ORDER, DISORDER, AND PHASE TRANSITION IN CONDENSED SYSTEM

Electron Paramagnetic Resonance of Cr^{3+} Ions in ABO_3 (A = Sc, Lu, In) Diamagnetic Crystals

A. M. Vorotynov[a]*, S. G. Ovchinnikov[a], V. V. Rudenko[a], and O. V. Vorotynova[b]

[a] *Kirenskii Institute of Physics, Siberian Branch, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia*
[b] *Siberian Federal University, Krasnoyarsk, 660041 Russia*
*e-mail: sasa@iph.krasn.ru
Received October 20, 2015

Abstract—A magnetic resonance method is applied to the investigation of a number of isostructural diamagnetic compounds ABO_3 (A = Sc, Lu, In) with small additions of Cr^{3+} ions ($S = 3/2$) sufficient to observe single-ion spectra. It is shown that the resonance spectra for isolated Cr^{3+} ions can be described to a good accuracy by the ordinary axial spin Hamiltonian for $3d$ ions in octahedral oxygen environment. The parameters of the spin Hamiltonian are determined. It is established that Cr^{3+} ions in these crystals are characterized by easy-axis-type anisotropy.

1. INTRODUCTION

Borates of transition metals with chemical formula ABO_3 (A = Fe, V, Cr, Ti) have attracted attention because of the variety of their physical properties that are manifested in this isostructural series of compounds [1]. However, a number of borates of $3d$ metals ABO_3, except for $FeBO_3$, remain poorly studied. For example, from among the whole series of $3d$ borates, magnetic anisotropy has been experimentally investigated to date only in $FeBO_3$ [2].

In the present study, we apply the electron paramagnetic resonance method to the experimental investigation of the anisotropic properties of Cr^{3+} ions in diamagnetic matrices of isostructural compounds of ABO_3 (A = Sc, Lu, In) borates. In this case, a Cr^{3+} ion is chosen due to the unusual magnetic properties of the isostructural crystal $CrBO_3$ [3]. In [4], the authors showed that the magnetic properties of the $CrBO_3$ crystal can be described on the basis of a simple model of a collinear two-sublattice antiferromagnet with magnetic moments along a third-order axis. The authors of [3] suggested, on the basis of static magnetic measurements, that it is more probable that, on the contrary, the antiferromagnetism vector of $CrBO_3$ lies in a plane close to the base plane.

We assume that the study of electron paramagnetic resonance in ABO_3 (A = Sc, Lu, In) diamagnetic crystals will allow one to determine the type of anisotropy of Cr^{3+} ions in these compounds.

2. SAMPLES AND THE EXPERIMENTAL METHOD

ABO_3 (A = Sc, Lu, In) crystals with small (about 5% at of A) addition of Cr^{3+} were grown by a technology similar to that of [5]. In this technology, a Cr^{3+} ion substitutes for the A ions. We obtained single crystals in the form of thin plates with a size of 2×2 mm and thickness of about 0.1 mm with a smooth shining surface of light gray color.

ABO_3 (A = Sc, Lu, In) isostructural crystals have a trigonal unit cell with $R\bar{3}c$ symmetry, the point group symmetry of the A ion being $(-3m)$. The parameters of the unit cell are presented in Table 1 [6] for Sc, In, and Lu. The C_3 axis of the crystal is normal to the plane of the plate of a sample (the c axis in Fig. 1).

The A ions are located in the octahedra formed by oxygen ions bound to boron ions by a strong covalent bond. The electron paramagnetic resonance measurements were carried out on a Bruker Elexsys E-580

Table 1. Unit cell parameters of ABO_3 crystals (data from [6])

ABO_3	Effective ion radius r, Å	Unit cell parameters, Å		c/a
		a	c	
Sc	0.745	4.759	15.321	3.22
In	0.800	4.823	15.456	3.21
Lu	0.861	4.915	16.211	3.30

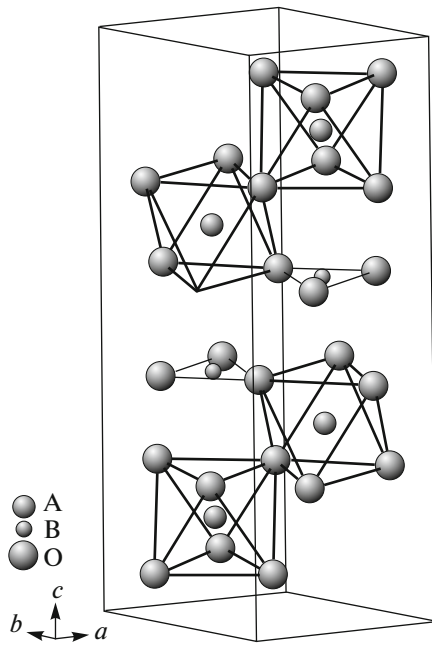The effective ion radius of Cr^{3+} is $r = 0.615$ Å.

Fig. 1. Crystal structure of ABO_3.

spectrometer operating in the X band at temperatures of 300 K and 77 K.

3. EXPERIMENTAL RESULTS

An example of a resonance spectrum of a Cr^{3+} ion in $ScBO_3$ at various temperatures for the external magnetic field vector in the base plane of the crystal is demonstrated in Fig. 2. The set of weak lines between intense single-ion absorption lines of Cr^{3+} ion (in magnetic fields from 2000 to 6000 Oe) belongs to the

spectrum of Cr^{3+}–Cr^{3+} ion pairs and is not discussed in the present paper.

The angular dependence of the resonance spectra measured under the rotation of the external magnetic field in the *aa* plane of ABO_3 (A = Sc, Lu, In) crystals revealed the axial symmetry about the crystallographic axis C_3. The angular dependence of the resonance fields of the transitions observed in the *ac* plane are shown in Fig. 3. Note that the observed spectra for the $ScBO_3$ compound have a two orders of magnitude higher intensity compared with the spectra of $InBO_3$ and $LuBO_3$ in spite of the fact that nearly identical Cr_2O_3 batch loading was used during the synthesis of the crystals.

The resonance spectra for isolated ions of Cr^{3+} can be described to a good accuracy by the following axial spin Hamiltonian for $3d$ ions:

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + D S_z^2, \quad (1)$$

where D is the axial constant of the spin Hamiltonian, $g_\parallel$ and $g_\perp$ are the values of the g factor for parallel and perpendicular orientations of the external magnetic field with respect to the C_3 axis of the crystal, β is the Bohr magneton, S_i and H_i are the projections of the spin of a Cr^{3+} ion and the external magnetic field to the C_3 axis of the crystal, and $S = 3/2$ is the spin of the Cr^{3+} ion.

The experimental and theoretical spectra were fitted with the use of the XSophe software [7]. The results are presented in Table 2.

The values of the g factors obtained are nearly isotropic and correspond to appropriate values for d^3 ions in the octahedral environment [8]. The spin Hamiltonian constant D correlates with those in the earlier investigated compounds Al_2O_3 [9] and $ZnGa_2O_4$ [10, 11], in which the Cr^{3+} ion is also in an octahedral
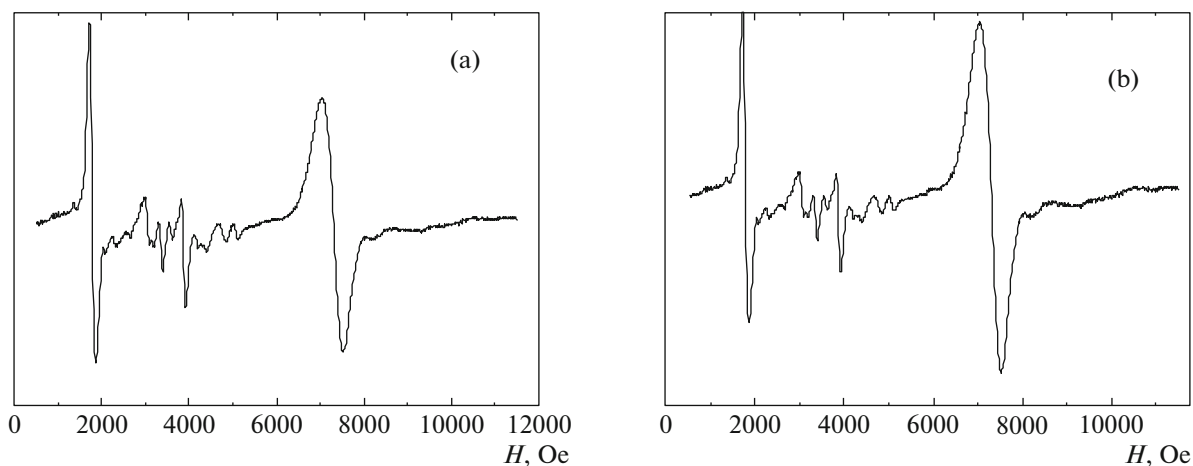

Fig. 2. Resonance spectra of a Cr^{3+} ion in $ScBO_3$ at various temperatures. An external magnetic field is applied in the base plane of the crystal; (a) $T = 300$ K, and (b) T = 77 K.

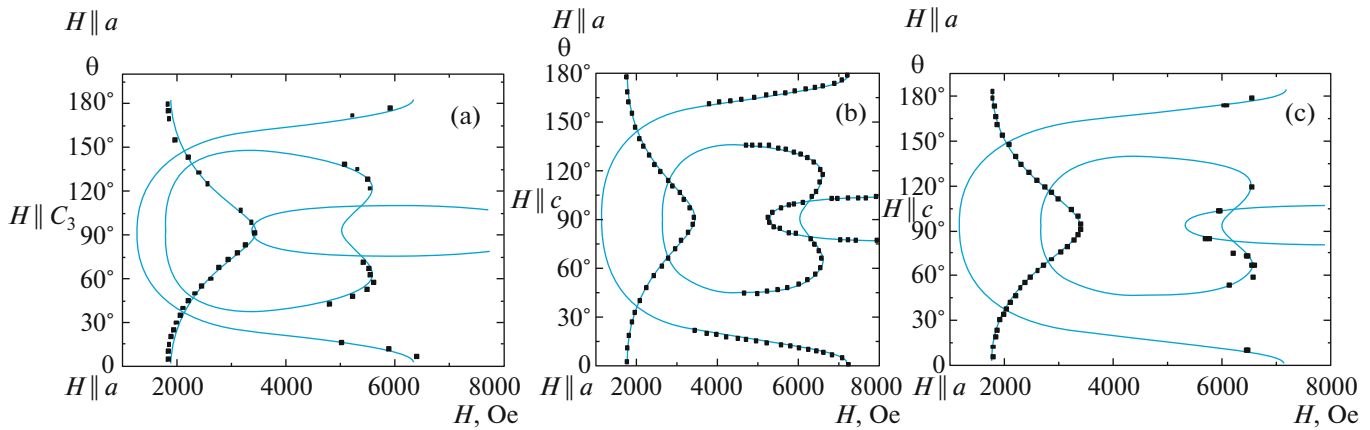**Fig. 3.** (Color online) Angular dependence of resonance fields observed in ABO_3 crystals; (a) A = In, (b) A = Sc, and (c) A = Lu. Dots represent experiment and solid curves, calculation (see Table 1).
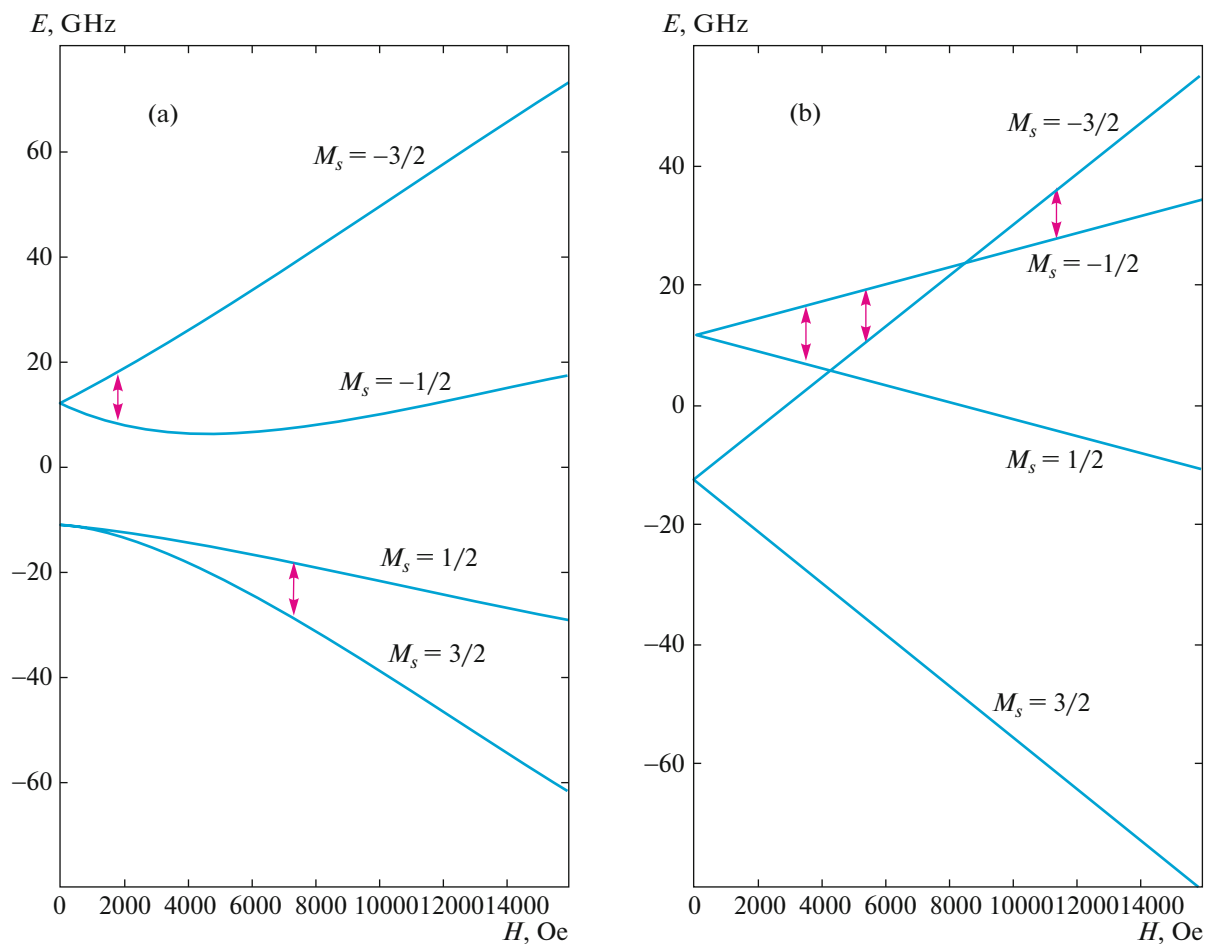

Fig. 4. (Color online) Calculated schemes of energy levels of a Cr^{3+} ion in $ScBO_3$; (a) external magnetic field is parallel to the base plane of the crystal, and (b) external magnetic field is parallel to the C_3 axis.

coordination. The sign of the constant D of the Cr^{3+} ion in ABO_3 (A = Sc, Lu, In) is determined from the ratio of the intensities of the transitions $-3/2 \leftrightarrow -1/2$ and $1/2 \leftrightarrow 3/2$ (see Figs. 2 and 4) at temperatures 300 K and 77 K.

As an example, Fig. 4 demonstrates the calculated schemes of energy levels of the Cr^{3+} ion in $ScBO_3$.

The value of D in the $InBO_3$ compound significantly differs from the values in $ScBO_3$ and $LuBO_3$,

Table 2. Parameters of the spin Hamiltonian for an isolated Cr^{3+} ion in the ABO_3 matrix at room temperature

A	$g_\parallel$	$g_\perp$	D, cm^{-1}
In	1.980(1)	1.982(1)	−0.314(1)
Sc	1.980(1)	1.982(1)	−0.402(2)
Lu	1.980(1)	1.982(1)	−0.407(3)

Note: The numbers in parentheses indicate an error estimate in the last digit.

which poorly correlates with the variation of the lattice parameters (see Table 1). In our view, this behavior can be accounted for by both the difference in the degree of covalent bonds of the Cr^{3+} ion in diamagnetic matrices of ABO_3 (A = Sc, Lu, In) and the difference in the hybridization degree of electron orbitals of ions in the matrix.

Thus, as a result of investigation of the single-ion magnetic resonance spectra of Cr^{3+} ions in ABO_3 (A = Sc, Lu, In) diamagnetic matrices, we have determined the parameters of the uniaxial spin Hamiltonian and have shown that Cr^{3+} ions in these crystals are characterized by easy-axis-type anisotropy.

REFERENCES

1. N. B. Ivanova, V. V. Rudenko, A. D. Balaev, N. V. Kazak, V. V. Markov, S. G. Ovchinnikov, I. S. Edelman, A. S. Fedorov, and P. V. Avramov, J. Exp. Theor. Phys. **94**, 299 (2002).

2. G. V. Bondarenko, S. G. Ovchinnikov, V. V. Rudenko, V. M. Sosnin, V. I. Tugarinov, and A. M. Vorotynov, J. Magn. Magn. Mater. **335**, 90 (2013).

3. A. D. Balaev, N. B. Ivanova, N. V. Kazak, S. G. Ovchinnikov, V. V. Rudenko, and V. M. Sosnin, Phys. Solid State **45**, 287 (2003).

4. T. A. Bither, C. G. Frederick, T. E. Gier, J. F. Weiher, and H. S. Young, Solid State Commun. **8**, 109 (1970).

5. V. V. Rudenko, Inorg. Mater. **34**, 1253 (1998).

6. T. A. Bither and H. S. Yang, J. Solid State Chem. **6**, 502 (1973).

7. M. Griffin, A. Muys, C. Noble, D. Wang, C. Eldershaw, K. E. Gates, K. Burrage, and G. R. Hanson, Mol. Phys. Rep. **26**, 60 (1999).

8. S. A. Altshuler and B. M. Kozyrev, *Electron Paramagnetic Resonance of Compounds of Intermediate Group Elements* (Nauka, Moscow, 1972) [in Russian].

9. M. J. Berggren, G. F. Imbusch, and P. L. Scott, Phys. Rev. **188**, 675 (1969).

10. J. C. M. Henning, J. H. den Boeff, and G. G. P. van Gorkom, Phys. Rev. B **7**, 1825 (1973).

11. G. L. McPherson and Wai-ming Heung, Solid State Commun. **19**, 53 (1976).

Translated by I. Nikitin