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

M. N. Popova^{1*}, K. N. Boldyrev¹, S. A. Klimin¹, T. N. Stanislavchuk², A. A. Sirenko²,

L. N. Bezmaternykh³

¹*Institute of Spectroscopy, RAS, Moscow, Troitsk, 142190, Russia*

²*Department of Physics, New Jersey Institute of Technology, Newark, New Jersey, 07102, USA*

³*Kirenskiy Institute of Physics, Siberian Branch of RAS, Krasnoyarsk, 660036, Russia*

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 $R\bar{3}2$ structure of a natural mineral huntite, namely, in $R\text{Fe}_3(\text{BO}_3)_4$ with $R = \text{Pr}, \text{Nd}, \text{and Sm}$. Pronounced peculiarities in the $\omega(T)$ dependences at the Neel temperature $T_N \approx 32 \text{ K}$ 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 renormalization of frequencies and intensities of coupled modes. Modeling of the spectra has revealed the value of about 15 cm^{-1} for the electron-phonon coupling constant in $\text{PrFe}_3(\text{BO}_3)_4$.

Keywords: rare-earth iron borates, spin-phonon interactions, electron-phonon coupling, optical spectroscopy

* Corresponding author. *E-mail address:* popova@isan.troitsk.ru

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 magnetic Néel temperature T_N were observed in the Raman spectra of multiferroic BiFeO_3 [4] and $R\text{CrO}_3$ (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 Tb^{3+} crystal-field 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].

Fig. 1. A fragment of the crystal structure of $R\text{Fe}_3(\text{BO}_3)_4$. Each R^{3+} ion is connected by $R\text{-O-Fe}$ 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 (00-1) 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 $\text{PrFe}_3(\text{BO}_3)_4$ where Fe-Pr interaction is antiferromagnetic [20,21].

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 FeO_6 octahedra running along the c -axis of the crystal, interconnected by two kinds of BO_3 triangles and RO_6 distorted prisms [8], see Fig.1. In the case of $R = \text{Pr}, \text{Nd}, \text{and Sm}$, the structure is described by the space group $R\bar{3}2$ 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 $R\bar{3}2 - P3_121$ 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 5x5x10 mm were oriented using the crystal morphology and optical polarization methods. A Fourier 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 π - ($\mathbf{k} \perp c$, $\mathbf{E} \parallel c$, $\mathbf{H} \perp c$) and σ - ($\mathbf{k} \perp c$, $\mathbf{E} \perp c$, $\mathbf{H} \parallel c$) polarizations, in a broad range of temperatures (2 – 300 K). FIR ellipsometry measurements were also performed, using 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 $R\text{Fe}_3(\text{BO}_3)_4$, $R = \text{Pr}, \text{Nd}, \text{Sm}$, that belong to the $R\bar{3}2$ (D_7^3) 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 Γ 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 $\text{NdFe}_3(\text{BO}_3)_4$ are presented in Ref. [10].

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

Figure 2 displays the temperature dependences of some phonon frequencies in $\text{NdFe}_3(\text{BO}_3)_4$ and $\text{PrFe}_3(\text{BO}_3)_4$. 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 $\text{EuFe}_3(\text{BO}_3)_4$. 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 $\text{EuFe}_3(\text{BO}_3)_4$ phonon frequencies at T_N .

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

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

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

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 $R\text{Fe}_3(\text{BO}_3)_4$ 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 E phonon 85 cm^{-1} (300 K) in $\text{PrFe}_3(\text{BO}_3)_4$ [Fig. 2(b)] and $\text{NdFe}_3(\text{BO}_3)_4$ [Fig. 2(a)].

3.2. Interaction between lattice phonons and crystal-field levels of R^{3+} ions in $R\text{Fe}_3(\text{BO}_3)_4$

Fig. 2 evidences a drastic difference in the temperature behavior of the lowest-frequency in-plane lattice vibration of $\text{PrFe}_3(\text{BO}_3)_4$ and $\text{NdFe}_3(\text{BO}_3)_4$. In $\text{PrFe}_3(\text{BO}_3)_4$, this vibration markedly softens upon lowering the temperature, whereas in $\text{NdFe}_3(\text{BO}_3)_4$ it strongly hardens. The lowest-frequency CF excitation of the Γ_3 symmetry (which is allowed to interact with E phonons) lies at 192 cm^{-1} for $\text{PrFe}_3(\text{BO}_3)_4$ [20], i.e., above the 85 cm^{-1} phonon mode, and at 65 cm^{-1} for $\text{NdFe}_3(\text{BO}_3)_4$ [30], i.e., below the considered mode. A mutual “repulsion” of the interacting excitations results in such a different behavior of the 85 cm^{-1} phonon in the praseodymium and neodymium compounds. A further support of such interpretation comes from the temperature-dependent FIR ellipsometry data on $\text{NdFe}_3(\text{BO}_3)_4$ [Fig. 3]. An interaction between the E phonon mode and the electronic excitation of the Γ_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

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.

Fig.4. The π -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 cm^{-1} below ~ 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 $\text{SmFe}_3(\text{BO}_3)_4$.

The most spectacular manifestations of the electron-phonon coupling are observed in the FIR spectra of $\text{PrFe}_3(\text{BO}_3)_4$. Figure 4 presents the π -polarized FIR reflection spectra due to A_2 nondegenerate phonon modes and the corresponding reflection intensity maps for $\text{PrFe}_3(\text{BO}_3)_4$ and, for a comparison, $\text{SmFe}_3(\text{BO}_3)_4$. In the spectra of the Sm compound, only a small kink at T_N in the $\omega(T)$ dependence for the A_2^2 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 ~ 100 K, well above $T_N = 32$ K, and shows a peculiarity at T_N . Figure 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). Figure 5 clearly demonstrates a shift and a narrowing of the quasi-phonon mode with lowering the temperature from RT to ~ 40 K and a progressive loss of its intensity below ~ 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)

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.

The only difference between the Sm and Pr compounds is that the former has no crystal-field (CF) levels below 135 cm^{-1} [17] but the latter possesses a level of 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 (Γ_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 ω_0 and ω_{12} are the frequencies (in 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 Pr^{3+} , respectively; W is the interaction constant between the electronic excitation ω_{12} and the Γ -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

$n_1 - n_2 = th \frac{\omega_{12}(T)}{2kT}$. The function $\omega_{12}(T)$ coincides with the temperature-dependent position of the Pr^{3+} crystal-field level found earlier from optical spectroscopy data [19,20]. The interaction constant W and original phonon frequency ω_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 $R\text{Fe}_3(\text{BO}_3)_4$, $R = \text{Pr, Nd, and Sm}$. Peculiarities in the temperature dependences of phonon frequencies at the Neel 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 cm^{-1} for the electron-phonon coupling constant was found from the modeling 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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Figure captions

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5