DEFECTS AND IMPURITY CENTERS, DISLOCATIONS, AND PHYSICS OF STRENGTH

Electron Paramagnetic Resonance of Mn²⁺ Ions in Single Crystals of Yttrium Aluminum Borate YAl₃(BO₃)₄

A. M. Vorotynov[a], G. A. Petrakovskiĭ[a], Ya. G. Shiyan[a], L. N. Bezmaternykh[a], V. E. Temerov[a], A. F. Bovina[a], and P. Aleshkevych[b]

[a] *Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*
e-mail: sasa@iph.krasn.ru

[b] *Institute of Physics, Polish Academy of Sciences, al. Lotnikow 32/46, Warsaw, 02-668 Poland*

Received April 13, 2006; in final form, May 15, 2006

Abstract—Single crystals of yttrium aluminum borate $YAl_3(BO_3)_4$ doped with manganese ions are studied using electron paramagnetic resonance spectroscopy. It is shown that manganese ions introduced at low concentrations into the sample predominantly occupy yttrium ion sites in the crystal structure. The shape of the electron paramagnetic resonance spectrum unambiguously indicates that the valence of manganese ions in this case is equal to 2+. The parameters of the spin Hamiltonian of Mn^{2+} ions in the $YAl_3(BO_3)_4$ matrix are determined at room temperature. The magnitude and sign of the fine structure parameter D allow the conclusion that the $YAl_3(BO_3)_4$ single crystals doped with manganese ions have a strong crystal field at the yttrium ion sites and easy-axis anisotropy.

1. INTRODUCTION

Crystals with magnetic subsystems formed by ions of different types exhibit remarkable magnetic properties. These properties are especially pronounced in rare-earth magnetic materials in which $4f$ ions of rare-earth metals interact with $3d$ transition metal ions. The majority of rare-earth metal ions are characterized by a strong anisotropy, and the magnetic anisotropy of the crystals formed by these ions, as a rule, is determined by the competition of anisotropic interactions between the rare-earth and transition metal ions.

Among the aforementioned crystals, there exists a class of borates with the structure of the natural mineral huntite $CaMg_3(CO_3)_4$. These compounds are of considerable interest not only in terms of their magnetic properties but also as multifunctional materials that are especially promising for use in constructing instruments due to their high thermal and chemical stabilities. The general formula for borates of this class is written as $AMe_3(BO_3)_4$, where A is a rare-earth metal and Me is a trivalent metal (Al, Ga, Cr, Fe, Sc) [1, 2]. Among them, aluminum borates $AAl_3(BO_3)_4$ have attracted the particular attention of researchers owing to their luminescence properties and possible application in laser technology.

Crystals of yttrium aluminum borate $YAl_3(BO_3)_4$ are characterized by a high hardness, nonhygroscopicity, and chemical stability. As was already mentioned, yttrium aluminum borate crystals have a huntite struc-

ture with space group $R32$ [3]. It is worth noting that, in the crystal structure of the $YAl_3(BO_3)_4$ borate, the Y^{3+} ions can be easily replaced by ions of other rare-earth metals, such as Nd^{3+}, Ho^{3+}, Er^{3+}, and Yb^{3+} ions. Moreover, it is known that $YAl_3(BO_3)_4$ borates doped with rare-earth metal ions are promising materials for use in laser engineering [4–6].

In this work, single crystals of the $YAl_3(BO_3)_4$ borate doped with manganese ions were studied using electron paramagnetic resonance spectroscopy.

2. SAMPLE SYNTHESIS AND DESCRIPTION OF THE CRYSTAL STRUCTURE

Trigonal single crystals of the $YAl_3(BO_3)_4$ borate doped with manganese ions were grown using the solution–melt method. The initial solution melt used for synthesizing our samples is characterized by a wide range of stability of the high-temperature trigonal phase of the $YAl_3(BO_3)_4$ borate and has the following composition: 85 wt % ($Bi_2Mo_3O_{12}$ + $0.5Li_2MoO_4$ + $2B_2O_3$) and 15 wt % $YAl_3(BO_3)_4$. A weighed portion of the initial solution melt (30 g) was prepared in a platinum crucible 50 ml in volume. The saturation temperature of this material varied in the range from 960 to 970°C. Manganese trioxide Mn_2O_3 was added to the reaction mixture at a temperature of 1000°C. The molar ratio between the Mn_2O_3 and Al_2O_3 oxides was equal to 0.28 in the first experiment and to 0.42, 0.69, and 1.15
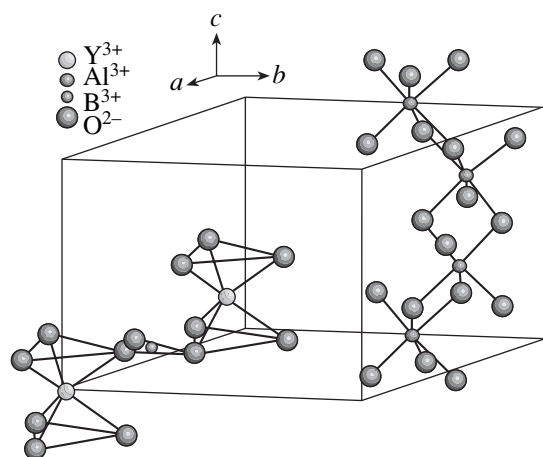
Fig. 1. Crystal structure of yttrium aluminum borate $YAl_3(BO_3)_4$. Not all atoms in the unit cell are shown. The unit cell parameters are as follows: $a = 9.295(3)$ Å, $c = 7.243(2)$ Å, $Z = 3$, and space group $R32$.

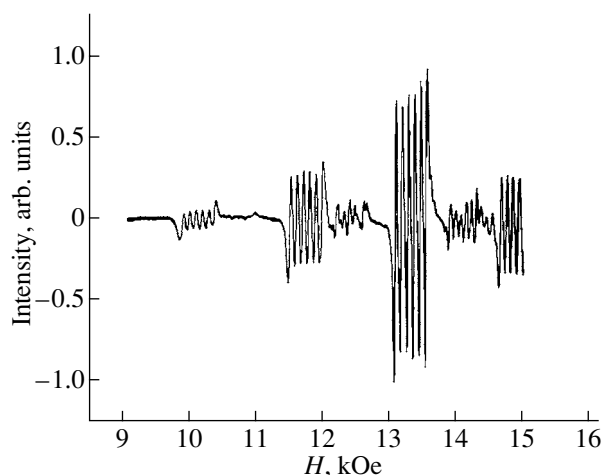**Fig. 2.** Electron paramagnetic resonance spectrum of the $YAl_3(BO_3)_4$ single crystal doped with manganese ions. Measurements were performed in magnetic fields applied parallel to the c axis at room temperature ($\nu = 36$ GHz).

in the second, third, and fourth experiments, respectively. The high-temperature trigonal phase remained stable even at a low degree of dilution, and the saturation temperature decreased with an increase in the concentration of the Mn_2O_3 dopant.

After the final homogenization, the solution melt was cooled to a temperature 10–15 K below the saturation temperature. Then, a platinum wire probe was immersed in the solution melt. The crystals spontaneously formed on the wire probe were further grown under gradual cooling at a rate of 0.5 K/h for 48 h. The wire probe together with the grown crystals was removed from the solution melt and cooled from the final growth temperature to room temperature outside the furnace. The transparent orange red crystals formed were 1–3 mm in size and had the form of hexagonal right-angle prisms.

It is remarkable that the doping of the $YAl_3(BO_3)_4$ single crystal with manganese leads to a decrease in both parameters of the trigonal unit cell. In particular, sample *4* (hereafter, the number of the sample corresponds to the number of the growth experiment in order of increasing manganese content) has the unit cell parameters $a = 9.276(2)$ Å and $c = 7.206(2)$ Å, whereas the $YAl_3(BO_3)_4$ single crystal without a manganese impurity has the parameters $a = 9.295(3)$ Å and $c = 7.243(2)$ Å. The main elements of the crystal structure of the yttrium aluminum borate under investigation are schematically shown in Fig. 1.

Considering the valence and distribution of manganese ions over lattice sites in grown crystals, we note that Aleksandrovskiĭ et al. [7] investigated the optical absorption and luminescence spectra of $GdGa_{0.5}Al_{0.5}(BO_3)_4$ trigonal crystals doped with manganese ions under similar conditions of solution melt crystallization and made the inference that the manga-

nese ions in these crystals are in divalent and tetravalent states. In the crystal structure of the $GdGa_{0.5}Al_{0.5}(BO_3)_4$ borate, larger sized Mn^{2+} ions occupy Gd^{3+} sites, whereas Mn^{4+} ions are located at the Ga^{3+} or Al^{3+} sites nearest to the Gd^{3+} sites.

3. EXPERIMENTAL TECHNIQUE, RESULTS, AND DISCUSSION

The electron paramagnetic resonance spectra of the $YAl_3(BO_3)_4$ single crystal doped with manganese ions were recorded on an RÉ-1308 EPR spectrometer operating in the Q band. The measurements were performed at room temperature in magnetic fields of up to 14 kOe for different orientations of the single crystal with respect to the external magnetic field.

Figure 2 shows a typical spectrum of the electron paramagnetic resonance in magnetic fields applied parallel to the trigonal axis c of the single crystal. The observed spectra consist of five lines with a fine structure. Each line is split into six hyperfine structure components. This structure is typical of manganese ions with the $3d^5$ electronic configuration (Mn^{2+}, electron spin $S = 5/2$, nuclear spin $I = 5/2$). Upon rotation of the magnetic field in the plane aligned with the c axis of the crystal, the resonance fields corresponding to the fine structure lines are characterized by the angular dependence $H_{res} \sim D(3\cos\theta - 1)$. Upon rotation of the magnetic field in the direction perpendicular to the c axis of the crystal, the positions of the resonance fields corresponding to the fine structure lines remain unchanged.

In the crystal structure of the $YAl_3(BO_3)_4$ borate, the yttrium ions are surrounded by six oxygen ions forming a trigonal bipyramid with symmetry $3a$ (32 or $R\bar{3}m$). The local quantization axes for all ions are aligned parallel to the c axis of the single crystal. The aluminum

ions are located in distorted octahedra composed of oxygen ions with symmetry 9d (.2 or R32). The local quantization axes of these octahedra form a twisted zig-zag chain along the c axis of the single crystal (Fig. 3). Therefore, if the manganese impurity ions were to replace the aluminum ions, the splitting of the fine structure lines in the electron paramagnetic resonance spectrum would be observed for any orientation of the magnetic field differing from **H ∥ c**. However, this splitting of the fine structure lines in the electron paramagnetic resonance spectra is not observed for intermediate orientations of the magnetic field. This fact indicates that the experimental electron paramagnetic resonance spectra are associated with the Mn^{2+} ions located at the yttrium ion sites.

In the case where the cubic symmetry with an axial distortion along the trigonal axis of the crystal is predominant, the spin Hamiltonian without regard for the fine structure can be represented in the following form [8]:

$$\mathcal{H} = \beta(\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}) - 2/3 B_4(O_4^0 + 20\sqrt{2}O_4^3)$$
$$+ (B_2^0 O_2^0 + B_4^0 O_4^0). \quad (1)$$

Here, $\beta(\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S})$ is the Zeeman energy; β is the Bohr magneton; $\mathbf{H}$ is the magnetic field vector; $\mathbf{g}$ is the spectroscopic splitting factor; $\mathbf{S}$ is the electron spin; $2/3 B_4(O_4^0 + 20\sqrt{2}O_4^3) + (B_2^0 O_2^0 + B_4^0 O_4^0)$ is the crystal potential reflecting the symmetry of the complex; O_2^0, O_4^0, and O_4^3 are the equivalent spin operators given by the formulas presented in [8]; and B_2^0, B_4^0, and B_4^3 are the coefficients of these operators.

The energy levels and frequencies of well-resolved transitions were calculated by Bleaney and Trenam [9] under the assumption of a dominant contribution from the Zeeman interaction in the framework of perturbation theory, including terms of the second order in A and D and terms of the first order in F, which in the general case are small (here, $A = 120B_4$ and $F = 180B_4^0$ are the parameters of the cubic crystal field and $D = 3B_2^0$ is the fine structure parameter).

Well-resolved transitions occur in the fields

$$M = \pm 5/2 \longleftrightarrow \pm 3/2:$$

$$g\beta H = g\beta H_0 \pm \{2D(1 - 3\cos^2\theta)$$
$$- 2pa - Fq/6\} - 32\delta_1 + 4\delta_2 + \varepsilon_1,$$

$$M = \pm 3/2 \longleftrightarrow \pm 1/2:$$

$$g\beta H = g\beta H_0 \pm \{D(1 - 3\cos^2\theta)$$
$$+ 5/2 pa + 5/24 Fq\} + 4\delta_1 - 5\delta_2 + \varepsilon_2,$$

$$M = +1/2 \longleftrightarrow -1/2:$$

$$g\beta H = g\beta H_0 + 16\delta_1 - 8\delta_2 + \varepsilon_3. \quad (2)$$
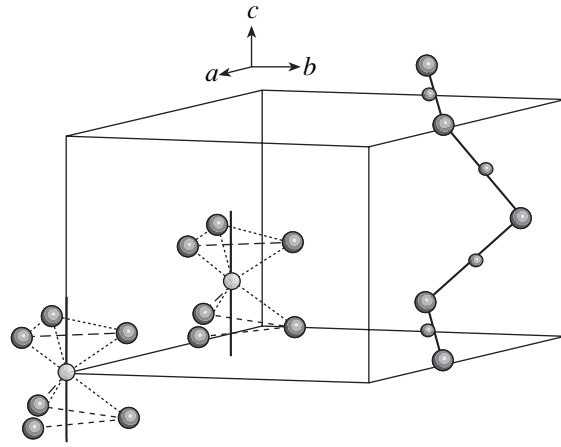

Fig. 3. Positions of the local quantization axes (solid lines) for ions at the yttrium and aluminum sites (designations are the same as in Fig. 1).

In these relationships, H is the magnetic field in which the line is observed at the frequency ν of the radiation used and $H_0 = h\nu/g\beta$ is the magnetic field in which the lines should be observed in the case where all the terms describing the fine structure are equal to zero.

The parameter p involved in the terms of relationships (2) is determined by the cubic crystal field and can be represented by the following expression [10]: $p = 1 - 5\varphi$, where $\varphi = l^2m^2 + m^2n^2 + n^2l^2$ and l, m, and n are the direction cosines of the magnetic fields vector H with respect to the axes of the cubic crystal field. The second-order terms introduced by the cubic crystal field have the form

$$\varepsilon_1 = a^2\{5/3\varphi(1 - 7\varphi)\}/g\beta H_0,$$
$$\varepsilon_2 = -a^2\{5/48(3 + 178\varphi - 625\varphi^2)\}/g\beta H_0, \quad (3)$$
$$\varepsilon_3 = a^2\{10/3\varphi(7 - 25\varphi)\}/g\beta H_0.$$

In relationships (2), θ is the angle between the magnetic field vector $\mathbf{H}$ and the trigonal axis of the crystal. Moreover, we introduced the following designations:

$$q = 35\cos^4\theta - 30\cos^2\theta + 3,$$
$$\delta_1 = D^2\cos^2\theta\sin^2\theta/g\beta H_0,$$
$$\delta_2 = D^2\sin^4\theta/4g\beta H_0.$$

The spin Hamiltonian parameters were calculated with the use of the resonance fields for the orientations **H ∥ c** and **H ⊥ c**, relationships (2), and the Maple program package for mathematical manipulations. As a

result, we obtained the following values of the spin Hamiltonian parameters:

$$g_\parallel = 1.9982 \pm 0.00005, \quad g_\perp = 1.9924 \pm 0.00005,$$

$$D = -783.7 \pm 0.1 \text{ Oe}, \quad |a| = 0.015 \pm 0.009 \text{ Oe},$$

$$|F| = 13.6 \pm 0.2 \text{ Oe}.$$

The hyperfine splittings averaged over all observed transitions are $|A_\parallel| = 95 \pm 4$ Oe and $|A_\perp| = 91 \pm 5$ Oe. The fine structure parameter $|D|$ turns out to be anomalously large as compared to the values characteristic of Mn^{2+} ions [11]. The sign of the fine structure parameter D was determined by measuring the relative intensities of the low-field and high-field lines of the fine structure. At liquid-helium temperature, the intensity of the low-field line appears to be considerably higher than the intensity of the high-field line. This finding unambiguously indicates that the fine structure parameter is negative in sign.

It should be noted that all the electron paramagnetic resonance spectra measured in our work contain lines whose intensities are one order of magnitude lower than the intensities of the main lines of the fine structure. Moreover, the extrema revealed in the angular dependence of the resonance fields do not coincide with the extrema obtained for the main lines of the fine structure and the splitting of these lines is observed for intermediate orientations of the magnetic field. We could not perform a detailed analysis of these weak lines, because they considerably overlap with the main lines of the fine structure. Quite possibly, the presence of additional weak lines in the electron paramagnetic resonance spectra of the single crystal under investigation is associated with the small number of Mn^{4+} ions located at the aluminum ion sites.

4. CONCLUSIONS

Thus, the results of the investigation performed have demonstrated that the electron paramagnetic resonance spectrum of an yttrium aluminum borate single crystal doped with manganese corresponds to divalent manganese ions located at yttrium ion sites in the crystal lattice of the compound and is adequately described by the Hamiltonian $\mathcal{H} = \beta(\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S}) - 2/3B_4(O_4^0 + 20\sqrt{2}O_4^3) + (B_2^0 O_2^0 + B_4^0 O_4^0)$.

The fine structure parameter $D = 3B_2^0 = -783.7 \pm 0.1$ Oe determined from the electron paramagnetic resonance spectra recorded for different orientations of the magnetic field turned out to be substantially larger than the values characteristic of Mn^{2+} ions. This indicates that the $YAl_3(BO_3)_4$ single crystals doped with manganese ions have a strong crystal field. The analysis of the relative intensities of the extreme lines in the electron paramagnetic resonance spectrum revealed that the crystal under investigation possesses an easy-axis anisotropy.

REFERENCES

1. G. Blasse and A. Bril, Phys. Status Solidi **20**, 551 (1967).
2. V. I. Chani, M. I. Timoshechkin, K. Inoue, K. Shimamura, and T. Fukuda, Neorg. Mater. **30**, 1570 (1994) [Inorg. Mater. **30**, 1466 (1994)].
3. N. I. Leonyuk and L. I. Leonyuk, Prog. Crystal Growth Charact. Mater. **31**, 179 (1995).
4. N. I. Leonyuk, E. B. Koporulina, K. L. Bray, and D. Hansen, J. Cryst. Growth **191**, 767 (1998).
5. A. Brenier, Opt. Commun. **141**, 221 (1997).
6. D. Jaque, J. Capmany, and S. Qarcia, Appl. Phys. Lett. **75**, 325 (1999).
7. A. S. Aleksandrovskiĭ, L. N. Bezmaternykh, A. S. Krylov, V. E. Temerov, and S. A. Kharlamova, in *Abstracts of the VIII International Workshop on Luminescence and Laser Physics, Irkutsk, Russia, 2002* (Irkutsk, 2002), p. 11 [in Russian].
8. A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transitions Ions* (Clarendon, Oxford, 1970; Mir, Moscow, 1972).
9. B. Bleaney and R. S. Trenam, Proc. R. Soc. London, Ser. A **223**, 1 (1954).
10. R. de L. Kronig and C. J. Bouwkamp, Physica's Gravenhage) **6**, 290 (1939).
11. S. A. Al'tshuler and B. M. Kozyrev, *Electron Paramagnetic Resonance* (Academic, New York, 1964; Nauka, Moscow, 1972).

Translated by O. Borovik-Romanova