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

M.N. Popova a,*, K.N. Boldyrev a, S.A. Klimin a, T.N. Stanislavchuk b, A.A. Sirenko b, L.N. Bezmernykh c

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 RFe3(BO3)4, with R=Pr, Nd, and Sm. Pronounced peculiarities in the ω(T) dependences at the Neél temperature TN = 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 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 PrFe3(BO3)4.

© 2014 Elsevier B.V. All rights reserved.

Keywords:
- Rare-earth iron borates
- Spin–phonon interactions
- Electron–phonon coupling
- Optical spectroscopy

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 Neél temperature TN were observed in the Raman spectra of multiferroic BiFeO3 [4] and RCO3 (R stands for a rare earth or yttrium) [5] and in the far infrared (FIR) spectra of EuFe3(BO3)4 [6]. Anticrossing between the magnetic exchange excitation and the Tb3+ crystal-field (CF) excitation in the FIR spectra of a multiferroic garnet Tb3Fe5O12 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 RFe3(BO3)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 FeO6 octahedra running along the c-axis of the crystal, interconnected by two kinds of BO3 triangles and RO3 distorted prisms [8], see Fig. 1. In the case of R=Pr, Nd, and 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 RFe3(BO3)4 compounds, they undergo a structural phase transition R32–P3121 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, NdFe3(BO3)4 (TN = 33 K) [12–14] and SmFe3(BO3)4 (TN = 32 ± 1 K) [15–17] order into the easy-plane antiferromagnetic structure while PrFe3(BO3)4 (TN = 32 ± 1 K) [18–21] orders into the easy-axis one. At 13.5 K [13] (16 K [14]) a commensurate magnetic structure of NdFe3(BO3)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

PrFe3(BO3)4, NdFe3(BO3)4, and SmFe3(BO3)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 × 5 × 10 mm2 were oriented using the crystal morphology and optical polarization methods. A Fourier
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]:

$$
\omega_n(T) = \omega_{\Omega 0}^2 + \sum_{y} C^n_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j)/(T)
$$

(1)

Here, spin products in the Heisenberg Hamiltonian are approximated by their temperature-dependent effective averages; $C^n_{ij}$ coefficients are characteristics of the spin–phonon interaction. In principle, $C^n_{ij}$ may have any sign, depending on the eigenvalue 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 $\alpha(T)$ 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 $\Gamma_{5d}$ CF levels) is observed. The quasielectronic mode gains its intensity at the expense of the $E$ phonon mode which looses 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 $A_2$ nondegenerate phonon modes and the corresponding reflection intensity maps for PrFe$_3$(BO$_3$)$_4$ and, for a comparison, SmFe$_3$(BO$_3$)$_4$.

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 ($D_3$) 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 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.

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 $\pi$–(KLL, ELC, HLL) and $\sigma$–(KLL, ELc, HLL) 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].

3.1. 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
In the spectra of the Sm compound, only a small kink at $T_N$ in the $\omega$ ($T$) dependence for the $A_2^0$ phonon mode is observed, whereas the lowest-frequency $A_2^0$ mode does not change at all with lowering the temperature. By contrast, for PrFe$_3$(BO$_3$)$_4$ a splitting of the reststrahlen (reflection) band corresponding to the $A_2^0$ 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 $<\varepsilon_2(\omega)>$ part of the pseudo-dielectric function of PrFe$_3$(BO$_3$)$_4$ obtained from the ellipsometry data at different temperatures. Position of the peak in $<\varepsilon_2(\omega)>$ coincides with the TO frequency, the width is proportional to the damping constant (a negative spike in $<\varepsilon_2(\omega)>$), is, probably, due to diffraction effects at a relatively small crystal area of the PrFe$_3$(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 cm$^{-1}$ [17] but the latter possesses a level of Pr$^{3+}$ at $\sim$48 cm$^{-1}$ [19,20], almost resonant with the $A_2^0$ 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 PrFe$_3$(BO$_3$)$_4$ can be found as roots of the following equation [32]:

$$\omega^2 - \omega_0^2 + 2\omega_0\omega_1(n_1 - n_2)W^2 = 0$$ (2)

Here $\omega_0$ and $\omega_1$ 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 $\Gamma_1^>$ and ground $\Gamma_2^>$ CF states of Pr$^{3+}$, respectively; $W$ is the interaction constant between the electronic excitation $\omega_1$ and the $\Gamma$-point $A_2^0$ optical phonon. This constant determines a change of the RE ion’s energy due to a modulation of the crystal field by the $A_2^0$ 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 $\omega_+ = \omega_1$ 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 $n_1 - n_2 = th(\omega_1(T)/2kT)$. The function $\omega_1(T)$ 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 $\omega_0$ were varied to achieve the best agreement with the experimental data. This fitting has yielded $\omega_0 = 45.5$ cm$^{-1}$ and $W = 14.6$ 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, RFe$_3$(BO$_3$)$_4$, R = 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 (dynamical mechanism). Manifestations of the electron-phonon interaction in NdFe$_3$(BO$_3$)$_4$ and a formation of a coupled electron–phonon mode in PrFe$_3$(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 PrFe$_3$(BO$_3$)$_4$, which points to an essential role played by the electron–phonon interaction in physics of multiferroics.

Acknowledgments

This work was supported by the Russian Science Foundation (Grant no. 14-12-01033). Experiments at U4-IR beamline NSLS-BNL (T.N.S. and A.A.S.) were performed under Contract no. DE-FG02-07ER46382 from the U.S. Department of Energy. The National Synchrotron Light Source is operated as a User Facility for the U.S. Department of Energy under Contract no. DE-AC02-98CH10886. M.N.P. thanks B.Z. Malkin for helpful discussions.

References


