===================== MAGNETISM =====================

# Exchange Interactions in the $Cr^{3+}$−$Cr^{3+}$ Ion Pair in the $ABO_3$ (A = Ga, In, Sc) Diamagnetic Matrix

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**Abstract**—The exchange interactions in the $Cr^{3+}$−$Cr^{3+}$ ion pairs in the isostructural $ABO_3$ (A = Ga, In, Sc) diamagnetic compounds have been examined using the magnetic resonance technique. The values of bilinear and biquadratic exchange interactions have been determined. It is shown that the biquadratic exchange in the $Cr^{3+}$−$Cr^{3+}$ pair in these compounds is caused by the exchange striction.

## 1. INTRODUCTION

The knowledge of the size and sign of the main exchange interactions between magnetic ions in *A* site of the $ABO_3$ (A = Fe, V, Cr, Ti) borates is necessary for understanding different types of magnetic ordering in these crystals [1]. The detailed data on these interactions can be obtained directly from the electron spin resonance (ESR) spectra recorded on diamagnetic analogs of these crystals, i.e., the $ABO_3$ (A = Ga, In, Sc) crystals weakly doped with magnetic ions. In our previous study [2], we reported the ESR data on the $Cr^{3+}$−$Cr^{3+}$ ion pairs in the $ABO_3$ (A = Sc, In, Ga) crystals. The parameters of the spin Hamiltonian of the pair and the degree of distortion of the native crystal lattice by the impurity pair were determined.

Here, we report on the data of temperature investigations of the intensities of resonance lines corresponding to the multiplets of the $Cr^{3+}$−$Cr^{3+}$ pair in the $ABO_3$ (A = Sc, In, Ga) crystals in order to determine the parameters of exchange interactions in it.

## 2. EXPERIMENTAL

The $ABO_3$ (A = Sc, In, Ga) single crystals with a minor (about 5 at % A) addition of $Cr^{3+}$ ions were grown from the $Cr_2O_3$−$M_2O_3$−$B_2O_3$−(70PbO−30PbF$_2$ wt %) flux. The synthesis procedure was described in detail in [3]. In this case, $Cr^{3+}$ ions replace A ions. We obtained single crystals in the form of thin plates 2 × 2 mm in size with a thickness of about 0.1 mm and a smooth light-gray shiny surface.

The isostructural $ABO_3$ (A = Sc, In, Ga) crystals have a trigonal unit cell (sp. gr. $R\overline{3}c$) with the point symmetry group of the A ion ($-3m$). The $ABO_3$ crystal structure is shown in Fig. 1.

The A ions are located in the octahedra formed by oxygen ions bound to boron ions by the strong covalent bond. The $Cr^{3+}$−$Cr^{3+}$ ion pair is located at the sites of the A ions in neighboring octahedra sharing the vertex oxygen ion through which the exchange interaction in the pair is implemented.

The effective Ga, In, and Sc ionic radii and the interionic distances for ion pairs are given in Table 1.

The ESR measurements were performed on a Bruker Elexsys E-580 spectrometer operating in the X range at temperatures of 300−3.6 K. The temperature stabilization was not worse than 0.1 K. An Oxford ITC 503C temperature controller and an Oxford ESR 900 continuous-flow cryostat were used. The feature of this cryostat is that the resonator remains at room

**Table 1.** Parameters of the unit cell of the $ABO_3$ crystals

| $ABO_3$ | Effective ionic radius of ion A, Å [4]* | Interionic distance A–A, Å** |
|---------|------------------------------------------|-------------------------------|
| Ga | 0.620 | 3.5459 |
| In | 0.800 | 3.7739 |
| Sc | 0.745 | 3.7424 |

*The effective radius of $Cr^{3+}$ ions is $r = 0.615$ Å. **According to the X-ray data on a diamagnetic crystal [2].
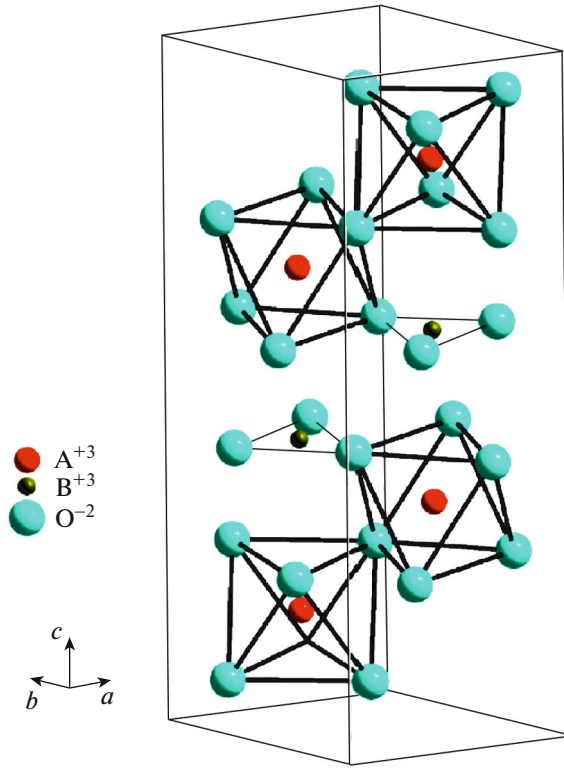
$A^{+3}$
$B^{+3}$
$O^{-2}$

**Fig. 1.** $ABO_3$ crystal structure. For simplicity, not all atoms in the unit cell are shown.

temperature with a constant Q factor of $Q \sim 9300$ over the entire investigated temperature range. The first derivative of the absorption signal was detected. After that, the resonance curve was integrated. The area under the integration curve was taken to be the signal intensity.

## 3. THEORY

When two $Cr^{3+}$ ions interact with the formation of a magnetic pair, the spins $s$ of each ion form four spin states (multiplet), each being characterized by the total spin quantum number $S$ ranging from $(s_1 + s_2)$, $(s_1 + s_2 - 1)$,... to zero. Assuming the energy intervals between these spin states to be large as compared with other magnetic interactions, we can write a separate spin Hamiltonian for each multiplet [2].

We write the interaction energy of chromium ions forming a pair as

$$H_{ex} = J\mathbf{S_1S_2} + j(\mathbf{S_1S_2})^2, \qquad (1)$$

where $J$ and $j$ are the isotropic bilinear and biquadratic exchange interactions, respectively. The need for taking into account the biquadratic exchange interaction follows, in the general case, from the fact that the spin value for each individual chromium ion in the pair is

$s_1 = s_2 = 3/2 > 1/2$. In this case, the energy levels of the multiplet with the full spin $S$ will be expressed as

$$W_S = \frac{1}{2}JS(S+1) + \frac{1}{4}jS(S+1)$$
$$\times [S(S+1) - 2s_1(s_1+1) - 2s_2(s_2+1)], \qquad (2)$$

$$W_1 = J - \frac{13}{2}j, \quad W_2 = 3J - \frac{27}{2}j, \quad W_3 = 6J - 9j$$

and the population (and, consequently, the intensity) of each of its sublevels (due to the Zeeman splitting at the ESR) is proportional to the quantity [5]

$$I_S \sim \frac{1}{kT} \frac{\exp\left(-\frac{W_S}{kT}\right)}{\sum\limits_s (2S+1)\exp\left(-\frac{W_S}{kT}\right)}, \qquad (3)$$

$$\sum_S = 1 + 3\exp^{-W_1/kT} + 5\exp^{-W_2/kT} + 7\exp^{-W_3/kT}.$$

It should be noted that, in the calculation of the energy level position in Eq. (2), we ignored the dipole–dipole interaction in the pair $D_e = g^2\beta^2/R^3$ and the single-ion anisotropy constant $D_s$ for each multiplet in the pair, which were determined in [2] and, in order of magnitude, are $D_e \sim 0.03$ cm$^{-1}$ and $D_s \sim 0.08$ cm$^{-1}$. Below, we show that this approximation is valid, since these interactions turn out to be weaker than other interactions in the $Cr^{3+}$–$Cr^{3+}$ pair by an order of magnitude.

## 4. RESULTS AND DISCUSSION

In our previous work [2], the transitions for pair multiplets with full spins of $S = 2$ and $3$ were identified and described. The results obtained were processed using the absorption lines located at the maximum distance from the other resonance spectrum lines in order to eliminate errors caused by the possible overlap of signals and errors of their integration. Such lines correspond to the transitions with $S = 2$ and $m = 1 \leftrightarrow 2$ (and $1 \leftrightarrow 0$ for $GaBO_3$ only). Figure 2 shows temperature dependences of the intensities of transitions between the magnetic levels $m$ $1 \leftrightarrow 2$ in the multiplet with $S = 2$ for the investigated compounds.

The fitted data on the exchange interactions are given in Table 2.

The sign of the obtained exchange integral $J$ corresponds to the antiferromagnetic interaction in a pair, which does not contradict the experiments showing that the $CrBO_3$ compound is an antiferromagnet with $T_N = 15$ K.

In this case, the paramagnetic Néel temperature $\theta = 2zJS(S+1)/3k$ determined using the equation of the molecular field theory ranges from $-69$ to $-48$ K. As is known [6], the paramagnetic Néel temperature of the $CrBO_3$ compound is $\theta = 40$ K. In this case, the correct calculation of the paramagnetic Néel tempera-
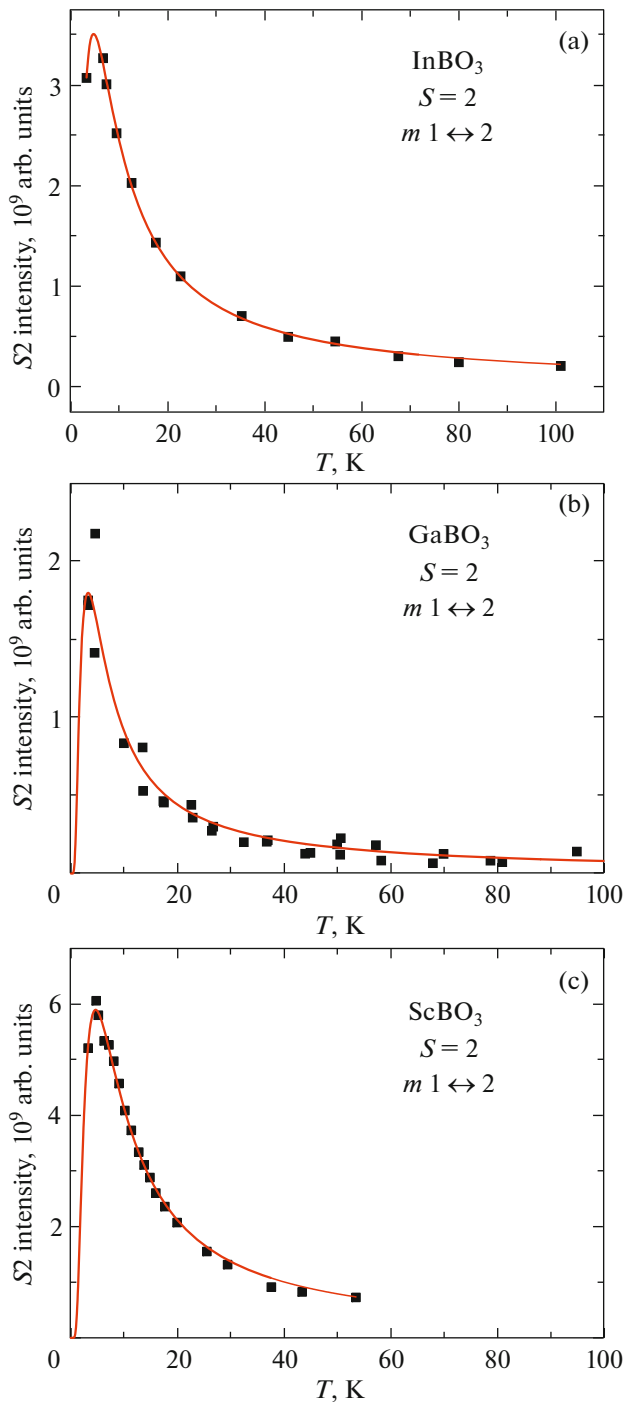
**Fig. 2.** Temperature dependences of the intensities of the transitions between magnetic levels $m\ 1 \leftrightarrow 2$ in a multiplet with $S = 2$ for (a) $InBO_3$, (b) $GaBO_3$, and (c) $ScBO_3$. Dots show the experiment and solid curves, fitting using Eq. (3).



**Fig. 3.** Dependence of the exchange interaction value $J$ on the real distance $R_{exp}$ between chromium ions in a pair.

ture apparently requires the interaction with the second neighbors to be taken into account.

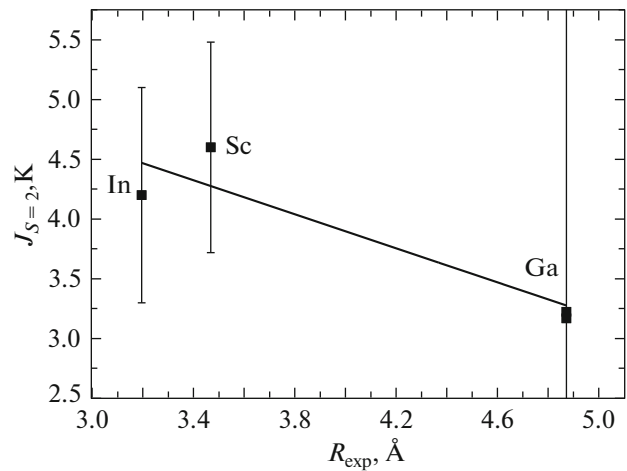Figure 3 shows the dependence of $J$ on the distance between chromium ions in the $Cr^{3+}$–$Cr^{3+}$ pair. As expected, the value of the exchange interaction decreases with increasing distance between the magnetic ions.

The biquadratic term in interaction Hamiltonian (1) can result from both the transfer of the fourth-order electron density [7, 8] and the magnetostriction [9].

In the first case, the resulting coefficient of the biquadratic exchange term $j$ is fairly difficult to calculate and, in the order of magnitude, it is $j \sim +b^4/U^2 E_H + J^2/E_H$, where $b$ is the corresponding transfer integral, $U$ is the energy of electron excitation of the ligand cation, and $E_H$ is the Hund energy (~2 eV). Therefore, the transfer processes lead to the positive $j$ value, which is about $10^{-3}$ K at the obtained $J$ values. The $j$ values are negative and have a significantly larger value (Table 2). Thus, the transfer processes obviously cannot describe the obtained $j$ value.

An alternative mechanism leading to the biquadratic exchange interaction was proposed in [9]. The free energy of a pair of chromium ions in the crystal lattice can be written as the sum of the elastic and exchange terms

$$F = 1/2 c R_0 (R - R_0)^2 - J(\mathbf{S}_1 \mathbf{S}_2), \quad (4)$$

where $c$ is the corresponding component of the elastic tensor. In the absence of exchange interaction, the quantity $R_0$ is the equilibrium distance in a pair of chromium ions. This distance can change in the presence of exchange interaction. Assuming $\partial F/\partial R = 0$, we obtain

$$R = R_0 + (J'/c R_0)(\mathbf{S}_1 \mathbf{S}_2), \quad (5)$$

where $J' = dJ/dR$.

Substituting the new $R$ value into Eq. (4), we see that the expression for free energy contains a term proportional to $(\mathbf{S}_1 \mathbf{S}_2)^2$ with the coefficient $j = -1/2(J'^2/c R_0)$. It can be seen that this term is negative.

**Table 2.** Exchange interactions in the pair of ions $Cr^{3+}$–$Cr^{3+}$ in the $ABO_3$ (A = Sc, In, Ga) crystals obtained by fitting the experimental data and Eq. (3)

| Parameter | $ScBO_3$ $m = 1 \leftrightarrow 2$ | $InBO_3$ $m = 1 \leftrightarrow 2$ | $GaBO_3$ | |
|---|---|---|---|---|
| | | | $m = 1 \leftrightarrow 2$ | $m = 1 \leftrightarrow 0$ |
| $J$, K | $4.6 \pm 0.88$ | $4.2 \pm 0.9$ | $3.17 \pm 5.8$ | $3.225 \pm 4.7$ |
| $j$, K | $-0.46 \pm 0.24$ | $-0.359 \pm 0.25$ | $-0.295 \pm 1.6$ | $-0.324 \pm 1.3$ |
| $R$, Å (from Table 1) | 3.7424 | 3.7739 | 3.5459 | |
| $|j/J|$ | 0.1 | 0.085 | 0.093 | 0.1 |
| $R_{exp}$, Å | $3.4688 \pm 0.07$ | $3.1959 \pm 0.07$ | $4.8732 \pm 0.2$ | |

$R$ and $R_{exp}$ are distances between ions in the pair. The value of $R_{exp}$ was obtained in [2].

To estimate the $j$ value, we use the average values of $J' = 9.7 \times 10^{-7}$ erg/cm (from Fig. 3), the average elastic modulus $c \sim 5 \times 10^{11}$ dyn/cm$^2$ for trigonal crystals [10], and the average experimental equilibrium distance $R_0 \sim 4 \times 10^{-8}$ cm (see Table 2). Then, the estimate is $j = -0.17$ K, which is quite similar to the experimental values.

Thus, we may state that, in our case, the main mechanism of the biquadratic exchange is the magnetostriction.

## 5. CONCLUSIONS

The temperature dependence of the intensities of resonance transitions in the spectra of pairs of chromium ions in the $ABO_3$ (A = Ga, In, Sc) compounds was investigated and the parameters of the bilinear and biquadratic exchange interactions in the $Cr^{3+}$–$Cr^{3+}$ pair were determined. It was shown that the main mechanism of the biquadratic exchange interaction in these compounds is the exchange striction.

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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