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## Spectral signatures of spin–phonon and electron–phonon interactions in multiferroic iron borates

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## ABSTRACT

High-resolution far-infrared reflection and polarized ellipsometry, as well as Raman scattering temperature-dependent measurements are used to study spin–phonon and electron–phonon interactions in rare-earth (RE) iron borates with the R32 structure of a natural mineral huntite, namely, in  $R\text{Fe}_3(\text{BO}_3)_4$  with  $R=\text{Pr}$ ,  $\text{Nd}$ , and  $\text{Sm}$ . Pronounced peculiarities in the  $\omega(T)$  dependences at the Néel temperature  $T_N \approx 32$  K are observed for all the compounds studied and the origin of these peculiarities is discussed. A coupling between lattice phonons and crystal-field excitations of a RE ion manifests itself by a re-normalization of frequencies and intensities of coupled modes. Modeling of the spectra has revealed the value of about  $15\text{ cm}^{-1}$  for the electron–phonon coupling constant in  $\text{PrFe}_3(\text{BO}_3)_4$ .

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## 1. Introduction

Charge–lattice–spin coupling plays a key role in a vast variety of phases and phenomena observed in multiferroics [1–3]. To study these interactions, different methods are used, in particular, optical ones. Thus, pronounced phonon anomalies around the Néel temperature  $T_N$  were observed in the Raman spectra of multiferroic  $\text{BiFeO}_3$  [4] and  $\text{RCrO}_3$  (R stands for a rare earth or yttrium) [5] and in the far infrared (FIR) spectra of  $\text{EuFe}_3(\text{BO}_3)_4$  [6]. Anticrossing between the magnetic exchange excitation and the  $\text{Tb}^{3+}$  crystal-field (CF) excitation in the FIR spectra of a multiferroic garnet  $\text{Tb}_3\text{Fe}_5\text{O}_{12}$  and a formation of hybrid  $f$ -electron–magnon excitations were recently demonstrated in Ref. [7].

The present paper deals with FIR and Raman studies of spin–phonon and electron–phonon interactions in rare-earth (RE) iron borates  $R\text{Fe}_3(\text{BO}_3)_4$  that belong to an interesting new family of multiferroics. These compounds crystallize in a huntite-type noncentrosymmetric trigonal structure characterized by a presence of helical chains of edge-sharing  $\text{FeO}_6$  octahedra running along the  $c$ -axis of the crystal, interconnected by two kinds of  $\text{BO}_3$  triangles and  $\text{RO}_6$  distorted prisms [8], see Fig. 1. In the case of  $R=\text{Pr}$ ,  $\text{Nd}$ , and  $\text{Sm}$ , the structure is described by the space group

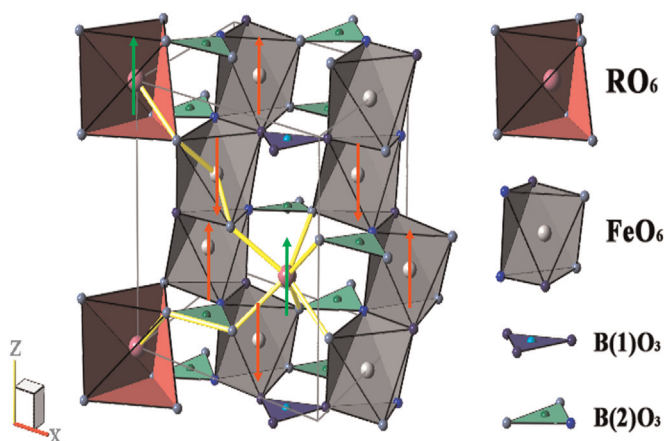
R32 at all the temperatures. Just this subfamily is studied in the present work. As for the rest  $R\text{Fe}_3(\text{BO}_3)_4$  compounds, they undergo a structural phase transition  $R32-P3_121$  with lowering the temperature [9,10]. A presence of two interacting magnetic systems (RE and iron ones) results in a large diversity of RE dependent magnetic and magnetoelectric properties of iron borates. All of them order magnetically at temperatures 30–40 K [11] but into different, sometimes complicated, magnetic structures depending on the R ions. Of the compounds studied here,  $\text{NdFe}_3(\text{BO}_3)_4$  ( $T_N = 33$  K) [12–14] and  $\text{SmFe}_3(\text{BO}_3)_4$  ( $T_N = 32 \pm 1$  K) [15–17] order into the easy-plane antiferromagnetic structure while  $\text{PrFe}_3(\text{BO}_3)_4$  ( $T_N = 32 \pm 1$  K) [18–21] orders into the easy-axis one. At 13.5 K [13] (16 K [14]) a commensurate magnetic structure of  $\text{NdFe}_3(\text{BO}_3)_4$  turns into an incommensurate spin helix that propagates along the  $c$  axis [13,14]. Large magnetoelectric and magnetodielectric effects were registered in the neodymium and samarium iron borates [22–25].

## 2. Experiment

$\text{PrFe}_3(\text{BO}_3)_4$ ,  $\text{NdFe}_3(\text{BO}_3)_4$ , and  $\text{SmFe}_3(\text{BO}_3)_4$  single crystals of good optical quality were grown in the Kirenskiy Institute of Physics in Krasnoyarsk, as described in Ref. [19]. Samples with dimensions up to  $5 \times 5 \times 10\text{ mm}^3$  were oriented using the crystal morphology and optical polarization methods. A Fourier

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**Fig. 1.** A fragment of the crystal structure of  $RFe_3(BO_3)_4$ . Each  $R^{3+}$  ion is connected by R–O–Fe bonds to six  $Fe^{3+}$  ions residing in the three chains of  $FeO_6$  octahedra (only two of them are shown) around this  $R^{3+}$  ion. These  $Fe^{3+}$  ions are situated in the (001) and (00 $\bar{1}$ ) planes above and below the  $R^{3+}$  ion, which supports a nonfrustrated magnetic interaction between the  $R^{3+}$  ion and antiferromagnetically ordered iron chains below  $T_N$ . Red and green arrows indicate directions of magnetic moments for  $Fe^{3+}$  and  $Pr^{3+}$  ions in the magnetically ordered state of  $PrFe_3(BO_3)_4$  where Fe–Pr interaction is antiferromagnetic [20,21]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

spectrometer Bruker IFS 125 HR with a liquid helium bolometer (4.2 K) as a detector and a closed helium cycle cryostat Cryomech ST403 were used to register optical reflectance spectra in the spectral region 0.6–3 THz (20–100  $cm^{-1}$ ) in the  $\pi$ -( $\mathbf{k}\perp\mathbf{c}$ ,  $\mathbf{E}\parallel\mathbf{c}$ ,  $\mathbf{H}\perp\mathbf{c}$ ) and  $\sigma$ -( $\mathbf{k}\perp\mathbf{c}$ ,  $\mathbf{E}\perp\mathbf{c}$ ,  $\mathbf{H}\parallel\mathbf{c}$ ) polarizations, in a broad range of temperatures (3–300 K). FIR ellipsometry measurements were also performed, using a self-made ellipsometer on the U4IR beamline of the National Synchrotron Light Source, Brookhaven National Laboratory, USA [26]. Raman measurements were performed in a backscattering configuration, as described in Ref. [10].

### 3. Results and discussion

As we intend to study interactions between lattice vibrational excitations and the spin and electronic subsystems of  $RFe_3(BO_3)_4$ ,  $R=Pr, Nd, Sm$ , that belong to the  $R32 (D_3^3)$  space symmetry group, we have to remind what phonons can be probed in them by optical measurements. These compounds have one formula unit in a primitive crystal cell (20 atoms), so their vibrational spectrum consists of 60 branches. 57 optical  $\Gamma$  point ( $k=0$ ) phonons are characterized by irreducible representations of the crystal factor group  $D_3$  as follows [10]:  $\Gamma_{\text{vibr}}=7 A_1(xx,yy,zz)+12 A_2(E\parallel z)+19 E(E\perp z, xy,xz,yz)$ . The  $A_2$  ( $E$ ) phonon modes are IR active for the electric vector of radiation polarized along (perpendicular to) the  $c$  crystalline axis.  $E$  modes are also Raman active, as well as  $A_1$  modes. Recently, the data on the IR active phonons in Pr, Nd, and Sm iron borates at room temperature (RT) were published [27]. The RT Raman data on  $NdFe_3(BO_3)_4$  are presented in Ref. [10].

#### 3.1. Spectral manifestations of a spin–phonon coupling in RE iron borates

Fig. 2 displays the temperature dependences of some phonon frequencies in  $NdFe_3(BO_3)_4$  and  $PrFe_3(BO_3)_4$ . Pronounced peculiarities are observed at the temperature  $T_N$  of the antiferromagnetic ordering. Two mechanisms, the static one and the dynamic one, of a coupling between lattice phonons and a magnetic ordering of the system have to be considered. The static mechanism originates from the magnetoelastic coupling in a multiferroic material. In a

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 is based on the phonon-induced modulation of the superexchange energies, which, in its turn, affects the elastic constants and, hence, the phonon frequencies [28]. In Ref. [6], an experimental evidence was presented for static atomic displacements in a magnetically ordered state of  $EuFe_3(BO_3)_4$ . Probably, such displacements exist in a magnetically ordered state of other RE iron borates. In Ref. [6], however, it was not possible to determine a quantitative contribution of this mechanism into observed shifts of  $EuFe_3(BO_3)_4$  phonon frequencies at  $T_N$ .

As for the dynamic mechanism, in the case of a nonresonant spin–phonon interaction the temperature dependence of the phonon frequency reads [29]:

$$\omega_n^2(T) = \omega_{n0}^2 + \sum_{ij} C_{ij}^n \langle S_i S_j \rangle (T) \quad (1)$$

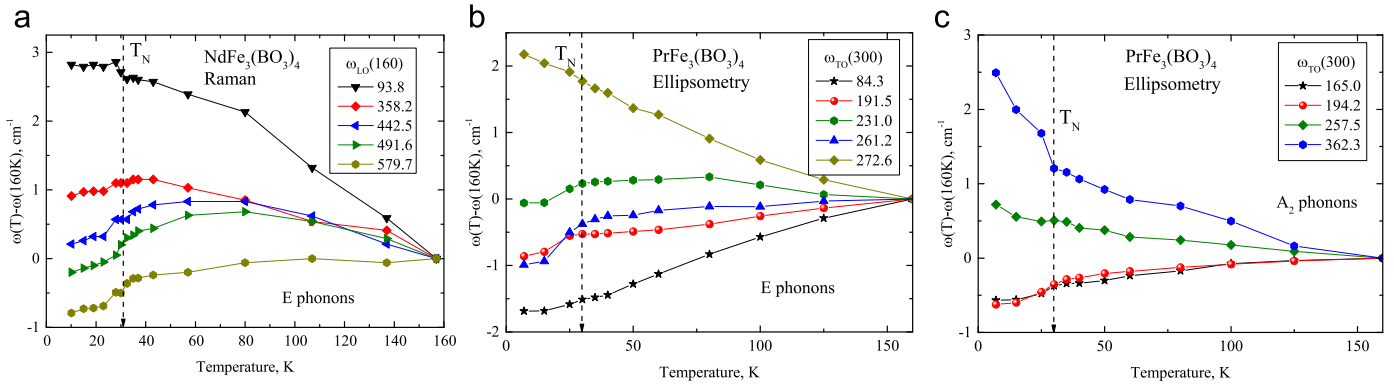
Here, spin products in the Heisenberg Hamiltonian are approximated by their temperature-dependent effective averages;  $C_{ij}^n$  coefficients are characteristics of the spin–phonon interaction. In principle,  $C_{ij}^n$  may have any sign, depending on the eigenvector of a particular phonon mode, which explains why both hardening and softening of phonon frequencies upon magnetic ordering are observed. To get quantitative information on the spin–phonon interaction in iron borates, a microscopic theory has to be developed.

Besides noticeable peculiarities at  $T_N$  in the phonon frequencies vs temperature dependences for  $RFe_3(BO_3)_4$  compounds, Fig. 2 demonstrates also a substantially different and  $R^{3+}$  ion dependent behavior of phonon frequencies above  $T_N$ . An interaction between lattice vibrations and electronic crystal-field excitations of  $R^{3+}$  ions could be the most probable reason for that. We begin the next Section with comparing  $\omega(T)$  curves for the lowest-frequency  $E$  phonon in  $PrFe_3(BO_3)_4$  [Fig. 2(b)] and  $NdFe_3(BO_3)_4$  [Fig. 2(a)].

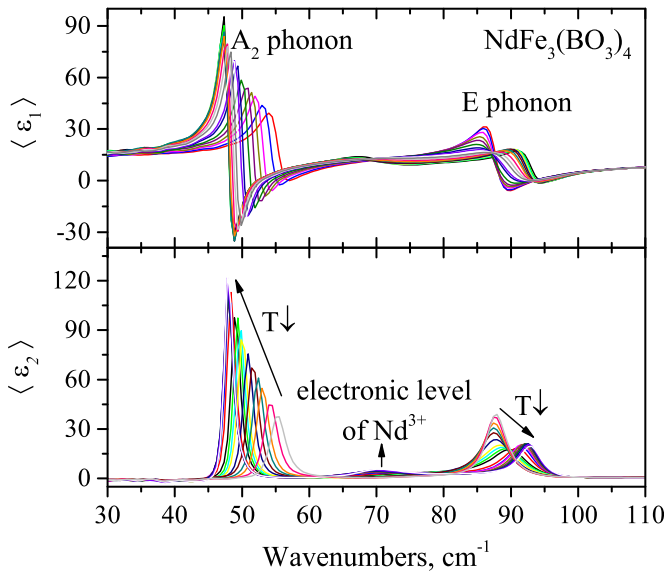
#### 3.2. Interaction between lattice phonons and crystal-field levels of $R^{3+}$ ions in $RFe_3(BO_3)_4$

Fig. 2 evidences a drastic difference in the temperature behavior of the lowest-frequency in-plane lattice vibration of  $PrFe_3(BO_3)_4$  and  $NdFe_3(BO_3)_4$ . In  $PrFe_3(BO_3)_4$ , this vibration markedly softens upon lowering the temperature, whereas in  $NdFe_3(BO_3)_4$  it strongly hardens. The lowest-frequency CF excitation of the  $\Gamma_3$  symmetry (which is allowed to interact with  $E$  phonons) lies at 192  $cm^{-1}$  for  $PrFe_3(BO_3)_4$  [20], i.e., above the 85  $cm^{-1}$  phonon mode, and at 65  $cm^{-1}$  for  $NdFe_3(BO_3)_4$  [30], i.e., below the considered mode. A mutual “repulsion” of the interacting excitations results in such a different behavior of the lowest-frequency  $E$  phonon in the praseodymium and neodymium compounds. A further support of such interpretation comes from the temperature-dependent FIR ellipsometry data on  $NdFe_3(BO_3)_4$  [Fig. 3]. An interaction between the  $E$  phonon mode and the electronic excitation of the  $\Gamma_3$  ( $E$  in phonon notations) symmetry (corresponding to the  $\Gamma_4$ – $\Gamma_{56}$  transition between the  $Nd^{3+}$  CF levels) is observed. The quasidelectronic mode gains its intensity at the expense of the  $E$  phonon mode which loses its intensity with lowering the temperature.

The most spectacular manifestations of the electron–phonon coupling are observed in the FIR spectra of  $PrFe_3(BO_3)_4$ . Fig. 4 presents the  $\pi$ -polarized FIR reflection spectra due to  $A_2$  non-degenerate phonon modes and the corresponding reflection intensity maps for  $PrFe_3(BO_3)_4$  and, for a comparison,  $SmFe_3(BO_3)_4$ .



**Fig. 2.** Temperature dependences of phonon lines' positions in (a)  $\text{NdFe}_3(\text{BO}_3)_4$  and (b) and (c)  $\text{PrFe}_3(\text{BO}_3)_4$ . (a) Raman and (b) and (c) FIR ellipsometry data are presented.



**Fig. 3.** The real  $\langle \epsilon_1(\omega) \rangle$  and imaginary  $\langle \epsilon_2(\omega) \rangle$  parts of the pseudo-dielectric function of  $\text{NdFe}_3(\text{BO}_3)_4$  obtained from the ellipsometry data at different temperatures.

In the spectra of the Sm compound, only a small kink at  $T_N$  in the  $\omega(T)$  dependence for the  $A_2^1$  phonon mode is observed, whereas the lowest-frequency  $A_2^1$  mode does not change at all with lowering the temperature. By contrast, for  $\text{PrFe}_3(\text{BO}_3)_4$  a splitting of the reststrahlen (reflection) band corresponding to the  $A_2^1$  mode is clearly seen. The splitting starts below  $\sim 100$  K, well above  $T_N = 32$  K, and shows a peculiarity at  $T_N$ . Fig. 5 shows the imaginary  $\langle \epsilon_2(\omega) \rangle$  part of the pseudo-dielectric function of  $\text{PrFe}_3(\text{BO}_3)_4$  obtained from the ellipsometry data at different temperatures. Position of the peak in  $\langle \epsilon_2 \rangle$  coincides with the TO frequency, the width is proportional to the damping constant (a negative spike in  $\langle \epsilon_2(\omega) \rangle$  is, probably, due to diffraction effects at a relatively small crystal area of the  $\text{PrFe}_3(\text{BO}_3)_4$  sample, in the long-wavelength region). Fig. 5 clearly demonstrates a shift and a narrowing of the quasi-phonon mode with lowering the temperature from RT to  $\sim 40$  K and a progressive loss of its intensity below  $\sim 40$  K. The quasi-electronic mode gains its intensity from the quasi-phonon mode. A pronounced shift of the quasi-electronic mode to higher frequencies is observed below the temperature of an antiferromagnetic ordering  $T_N$  (see Fig. 4 and inset of Fig. 5).

The only difference between the Sm and Pr compounds is that the former has no crystal-field levels below  $135 \text{ cm}^{-1}$  [17] but the latter possesses a level of  $\text{Pr}^{3+}$  at  $\sim 48 \text{ cm}^{-1}$  [19,20], almost resonant with the  $A_2^1$  phonon. The symmetry of the corresponding

electronic excitation ( $\Gamma_2$ ) coincides with that of the phonon ( $A_2$ ), which favors formation of coupled electron–phonon modes (see, e.g., Refs. [31,32]). Frequencies of the coupled electron–phonon excitations in  $\text{PrFe}_3(\text{BO}_3)_4$  can be found as roots of the following equation [32]:

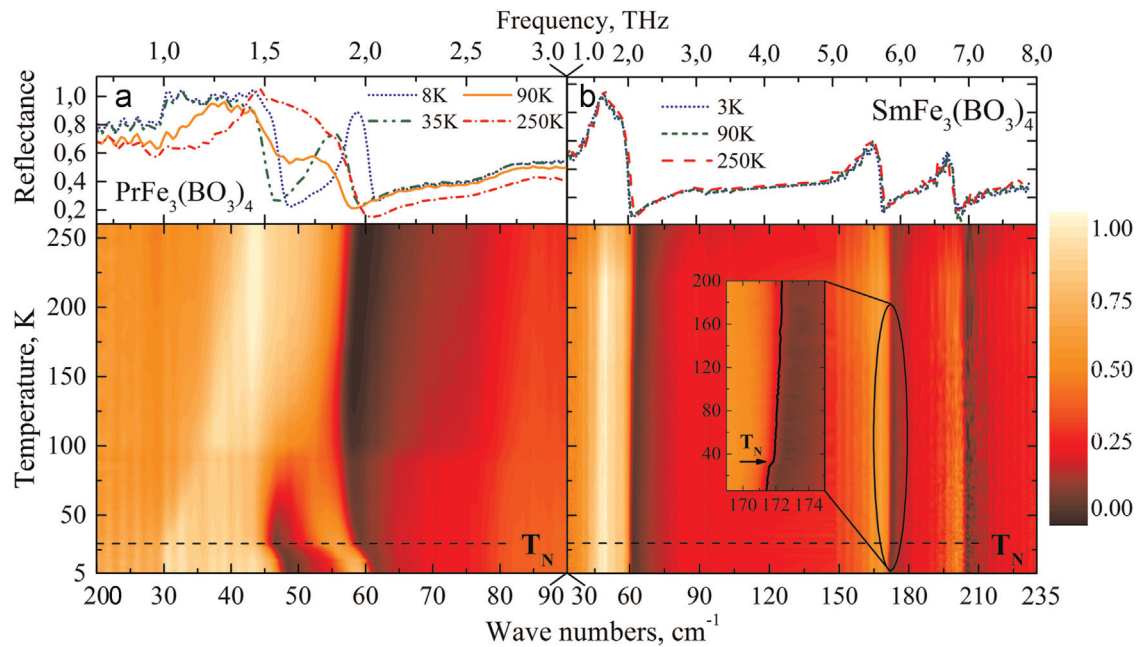
$$\omega^2 - \omega_0^2 + \frac{2\omega_0\omega_{12}(n_1 - n_2)|W|^2}{\omega^2 - \omega_{12}^2} = 0 \quad (2)$$

Here  $\omega_0$  and  $\omega_{12}$  are the frequencies (in  $\text{cm}^{-1}$ ) of the vibrational and electronic excitations, respectively, in the absence of interaction;  $n_1$  and  $n_2$  are relative populations of the excited  $|\Gamma_1\rangle$  and ground  $|\Gamma_2\rangle >$  CF states of  $\text{Pr}^{3+}$ , respectively;  $W$  is the interaction constant between the electronic excitation  $\omega_{12}$  and the  $\Gamma$ -point  $A_2^1$  optical phonon. This constant determines a change of the RE ion's energy due to a modulation of the crystal field by the  $A_2^1$  lattice vibration [32]. At high temperatures,  $n_1 \approx n_2$ , the electron–phonon interaction vanishes, and we have pure phonon and electronic excitations with frequencies  $\omega_+ = \omega_{12}$  and  $\omega_- = \omega_0$ , respectively. Using Eq. (2), we have modeled the experimental data of Fig. 4. In the case of the Boltzman distribution of populations of electronic levels, the difference of populations  $n_1 - n_2$  is given by  $n_1 - n_2 = th(\omega_{12}(T)/2kT)$ . The function  $\omega_{12}(T)$  coincides with the temperature-dependent position of the  $\text{Pr}^{3+}$  crystal-field level found earlier from optical spectroscopy data [19,20]. The interaction constant  $W$  and original phonon frequency  $\omega_0$  were varied to achieve the best agreement with the experimental data. This fitting has yielded  $\omega_0 = 45.5 \text{ cm}^{-1}$  and  $W = 14.6 \text{ cm}^{-1}$ .

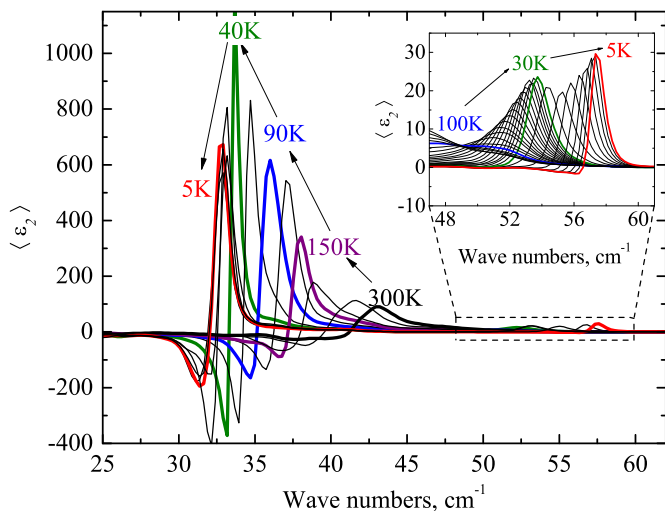
#### 4. Conclusions

Using far-infrared reflection and ellipsometry and Raman scattering spectroscopies, we have performed a study of interactions between the lattice vibrations and the spin system, as well as electronic RE ion crystal-field excitations in multiferroic RE iron borates with the R32 structure,  $\text{RFe}_3(\text{BO}_3)_4$ ,  $\text{R} = \text{Pr, Nd, and Sm}$ . Peculiarities in the temperature dependences of phonon frequencies at the Néel temperature  $T_N$  were observed for all the compounds studied. Either hardening or softening below  $T_N$  were registered for different modes. The values of the force constants can either grow or diminish in the magnetically ordered state because of (i) atomic displacements due to a local magnetic striction (static mechanism) and (ii) modulation of the exchange interaction by a given vibration (dynamic mechanism). Manifestations of the electron–phonon interaction in  $\text{NdFe}_3(\text{BO}_3)_4$  and a formation of a coupled electron–phonon mode in  $\text{PrFe}_3(\text{BO}_3)_4$  were detected. A rather large value of about  $15 \text{ cm}^{-1}$  for the electron–phonon coupling constant was found from the modeling





**Fig. 4.** The  $\pi$ -polarized FIR reflection spectra (upper parts) and the corresponding reflection intensity maps in the frequency–temperature axes (lower parts) for (a)  $\text{PrFe}_3(\text{BO}_3)_4$  and (b)  $\text{SmFe}_3(\text{BO}_3)_4$ ,  $T_N = 32 \pm 1$  K for both compounds. A splitting of the  $\text{PrFe}_3(\text{BO}_3)_4$  reststrahlen band near  $50 \text{ cm}^{-1}$  below  $\sim 100$  K is seen. Inset in (b) reveals a small kink at  $T_N$  in the  $\omega(T)$  dependence for the  $A_2^2$  phonon mode of  $\text{SmFe}_3(\text{BO}_3)_4$ .



**Fig. 5.** The imaginary  $\langle \epsilon_2(\omega) \rangle$  part of the pseudo-dielectric function of  $\text{PrFe}_3(\text{BO}_3)_4$  obtained from the ellipsometry data at different temperatures. Inset shows an expanded view of the emerging high-frequency branch of the spectrum.

of a coupled mode behavior in  $\text{PrFe}_3(\text{BO}_3)_4$ , which points to an essential role played by the electron–phonon interaction in physics of multiferroics.

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