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## Features of electronic paramagnetic resonance in the $\text{ErAl}_3(\text{BO}_3)_4$ single crystal

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An additional resonance line was found in the EPR spectrum of the  $\text{ErAl}_3(\text{BO}_3)_4$  crystal at a temperature of 4.2 K, along with the main line. The appearance of an additional line is associated with the possible formation of magnetic clusters in the crystal. *Published by AIP Publishing.*

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Rare-earth aluminoborates  $\text{RAI}_3(\text{BO}_3)_4$  (R—rare-earth element) with trigonal space group  $R\bar{3}2$  ( $D^7$ ) without an inversion center have well-pronounced nonlinear<sup>1</sup> and luminescent<sup>2</sup> optical properties. A giant magnetoelectric effect was recently found in these crystals.<sup>3</sup> In addition, more recently, it has been shown that these crystals represent promising materials for magnetic cooling.<sup>4</sup> In general, the magnetic ordering of rare-earth aluminoborates occurs at very low temperatures.

One of the interesting representatives of the family of aluminoborates is  $\text{ErAl}_3(\text{BO}_3)_4$ , which remains a paramagnet at a temperature of 2 K.<sup>5</sup> A huge magnetoelectric effect was found in this compound.<sup>5</sup> The  $\text{ErAl}_3(\text{BO}_3)_4$  single crystal demonstrates highly anisotropic magnetic properties.<sup>5</sup> It should be noted that optical and magneto-optical spectroscopy, as well as luminescence of erbium aluminoborate, have been studied previously;<sup>6,7</sup> however, studies performed using the electronic paramagnetic resonance (EPR) method have not been reported in the literature.

The purpose of this work was to identify the EPR features of the  $\text{ErAl}_3(\text{BO}_3)_4$  single crystal. The EPR study in erbium aluminoborate makes it possible to determine the  $g$ -factor of the rare-earth ion, which is important for the interpretation of the magnetic and thermodynamic properties of the object. The resonance method can also provide valuable information on the spin-spin interaction between rare-earth  $\text{Er}^{3+}$  ions.

The  $\text{ErAl}_3(\text{BO}_3)_4$  single crystal was prepared by the solution-melt crystallization method.<sup>8</sup> The orientation of crystalline axes was determined by X-ray diffraction. The sample was a plate with an area of  $2 \times 3$  mm and a thickness of 0.2 mm. The crystal trigonal axis was perpendicular to the plate plane and coincided with the crystallographic axis  $c$ . The EPR spectra studies were carried out at a temperature of 4.2 K in the frequency range of 40–120 GHz on a complex of standard direct-gain spectrometers. Only perpendicular polarization of the microwave field was used. The external magnetic field  $\mathbf{H}$  was created by a superconducting solenoid. The spectral measurements presented in the article were obtained at different orientations of  $\mathbf{H}$  in the plane formed by the  $c$  and the second-order axis  $a \perp c$ .

It is known that the main multiplet of the  $\text{Er}^{3+}$  ion in  $\text{ErAl}_3(\text{BO}_3)_4$  is  $^4I_{15/2}$  with the spin  $S = 3/2$ , the orbital angular momentum  $L = 6$ , and the total angular momentum  $J = 15/2$ . The main doublet of the multiplet split by the crystal field is separated from the first excited doublet by  $\sim 46 \text{ cm}^{-1}$ .<sup>7</sup> The crystal-field constant values in  $\text{ErAl}_3(\text{BO}_3)_4$  are almost the same as in the erbium-doped single crystal  $\text{YAl}_3(\text{BO}_3)_4$ . Only one absorption line was observed in the EPR spectrum of a doped crystal, which is associated with transitions between the levels of the ground doublet.<sup>9</sup> Therefore, it may be assumed that the result of the study of resonance properties of the  $\text{ErAl}_3(\text{BO}_3)_4$  crystal will be similar.

Indeed, as illustrated in Fig. 1, the EPR spectra measured in the  $\text{ErAl}_3(\text{BO}_3)_4$  single crystal exhibit an intense line associated with the transition between the levels of the lowest doublet. In this case, the resonance field  $H_r$  at a frequency  $\nu = 69.00$  GHz is approximately 30 kOe at  $\mathbf{H} \parallel c$  and approximately 5 kOe at  $\mathbf{H} \parallel a$  [Fig. 1(a)]. However, in addition to the main line, an additional line of much weaker intensity is observed on the presented spectra. Thus, a local intensity maximum is clearly visible: approximately 14 kOe at  $\mathbf{H} \parallel c$  and approximately 2 kOe at  $\mathbf{H} \parallel a$ . Fig. 1(b) shows the change in the EPR spectrum at a frequency  $\nu = 61.03$  GHz with a deviation of  $\mathbf{H}$  from the  $a$  axis ( $\mathbf{H} \perp c$ ) up to  $\mathbf{H} \parallel c$ . A local maximum of intensity is observed on all spectra, a single structure of both lines is preserved, and there are no signs of their intersection. An increase in the angle between the  $\mathbf{H}$  direction and the axis  $a$  leads to an increase in the  $H_r$  values for both the main and additional lines.

The EPR frequency-field dependencies (FFD) of the  $\text{ErAl}_3(\text{BO}_3)_4$  single crystal were restored for the  $\mathbf{H}$  orientation along and perpendicular to the  $c$  axis on the basis of the experimental data obtained in the frequency range of 40–120 GHz and in magnetic fields up to 40 kOe. They are presented in Fig. 2. It should be noted that the additional line, unlike the main line, has a non-zero initial splitting. Extrapolation of the experimental data to  $H = 0$  gives the splitting value of approximately 7 GHz at  $\mathbf{H} \parallel c$  and of approximately 20 GHz at  $\mathbf{H} \parallel a$ . The  $g$ -factor values of the main and additional lines were determined for both orientations of  $\mathbf{H}$  according to the  $\nu(H_r)$  slope. The value of  $g$ -factor  $g_{\parallel}$  of the main line at  $\mathbf{H} \parallel c$  is

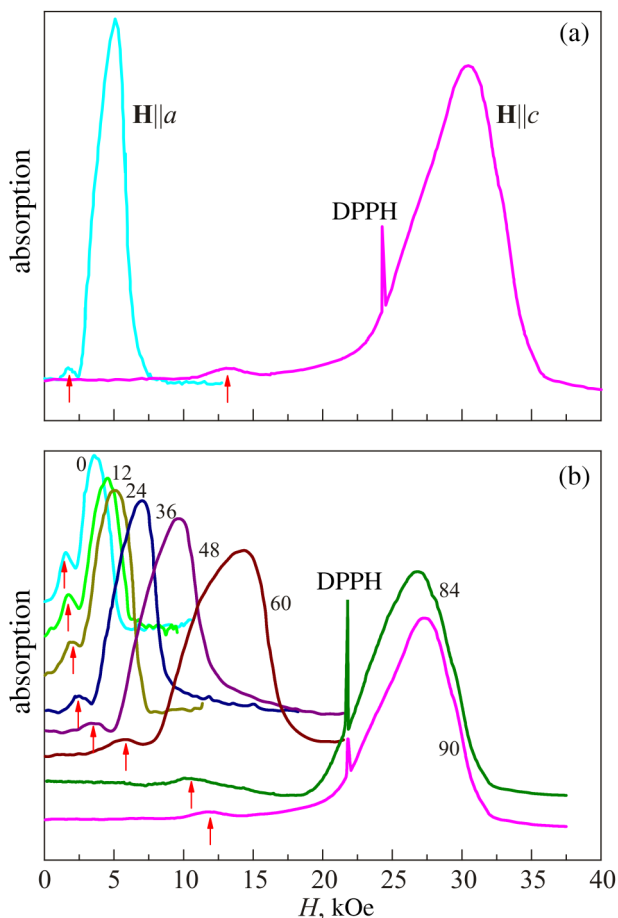


Fig. 1. The EPR absorption spectra in the  $\text{ErAl}_3(\text{BO}_3)_4$  single crystal, measured at  $T=4.2\text{ K}$ : (a) the external field  $\mathbf{H}$  is directed along the  $c$  axis and along the  $a$  axis, the frequency  $\nu = 69.00\text{ GHz}$ . For the convenience of presenting the results, the spectral line intensity measured at  $\mathbf{H}\parallel a$  is increased in comparison with the line intensity at  $\mathbf{H}\parallel c$ ; (b) spectra measured for different directions of the field  $\mathbf{H}$  in the  $ac$  plane at a frequency  $\nu = 61.03\text{ GHz}$ . The digits indicate the angle (in degrees) between the  $\mathbf{H}$  direction and the  $a$  axis. The arrows indicate the maxima of the additional absorption line. Narrow lines correspond to the signal from the diphenylpicrylhydrazyl (DPPH) reference sample.

approximately 1.6, and of the additional line is approximately 3.4. The value of  $g$ -factor  $g_{\perp}$  of the main line at  $\mathbf{H}\parallel a$  is approximately 9.5, and of the additional line is approximately 19.6. Thus, the  $g$ -factor of the additional line almost twice exceeds the  $g$ -factor of the main line for both orientations of the external field. The obtained values of the  $g$ -factor of the main line are in good agreement with the data for the erbium-doped single crystal  $\text{YAl}_3(\text{BO}_3)_4$  ( $g_{\parallel} \approx 1.4$ ,  $g_{\perp} \approx 9.5$ ).<sup>9</sup>

It was reported earlier that, when the  $\text{YAl}_3(\text{BO}_3)_4$  crystal is doped with erbium, the  $\text{Er}^{3+}$  ions occupy the  $\text{Al}^{3+}$  positions.<sup>10</sup> Such a substitution in erbium alumborate leads to the appearance of groups of erbium ions located closer to each other than in the crystal lattice of  $\text{ErAl}_3(\text{BO}_3)_4$ , which does not contain impurities. In addition, similar groups may arise, for example, when  $\text{Er}^{3+}$  ions are introduced into the crystal lattice interstice. It is obvious that, the shorter the distance between ions, the stronger the spin-spin interaction between them. Therefore, a correlation may arise, and magnetic clusters can be formed in the paramagnetic matrix, in the case of this substitution or insertion of  $\text{Er}^{3+}$  ions between the spins. The presence of such magnetic clusters in the EPR spectrum may lead to the appearance of an additional line

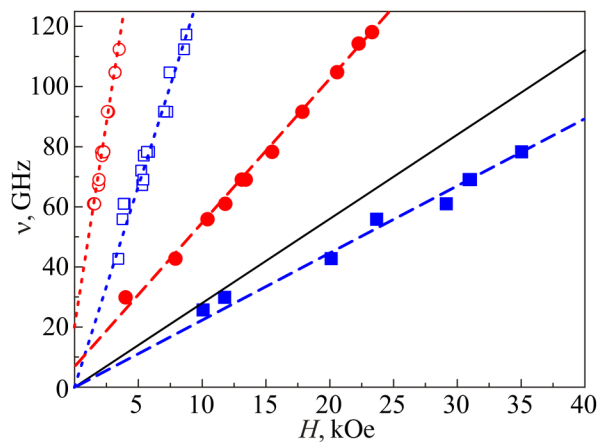


Fig. 2. Frequency-field dependencies of the EPR spectrum in the  $\text{ErAl}_3(\text{BO}_3)_4$  single crystal at  $T=4.2\text{ K}$  for  $\mathbf{H}\parallel c$  ( $\blacksquare, \bullet$ ) and  $\mathbf{H}\parallel a$  ( $\square, \circ$ ). The square symbols correspond to the main resonance line, the round symbols correspond to the additional one. For comparison, a solid straight line shows the dependence in DPPH ( $g=2$ ).

with nonzero initial splitting and double  $g$ -factor.<sup>11</sup> The fact that the additional line is associated with an impurity is indicated by the ratio between the intensities of the main and additional lines. The intensity of the additional line is two orders of magnitude less than that of the main line. This ratio may be considered a rough estimate of the amount of impurity. It can be noted that 0.1–1% of the impurity is completely permissible with crystal growth. Another possible indirect confirmation of the appearance of erbium ions on aluminum positions is presented in the paper.<sup>12</sup>

The authors pointed out the appearance of satellites near the main lines of the absorption spectrum in the visible region in the  $\text{Er:YAl}_3(\text{BO}_3)_4$  crystal in the case of high degree doping of the crystal by erbium ions. They associated these satellites with the Er-Er interaction. However, such satellites may also appear in the case of a minor substitution of aluminum by erbium. Since the crystal field acting on the  $\text{Er}^{3+}$  ions at erbium and aluminum positions is different, the absorption lines of erbium ions at the aluminum positions are shifted in comparison with the absorption lines of erbium ions at their own positions. Thus, an additional resonance line of weak intensity with initial splitting was observed in the EPR spectra of the  $\text{ErAl}_3(\text{BO}_3)_4$  single crystal along with the main one. An additional line was observed in external fields applied in different directions in the plane formed by the trigonal axis  $c$  of the crystal and the second-order axis  $a$ . The frequency-field dependencies of  $\text{ErAl}_3(\text{BO}_3)_4$  are restored for cases when the external field is directed along the  $c$  and  $a$  axes. The values of the spectroscopic splitting axial tensor components: for the main line  $g_{\parallel} \approx 1.6$ ,  $g_{\perp} \approx 9.5$ , for the additional line  $g_{\parallel} \approx 3.4$ ,  $g_{\perp} \approx 19.6$ . It is assumed that the appearance of a low-intensity additional line is associated with the formation of magnetic clusters.

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