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Spectroscopy of $RFe_3(BO_3)_4$ multiferroics: phase transitions, spin-phonon interaction, coupled electron-phonon modes

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Abstract. Review of the work performed in the author's laboratory is given, on high-resolution Fourier spectroscopy studies of multiferroics from the family of rare-earth iron borates with the structure of the natural mineral huntite. For these multiferroics, we reveal spectral signatures of interactions between electronic, spin, and lattice degrees of freedom. We have observed and investigated coupled electron-phonon modes in $PrFe_3(BO_3)_4$ and $TbFe_3(BO_3)_4$. The structure of the magnetically ordered phase of $EuFe_3(BO_3)_4$ is determined.

Multiferroics, i.e., materials, in which at least two order parameters coexist, are interesting both for the fundamental solid state physics and in view of possible applications. As a rule, different subsystems (electronic, spin, lattice) of a multiferroic strongly interact with each other. This, in particular, opens a possibility to control an electric polarization by a magnetic field and *vice versa.* The history of multiferroics goes back to the P. Curie's paper of 1894 but only in the middle of the last century Soviet scientists at first predicted in what compounds (named by them "magnetoelectrics") the magnetoelectric effect can be observed and then observed it for the first time. These studies are summarized in the review [1]. The word "multiferroics" appeared in 1994, it allows considering other than magnetic and electric order parameters. At the beginning of this century, a new burst of interest in multiferroics was caused by the synthesis of compounds with a large magnetoelectric effect and by a discovery of new classes of multiferroics (see, e.g., the reviews [2] and [3]). At the same time, linear and nonlinear optical spectroscopy of multiferroics develops; new magneto-optical effects characteristic just for multiferroics are discovered.

In our laboratory, starting from the beginning of 2000-ies, studies of different multiferroics are carried out by the method of the broad-band high-resolution Fourier spectroscopy. Below, we review several our works on the study of new multiferroics from the family of the rare-earth (RE) iron borates with structural type of the natural mineral huntite. These compounds possess a noncentrosymmetric trigonal structure which incorporates helical chains of the FeO_6 octahedra joined by their edges, running along the *c* axis. The chains are linked by BO_6 triangles and RO_6 prisms. All RE iron borates antiferromagnetically order at $T_N = 30 – 40$ K. Those of them that have an ionic radius of the R^{3+} ion smaller than the one of Sm^{3+} undergo a structural phase transition. We have

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shown that this is a so called "weak" first-order phase transition [4] and have discussed a possible nature of quasi-soft modes [5]. The temperature of the structural phase transition T_s and some of the optical properties turned out to depend on the crystal growth technology [6], which, from one hand, has to be taken into account when interpreting experimental data and, from the other hand, opens a possibility to control T_s.

The antiferromagnetic phase transition is accompanied by noticeable changes in the electronic and phonon spectra of RE iron borates. One observes splittings [7, 8] and shifts [9, 10] of spectral lines corresponding to the $f-f$ optical transitions of RE ions and appearance of forbidden lines [9, 10]. High-resolution electronic spectra of $EuFe_3(BO_3)_4$ allowed us to find that below T_N iron magnetic moments order into a collinear structure along one of the C_2 axes in the *ab* plane [6]. The temperature dependences of the phonon frequencies exhibit peculiarities at T_N, which testifies the spin-phonon interaction [4, 5, 11]. Static and dynamic mechanisms of such interaction are discussed and an experimental proof of a role of the static mechanism is given [11].

We have also undertaken a study of the interaction of phonons and electronic 4*f* excitations of the RE ions in RE iron borates. A temperature-dependent interference between two types of excitations was observed in $PrFe_3(BO_3)_4$ in which the frequency of 4*f* crystal-field electronic excitation of Pr^{3+} falls into the TO-LO frequency interval of the optical A_2^1 phonon mode near 50 cm^{-1}. Experimental data were explained on the basis of a theoretical model of coupled electron-phonon modes. The fitting procedure revealed the value 14.8 cm^{-1} for the electron-phonon coupling constant. This rather large value points to an essential role played by the electron-phonon interaction in the physics of multiferroics [12]. Subsequent *ab initio* calculations have shown that in the mentioned A_2^1 mode translations of the RE ion dominate [13]. Considerably more complicated picture was observed in the spectra of $TbFe_3(BO_3)_4$ in which doubly degenerate lattice phonon and 4*f* electronic crystal-field excitation of Tb^{3+} fall into resonance. An electron-phonon interaction causes delocalization of the CF excitation, an observable Davydov splitting, and formation of coupled electron-phonon modes [5].

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