction of rare-earth ions with iron ions. The magnetic properties of ferrobates depend on the magnetic ion. The strong spin-orbit coupling in rare-earth ions should lead to an interaction of magnetic excitations and vibrations of the crystal lattice. The coupling of the magnetic excitations and IR active vibrational modes determines the magneto-electric properties of these materials. Ferrobates, where this coupling is quite strong, are multiferroics.<sup>1,2</sup> To determine the magnitudes and mechanisms of the magneto-electric coupling it is necessary to know the structure of the IR active vibrational spectrum of crystals and the mechanism by which it forms. In the present work the IR active vibrational spectra of one of the members of the series of rare-earth ferrobates—the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal—are investigated.

### EXPERIMENTAL RESULTS

A  $\text{TbFe}_3(\text{BO}_3)_4$  single crystal was grown from a seeded melt in platinum crucibles.<sup>3</sup> The single crystal obtained was cut in the form of a  $1 \times 4 \times 5$  mm plate whose surface was perpendicular to the trigonal axis  $c$ . The reflection spectra were measured in a diffraction IR spectrometer in the energy range 200–2000  $\text{cm}^{-1}$ . A sample was placed in the vacuum part of a cryostat. Infrared radiation entered the cryostat through a CsI crystal window. The values obtained for the reflection from the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal were normalized to the reflection from an aluminum window. Figure 1 displays

the reflection spectra measured at room temperature in  $E \perp c$  polarization. As Fig. 1b shows, two wide bands peaking at 1250 and 1450  $\text{cm}^{-1}$  and a weak band peaking at 1700  $\text{cm}^{-1}$  are seen in the reflection spectrum in the range 1200–1800  $\text{cm}^{-1}$ . There are four weak reflection bands peaking at 670, 720, 733, and 750  $\text{cm}^{-1}$  in the region 600–800  $\text{cm}^{-1}$ . In addition, a wide band peaking at 430  $\text{cm}^{-1}$  and two quite narrow bands peaking at 280 and 225  $\text{cm}^{-1}$  are observed in the region 200–500  $\text{cm}^{-1}$ .

The reflection bands in the spectrum do not show any substantial changes as temperature decreases to 10 K (Fig. 2).

### DISCUSSION

At high temperatures rare-earth ferrobates possess the trigonal symmetry of the mineral hantite  $\text{CaMg}_3(\text{CO}_3)_4$ , whose space group is  $D_3^7(R32)$  with three molecules per unit cell.<sup>4</sup> The crystal lattice parameters of  $\text{TbFe}_3(\text{BO}_3)_4$  are  $a = 9.552 \text{ \AA}$  and  $c = 7.573 \text{ \AA}$ . It should be underscored that the primitive cell contains one molecule of the material, and it is the volume of the primitive cell that must be used in order to calculate the vibrational spectrum.

At low temperatures a first-order structural phase transition occurs in ferrobates with rare-earth ions from Eu to Yb.<sup>5,6</sup> The phase transition is accompanied by a lowering of the symmetry  $R32 \rightarrow P3_12_1$ . A similar phase transition occurs in a  $\text{TbFe}_3(\text{BO}_3)_4$  crystal at temperature 196 K.<sup>5</sup> If it is assumed that the lowering of symmetry in terbium ferrobate at a structural phase transition is identical in other ferrobates, then the symmetry of the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal in the low-temperature phase will be  $P3_12_1$  while the unit cell contains three formula units and is identical to the primitive cell. The volume of the primitive cell increases as a result of the phase transition.

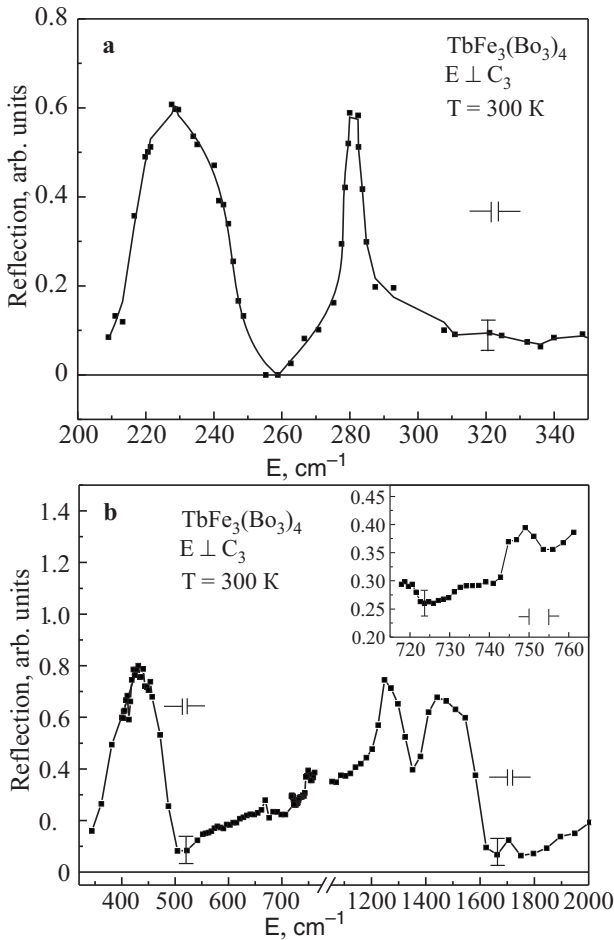


FIG. 1. Reflection spectrum at  $T=300$  K in  $E \perp c$  polarization, section of the spectrum from 200 to 350  $\text{cm}^{-1}$  (a) and section of the spectrum from 350 to 2000  $\text{cm}^{-1}$  (b).

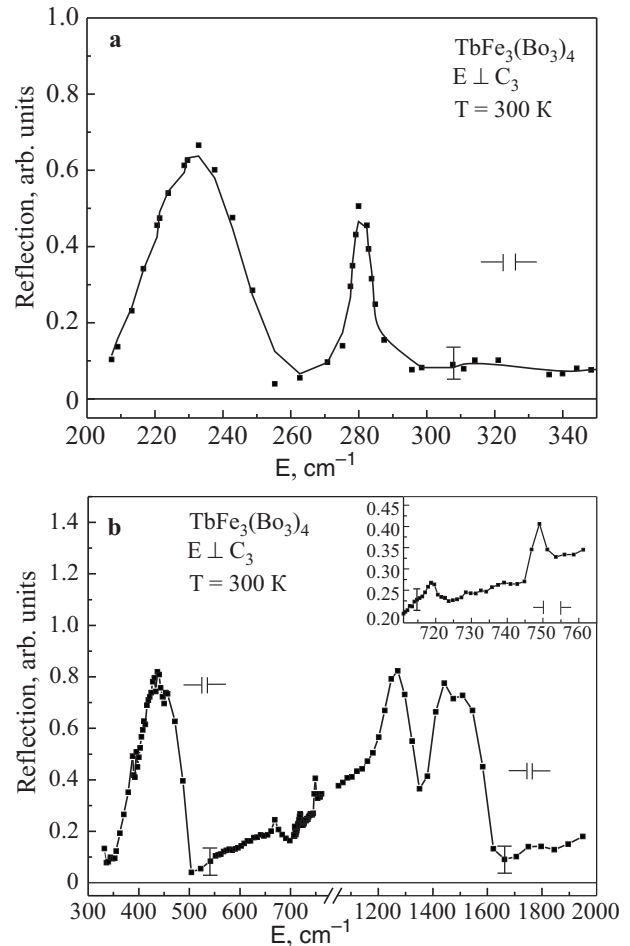


FIG. 2. Reflection spectrum at 10 K in  $E \perp C$  polarization, section of the spectrum from 200 to 350  $\text{cm}^{-1}$  (a) and section of the spectrum from 350 to 2000  $\text{cm}^{-1}$  (b).

The main structural element in the rare-earth ferrobates are spiral chains, consisting of  $\text{FeO}_6$  octahedra (Fig. 3), directed along the  $c$  axis. Three such chains are coupled with one another by  $\text{RO}_6$  triangular prisms, and the  $\text{BO}_3$  equilateral triangles supplement this coupling. After a structural phase transition one of the iron chains shifts along the  $c$  axis relative to the other chains.<sup>7</sup> The changes in the relative arrangement of the chains of iron ions destroy the equivalence of the neighboring iron chains and lower the symmetry of the crystal. In the low-temperature phase two crystallographically non-equivalent iron ions appear in the unit cell. In addition, the local symmetry of the rare-earth ion is lowered from  $D_3$  in the high-temperature phase to  $C_2$  in the low-temperature phase. As indicated above, a structural phase transition occurs with multiplication of the primitive cell of the crystal. The volume increase is accompanied by doubling of the cell parameter in a direction perpendicular to the trigonal axis  $c$ .

Previous investigations and analysis of the Raman scattering spectra of single crystals of ferrobates<sup>7,8</sup> have shown that the modes observed at room temperature correspond to trigonal structure belonging to the space group  $D_3^7$  with one molecule in a primitive cell. A primitive cell contains 20 ions, and 60 normal vibrational modes should be observed. The vector of mechanical displacements can be decomposed

with respect to irreducible representations of the factor group of the crystal as follows:

$$\Gamma = 7A_1 + 13A_2 + 20E.$$

Here the non-degenerate  $A_2$  and doubly degenerate  $E$  modes are acoustic; all other modes are optical. Seven of these non-degenerate modes with symmetry  $A_1$  are Raman active, while 12 modes with symmetry  $A_2$  and 19 doubly degenerate modes with symmetry  $E$  should be observed in the Raman and IR spectra.

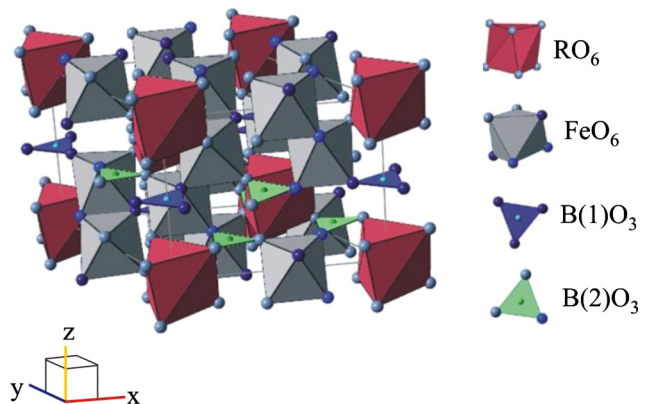


FIG. 3. Crystal structure of  $R\text{Fe}_3(\text{BO}_3)_4$ .

As indicated above, the IR spectrum of a  $\text{TbFe}_3(\text{BO}_3)_4$  crystal remains practically unchanged as temperature decreases from 300 to 10 K. For this reason it can be conjectured that this spectrum is determined mainly by internal vibrations of the complexes  $\text{BO}_3^{3-}$ ,  $\text{FeO}_6^{9-}$ , and  $\text{TbO}_6^{9-}$ . The localization of the vibrational modes could be due to the large distance separating the centers of these complexes from one another in the crystal structure of ferrobortate (Fig. 3). On this basis we shall attempt to analyze the experimental data under the assumption that the high-frequency vibrational spectrum of the crystal  $\text{TbFe}_3(\text{BO}_3)_4$  is formed by the internal vibrations of the oxide complexes  $\text{BO}_3^{3-}$ ,  $\text{FeO}_6^{9-}$ , and  $\text{TbO}_6^{9-}$  while the low-frequency spectrum is formed by the external lattice vibrations. The reduced masses of the complexes  $\text{BO}_3^{3-}$ ,  $\text{FeO}_6^{9-}$ , and  $\text{TbO}_6^{9-}$  form the ratios 1:4:6, respectively. For this reason the internal vibrations of  $\text{BO}_3^{3-}$  have the highest frequencies, since the reduced mass of the complex  $\text{BO}_3^{3-}$  is much lower than that  $\text{TbO}_6^{9-}$  while the force constants are approximately equal, since the degree of oxidation of all complexes is the same. Evidently, the heaviest molecule  $\text{TbO}_6^{9-}$  will also have the lowest frequency among these complexes.

In the high-temperature range  $\text{TbFe}_3(\text{BO}_3)_4$  possesses two crystallographic nonequivalent  $\text{BO}_3^{3-}$  complexes with different local symmetry. The unit cell contains one such complex in the form of an equilateral triangle with  $D_3$  local symmetry and three equivalent complexes in the form of isosceles triangles with  $C_2$  local symmetry. Thus according to the analysis presented in Ref. 7 four internal vibrational modes with  $E$  symmetry of the trigonal complexes  $\text{BO}_3^{3-}$  with local symmetry  $D_3$  as well as 12 vibrational modes of three equivalent trigonal complexes  $\text{BO}_3^{3-}$  with  $C_2$  local symmetry neglecting Davydov splitting should be observed in the spectra of these compounds in the high-temperature phase. In the IR spectra for the trigonal complexes  $\text{BO}_3^{3-}$  with  $D_3$  local symmetry only three internal vibrational modes with  $E$  symmetry are allowed. Among them the rotational mode will lie in the low-frequency range, falling outside the frequency range investigated in present work. For the complexes  $\text{BO}_3^{3-}$  with  $C_2$  local symmetry three internal vibrational modes with  $E$  symmetry can also be observed. Two of these modes are split into doublets as a result of the low local symmetry. In addition, as in the preceding case, a rotational low-frequency mode cannot be observed in the experimental frequency range.

Thus two internal vibrational modes, having  $E$  symmetry, of the trigonal complexes  $\text{BO}_3^{3-}$  with  $D_3$  local symmetry and four internal vibrational modes of three equivalent complexes  $\text{BO}_3^{3-}$  with  $C_2$  local symmetry can be observed in the present experiment.

The  $\text{FeO}_6^{9-}$  molecules also possess  $C_2$  local symmetry. In a free state they have two modes which are active in the IR region of the spectrum. In a crystal these modes must be split into doublets. The complexes  $\text{TbO}_6^{9-}$  have  $D_3$  local symmetry, and two vibrational modes can be observed in their IR spectrum. Thus, neglecting Davydov splitting, 12 internal vibrational modes of the complexes  $\text{BO}_3^{3-}$ ,  $\text{FeO}_6^{9-}$ , and  $\text{TbO}_6^{9-}$  should be observed in the vibrational spectrum of the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal.

On this basis we shall give an interpretation of the vibrational spectrum of the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal in the high-temperature phase. The planar molecule  $\text{BO}_3^{3-}$  in a free state possesses the following frequency:  $\nu_1(A_1)=1060\text{ cm}^{-1}$ ,  $\nu_2(A_2)=648-668\text{ cm}^{-1}$ ,  $\nu_3(E)=1428-1490\text{ cm}^{-1}$ , and  $\nu_4(E)=545-606\text{ cm}^{-1}$ .<sup>9</sup> The  $\nu_3$  and  $\nu_4$  vibrations are IR active. The  $\nu_3$  vibration is a stretching vibration, while  $\nu_4$  is a deformation vibration. The following general behavior is observed for these vibrations. Since the oscillator strengths of the stretching vibrations are much greater than the oscillation strengths of the deformation vibrations of the molecules, in the reflection spectrum the stretching vibrations have a high intensity. Therefore the two intense reflection bands which we observed with peak energies 1250 and 1450  $\text{cm}^{-1}$  are due to the stretching vibrations  $\nu_3$  of the  $\text{BO}_3^{3-}$  molecules with  $D_3$  and  $C_2$  local symmetry, respectively. The 1450  $\text{cm}^{-1}$  band has a doublet structure (Fig. 1b), which, apparently, is a consequence of its splitting because of the low local symmetry of  $\text{BO}_3^{3-}$  ( $C_2$ ). The weak reflection bands in the energy range 650–750  $\text{cm}^{-1}$  are associated with deformation vibrations  $\nu_4$  of the  $\text{BO}_3^{3-}$  molecules (Fig. 1b). The reflection band with a maximum at 750  $\text{cm}^{-1}$  can be associated to the vibrations of  $\text{BO}_3^{3-}$  with  $C_2$  local symmetry, while the band with a reflection maximum at 720  $\text{cm}^{-1}$  can be associated to the vibration of the complex with  $D_3$  local symmetry.

Since the reflection bands with maxima at frequencies 440 and 280  $\text{cm}^{-1}$  fall into the spectral range 200–600  $\text{cm}^{-1}$ , it can be conjectured that they are due to the internal vibrations of octahedral complexes  $\text{FeO}_6^{9-}$ .<sup>10</sup> These octahedral complexes possess six additional modes, two of which are IR active. The mode with the frequency 440  $\text{cm}^{-1}$  is the  $\nu_3$  stretching vibration while the 290  $\text{cm}^{-1}$  mode is the  $\nu_4$  deformation vibration of the octahedron  $\text{FeO}_6^{9-}$ . Even though the  $\text{FeO}_6^{9-}$  complex possesses the low  $C_2$  local symmetry, splitting of these modes is not observed in the reflection spectrum.

As mentioned above, the  $\text{FeO}_6^{9-}$  octahedra in the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal form a chain structure along the trigonal  $c$  axis of the crystal. Since the distance between the octahedra in the chains (3.18 Å) is much shorter than the distance between the chains (4.83 Å), the vibrational branches are quasi-one-dimensional. This can be seen by evaluating the dynamic coupling of the vibrations of the  $\text{FeO}_6^{9-}$  octahedra, which is proportional to  $R^{-6}$ , where  $R$  is the distance between the octahedra. It is easy to see that the dynamic coupling in a chain is an order of magnitude greater than between chains.

It is supposed that the intense reflection band peaking at 225  $\text{cm}^{-1}$  is due to stretching vibrations of distorted octahedral complexes  $\text{TbO}_6^{9-}$ . This supposition is based on the fact that masses of the  $\text{Tb}^{3+}$  ions are much larger than the masses of the  $\text{Fe}^{3+}$  ions, and for this reason the vibrational frequencies of the  $\text{TbO}_6^{9-}$  complexes are lower than those of the  $\text{FeO}_6^{9-}$  complexes. The validity of the interpretation presented in this work for the high-frequency vibrational modes of the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal is confirmed by the Raman studies of this compound.<sup>7</sup> In the Raman spectrum of the crystal the IR active vibrational modes corresponding to the internal vibrations of  $\text{BO}_3^{3-}$  molecules manifest as quite strong scattering bands. This is because there is no inversion operation

among the local symmetry elements of the complex  $\text{BO}_3^{3-}$ . For this reason, in a free state of the molecules  $\text{BO}_3^{3-}$ , there is no alternative prohibition, and the vibrational modes are active in the IR and Raman scattering. The IR active vibrational modes, corresponding to the vibrations of the octahedral complexes  $\text{FeO}_6^{9-}$  with energies 440 and  $280\text{ cm}^{-1}$ , manifest in the Raman spectrum as quite weak scattering bands. This is because the inversion operation is present in the local symmetry of the complex  $\text{FeO}_6^{9-}$ , and for this reason alternative prohibition should be observed in it. In the crystal the local symmetry of the complex  $\text{FeO}_6^{9-}$  is  $C_2$ , but its distortions are negligible and the removal of the alternative prohibition manifests weakly. The IR active vibrational mode of the  $\text{TbO}_6^{9-}$  molecule with frequency  $225\text{ cm}^{-1}$  is not observed in the Raman spectrum. It is believed that the local symmetry of  $\text{TbO}_6^{9-}$  ( $D_3$ ) promotes weak distortion of this molecule and preservation of the alternative prohibition. This Raman studies likewise support the fact that the IR spectrum in ferroborate  $\text{TbFe}_3(\text{BO}_3)_4$  is formed by the internal vibrations of the complexes  $\text{BO}_3^{3-}$ ,  $\text{FeO}_6^{9-}$ , and  $\text{TbO}_6^{9-}$ .

Since the structural phase transition in ferroborates occurs with multiplication of the primitive cell of the crystal, modes due to the folding of the Brillouin zone, so-called Davydov splitting, should arise in the vibrational spectrum of the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal. However, Davydov splitting is not observed in the internal vibrational modes of the complexes  $\text{BO}_3^{3-}$ ,  $\text{FeO}_6^{9-}$ , and  $\text{TbO}_6^{9-}$ . This is due to the localization of the internal vibrational modes of these complexes. For this reason the splittings are negligible and are observed in the region of the internal vibrational modes only in the Raman scattering spectra on account of the quite narrow light-scattering bands.<sup>7</sup> The appearance of new bands in the IR spectra, due to the folding of the Brillouin zone, below the structural phase transition at low temperatures can be expected in the region of external vibrational branches at frequencies less than  $200\text{ cm}^{-1}$ . No effect of magnetic ordering, which in the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal appears below 40 K,<sup>12</sup> on the vibrational spectrum was observed in the experimental spectral range. On modes corresponding to the vibrations of the iron lattice the effect of magnetic ordering is weak be-

cause of the zero orbital moment of the iron ions in the ground state. The greatest effect of magnetic ordering can be expected on the internal modes, corresponding to the vibrations of the sublattice of rare-earth ions, in the spectral region below  $200\text{ cm}^{-1}$ .

In summary, it has been shown in this work that the observed vibrational modes in the IR spectrum of the crystal  $\text{TbFe}_3(\text{BO}_3)_4$  are internal vibrations of the complexes  $\text{BO}_3^{3-}$ ,  $\text{FeO}_6^{9-}$ , and  $\text{TbO}_6^{9-}$ . For this reason local static crystal fields of ionic complexes play the decisive role in the formation of the high-frequency IR-active vibrational spectrum of the  $\text{TbFe}_3(\text{BO}_3)_4$  crystal, while dynamical interactions between them are very weak.

<sup>a</sup>Email: pashchenko@ilt.kharkov.ua

<sup>1</sup>A. K. Zvezdin, S. S. Krotov, A. M. Kadomtseva, G. P. Vorob'ev, Yu. F. Popov, A. P. Pyatakov, L. N. Bezmaternykh, and E. A. Popova, *JETP Lett.* **81**, 272 (2005).

<sup>2</sup>F. Yen, B. Lorenz, Y. Y. Sun, C. W. Chu, L. N. Bezmaternykh, and A. N. Vasiliev, *Phys. Rev. B* **73**, 054435 (2006).

<sup>3</sup>D. Balaev, L. N. Bezmaternykh, I. A. Gudim, V. L. Temerov, S. G. Ovchinnikov, and S. A. Kharlamova, *J. Magn. Magn. Mater.* **258–259**, 532 (2003).

<sup>4</sup>W. A. Dollas and R. J. Reeder, *Am. Mineral.* **71**, 163 (1986).

<sup>5</sup>Y. Hinatsu, Y. Doi, K. Ito, M. Wakeshima, and A. Alemi, *J. Solid State Chem.* **172**, 438 (2003).

<sup>6</sup>A. N. Vasiliev, E. A. Popova, I. A. Gudim, L. N. Bezmaternykh, and Z. Hiroi, *J. Magn. Magn. Mater.* **300**, e382 (2006).

<sup>7</sup>Daniele Fausti, Agung A. Nugroho, Paul H. M. van Loosdrecht, Sergei A. Klimin, Marina N. Popova, and Leonard N. Bezmaternykh, *Phys. Rev. B* **74**, 024403 (2006).

<sup>8</sup>S. A. Klimin, D. Fausti, A. Meetsma, L. N. Bezmaternykh, and P. H. M. Palstra, *Acta Crystallogr. B* **61**, 481 (2005).

<sup>9</sup>K. Nakamoto, *IR Spectra and RS Spectra of Inorganic and Coordination Compounds* [Russian translation], Mir, Moscow (1991).

<sup>10</sup>V. Barron, J. L. Rendon, J. Torrent, and C. J. Serna, *Clays Clay Miner.* **32**, 475 (1984).

<sup>11</sup>A. N. Vasil'ev and E. A. Popov, *Fiz. Nizk. Temp.* **32**, 968 (2006) [*Low Temp. Phys.* **32**, 715 (2006)].

<sup>12</sup>C. Ritter, A. Balaev, A. Vorotynov, G. Petrakovskii, D. Velikanov, V. Temerov and I. Gudim, *J. Phys.: Condens. Matter* **19**, 196227 (2007).

Translated by M. E. Alferieff