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Research article

Non-coplanar antisymmetric exchange in the ferromagnet $PbMnBO_4$

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ABSTRACT

To determine the direction of DM vector in the magnets with two non-coplanar super-exchange paths, a criterion based on an asymmetry of distribution of ligands between interacting spins is proposed. The direction of DM vector in $PbMnBO_4$ corresponds to structural formula following from this criterion. The exchange paths, allowing the existence of the two-bridge DM interaction between neighboring Mn^{3+}-ions in the chains, are considered. The possible mechanisms of antisymmetric exchange via two ligands in this crystal are discussed.

1. Introduction

The various optical, elastic, electrical, magnetic, and multiferroic properties of a group of borates with the multite structure $AMBO_4$ are studied intensively during more than two decades [1–15]. Magnetic crystals with $M = Cr, Mn, Fe$ [2–12], as well as mixed and diamagnetically diluted compounds [13–15], have a pronounced magnetic anisotropy, which is caused by one- and two-ion interactions. The knowledge of the anisotropic interactions parameters is important both for the interpretation of the magnetic and magnetoelectric properties and for understanding of the mechanisms of the interactions. Among orthoborates, $PbMnBO_4$ (Fig. 1) is the only magnet with ferromagnetic ordering, which determines its special significance in the study of the anisotropy of magnetic multites. Previously [16] it was shown that the main contributions in the total change of anisotropy energy upon the magnetization reorientation in magnetic field are a single-ion anisotropy (SIA) and anisotropic exchanges both symmetric (SAE) and antisymmetric (Dzyaloshinsky–Moriya (DM) interaction [17,18]). The direction and magnitude of the vector $\mathbf{D_{n,n'}}$ of DM interaction

$$H_{DM} = \mathbf{D}_{n,n'}[\mathbf{S}_n \times \mathbf{S}_{n'}] \quad (1)$$

largely determine the magnetic structure and anisotropy of 3d insulators [19]. Keffer [20] proposed a simple phenomenological relation for the vector $\mathbf{D_{n,n'}}$ for two spins interacting via one intermediate ligand O_i

$$\mathbf{D}_{n,n'} \propto [\mathbf{r}_n \times \mathbf{r}_{n'}], \quad (2)$$

where $\mathbf{r}_{n,n'}$ are vectors for $S_{n,n'} - O_i$ bonds. Later on Moskvin [21,22] derived a microscopic formula for vector in frames of the second order perturbation theory as a combine effect of the single-bridge superexchange and spin–orbital coupling (SOC) for S-ion magnets with orbitally non-degenerate ground state. If the superexchange occurs through the several ligands, the total vector $\mathbf{D_{n,n'}}$, as a rule, is considered as a sum of additive contributions from each separate single-bridge exchange $\mathbf{D}_i$, fulfilled the Keffer rule (2). In the works [23–27] it was shown that the two-bridge exchange can largely exceed the single-bridge one. When the magnetic ions and ligands lie in common plane (coplanar case), the vectors and the total vector are orthogonal to the plane [28] or absent in the case of symmetric paths [26,29] in accordance with symmetry constraints [18]. If the magnetic ions and ligands do not lie in the same plane (non-coplanar case) the direction of the two-bridge DM vector $\mathbf{D}_{i,j}$ and, hence, the total vector $\mathbf{D_{n,n'}}$ can not be determined a priory from symmetry arguments. Besides the chain character of dominant isotropic and anisotropic two-ion magnetic interactions the crystal structure of $PbMnBO_4$ has other intriguing feature - the two-bridge non-coplanar exchange between Mn^{3+}-ions via oxygen O_1 and O_3 ions (Fig. 2). An angle between $O_1 - Mn - O_1$ and $O_3 - Mn - O_3$ - planes is equal to 20°.

In the work [16] the magnitude and direction of DM vector was obtained by the analysis of the experimental field dependences of magnetization along the hard directions in the crystal, taking into account the other - SIA, SAE, and dipole - dipole interaction. But the orientation of the vector of DM interaction was not explained. The aim of this work is to propose a criterion of definition of DM vector direction for the non-coplanar two-bridge exchange and obtain an analytical expression for the direction, following from this criterion.

2. Isotropic and antisymmetric exchanges

The crystal structure of magnetic multites with M=Cr, Mn and Fe was studied in detail by Park et al. in Ref. [2]. The unique magnetic

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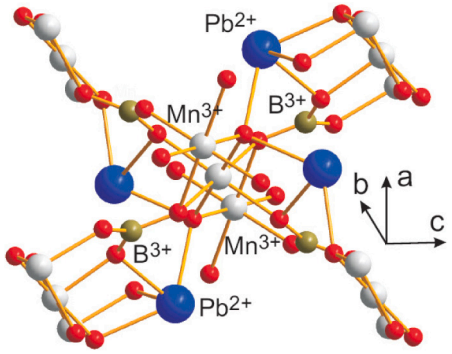

Fig. 1. Crystal structure of $PbMnBO_4$.

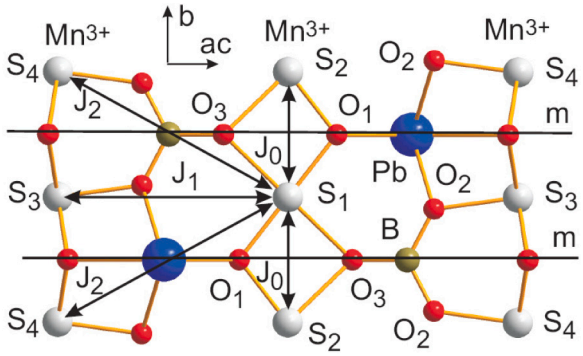

Fig. 2. Isotropic intrachain (J_0) and interchain (J_1 and J_2) exchanges. The mirror planes of symmetry m are shown.

properties of $PbMnBO_4$ crystal (space group Pnma) are caused by the specific features of its structure. The main fragments of the crystal structure are linear chains of distorted edge-sharing MnO_6 octahedra (Fig's 1,2). The chains are linked by the BO_3 and PbO_4 groups. The nearest interchain Mn-Mn separation is 5.45 Å, while the intrachain one is 2.97 Å. The static Jahn–Teller effect causes both strong magnetic anisotropy and formation of ferromagnetic exchange coupling in the chains [2,3,5,6]. The isotropic ferromagnetic exchange between nearest spins in the chains J_0 and total interchain exchange were determined within Ginsburg–Landau field theory taking into account the magnetic ordering temperature T_c = 30.3 K and Curie–Weiss temperature Θ = 49 K [8]

$$H_{ex} = J_0(\mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_3\mathbf{S}_4) + \frac{z_1}{2}J_1(\mathbf{S}_1\mathbf{S}_3 + \mathbf{S}_2\mathbf{S}_4) + \frac{z_2}{2}J_2(\mathbf{S}_1\mathbf{S}_4 + \mathbf{S}_2\mathbf{S}_3), \quad (3)$$

$$J_0 + d = -20.2\ \text{K}, \quad z_1J_1 + z_2J_2 = -8.8\ \text{K}.$$

Here J_1, J_2 - two possible exchanges between chains (Fig. 2), z_n - number of interchain neighbors, d - isotropic part of dipole–dipole interaction.

Antisymmetric exchange interactions was taken into account only between spins with the dominant intrachain exchange (1–2 and 3–4 in Fig. 2). The vectors of DM interaction lie in the symmetry mirror *ac* plane *m* between interacting ions. The symmetry center on the magnetic ions provides a staggered character of DM vector $\mathbf{D}_{j,j+1} = (-1)^j\mathbf{D}_{n,n'}$, where j denotes the Mn^{3+} cites along the magnetic chain.

$$H_{DM} = \mathbf{D}_{12}[\mathbf{S}_1 \times \mathbf{S}_2] + \mathbf{D}_{34}[\mathbf{S}_3 \times \mathbf{S}_4].$$

The sliding planes a and n of the crystal between chains change the vector projection $D^a_{12} = -D^a_{34}$. The parameters of anisotropic exchanges that describe the experiment depend on the choice of the isotropic interchain interaction scheme (Fig. 2). In the density functional theory [3,6], the energies of strictly collinear magnetic structures were considered without anisotropic contributions. The interchain exchange energies obtained from the energy difference of collinear structures are comparable to the energies of neglected interactions [16]. Two limit distributions of interchain exchanges fulfilled the condition (3) fix an interval of allowable values of DM interaction parameters

$$D_{12} = D_{34} = 2.33 \pm 0.2\ \text{K}, \quad \phi_{DM} = 1.48 \pm 0.02\ \text{rad}, \quad (4)$$

where an angle of DM vector orientation ϕ_{DM} is calculated from orthorhombic a axis. Note two important features of DM interaction parameters. Firstly, the absolute value (4) far exceeds the conventional estimate $D \propto (\delta g/g)J_0$ [18], as the g-shift for Mn^{3+}-ions is small [30–32]. The 90° geometry and quantum interference between different exchange paths in Mn^{3+} chains strongly enhance the value of anisotropic exchange constants. These values remain stable on light deviation from the exact 90° bond angle, whereas the isotropic exchange constant is reduced and even crosses zero by small changes of the bond geometry [29]. This explain the difficulty to estimate the anisotropic exchange parameters from g-shift and the isotropic exchange, because here the isotropic exchange constant between the ground states of neighboring ions via bridge of ground states is not comparable to the exchange between neighboring excited states via second bridge, which is necessary for estimation of $\mathbf{D}_{\mathbf{n},\mathbf{n}'}$. It means that in $PbMnBO_4$ the vector of two-bridge exchange $\mathbf{D}_{O1O3}$ have to takes a dominant contribution in the total DM vector in comparison with the possible separate single-bridge vectors $\mathbf{D}_{O1}$ and $\mathbf{D}_{O3}$. Secondly, the direction of DM vector still the same for any distributions of ferromagnetic interchain exchanges in the framework of constraint (3). The last is a result of structural character of this parameter - the direction of the DM vector is determined by the crystal structure and is independent on the model of interchain exchange distribution.

3. Direction of antisymmetric exchange vector

The orientation of the axes of anisotropic exchanges strongly affects the nonlinearity of the magnetization curves and the fields of the reorientation completion H_b and H_c. In a general case the total DM vector is determined by a sum of the single-bridge exchanges over the oxygen ions O_1 and O_3, and two-bridge exchange over both ligands

$$\mathbf{D}_{12} = \mathbf{D}_{O1} + \mathbf{D}_{O3} + \mathbf{D}_{O1,O3}.$$

In the work [6] authors concluded that the intrachain isotropic exchange in the ground state via O_3 plays the main role. If the DM interaction occurs via this ligand only, in accordance with the Keffer rule the vectors in neighboring chains $\mathbf{D}_{12}$ and $\mathbf{D}_{34}$ make angles of ±0.52 rad with the *c* axis (ϕ_{DM} = 2.09 rad). Such large noncollinearity of the anisotropy axes in neighbouring chains would lead to a strong nonlinearity of the field dependence of magnetization in the field $\mathbf{H}\|\mathbf{c}$ and the first-order phase transition at H_c. The total antisymmetric exchange vector (4), following from the experimental curves analysis, may be obtained as a sum of two separate single-bridge vectors $\mathbf{D}_{O1}$ and $\mathbf{D}_{O3}$ only, with the directions fulfilled the Keffer rule (2) (Fig. 3). In this case single-bridge vectors partially compensate each other, and the values of the exchanges $D_{O1} = 0.18\ J_0, D_{O3} = 0.25\ J_0$, taken into account a proportionality of the values to corresponding isotropic exchanges $D_{O1(O_3)} \propto 0.4\ J_{O_1(O_3)}$, seems a unrealistic large for Mn^{3+} ions. Besides, a sum of two corresponding tensors of symmetric anisotropic exchanges would give a total biaxial tensor of SAE, unlike the result of work [16].

The DM interaction arises at the combination of low symmetry and SOC. The direction of DM vector must reflect a decrease of local symmetry of interacting magnetic ions. So, the direction followed from the rule for single-bridge coupling (2) determines the axis *z*, relatively that the displacement of ligand in the *xy*-plane is maximally asymmetric. For the two-bridge exchange we define the function of local symmetry

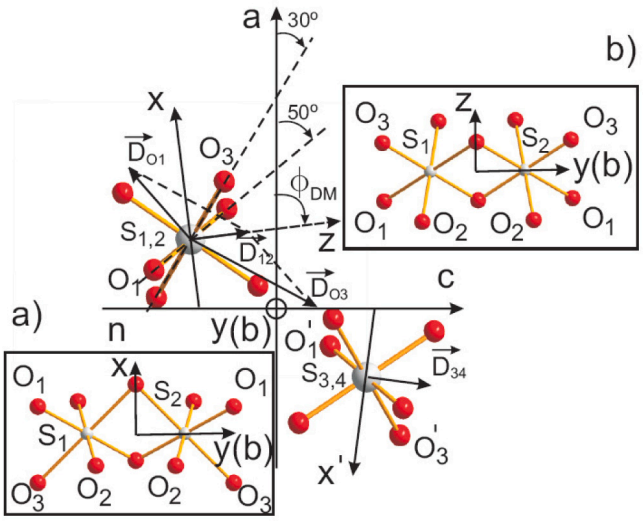

Fig. 3. Orientation of antisymmetric exchanges in the mirror plane of symmetry.

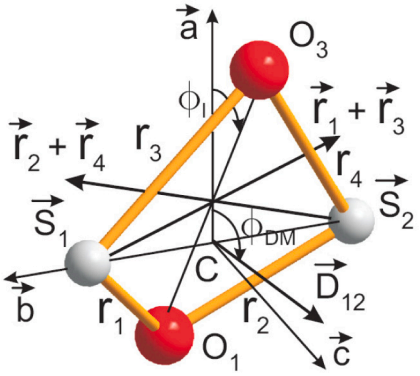

Fig. 4. Orientation of non-coplanar antisymmetric exchange in a ferromagnet $PbMnBO_4$.

as a sum of ligands projections on the vector lying in the mirror plane m and directed from a center between interacting spins $\mathbf{S}_1$ and $\mathbf{S}_2$ C

$$F(\phi) = \sum_{n=1,2} \mathbf{r}_n \cdot \mathbf{e}_\phi = r \cdot cos(\phi + \delta), \tag{5}$$

where ϕ is an angle between the vector direction and axis **a**. For $PbMnBO_4$ crystal structure r=0.69 Å, $\delta = 0.088$ rad. The function $F(\phi)$ has a maximum at the $\phi = -\delta$. This direction determines an axis x with the maximal total displacement of ligand projections (Fig. 3, inset *a*)). Corresponding orthogonal direction z with $F(\phi = 1.48\ \text{rad}) = 0$ results the direction with symmetric projections (Fig. 3, inset *b*)). $F(\phi_{DM}) = 0$ means that $[(\mathbf{r}_1 + \mathbf{r}_3) \times \mathbf{D}_{12}] = 0$, and, taking into account a symmetry permutation $\mathbf{r}_1 \to \mathbf{r}_2$ and $\mathbf{r}_3 \to \mathbf{r}_4$, results

$$\mathbf{D}_{12} \propto [(\mathbf{r}_1 + \mathbf{r}_3) \times (\mathbf{r}_2 + \mathbf{r}_4)], \tag{6}$$

where $\mathbf{r}_1, \mathbf{r}_3$ and $\mathbf{r}_2, \mathbf{r}_4$ are vectors from spins $\mathbf{S}_1$ and $\mathbf{S}_2$ to ligands O_1 and O_3, accordingly (Fig. 4).

A distinctive feature of vector product (6) is its dependence both a mutual ligand planes orientation and a ratio of distances between magnetic ion and ligands. For the DM vector orientation ϕ_{DM} in the mirror plane we can express Eq. (6) as follows

$$\tan(\phi_{DM} - \phi_l) = \frac{n - n^{-1}}{2 \sin \phi}, \tag{7}$$

where ϕ_l is an angle of orientation of line connecting the ligands O_1O_3 (Fig. 4), $n = r_3^m / r_1^m$ is the ratio of vector projections on the mirror plane and ϕ is an angle between ligand planes. Note, that ϕ_{DM} is independent on the vector components along the **b** axis. In general case the DM vector locates in the sector between two limit directions. In the first limit of equal distances between magnetic ion projections and both ligands ($n = 1$) in non-coplanar planes the DM vector is directed along the line connecting the ligands. In the second limit case of coplanar two-bridge interactions ($\phi = 0$) via non-equivalent paths, the vector will normal to the plane of interacting ions (and, hence, the line O_1O_3). At the interaction via two symmetric paths the expression (6) is vanish, that corresponds to appearance of local inversion center between interacting ions. Depending on the sign of ϕ and ratio $n \vee 1$, there are four possible sectors of DM vector orientation on the mirror plane. The direction of DM vector in $PbMnBO_4$ $\mathbf{D}_{12}$, following from the analysis of experimental dependences of magnetization [16], fulfills to the structural relations (6) and locates in the sector $n > 1, \phi > 0$.

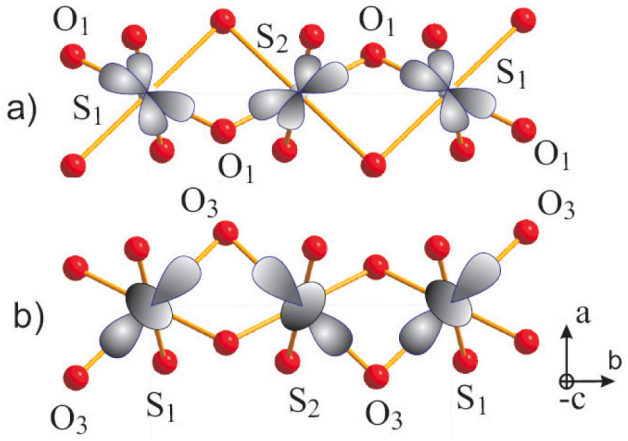

Fig. 5. The charge distribution picture for excited (a) and ground (b) e_g-states.

The expression (10) points on the dominant contribution of two-bridge DM exchange in $PbMnBO_4$ and its non-additive character. If one of the ligands is absent, the expression is not transforms into Keffer rule (2), as at $r_i \to \infty$ absolute value D_{12} tends to zero due to higher power of ligands spacing r_i in denominator, as for single-bridge interaction [33,34].

4. Discussions

The anisotropic interactions of ionic crystals are strongly depend on a structure of orbital levels and their electron population. Both the value and direction of the DM vector are determined by the electronic structure and geometry of interacting ions. The ground electron configuration of manganese ion in a strong crystal field is $t_{2g}^3 e_g^1$. In the cubic symmetry the five d orbitals split into the low-energy t_{2g} orbitals and the high-energy e_g orbitals. A tetragonal distortion (a static Jahn–Teller effect) splits upper electron states $|0\rangle \propto |3z^2 - r^2\rangle/\sqrt{6}$ and $|2^s\rangle = (|2\rangle + |-2\rangle)/\sqrt{2} \propto |x^2 - y^2\rangle/\sqrt{2}$ breaking a degeneracy in a pure octahedral field. Here and after the local z axis is directed along the long $Mn - O_3$ bond. The orthorhombic distortion ($Mn - O_2 > Mn - O_1$) entangle the functions. So, yields

$$\begin{aligned} \Psi_g &= c_1|0\rangle - c_2|2^s\rangle, \\ \Psi_e &= c_2|0\rangle + c_1|2^s\rangle, \end{aligned} \tag{8}$$

- the functions of ground and excited states, respectively, with $c_1 = 0.988, c_2 = 0.153$ [35]. In order the DM ring-exchange via ground and excited states arises, it is necessary to transfer an electron on the excited state with function directed to O_1 - ions. The charge distribution pictures for excited (a) and ground (b) states are shown in Fig. 5. In the upper picture (a) the excited Ψ_e states of Mn^{3+} ions is coupled via O_1

ions, in the lower picture (b) the ground states Ψ_g states is coupled with the ground states of the other neighboring ions via O_3 ions. The SOC is necessary to excite the orbital angular momentum at one of two sites. But the e_g-functions (8) do not interact under spin–orbital interaction λ**LS**. The transition on Ψ_e state is possible from t_{2g} states $|xy\rangle, |xz\rangle$ and $|yz\rangle$. The possibility of mixing Ψ_g and Ψ_e states by SOC is appeared after further lowering of local symmetry. The deviations of angles between octahedral axes from 90° (86.6°, 84.2°, 89° for $O_1-Mn-O_2, O_1-Mn-O_3, O_2-Mn-O_3$, respectively [2]) points at the presence of triclinic components of crystal field, that may mix e_g and t_{2g} functions. The entanglement of the orbital functions also may follows from on-site Coulomb repulsion, as it was suggested for $CuGeO_3$ by Eremina with co-authors [27]. In this case the orbital angular momenta are not quenched and are not conserved quantities [36]. So, the probability of transition between two upper renormalized states due to SOC is appeared, and the SOC turn on two-bridge DM interaction via both O_1 and O_3 ligands.

5. Conclusions

The directions of vectors of intrachain antisymmetric exchanges correspond to maximally asymmetric distributions of projections of intermediate oxygen ions on the planes, which are orthogonal to the DM vectors. The directions of DM vectors in $PbMnBO_4$ are in quantitative agreement with analytical expression following from this criterion. The anisotropic super-exchange via two non-coplanar paths strongly enhances the value of the antisymmetric exchange constant and leads to novel orientation of DM vector.

CRediT authorship contribution statement

S.N. Martynov: Writing – original draft, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

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