



## Terahertz spectroscopy of multiferroic $\text{EuFe}_3(\text{BO}_3)_4$

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### ABSTRACT

The terahertz spectra of a rare-earth iron borate with the huntite structure are obtained for the first time. We study the low-temperature (4.0–90 K)  $\alpha$ -polarized transmittance spectra of the  $\text{EuFe}_3(\text{BO}_3)_4$  single crystal in the region 0.9–6.0 THz. Pronounced shifts of phonon frequencies and appearance of new phonon modes at the temperature  $T_S = 58$  K of the  $R32 \rightarrow P3_121$  structural phase transition are observed. Additional shifts of phonon frequencies occur at the temperature  $T_N = 34$  K of the magnetic ordering of the Fe subsystem, thus evidencing the spin–phonon coupling in this multiferroic material.

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## 1. Introduction

Rare-earth (RE) iron borates with noncentrosymmetric trigonal structure of the natural mineral huntite constitute an interesting family of new multiferroics. The structure of these  $R\text{Fe}_3(\text{BO}_3)_4$  compounds incorporates the chains of edge-sharing  $\text{FeO}_6$  octahedra running along the  $c$ -axis of the crystal. The chains are interconnected via  $\text{BO}_3$  triangles and  $\text{RO}_6$  distorted prisms. At high temperatures, the structure of all the iron borates is described by the  $R32$  space group with a single  $D_3$  symmetry position for the RE ion. For the rare earths with the ionic radius greater than that of Eu, the  $R32$  structure of  $R\text{Fe}_3(\text{BO}_3)_4$  is preserved down to the lowest measured temperatures. For the “small” rare-earth ions, RE iron borates undergo a structural phase transition into the  $P3_121$  phase [1–3] at the temperature  $T_S$  depending on the ionic radius of  $R^{3+}$  and varying from 445 K for  $R = \text{Y}$  to 88 K for  $R = \text{Eu}$ , according to DTA and specific heat measurements on powder samples [1]. In the  $P3_121$  structure, there are two types of nonequivalent iron chains and though a single structural position for the RE ion survives, its symmetry lowers from  $D_3$  to  $C_2$  [2]. The RE iron borates order antiferromagnetically at  $T_N \sim 30$ –40 K [1].

The presence of two interacting magnetic subsystems (RE and Fe ones) results in a great variety of magnetic and magnetoelectric properties of  $R\text{Fe}_3(\text{BO}_3)_4$ , depending on a particular RE ion. This stimulates an intensive study of the RE iron borates by different methods. Magnetic, magnetoelectric and magnetoelectric, dielectric, specific heat, neutron, hard x-ray, and Raman scattering, electron paramagnetic and antiferromagnetic resonance

measurements, optical spectroscopy of the  $f$ – $f$  transitions were successfully used (see, e.g., [3–11] and references therein).

In this Letter, on the example of  $\text{EuFe}_3(\text{BO}_3)_4$ , we show that far infrared (FIR) spectra deliver a rich information on the phase transitions and spin–lattice coupling in RE iron borates.

Our previous study of the optical spectra in the mid-infrared region of the  $\text{Eu}^{3+}$  ion in the  $\text{EuFe}_3(\text{BO}_3)_4$  single crystal has revealed a first-order structural phase transition at  $T_S = 58$  K with a pronounced hysteresis loop [12]. The spectra of the probe Kramers ion  $\text{Er}^{3+}$  in  $\text{EuFe}_3(\text{BO}_3)_4$  [13] and, then, recent magnetic and EPR measurements of pure  $\text{EuFe}_3(\text{BO}_3)_4$  [14] have shown that the iron magnetic subsystem orders antiferromagnetically into the easy-plane magnetic structure at  $T_N = 34$  K [13] (37 K [14]).

## 2. Experiment

The  $\text{EuFe}_3(\text{BO}_3)_4$  single crystal of good optical quality was grown in the Kirensky Institute of Physics in Krasnoyarsk from solution-melts on the basis of the  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ – $\text{Li}_2\text{MoO}_4$ – $\text{B}_2\text{O}_3$  flux, as described in Ref. [15]. From an optically oriented crystal, a 72  $\mu\text{m}$  thick platelet was cut perpendicular to the  $c$ -axis.

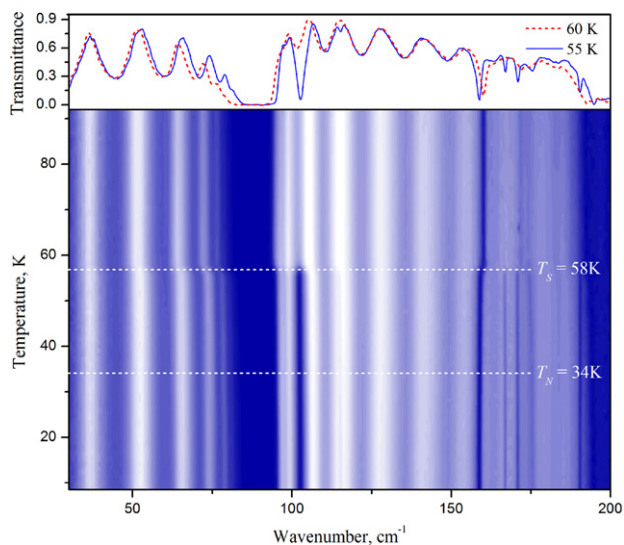
A Fourier spectrometer Bruker IFS 125 HR with a liquid helium cooled bolometer (4.2 K) as a detector and a closed helium cycle cryostat Cryomech ST403 were used to register optical transmittance spectra in the region 30–200  $\text{cm}^{-1}$  (0.9–6 THz) at the temperatures 4–90 K. Spectra were studied in the  $\alpha$  ( $\mathbf{k} \parallel c$ ,  $\mathbf{E}, \mathbf{H} \perp c$ ) polarization.

## 3. Results and discussion

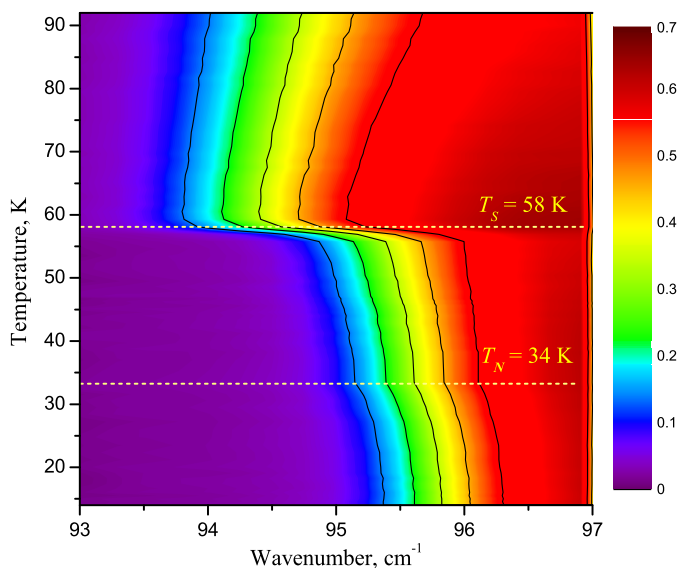
Fig. 1 displays the  $\alpha$ -polarized transmittance spectra of  $\text{EuFe}_3(\text{BO}_3)_4$  at two temperatures,  $60 \text{ K} > T_S$  and  $T_N < 55 \text{ K} < T_S$ ,

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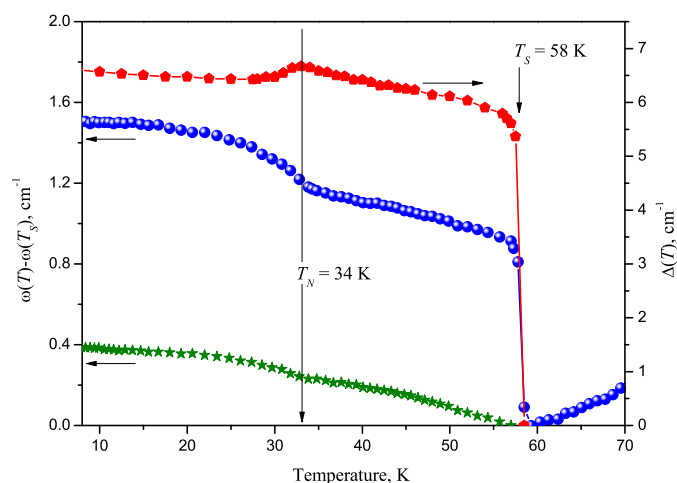
**Fig. 1.** Transmission spectra of  $\text{EuFe}_3(\text{BO}_3)_4$  in the terahertz range at the temperatures  $60 \text{ K} > T_S$  and  $T_N < 55 \text{ K} < T_S$  (upper part) and the intensity map (lower part). Shifts of phonon frequencies and emergence of new phonon modes are seen.



**Fig. 2.** Transmission spectra of  $\text{EuFe}_3(\text{BO}_3)_4$  as intensity map in the spectral region of the high-frequency boundary of the  $90 \text{ cm}^{-1}$  phonon. Solid curves are lines of equal transmittance at different temperatures.

together with the intensity map smoothly scanned vs. temperature. First-order structural phase transition  $R32 \rightarrow P3_121$  at  $T_S = 58 \text{ K}$  manifests itself by sharp shifts of phonon frequencies and by a sudden appearance of new vibrational modes (at  $102.7, 115.2, 167, 171, 175,$  and  $190 \text{ cm}^{-1}$ ) of the lower symmetry  $P3_121$  structure. Similar modes were observed in the Raman spectra of  $\text{RFe}_3(\text{BO}_3)_4$  ( $R = \text{Nd, Gd, Tb, Er, Y}$ ) [3]. Some more details of the frequency shift of the  $90 \text{ cm}^{-1}$  phonon are visible in Fig. 2. With lowering the temperature, this phonon mode softens at approaching  $T_S$  and, then, after a “jump” at  $T_S$  hardens below  $T_S$  (see also Fig. 3, balls). Such quasi-soft mode behavior, possibly, points to a relation of this particular mode connected with vibrations of the RE ion [3] to ionic displacements responsible for the antiferroelectric phase below  $T_S$  [2].

A significant difference between  $T_S = 58 \text{ K}$  ([12,13] and this study) observed for our single crystalline samples and  $T_S = 88 \text{ K}$  [1] reported for powder samples of  $\text{EuFe}_3(\text{BO}_3)_4$  is, probably, due to the presence of bismuth impurity in our samples grown from



**Fig. 3.** Shifts of the high-frequency boundary of the  $90 \text{ cm}^{-1}$  phonon in  $\text{EuFe}_3(\text{BO}_3)_4$  (balls) and of the  $102 \text{ cm}^{-1}$  “new” phonon mode appearing below the temperature  $T_S$  of the structural phase transition (stars), and the splitting  $\Delta(T)$  of the  $\Gamma_3(^5D_1)$  crystal-field doublet of  $\text{Eu}^{3+}$  near  $18986 \text{ cm}^{-1}$  (pentagons) as functions of temperature.

the  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$  containing flux [15] contrary to the samples of Ref. [1] where the  $\text{K}_2\text{Mo}_3\text{O}_{10}$  flux was used. The presence of “big”  $\text{Bi}^{3+}$  ions ( $r = 1.03 \text{ \AA}$ ) enhances the effective ionic radius of the RE ion, which leads to the lowering of the structural transition’s temperature [1]. The estimate using the  $T_S$  ( $r$ ) dependence from Ref. [1] and the measured  $T_S = 58 \text{ K}$  for our  $\text{EuFe}_3(\text{BO}_3)_4$  samples yields  $\sim 5\%$  for the concentration of bismuth impurity in the samples. The latest studies have shown that this amount can be considerably lowered by improving the growth technology [16].

Figs. 2 and 3 clearly demonstrate also another peculiarity in the temperature dependence of the  $90 \text{ cm}^{-1}$  phonon frequency, namely, at the temperature  $T_N$  of the magnetic ordering. A similar feature at  $T_N$  is present in the frequency vs. temperature curves,  $\omega(T)$ , for other phonon modes, including those appearing at the temperature  $T_S$  of the structural phase transition (see, e.g.,  $\omega(T) - \omega(T_S)$  plot in Fig. 3 for the “new” phonon mode at about  $102.7 \text{ cm}^{-1}$ , stars). The observed peculiarity at  $T_N$  in the  $\omega(T)$  dependences points to the spin-phonon coupling. Two mechanisms of such coupling, the static one and the dynamic one, are to be considered. The static mechanism comes from the magnetoelastic coupling in a multiferroic material. In the magnetically ordered state, internal local magnetic fields give rise to static atomic displacements (some kind of a local magnetic striction) which may change interatomic distances and elastic constants and thus influence the phonon frequencies. The dynamic mechanism of spin-phonon coupling originates from the phonon-induced modulation of the Fe–O–Fe superexchange energy, which, in its turn, affects the elastic constants and, hence, the phonon frequencies [17]. Additional studies are necessary to estimate quantitatively contributions of these two mechanisms.

There exists, however, a direct confirmation of static atomic displacements in the magnetically ordered state of  $\text{EuFe}_3(\text{BO}_3)_4$ . Fig. 3 shows also the splitting  $\Delta(T)$  of the isolated  $\Gamma_3(^5D_1)$  crystal-field (CF) doublet of the  $\text{Eu}^{3+}$  ion in the high-temperature  $R32$  phase of  $\text{EuFe}_3(\text{BO}_3)_4$  vs. temperature. This splitting starts abruptly at  $T_S$  and, then, smoothly grows with further decreasing the temperature, until it begins to diminish again after showing a pronounced peculiarity at  $T_N$ . A sudden appearance of the splitting at  $T_S$  manifests the local symmetry lowering for the  $\text{Eu}^{3+}$  ion at the structural phase transition. Subsequent growth of the  $\Gamma_3$  doublet splitting in the interval of temperatures between  $T_S$  and  $T_N$  shows unambiguously that the crystal field continues to change due to, evidently, growing lattice distortions below  $T_S$ . Such behavior

correlates with recent discovery, by hard x-ray experiments [7], of growing lattice distortions below  $T_S$ , of even lower than  $P3_121$  symmetry, in  $RFe_3(BO_3)_4$  ( $R = Gd, Tb, Er, Y$ ) and with a recent observation of the intensity growth for the forced electric dipole  $f-f$  transitions of the  $Tb^{3+}$  ion in  $TbFe_3(BO_3)_4$  below  $T_S$ , showing a peculiarity also at  $T_N$  [18]. While the lattice distortions characterized by the intensity of the (001) x-ray reflection get stabilized below  $T_N$  [7], the intensity of forced electric dipole  $f-f$  transitions continues to grow with decreasing the temperature below  $T_N$  [18], evidently, due to growing static distortions of some different symmetry stimulated by local magnetic striction. These latter additional distortions below  $T_N$  provoke changes of the static crystal field at the  $Eu^{3+}$  site resulting in a diminished splitting  $\Delta(T)$  of the  $\Gamma_3(^5D_1)$  CF doublet. Note that the local magnetic field that appears at the  $Eu^{3+}$  site in the magnetically ordered state of  $EuFe_3(BO_3)_4$  acts in an opposite direction, i.e., enhancing the splitting  $\Delta(T)$ .

#### 4. Conclusions

In summary, we report on the first terahertz spectroscopy study of a compound from the family of new multiferroics with general formula  $RFe_3(BO_3)_4$ . The temperature-dependent (4–90 K) transmission spectra of the  $EuFe_3(BO_3)_4$  single crystal demonstrate pronounced peculiarities at the temperatures  $T_S = 58$  K and  $T_N = 34$  K of the first-order structural and, respectively, magnetic ordering phase transitions. New phonon modes of the  $P3_121$  structure appear below  $T_S$ , while the frequencies of the preserved phonons suffer a sharp shift at  $T_S$ . The observed peculiarities at  $T_N$  in the phonon frequencies vs. temperature curves give evidence for the spin–phonon coupling. The mechanism of this coupling is, most probably, connected with atomic displacements stimulated by the internal magnetic field arising in the magnetically ordered state below  $T_N$ .

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#### References

- [1] Y. Hinatsu, Y. Doi, K. Ito, M. Wakeshima, A. Alemi, J. Solid State Chem. 172 (2003) 438.
- [2] S.A. Klimin, D. Fausti, A. Meetsma, L.N. Bezmaternykh, P.H.M. van Loosdrecht, T.T.M. Palstra, Acta Crystallogr., Sect. B 61 (2005) 481.
- [3] D. Fausti, A. Nugroho, P.H.M. Loosdrecht, S.A. Klimin, M.N. Popova, L.N. Bezmaternykh, Phys. Rev. B 74 (2006) 024403.
- [4] R.Z. Levitin, E.A. Popova, R.M. Chtsherbov, A.N. Vasiliev, M.N. Popova, E.P. Chukalina, S.A. Klimin, P.H.M. Loosdrecht, D. Fausti, L.N. Bezmaternykh, JETP Lett. 79 (2004) 423.
- [5] E.A. Popova, N. Tristan, A.N. Vasiliev, V.L. Temerov, L.N. Bezmaternykh, N. Leps, B. Büchner, R. Klingeler, Eur. Phys. J. B 62 (2008) 123.
- [6] A.M. Kadomtseva, Y.F. Popov, G.P. Vorob'ev, A.P. Pyatakov, S.S. Krotov, K.I. Kamilov, V.Y. Ivanov, A.A. Mukhin, A.K. Zvezdin, A.M. Kuz'menko, L.N. Bezmaternykh, I.A. Gudim, V.L. Temerov, Low Temp. Phys. 36 (2010) 511.
- [7] U. Adem, L. Wang, D. Fausti, W. Schottenhamel, P.H.M. van Loosdrecht, A. Vasiliev, L.N. Bezmaternykh, B. Büchner, C. Hess, R. Klingeler, Phys. Rev. B 82 (2010) 064406.
- [8] C. Ritter, A. Vorotynov, A. Pankrats, G. Petrakovskii, V. Temerov, I. Gudim, R. Szymczak, J. Phys.: Condens. Matter 22 (2010) 206002.
- [9] M. Janoschek, P. Fisher, J. Schefer, B. Roessli, V. Pomjakushin, M. Meven, V. Petricek, G. Petrakovskii, L. Bezmaternykh, Phys. Rev. B 81 (2010) 094429.
- [10] J.E. Hamann-Borrero, M. Philipp, O. Kataeva, M.V. Zimmermann, J. Geck, R. Klingeler, A. Vasiliev, L. Bezmaternykh, B. Büchner, C. Hess, Phys. Rev. B 82 (2010) 094411.
- [11] M.N. Popova, T.N. Stanislavchuk, B.Z. Malkin, L.N. Bezmaternykh, Phys. Rev. Lett. 102 (2009) 187403; M.N. Popova, T.N. Stanislavchuk, B.Z. Malkin, L.N. Bezmaternykh, Phys. Rev. B 80 (2009) 195101.
- [12] M.N. Popova, J. Rare Earths 27 (2009) 607.
- [13] M.N. Popova, J. Magn. Magn. Mater. 321 (2009) 716.
- [14] V.P. Dyakonov, R. Szymczak, A.D. Prokhorov, E. Zubov, A.A. Prokhorov, G. Petrakovskii, L. Bezmaternykh, M. Berkowski, V. Varyukhin, H. Szymczak, Eur. Phys. J. B 78 (2010) 291.
- [15] L.N. Bezmaternykh, V.L. Temerov, I.A. Gudim, N.A. Stolbovaya, Crystallogr. Rep. 50 (Suppl. 1) (2005) 97.
- [16] K.N. Boldyrev, M.N. Popova, L.N. Bezmaternykh, M. Bettinelli, Quantum Electronics 41 (2011) 120.
- [17] D.J. Lockwood, M.G. Cottam, J. Appl. Phys. 64 (1998) 5876.
- [18] M.N. Popova, T.N. Stanislavchuk, B.Z. Malkin, L.N. Bezmaternykh, J. Phys.: Condens. Matter 24 (2012) 196002.