

High-resolution spectroscopy, crystal-field calculations, and quadrupole helix chirality of $\text{DyFe}_3(\text{BO}_3)_4$

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Abstract. High-resolution polarized transmission spectra of $\text{DyFe}_3(\text{BO}_3)_4$ single crystals were investigated in broad spectral (10-23000 cm^{-1}) and temperature (3.5-300 K) ranges. Energies of the dysprosium levels in the paramagnetic and antiferromagnetic phases were determined. On the basis of these data and preliminary calculations in the frameworks of the exchange-charge model, we determined the crystal-field and Dy-Fe exchange interaction parameters of the Dy^{3+} ions at sites with the point C_2 symmetry corresponding to the enantiomorphic $P3_121$ and $P3_221$ space groups. The values of electronic quadrupole moments of the Dy^{3+} ions were calculated, which enabled us to interpret results of the work [Usui et al., Nature Mater. 13, 611 (2014)] on the observation of domains of different quadrupole chirality in $\text{DyFe}_3(\text{BO}_3)_4$.

The crystals $\text{DyFe}_3(\text{BO}_3)_4$ belong to the family of multiferroic rare-earth iron borates that crystallize in the trigonal $R32$ structure of the natural mineral huntite. With decreasing the temperature to $T_S=285$ K, $\text{DyFe}_3(\text{BO}_3)_4$ undergoes a structural phase transition from the $R32$ phase to the enantiomorphic space-group pair $P3_121$ and $P3_221$. It has been shown recently by resonant x-ray diffraction that, below T_S , single-crystal samples of $\text{DyFe}_3(\text{BO}_3)_4$ contain macroscopic domains which differ by right-handed ($P3_121$) or left-handed ($P3_221$) helical structures of electronic quadrupole moments of the Dy^{3+} ions [1]. Quadrupole moments at the Dy sites are induced by a low-symmetry C_2 component of the crystal field that appears below T_S and distorts the electronic density distribution in the Dy^{3+} ions. It is possible to calculate values of these moments on the base of the crystal-field (CF) parameters. A limited available information on the CF levels of Dy^{3+} ions in $\text{DyFe}_3(\text{BO}_3)_4$ prevents from doing CF calculations in the frame of the C_2 symmetry CF Hamiltonian with 15 parameters.

We have measured temperature-dependent transmission spectra of $\text{DyFe}_3(\text{BO}_3)_4$ single crystals corresponding to optical transitions from the ground multiplet to all the excited multiplets up to about 22200 cm^{-1} and to the far-infrared transitions within the ground multiplet. Almost all of the spectral lines observed in the absorption spectra of both the

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paramagnetic and antiferromagnetic ($T < T_N = 39$ K) phases of $\text{DyFe}_3(\text{BO}_3)_4$ were unambiguously identified and the corresponding energies of excitations of the Dy^{3+} ions were determined. This dataset formed a basis for the CF calculations and modeling of exchange interactions. Here, we confine ourselves with the paramagnetic phase.

The spectrum of a Dy^{3+} ion in a dielectric crystal can be described using the Hamiltonian $H = H_{\text{FI}} + H_{\text{CF}}$, where H_{FI} is the free-ion Hamiltonian but $H_{\text{CF}} = \sum_{p,q} C_q^p B_q^p$ is the CF Hamiltonian determined by 15 independent CF parameters B_q^p (C_q^p are the spherical tensor operators of rank p). The initial values of the CF parameters were calculated in the framework of the exchange-charge model [2]. Then, the energies of transitions between the levels of the Dy^{3+} ions, obtained from the numerical diagonalization of the Hamiltonian H operating in the total space of 2002 states of the electronic $4f^9$ configuration, were compared with the measured optical spectra of $\text{DyFe}_3(\text{BO}_3)_4$ in the paramagnetic phase, and the initial CF parameters were varied to fit the experimental data. Values of the six CF parameters ($B_0^2 = 404$, $B_0^4 = -1192$, $B_{-3}^4 = B_3^4 = 554i$, $B_0^6 = 328$, $B_{-3}^6 = B_3^6 = 70i$, $B_6^6 = B_{-6}^6 = 232 \text{ cm}^{-1}$) which determine the dominant trigonal CF component change monotonously along the series of RE iron borates. The remaining nine parameters of the CF component of the C_2 symmetry ($B_{-1}^2 = B_1^2 = 58.4i$, $B_2^2 = B_{-2}^2 = 69.4$, $B_{-1}^4 = B_1^4 = -49.2i$, $B_2^4 = B_{-2}^4 = 101.2$, $B_4^4 = B_{-4}^4 = 15.9$, $B_{-1}^6 = B_1^6 = -7.4i$, $B_2^6 = B_{-2}^6 = -14$, $B_4^6 = B_{-4}^6 = 31.4$, $B_5^6 = B_{-5}^6 = -79i$) are found with lower accuracy because they little influence the multiplet splittings. However, just this CF component determines some specific properties of RE iron borates in the $P3_121$ (or $P3_221$) phase, in particular, the anisotropy of the magnetic spectroscopic factors of Kramers doublets of the Dy^{3+} ions in the ab -plane and the quadrupole helix chirality in $\text{DyFe}_3(\text{BO}_3)_4$ [1].

The low-symmetry C_2 -component of the crystal field distorts the electronic density distribution in the Dy^{3+} ions and induces non-zero non-axial components of the electronic quadrupole moment at the dysprosium sites. The quadrupole helix chirality appears due to rotations of the local C_2 symmetry axis by $2\pi/3$ and $4\pi/3$ at the $3a$ dysprosium sites shifted relative one another along the c -axis by $c/3$ and $2c/3$, respectively. The results of calculations of the average values of the quadrupole moment components $\langle Q \rangle = \text{Tr}[Q \exp(-H/k_B T)] / \text{Tr}[\exp(-H/k_B T)]$ at different temperatures T (k_B is the Boltzman constant) using the set of the CF parameters given above agree satisfactorily with the experimental data presented in Ref. [1] (see Table 1) and confirm supposition [1] that changes of $\langle Q_{x^2-y^2} \rangle$ and $\langle Q_{yz} \rangle$ with temperature are mainly induced by redistribution of populations of CF sublevels of the Dy^{3+} ion ground multiplet.

Table 1. Quadrupole moments (arbitrary units) of Dy^{3+} in the $P3_121$ phase of $\text{DyFe}_3(\text{BO}_3)_4$.

Temperature	$\langle Q_{x^2-y^2} \rangle$		$\langle Q_{yz} \rangle / \langle Q_{x^2-y^2} \rangle$	
	Measured [1]	Computed	Measured [1]	Computed
50 K	-1.22	-1.18	-1.23	-1.415
100 K	-0.906	-0.910	-1.20	-1.202
150 K	-0.678	-0.695	-1.10	-1.096
200 K	-0.50	-0.548	-0.90	-1.031

This paper was supported by the Russian Science Foundation (14-12-01033).

References

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