

CRYSTAL-FIELD EFFECTS IN RARE-EARTH IRON BORATES: HIGH-RESOLUTION SPECTROSCOPY STUDY

M. N. Popova

*Institute of Spectroscopy, Russian Academy of Sciences,
5, Fizicheskaya Str., Troitsk, Moscow, 108840, Russia
e-mail: popova@isan.troitsk.ru*

In my lecture, I'll briefly review recent results on high-resolution spectroscopy studies of rare-earth (RE) iron borates obtained in my laboratory in collaboration with several other institutions. The RE iron borates belong to the borate family with general formula $RM_3(BO_3)_4$ where R is a rare earth or Y but $M = Al, Ga, Sc, Fe, \text{ or } Cr$. These compounds crystallize in the trigonal $R32$ structure of the natural mineral huntite. The most known representatives of this family are aluminum borates, which are used in self-frequency doubling and microchip lasers. Additional interest of scientists in the huntite borates is connected with an appreciable magnetoelectric effect found in RE iron, aluminum, and gallium borates.

With decreasing the temperature, iron borates with $R=Eu-Er$ or Y undergo a structural phase transition from the $R32$ phase to a less symmetric but also trigonal one corresponding to the enantiomorphic space-group pair $P3_121$ and $P3_221$. Resonant x-ray diffraction experiments on single-crystal samples of $DyFe_3(BO_3)_4$ revealed macroscopic domains with (sub)millimeter dimensions, which differ by right-handed ($P3_121$) or left-handed ($P3_221$) helical structures of electronic quadrupole moments of the Dy^{3+} ions at temperatures below the structural transition temperature $T_S=285$ K [1]. It is important to note that a multidomain chiral structure may noticeably reduce multiferroic properties of a crystal.

We have carried out temperature- and polarization-dependent high-resolution optical spectroscopy studies of $DyFe_3(BO_3)_4$. The crystal-field (CF) parameters for the Dy^{3+} ions in the C_2 symmetry positions of the $P3_121$ ($P3_221$) phase of $DyFe_3(BO_3)_4$ were obtained from calculations based on the analysis of the measured $f-f$ transitions. Using these parameters, we calculate temperature dependencies of the electronic quadrupole moments of the Dy^{3+} ions induced by the low-symmetry (C_2) CF component and show that the quadrupole helix chirality can be explained quantitatively. We also consider the helix chirality of the single-site magnetic susceptibility tensors of the Dy^{3+} ions in the paramagnetic $P3_121$ ($P3_221$) phase and suggest the neutron and resonant x-ray diffraction experiments in a magnetic field to reveal the helix chirality of field-induced magnetic moments [2].

Another feature of the $P3_121$ ($P3_221$) phase is that in the case of a collinear easy-plane structure of the ordered iron magnetic moments there are two sets of exchange splittings of CF energy levels of the R^{3+} ions in $RFe_3(BO_3)_4$. We have succeeded in observing this phenomenon in high-resolution spectra of $EuFe_3(BO_3)_4$. We also detect a strong effect of impurities (that enter the crystal from a flux in the course of the crystal growth) on T_S and demonstrate a coexistence of both $R32$ and $P3_121$ ($P3_221$) phases down to the lowest temperatures in a $EuFe_3(BO_3)_4$ crystal grown with the $Bi_2Mo_3O_{12}$ based flux, due to inhomogeneous distribution of impurity Bi^{3+} ions. Our study can be considered as a demonstration of the abilities of optical spectroscopy in delivering new information on a magnetic compound, even in the cases when other methods fail.

I would like to thank my colleagues who participated in the studies [2,3]. A financial support by the Russian Science Foundation under Grant No. 14-12-01033 is acknowledged.

[1] T. Usui, Y. Tanaka, H. Nakajima, et al., *Nature Materials* **13**, 611 (2014).

[2] M.N. Popova, E.P. Chukalina, K.N. Boldyrev, T.N. Stanislavchuk, B.Z. Malkin, I.A. Gudim, <http://arxiv.org/abs/1611.07092>; Submitted to *Phys. Rev. B*.

[3] M.N. Popova, B.Z. Malkin, K.N. Boldyrev, T.N. Stanislavchuk, D.A. Erofeev, V.L. Temerov, and I.A. Gudim, *Phys. Rev. B* **94**, 184418 (2016).