

ORDER, DISORDER, AND PHASE TRANSITION  
IN CONDENSED SYSTEM

# Electron Paramagnetic Resonance of $\text{Cr}^{3+}$ Ions in $\text{ABO}_3$ ( $A = \text{Sc, In, Ga}$ ) Diamagnetic Crystals<sup>1</sup>

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**Abstract**—A magnetic resonance method is applied to the investigation of a number of isostructural diamagnetic compounds  $\text{ABO}_3$  ( $A = \text{Sc, In, and Ga}$ ) with small additions of  $\text{Cr}^{3+}$  ions ( $S = 3/2$ ) sufficient to observe single-ion and pair spectra. It is shown that the resonance spectra for isolated  $\text{Cr}^{3+}$  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 for single  $\text{Cr}^{3+}$  ion and  $\text{Cr}^{3+}$ – $\text{Cr}^{3+}$  pair. Lattice distortions of the parent  $\text{ABO}_3$  crystals caused by the  $\text{Cr}^{3+}$  impurities is discussed.

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## 1. INTRODUCTION

Borates of transition metals with chemical formula  $\text{ABO}_3$  ( $A = \text{Fe, V, Cr, Ti}$ ) 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  $\text{ABO}_3$ , except for  $\text{FeBO}_3$ , remain poorly studied. For example, from among the whole series of  $3d$  borates, magnetic anisotropy has been experimentally investigated to date only in  $\text{FeBO}_3$  [2]. In the present study, we apply the electron paramagnetic resonance method to the experimental investigation of the anisotropic properties of  $\text{Cr}^{3+}$  ions in diamagnetic matrices of isostructural compounds of  $\text{ABO}_3$  ( $A = \text{Sc, In, Ga}$ ) borates. In this case, a  $\text{Cr}^{3+}$  ion was chosen due to the unusual magnetic properties of the isostructural crystal  $\text{CrBO}_3$  [3]. For example, in [4] the authors showed that the magnetic properties of the  $\text{CrBO}_3$  crystal can be described on the basis of a simple model of a collinear two-sublattice antiferromagnet with magnetic moments along a [111] 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  $\text{CrBO}_3$  lies in a plane close to the base plane.

The present paper is the continuation of the investigations presented by us in [5]. In [5] only single ion spectra for  $A = \text{In, Sc, and Lu}$  were discussed and was pointed out the presence of a  $\text{Cr}^{3+}$ – $\text{Cr}^{3+}$  pair spectra.

In this paper we present the new data of the Electron Spin Resonance (ESR) spectra of single  $\text{Cr}^{3+}$  ions in diamagnetic matrix  $\text{GaBO}_3$  and pair spectra of  $\text{Cr}^{3+}$ – $\text{Cr}^{3+}$  ions were treated and discussed for  $A = \text{Sc, In, Ga}$  compounds.

## 2. MATERIALS AND METHODS

$\text{ABO}_3$  ( $A = \text{Sc, In, Ga}$ ) crystals with small (about 5 at % of  $A$ ) addition of  $\text{Cr}^{3+}$  ions were grown from the solution-melt with composition  $\text{Cr}_2\text{O}_3$ – $\text{M}_2\text{O}_3$ – $\text{B}_2\text{O}_3$ –(70PbO–30PbF<sub>2</sub> wt %). The detailed synthesis technology is described in [6]. In this technology, a  $\text{Cr}^{3+}$  ions substitute the  $A$  ions. We obtained single crystals in the form of thin plates with a size of  $2 \times 2$  mm and thickness of about 0.1 mm with a smooth shining surface of light gray color.  $\text{ABO}_3$  ( $A = \text{Sc, In, Ga}$ ) isostructural crystals have a rhombohedral symmetry in space group  $R\bar{3}c$ , the point group symmetry of the  $A$  ion is  $(-3m)$ . Parameters of the unit cell were determined by using X-ray Smart APEX II (Bruker) (Mo  $K_\alpha$  radiation) installation at room temperature and are presented in Table 1 for Sc, In, Ga.

The  $C_3$ -axis of the crystal is normal to sample plate (the  $c$ -axis in Fig. 1). The  $A$  ions are located in the octahedrons formed by oxygen ions connected with boron ions by a strong covalent bond.

In addition, there is a possibility for nearest  $\text{Cr}^{3+}$  ions to form a magnetically coupled pairs. The projection of the pair's axes onto basal plane of the crystal is

<sup>1</sup> The article was translated by the authors.

**Table 1.** Unit cell parameters of  $ABO_3$  crystals

$ABO_3$	Effective ion radius $r$ , Å [7]	Unit cell parameters, Å		$c/a$	Distance, Å	$\theta$ , deg
		$a$	$c$			
Sn	0.745	4.7532(5)	15.2669(2)	3.212	3.7424	47.163
In	0.800	4.806	15.348	3.194	3.7739	47.33
Ga	0.620	4.578(1)	14.183(5)	3.098	3.5459	48.2

Note: The effective ion radius of  $Cr^{3+}$  is  $r = 0.615$  Å,  $\theta$  is angle between pair axis and  $C_3$ -axis of the crystal

presented in Fig. 2. All pairs are magnetically equivalent. The  $Cr^{3+}-Cr^{3+}$  distances and angles between  $C_3$  axis of the crystal and pair axes are shown in Table 1.

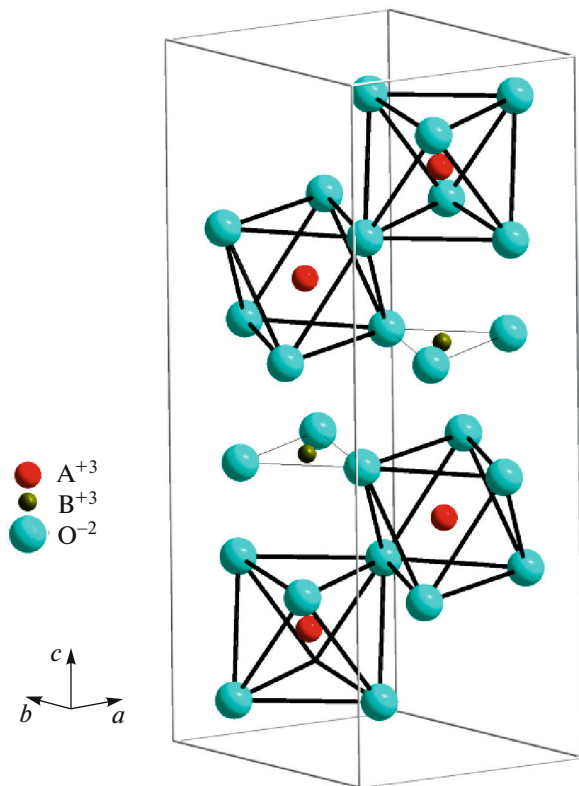
The electron paramagnetic resonance measurements were carried out on a Bruker Elexsys E-580 spectrometer operating at  $X$ -band at temperatures 300 and 77 K.

### 3. RESULTS

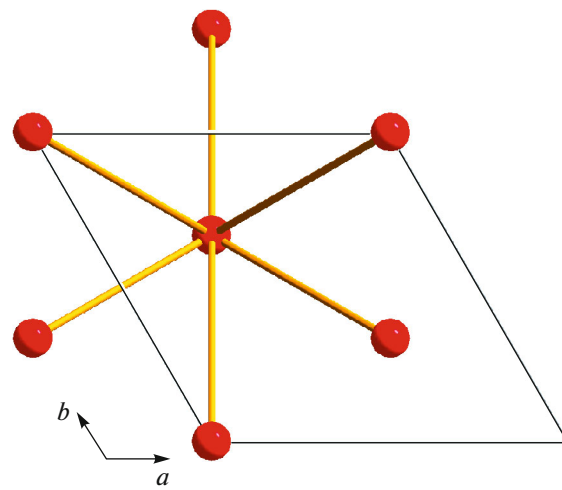
#### 3.1. Single-Ion Spectra

In this chapter we present the experimental results for the single ion ESR spectra of  $Cr^{3+}$  ions obtained in  $ABO_3$  (Sc, In, Ga) compounds. So far this paper is the continuation of the investigations presented by us in

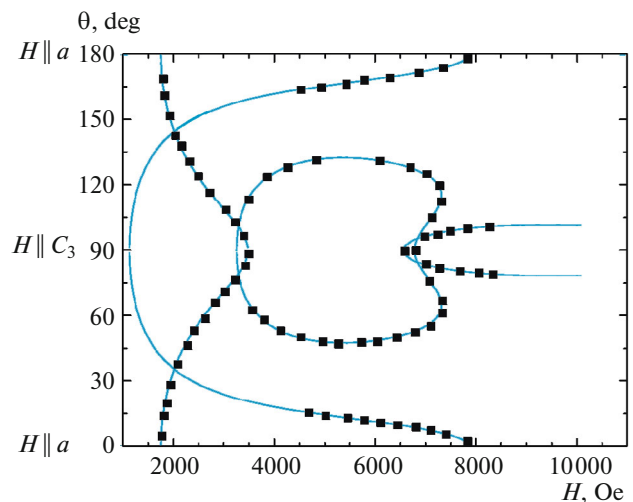
[5], let us consider more detailed only experimental data for the  $GaBO_3$  crystal, that was not discussed previously.



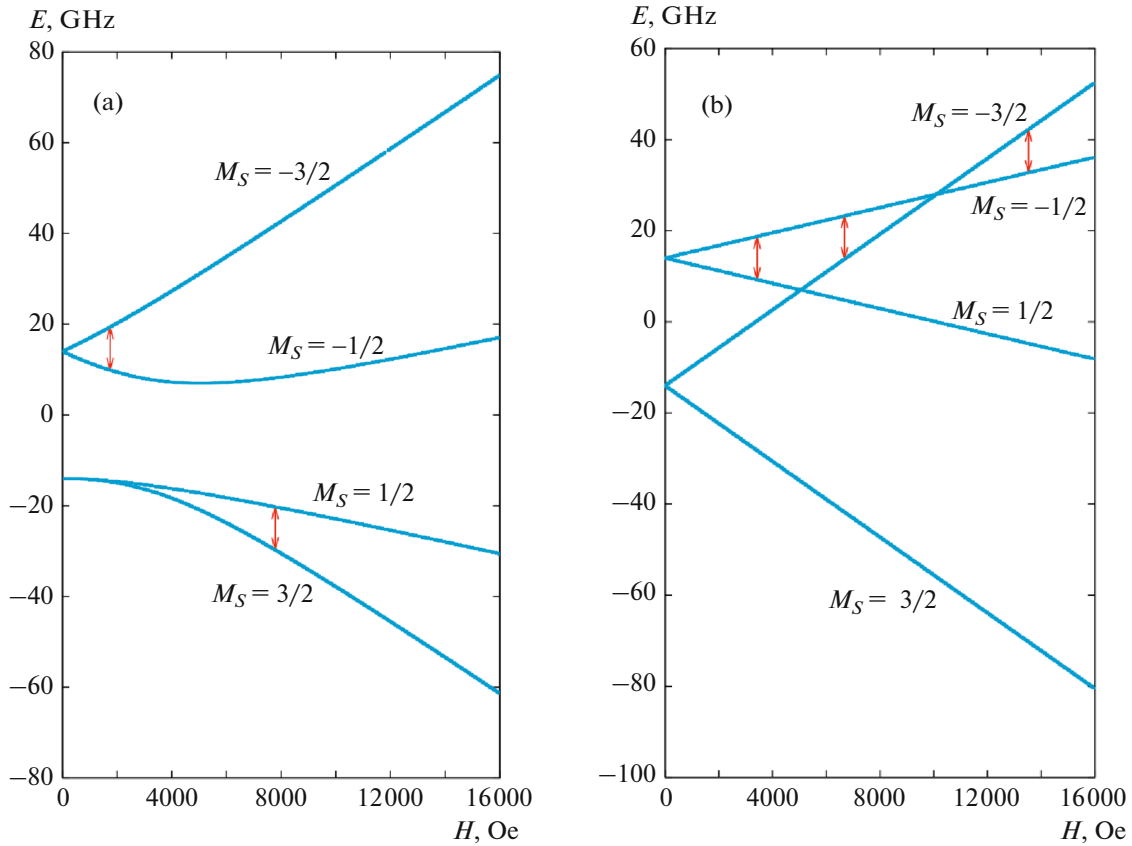
**Fig. 1.** (Color online) Crystal structure of  $ABO_3$ .



**Fig. 2.** (Color online) Projection of the axes of  $Cr^{3+}$  ions pairs onto basal plane of the crystal. Only  $Cr^{3+}$  ions are shown.



**Fig. 3.** (Color online) Angular dependence of resonance fields of the ESR signals observed in  $GaBO_3$  ( $ac$ ) plane of the crystal. Dots represent experiment and solid curves—calculation (see Table 2).



**Fig. 4.** (Color online) Calculated schemes of energy levels of a  $\text{Cr}^{3+}$  ion in  $\text{GaBO}_3$ ; (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.

The angular dependence of the resonance fields of the single  $\text{Cr}^{3+}$  ions transitions observed in the  $(ac)$  plane are shown in Fig. 3. The resonance spectra for isolated ions of  $\text{Cr}^{3+}$  can be described by the following axial spin Hamiltonian for  $3d$  ions:

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

where  $D$  is the axial constant of the spin Hamiltonian,  $g_{\parallel}$  and  $g_{\perp}$  are the values of the  $g$ -tensor for parallel and perpendicular orientations of the external magnetic field with respect to the  $C_3$  axis of the crystal,  $\beta$  is the Bohr magneton,  $S_i$  and  $H_i$  are the projections of the spin of a  $\text{Cr}^{3+}$  ion and the external magnetic field to the  $C_3$  axis of the crystal, and  $S = 3/2$  is the spin of the  $\text{Cr}^{3+}$  ion. The experimental and theoretical spectra were fitted with the use of the XSophe software [8]. The results are presented in Table 2.

The values of the  $g$ -tensor obtained are nearly isotropic and correspond to appropriate values for  $d^3$  ions in the octahedral environment [9]. The spin-Hamiltonian constant  $D$  correlates with those in the earlier investigated compounds  $\text{Al}_2\text{O}_3$  [10] and  $\text{ZnGa}_2\text{O}_4$  [11, 12], in which the  $\text{Cr}^{3+}$  ion is also in an octahedral

coordination. The  $D$  sign for  $\text{Cr}^{3+}$  ion in  $\text{GaBO}_3$  was determined by comparison of the resonance lines intensities of  $M_S = 1/2 \leftrightarrow 3/2$  and  $M_S = -1/2 \leftrightarrow -3/2$  transitions at 300 and 77 K respectively as in [5].

As an example, Fig. 4 demonstrates the calculated schemes of energy levels of the  $\text{Cr}^{3+}$  ion in  $\text{GaBO}_3$ .

### 3.2. Pair Spectra

In compounds with  $A = \text{Sc}, \text{In}, \text{Ga}$  the  $\text{Cr}^{3+}-\text{Cr}^{3+}$  pair spectra were observed. The example of the pair spectra for  $\text{ScBO}_3$  at room temperature is presented in

**Table 2.** Parameters of the spin Hamiltonian (1) for an isolated  $\text{Cr}^{3+}$  ion in the  $\text{ABO}_3$  matrix at room temperature

A	$g_{\parallel}$	$g_{\perp}$	$D, \text{cm}^{-1}$
In [5]	1.980(1)	1.982(1)	-0.314(1)
Sc [5]	1.980(1)	1.982(1)	-0.402(2)
Ge (new data)	1.980(1)	1.982(1)	-0.467(1)

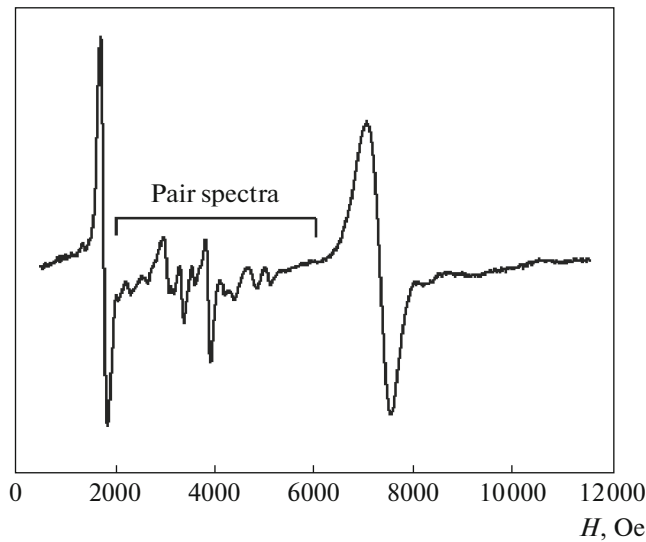


Fig. 5. The example of the  $\text{Cr}^{3+}\text{-Cr}^{3+}$  pair spectra for  $\text{ScBO}_3$  at room temperature in basal plane of the crystal.

Fig. 5. The intense line in the right and left sides corresponds to the single ion transitions.

$\text{Cr}^{3+}\text{-Cr}^{3+}$  pair forms by the nearest neighbors with the distances  $r = 3.7424, 3.774,$  and  $3.5459 \text{ \AA}$  for A = Sc, In, and Ga compounds respectively (see Table 1). The angle between pair axes and  $C_3$  axis of the crystals is equal approximately  $\theta \approx 47^\circ$  for all compounds. When two  $\text{Cr}^{3+}$  ions interact to form a magnetically coupled pair, the spins ( $s$ ) on each ion combine as vectors to produce a manifold of four spin states each characterized by a total spin quantum number  $S$ , which value varies from  $(s_1 + s_2), (s_1 + s_2 - 1) \dots$  to 0. Assuming that the energy intervals between these spin states are large compared with the other magnetic interactions, a separate spin Hamiltonian may be written for each spin state. In our case, it was possible to identify resonance spectra for pair multiplets with total spin  $S = 2$  and 3 only. The angle dependencies of the resonance fields of the signals in basal plane of the crystals are shown in Figs. 6–8.

Fitting of the experimental spectra were carried out with XSophe program [8] and the spin Hamiltonian (2).

$$H = -g_{\parallel}\beta H_z S_z - g_{\perp}\beta(H_x S_x + H_y S_y) + D_S S_z^2 + E_S(S_x^2 - S_y^2) + 1/60[B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4], \quad (2)$$

where  $g_{\parallel}$  and  $g_{\perp}$  are the values of the  $g$ -tensor for parallel and perpendicular orientations of the external magnetic field with respect to the  $C_3$  axis of the crystal,  $\beta$  is the Bohr magneton. Spin operators  $O_4^0, O_4^2,$  and  $O_4^4$  are mentioned in [13]. Third and fourth terms in (2) describe the value of the “fine” structure for the total spin  $S$  of pair’s multiplet and have the form [13]

$$D_S = (3\alpha_S D_e + \beta_S D_c), \quad E_S = (\alpha_S E_e + \beta_S E_c), \quad (3)$$

where  $D_e, E_e$  are the dipole-dipole interaction constants (assuming isotropic exchange interaction) in point approximation,  $D_c, E_c$ —“single ion” multiplet terms and

$$\alpha_S = \frac{1}{2} \frac{S(S+1) + 4s_i(s_i+1)}{(2S-1)(2S+3)}, \quad (4)$$

$$\beta_S = \frac{3S(S+1) - 3 - 4s_i(s_i+1)}{(2S-1)(2S+3)}.$$

The  $N \leftrightarrow J$  symbols in Figs. 6–8 denote transitions between corresponding  $M_S$  numbers in pair multiplets. Note, that the real experimental spectrum for each crystal consists from three identical spectra from Figs. 6–8 corresponding to  $\text{Cr}^{3+}\text{-Cr}^{3+}$  pairs rotated by 60 degrees in basal plane (see Fig. 2).

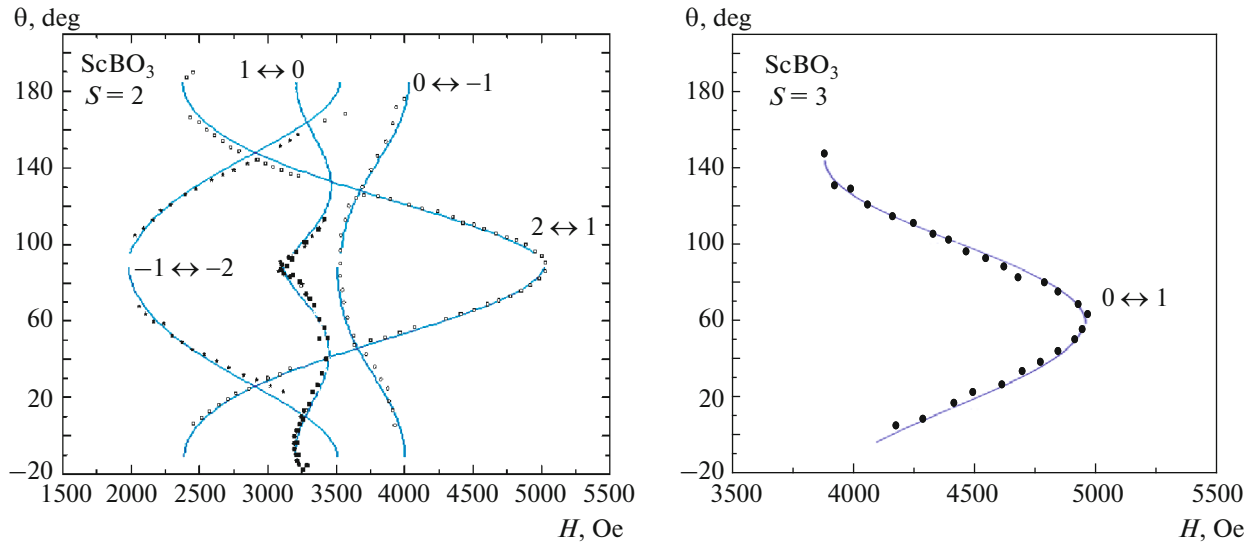
The best fitting spin-Hamiltonian (2) values are presented in Table 3.

#### 4. DISCUSSION

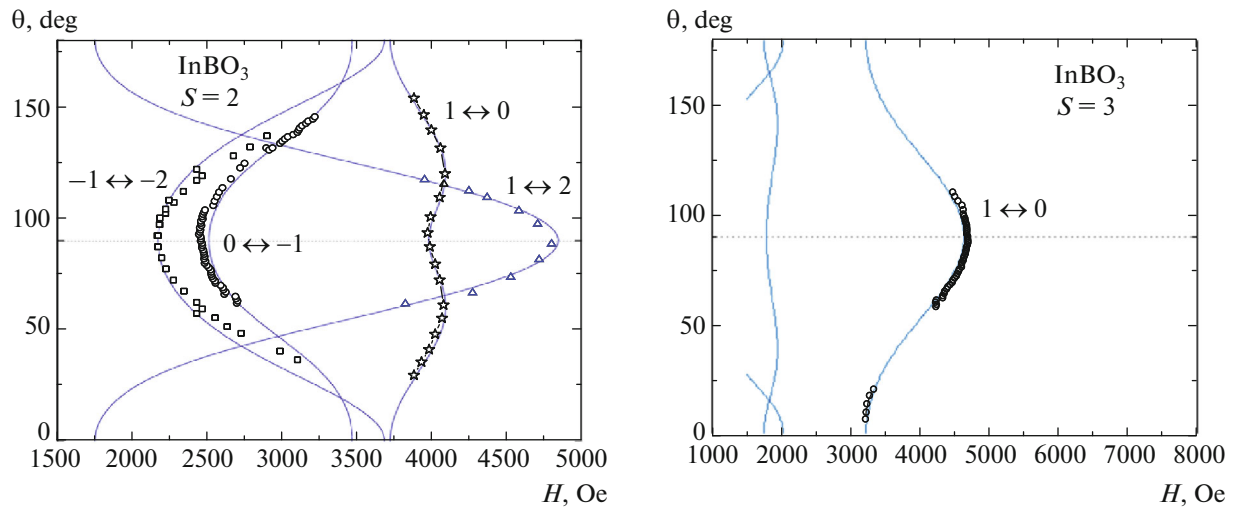
Let us, firstly, discuss the experimental results for  $\text{Cr}^{3+}\text{-Cr}^{3+}$  pairs in  $\text{ABO}_3$  crystals. The  $D_e$  term can be obtained directly from  $D_{S=2}$  value (Eq. (3)) since there is no lattice contribution ( $\beta = 0$  for  $S = 2$  (Eq. (4))).

Table 3. Spin-Hamiltonian (2) values ( $\text{cm}^{-1}$ ) for the  $\text{Cr}^{3+}\text{-Cr}^{3+}$  pairs in  $\text{ABO}_3$  crystals. The numbers in parentheses are the estimated errors in the last decimal place of the reported parameters.  $g_{\parallel} = 1.980$  and  $g_{\perp} = 1.982$  for all crystals

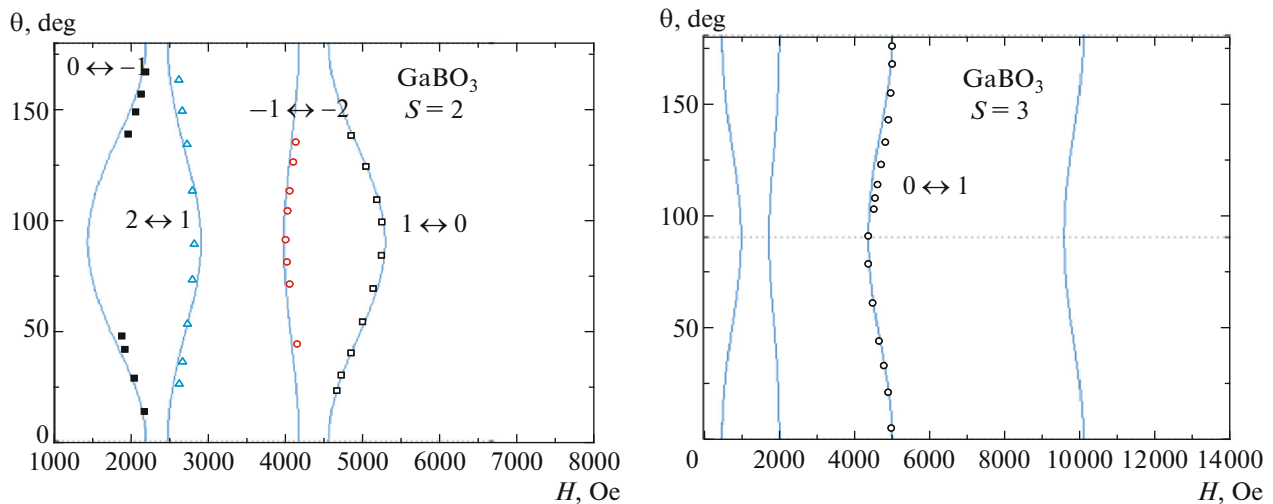
A	$S = 2$					$S = 3$			
	$D_S$	$E_S/D_S$	$B_4^0$	$B_4^2$	$B_4^4$	$D_S$	$E_S/D_S$	$B_4^0$	$B_4^2$
Ga	-0.022(3)	-0.03(3)	-0.18(3)	0.10(3)	0	-0.22(1)	0.028	0.0073	0
Sc	-0.061(1)	-0.097	0.047(1)	-0.05(1)	0.02	-0.197(1)	0.06(1)	0.01	-0.018
In	-0.078(1)	-0.0656	-0.0341	-0.009	-0.01	-0.173(6)	-0.1	-0.005	0.03



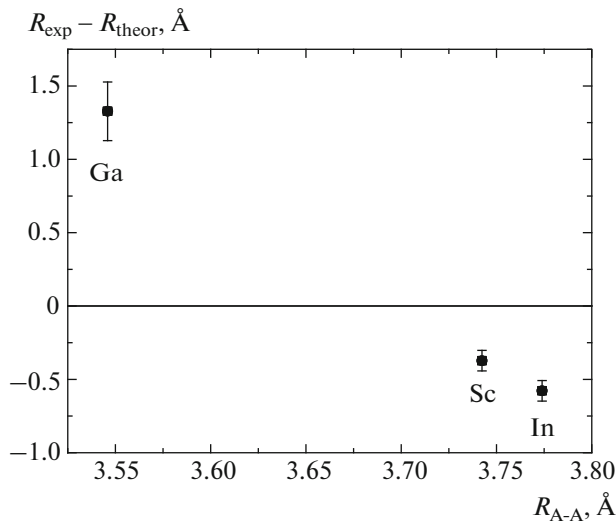
**Fig. 6.** (Color online) Angle dependencies of the resonance fields in basal plane of the crystals for  $\text{ScBO}_3$  crystal at room temperature. Dots—experiment, solid lines—fitted curves by using of spin Hamiltonian (2) with parameters from Table 3.



**Fig. 7.** (Color online) Angle dependencies of the resonance fields in basal plane of the crystals for  $\text{InBO}_3$  crystal at room temperature. Dots—experiment, solid lines—fitted curves by using of spin Hamiltonian (2) with parameters from Table 3.



**Fig. 8.** (Color online) Angle dependencies of the resonance fields in basal plane of the crystals for  $\text{GaBO}_3$  crystal at room temperature. Dots—experiment, solid lines—fitted curves by using of spin Hamiltonian (2) with parameters from Table 3.



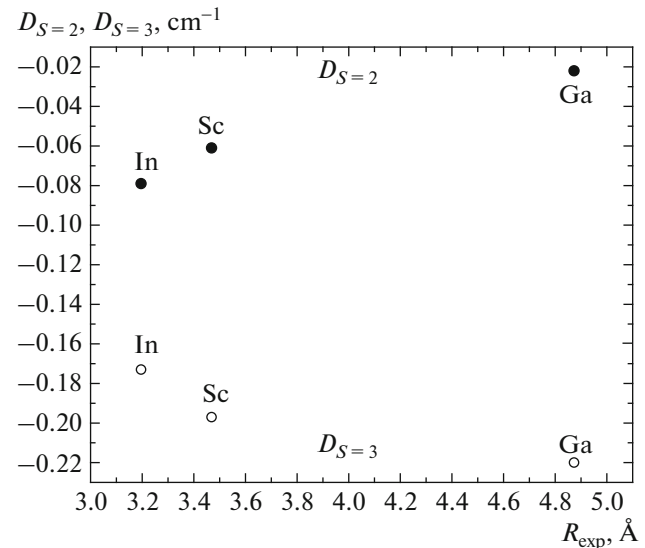
**Fig. 9.** Lattice distortion of the crystal caused by the  $\text{Cr}^{3+}-\text{Cr}^{3+}$  pair (see Table 4). Here  $R_{A-A}$  is the interionic  $A^{3+}-A^{3+}$  distances from Table 1.

For a pair system which exhibits a nearly isotropic  $g$ -tensor the anisotropic zero-field term  $D_e$  is almost entirely due to dipole-dipole interaction. If the paramagnetic ions which form the pair are treated as point dipoles, the value of  $D_e$  can be calculated from the following expression.  $D_e = -g^2\beta^2/R^3$  (where  $R$  is the interionic separation). From the  $D_e$  (for  $S = 2$ ) values observed for the  $\text{Cr}^{3+}-\text{Cr}^{3+}$  pairs in  $\text{ABO}_3$  a distances can be calculated for separation between two  $\text{Cr}^{3+}$  ions. The results are presented in Table 4. Note, that  $\text{Cr}^{3+}-\text{Cr}^{3+}$  distance in pure  $\text{CrBO}_3$  crystal is equal to  $3.5535 \text{ \AA}$  [14].

In Table 4  $R_{\text{theor}}$  is the interionic  $A^{3+}-A^{3+}$  separation X-ray data from Table 1,  $D_e^{\text{theor}} = -g^2\beta^2/R_{\text{theor}}^3$ ,  $D_{S=2}^{\text{theor}} = 3/2D_e^{\text{theor}}$ ,  $R_{\text{exp}}$  are the interionic  $\text{Cr}^{3+}-\text{Cr}^{3+}$  distance values calculated from  $D_{S=2}^{\text{exp}}$ . From Table 4 one can see the lattice distortions caused by the impurity  $\text{Cr}^{3+}-\text{Cr}^{3+}$  pairs in the parent  $\text{ABO}_3$  lattice. Figure 9 presents these distortions vs. interionic separation of the crystals.

**Table 4.**  $D_e$  values for the  $\text{Cr}^{3+}-\text{Cr}^{3+}$  pairs in  $\text{ABO}_3$  crystals

A	$R_{\text{theor}}, \text{ \AA}$ (from Table 1)	$D_e^{\text{theor}}, \text{ cm}^{-1}$	$D_{S=2}^{\text{theor}}, \text{ cm}^{-1}$	$D_{S=2}^{\text{theor}}, \text{ cm}^{-1}$ (from Table 3)	$R_{\text{exp}}, \text{ \AA}$
Ga	3.5459	-0.03807	-0.057105	-0.022	$4.8732 \pm 0.2$
Sc	3.7424	-0.03238	-0.04857	-0.061	$3.4688 \pm 0.07$
In	3.7739	-0.03158	-0.04737	-0.078	$3.1959 \pm 0.07$



**Fig. 10.**  $D_{S=2}$ —closed circles and  $D_{S=3}$ —open circles vs. calculated  $\text{Cr}^{3+}-\text{Cr}^{3+}$  pair distance for  $\text{ABO}_3$  ( $A = \text{In}, \text{Sc}, \text{Ga}$ ) crystals.  $R_{\text{exp}}$  is the real  $\text{Cr}^{3+}-\text{Cr}^{3+}$  distance, determined in Table 4.

One can notice a tendency: the smaller the interionic  $A^{3+}-A^{3+}$  distances, the stronger the distortions. Moreover, the sign of distortion is changing at  $A^{3+}-A^{3+}$  distance approximately equal to  $3.7 \text{ \AA}$ .

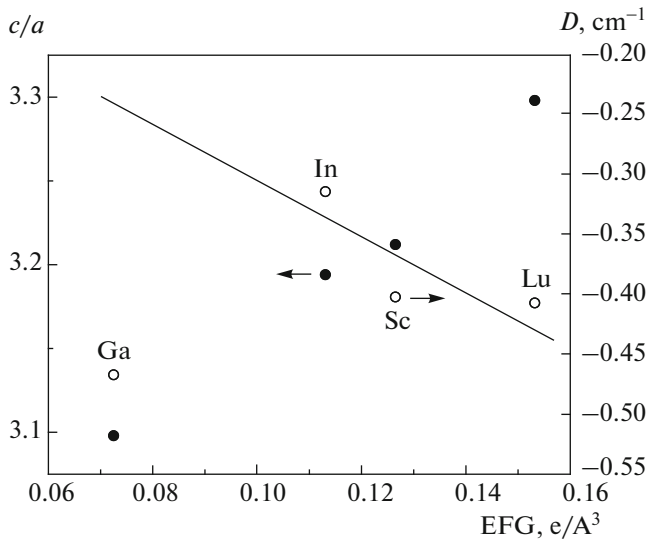
From the Eq. (3) the  $D_c$  values can be found also ( $D_{S=2}^{\text{exp}}$  value was used) (see Table 5).

It is seen, that  $D_c$  values are close enough to the axial constants  $D$  of the spin-Hamiltonian (1) for the single  $\text{Cr}^{3+}$  ion in  $\text{ABO}_3$  crystals except for the  $\text{GaBO}_3$ . The reasonable origin of this difference for the  $\text{GaBO}_3$  crystal may be explained if we take into account the strong lattice distortion observed for  $\text{Cr}^{3+}-\text{Cr}^{3+}$  pair in  $\text{GaBO}_3$ .

Figure 10 shows the dependencies of the pair spin-Hamiltonian (2) term  $D_s$  on  $\text{Cr}^{3+}-\text{Cr}^{3+}$  distance, calculated in Table 4.

Now, let us consider the axial constant  $D$  of the single ion spin-Hamiltonian (1). Assuming the model of the point dipole and considering only six nearest oxy-





**Fig. 11.**  $D$ —open circles (axial constant of the single ion spin Hamiltonian (1)) and  $c/a$ —closed circles (lattice parameters) vs. EFG in  $ABO_3$  ( $A = \text{Ga, In, Sc, Lu}$ ) crystals. The straight line is guide for eyes only for open circles (In, Sc, Lu).

gen ions (forming octahedral environment of  $\text{Cr}^{3+}$  ion) it is possible roughly to estimate the electric field gradient (EFG) for  $\text{Cr}^{3+}$  site using the X-ray data (Table 1). Obviously, the EFG value substantially determines the  $D$  value. Figure 11 presents  $D$  and  $c/a$  dependencies on EFG for  $ABO_3$  ( $A = \text{Ga, In, Sc, Lu}$ ) crystals.

The general trend is an increase in EFG as the  $c/a$  ratio increases. At the same way, the absolute value of the axial constant  $D$  increases with the EFG growing except for  $\text{Cr}^{3+}$  ion in  $\text{GaBO}_3$ . This fact may be explained if we assume that the strong lattice distortion observed for  $\text{Cr}^{3+}-\text{Cr}^{3+}$  pair in  $\text{GaBO}_3$  (see Fig. 9 and Table 4) may be implemented for single  $\text{Cr}^{3+}$  ion in  $\text{GaBO}_3$  too. In this case, the EFG value calculated from X-ray data (Table 1) may sufficiently differs from the real one.

**Table 5.**  $D_c$  values for the  $\text{Cr}^{3+}-\text{Cr}^{3+}$  pairs in  $ABO_3$  crystals

A	$D_c, \text{cm}^{-1}$	$D, \text{cm}^{-1}$ (data from Table 2)
Ga	-0.517	-0.467
Sc	-0.401	-0.402
In	-0.3155	-0.314

## 5. CONCLUSIONS

Single ion and pair spectra of  $\text{Cr}^{3+}$  ions in  $ABO_3$  ( $A = \text{Sc, In, Ga}$ ) diamagnetic crystals were explored by using electron paramagnetic resonance technique. Spin-Hamiltonian values for single ions and  $\text{Cr}^{3+}-\text{Cr}^{3+}$  pairs at room temperature were determined. The lattice distortions of the parent  $ABO_3$  ( $A = \text{Sc, In, Ga}$ ), caused by  $\text{Cr}^{3+}$  impurity were discussed. This work will be prolonged by the pair's resonance line intensities vs. temperature investigation in order to determine the signs and the values of the  $\text{Cr}^{3+}-\text{Cr}^{3+}$  exchange integrals  $J$ .

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