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Holmium iron borate: high-resolution spectroscopy and crystal-field parameters

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Abstract. High-resolution transmission spectra of $HoFe_3(BO_3)_4$ single crystals were measured in broad spectral (5000-23000 cm^{-1}) and temperature (1.7-300 K) ranges. Crystal-field energies of the Ho^{3+} ions were determined for a paramagnetic and easy-axis antiferromagnetic phases of the compound. On the basis of these data and of preliminary crystal-field calculations in the frame of the exchange-charge model, crystal-field parameters were found. A parameter of the isotropic Ho-Fe exchange interaction was estimated.

Holmium iron borate belongs to the family of new multiferroic materials – rare-earth (RE) borates with a trigonal structure of the mineral huntite. It crystalizes in the $R32$ symmetry space group (SG). The compound exhibits a substantial magnetoelectric effect at temperatures below $T_N = 39$ K where an antiferromagnetic ordering into an easy-plane magnetic structure takes place. To interpret magnetoelectric properties of RE compounds one needs the information on RE ion crystal-field (CF) levels and wave functions [1]. Detailed research on CF levels of Ho^{3+} in $HoFe_3(BO_3)_4$ has not been carried out before. The task is complicated by the fact, that the crystal has a low-symmetry structure with the SG $P3_121$ at room temperature, while the structural phase transition $R32 \rightarrow P3_121$ occurs at $T_s \sim 360$ K [2]. The point symmetry group of the holmium site in the $P3_121$ structure of $HoFe_3(BO_3)_4$ is C_2. Below $T_{SR} = 5$ K, the magnetic structure of holmium iron borate changes to an easy-axis one.

High-quality $HoFe_3(BO_3)_4$ single crystals were grown from fluxes based on $Bi_2Mo_3O_{12}$. The transmission spectra of oriented single crystals were registered using a high-resolution Fourier-transform spectrometer Bruker IFS 125HR in the spectral range 5000–23000 cm^{-1} with a resolution up to 0.2 cm^{-1}, which is sufficient to detect all spectral details. The crystal sample was placed into either a closed-cycle cryostat Cryomech ST403 (3.5 – 300 K) or a helium-filled optical cryostat with helium vapor pumping (1.7 – 4.2 K). The analysis of temperature dependences of polarized light absorption allowed us to identify the crystal-field levels of the Ho^{3+} ion in the paramagnetic phase of $HoFe_3(BO_3)_4$. In particular, the energies of CF levels of the ground multiplet $^5I_8$ are 0, 7.5, 14, 18, 54, 66, 95, 137, 154,

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175, 207, 246, 272, 311, 322, 340, and 354 cm^{-1}. The energies of upper levels from this dataset were specified using cooperative satellites in the high-frequency part of the absorption spectra. These satellites correspond to a simultaneous excitation of the two interacting holmium ions by one photon [3]. The knowledge of CF levels of the ground multiplet is important for interpretation of magnetic and thermodynamic properties of the compound. We have also determined the CF energies of Ho^{3+} ions in the easy-axis phase of the crystal ($T<T_{SR}$). As for the easy-plane phase, more work is necessary to identify all the observed spectral lines in a very complicated spectrum in the temperature range $T_{SR} <T< T_N$.

The energy spectrum of the Ho^{3+} ion in the crystal field of the C_2 symmetry in HoFe$_3$(BO$_3$)$_4$ is defined by 15 parameters B_q^p in the CF Hamiltonian, which is represented by a linear combination of spherical tensor operators $C_q^{(p)}$ in the Cartesian coordinate system with $x\|a$ and $z\|c$ axes. The parameters calculated with the exchange-charge model [4] were used as initial parameters. Then, the energies of transitions between the levels of the Ho^{3+} ions, obtained from a numerical diagonalization of the complete Hamiltonian operating in the space of 1001 states of the 4f^{10} electronic configuration, were compared with the measured optical spectra of HoFe$_3$(BO$_3$)$_4$ in the paramagnetic phase, and the initial CF parameters were varied to fit the experimental data. The following set of the CF parameters (in cm^{-1}) was obtained: $B_0^2 = 376$, $B_0^4 = -1112$, $B_{-3}^4 = B_3^4 = 526i$, $B_0^6 = 336$, $B_{-3}^6 = B_3^6 = 65i$, $B_6^6 = B_{-6}^6 = 232$ (they define the trigonal component of the crystal field); $B_{-1}^2 = B_1^2 = 71i$, $B_2^2 = B_{-2}^2 = 65$, $B_{-1}^4 = B_1^4 = -52i$, $B_2^4 = B_{-2}^4 = 71$, $B_4^4 = B_{-4}^4 = -16$, $B_{-1}^6 = B_1^6 = -21i$, $B_2^6 = B_{-2}^6 = -9.6$, $B_4^6 = B_{-4}^6 = -27$, $B_{-5}^6 = B_5^6 = -70i$ (these parameters are responsible for the low-symmetry C_2 component).

All the ions of holmium in the paramagnetic and easy-axis antiferromagnetic phases of HoFe$_3$(BO$_3$)$_4$ are optically equivalent in the absence of an external magnetic field. The frequency shifts of the electronic transitions (shifts of energy levels in the exchange field) observed between the temperatures T=50 K > T$_N$ and T = 1.5 K < T$_{SR}$ were interpreted considering the isotropic exchange interaction between the Ho^{3+} ions and Fe^{3+} ions in the S state, $H_{\text{RE-Fe}} = -J\boldsymbol{S}_{Ho} \cdot \boldsymbol{S}_{\text{Fe}}$ ($\boldsymbol{S}_{Ho}$ и $\boldsymbol{S}_{Fe}$ are spin moment operators for the holmium and iron ions). The value of the isotropic exchange interaction parameter $J = 0.2\ \text{cm}^{-1}$ was determined from a comparison of calculated spectral line shifts with the experimental data.

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