Magnetic and Electronic Properties of Frustrated Spin Dimer Compound

$\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$: A First-principles Calculation

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Abstract

The magnetic and electronic properties of $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ with a three dimensional network of isolated FeO_4 tetrahedra are systematically studied on the basis of first principles density functional calculations. Our results demonstrated that $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ is semiconducting, and Fe^{3+} ions favor high spin states. By evaluating its spin exchange interactions, we found that the dominated spin interaction in $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ comes from Fe-O-Fe bridge, which is antiferromagnetic coupling. Moreover, in the ab plane, the Fe^{3+} ions form an almost two dimensional triangle plaquettes and the three intra-layer spin exchange interactions are all antiferromagnetic, which results in the geometric frustration due to the three spin directions in the triangle cannot compromise with each other. Consequently, the interaction of strong spin dimer and geometric frustration leads to the observed spin glass behavior.

1. Introduction

The novel magnetic oxide $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ was recently synthesized by Wang *et al.* for the first time and the crystal structure was determined by x-ray diffraction.¹ Wang *et al.* also investigated the magnetic properties of $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$. According to the magnetic susceptibility depending on the temperature, $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ shows a spin glass behavior above ~ 20 K (i.e., $T_f \approx 20$ K), and the Curie-Weiss temperature θ of $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ is predicted to be about -75 K. Although geometrically spin frustrations has been taken as the possible origin of spin glass, it is still quite questioned. As we know, geometrically spin frustrations typically leads to non-collinear spin structure. Therefore, the intrinsic mechanics response for the observed spin-glass is still unclear.

Carefully looking at the geometric structure of this compound, we found that FeO_4 tetrahedron shares its three basal oxygen atoms with BO_3 triangles forming a two-dimensional layer in the ab plane and the layers are connected by the apical Fe–O bonds along the c direction. Generally, d orbitals of Fe atoms in FeO_4 tetrahedron are split into two energy levels e_g and t_{2g} . Consequently, the Fe atoms of $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ exist as high-spin Fe^{3+} (d^5 , $S = 5/2$) or low spin Fe^{3+} (d^5 , $S = 1/2$) states. In ab plane, each FeO_4 tetrahedron shares its three basal oxygen atoms with BO_3 triangles forming an almost two-dimensional (2D) layer and the three different Fe1, Fe2 and Fe3 atoms form a 2D triangle net (**Fig. 1a**). The 2D layers which alternate with layers of K^+ ions are connected by the apical Fe-O bonds along the c direction (**Fig. 1b**).

As we can see, the Fe1 atoms are connected with each other through Fe1-O-Fe1 bridge, while the Fe2 and Fe3 are fitted together through Fe2-O-Fe3 bridge. As a result, the two FeO_4 tetrahedron joining together by Fe-O-Fe bridges in the neighbor layers form

a typical spin dimer²⁻⁴. In addition, all possible spin exchange interactions were considered for $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ basing on the atomic environment. In the each layer of Fe atoms, the three different Fe atoms compose of a triangle plaquette and one might consider the three kinds of intra-layer exchanges J_3 , J_4 and J_5 (**Fig. 1a**). As for the inter-layer exchanges, there are the four different interactions J_{1a} , J_{1b} , J_{2a} , J_{2b} shown in **Fig. 1b**. The J_{1a} , J_{1b} are the intra-dimer interactions and the J_{2a} , J_{2b} are the inter-dimer interactions respectively. Depending on the geometrical parameters associated with the seven spin exchange paths which are listed in **Table 1**, the interaction between the dimer should be very strong because of their $\angle\text{Fe-O-Fe}$ angles involving in the spin exchange paths are 180° .

In order to further investigate the magnetic and electronic property this new compound, it is very important to carry out a systematically theoretical calculation for $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$. Therefore, in this paper, we studied the electronic property and evaluate the spin exchange interactions of $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ by employing the mapping analysis based on density functional electronic structure calculations.

2. Computational Details

Our spin-polarized density functional calculations employed the projector augmented wave method implemented in Vienna *ab initio* simulation package⁵ with the generalized gradient approximation (GGA)⁶ for the exchange-correlation functional, the plane-wave cutoff energy of 500 eV, a set of $4 \times 4 \times 2$ k-points,⁷ and the threshold 10^{-5} eV for energy convergence. In general, the electron correlation associated with 3d states is not well described by density functional calculations, and this deficiency is commonly

corrected by using the GGA plus on-site repulsion U (GGA+U) method. Therefore we also carried out GGA+U calculations with $U = 2.5$ and 4.5 eV.

3. Electronic property

Fig. 2 shows the plots of the total density of states (DOS) and the projected density of states (PDOS) for the Fe 3d states, obtained from GGA+U calculations (with $U = 0, 2.5$ eV) for the ferromagnetic FM state of $K_2Fe_2B_2O_7$. It indicates that all spin-up states of the Fe^{3+} ions are occupied while the spin-down states are unoccupied, which both the GGA and the GGA+U calculations present the same picture. Therefore, $K_2Fe_2B_2O_7$ consists of high-spin Fe^{3+} (d^5) ions. Besides, we also found that ferromagnetic $K_2Fe_2B_2O_7$ is a magnetic insulator with a certain band gap. As expected, the band gap is predicted to be greater by the GGA+U than by the GGA calculations.

4. Evaluation of spin exchange parameters

To extract the values of $J_{1a} - J_5$ on the basis of density functional calculations, we first calculated the total energies of the eight ordered spin states of $K_2Fe_2B_2O_7$ depicted in **Fig. 3**. The relative energies of the eight ordered spin states of $K_2Fe_2B_2O_7$ (**Fig. 3**), obtained from our GGA+U (with $U = 0.0, 2.5$ and 4.5 eV), are summarized **Table 1**. To determine the values of $J_{1a} - J_5$, we express the energies of the eight ordered spin states in terms of the spin Hamiltonian,

$$\hat{H} = - \sum_{i < j} J_{ij} \hat{S}_i \cdot \hat{S}_j, \quad (1)$$

in which J_{ij} ($= J_{1a} - J_5$) is the exchange parameter for the interaction between the spin

sites i and j , while $\hat{S}_i$ and $\hat{S}_j$ are the spin angular momentum operators at the spin sites i and j , respectively. By applying the energy expressions obtained for spin dimers with N unpaired spins per spin site (in the present case, $N = 5^8$), the total spin exchange energies (per formula unit) of the eight ordered spin states are written as

$$\begin{aligned}
 E_{\text{FM}} &= (-2J_{1a}-4J_{1b}-4J_{2a}-2J_{2b}-12J_3-12J_4-12J_5) \ 25/4 \\
 E_{\text{AF1}} &= (2J_{1a}+4J_{1b}+4J_{2a}+2J_{2b}+12J_3+0J_4+0J_5) \ 25/4 \\
 E_{\text{AF2}} &= (-2J_{1a}+4J_{1b}-4J_{2a}+2J_{2b}-12J_3-12J_4-12J_5) \ 25/4 \\
 E_{\text{AF3}} &= (2J_{1a}+4J_{1b}+4J_{2a}+2J_{2b}-12J_3+12J_4+12J_5) \ 25/4 \\
 E_{\text{AF4}} &= (-2J_{1a}+0J_{1b}+0J_{2a}+2J_{2b}-0J_3+12J_4+0J_5) \ 25/4 \\
 E_{\text{AF5}} &= (2J_{1a}+4J_{1b}+4J_{2a}+2J_{2b}-12J_3-12J_4-12J_5) \ 25/4 \\
 E_{\text{AF6}} &= (2J_{1a}+0J_{1b}+0J_{2a}+4J_{2b}-12J_3+6J_4+6J_5) \ 25/4 \\
 E_{\text{AF7}} &= (0J_{1a}-4J_{1b}+4J_{2a}+0J_{2b}-12J_3+6J_4+6J_5) \ 25/4
 \end{aligned} \tag{2}$$

Therefore, the values of $J_{1a} - J_5$ listed in **Table 2** are determined by equating the relative energies of the eight ordered spin states obtained from GGA+U calculations to the corresponding relative energies obtained from the total spin exchange energies.

Our calculations show that all spin interactions favor antiferromagnetic (AFM) coupling. As shown in the **Table 1**, the angles of Fe-O-Fe bridges in all spin exchange paths are larger than 90° . Consequently, the spin orbital can be well overlapped, and lead to AFM coupling. Besides, we also demonstrated that the intra-dimer interactions J_{1a} and J_{1b} are the strongest spin interaction, compared with other spin exchange interaction. As

shown in **Table 3**, the calculated J_{1a} and J_{1b} indicate that such spin exchange paths form spin dimer. Furthermore, the exchanges J_3 , J_4 and J_5 form a triangle in ab plane and all of them are AFM. As a result, the (J_3 , J_4 , J_5) triangle gives some rise to the spin frustration⁹⁻¹⁰, which is consistent with the experimental results.

5. Discussions

The calculated spin-exchange parameters J_{1a} - J_5 are related to the structural parameters associated with their spin exchange paths. The intra-dimer spin exchange J_{1a} and J_{1b} are of the superexchange (SE) type involving Fe-O-Fe paths, while the intra-layer exchange J_{2a} and J_{2b} as well as J_3 - J_5 are of the supersuperexchange (SSE) type involving Fe-O $\cdots$ O-Fe paths¹¹⁻¹². In general, the strength of an Fe-O-Fe superexchange (SE) between two transition-metal atoms Fe depends on the $\angle$ Fe-O-Fe angle and the Fe-O bond length¹³. As listed in Table 1, the $\angle$ Fe-O-Fe angles of SE paths J_{1a} and J_{1b} are 180° , and the Fe-O bond lengths are around 1.79 Å, so it is not surprising that both J_{1a} and J_{1b} are very strongly AFM. The SSE interactions cannot be ignored without justifiable reasons because that the SSE interactions can be much stronger than the SE interactions in some magnetic oxides. In our case, the SSE interactions (J_{2a} , J_{2b} , J_3 - J_5) are almost negligible.

As found for other magnetic materials¹⁴⁻¹⁷, the strength of SSE is mainly depending on the O 2p contributions from the O atoms of the M-O (M denotes the magnetic atom) bonds. To explore the intrinsic reason response for the weak SSE interactions, we determine the magnetic orbitals of the FeO₄ tetrahedra by extended Hückel tight-binding calculations.¹⁸ As presented in Figure 5a, the magnetic orbitals of FeO₄ tetrahedra are

given by the anti-bonding Fe 3d and O 2p orbitals. The overlapping of O 2p orbitals involving the SSE path is almost zero because the O 2p orbitals are nearly perpendicular to each other. For simplicity, only the magnetic orbitals of FeO_4 tetrahedra for the SSE interaction J_3 is given. Though not shown, the same thing is found for the other SSE interactions.

The comparison of the GGA and GGA+U calculations shows that the magnitudes of the exchanges decrease with increasing the on-site repulsion U on Fe. However, the intra-dimer interactions J_{1a} and J_{1b} are always the extremely dominant one independent of the U values. In the Figure 5, we present the spin lattice of Fe^{3+} ions for $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ and the strongest interactions J_{1a} and J_{1b} arise within the dimer.

Now, we discuss the origin of observed magnetism in experiments. As we know, typically, spin frustration will lead to non-collinear spin structure. Here, for $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$, the dominated spin interaction comes from the spin dimer, which is coupled with AFM interaction. Therefore, the AFM spin dimer cannot comprise with each other in the geometric frustration. As a result, spin glass structure is favored. It is worth to be noted that only AFM spin dimer or spin frustration cannot lead to the spin-glass.

6. Concluding remarks

The spin exchanges $J_{1a} - J_5$ of $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ extracted from our calculations reveal that intra-dimer interactions J_{1a} , J_{1b} are strongly AFM, and the remaining five spin exchanges J_{2a} , J_{2b} , J_3 , J_4 and J_5 are relative weak. Besides, the intra-layer interactions J_3 , J_4 and J_5 are AFM and form a triangle net in ab plane. It indicates that the system is a typical spin dimer model with geometric frustration, which is response for the observed spin glass behavior.

Acknowledgments

This work was supported by the NSFC (21203096, 11204137, 11474165), by NSF of Jiangsu Province (BK20130031, BK20131420, BK2012392), by the NJFU outstanding young scholars funding. We also acknowledge the support from the Shanghai Supercomputer Center.

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Table 1. Geometrical parameters associated with the seven spin exchange paths.

SE	Fe...Fe	Fe-O-Fe	$\angle$ Fe-O-Fe
J_{1a}	3.583	1.792, 1.792	180
J_{1b}	3.599	1.799, 1.800	180
SSE	Fe...Fe	Fe-O...O-Fe	$\angle$ Fe-O...O, $\angle$ O...O-Fe
J_{2a}	4.913	1.872, 3.933, 1.868	102, 101.6

		1.872,3.933,1.878	102,101.6
		1.872,3.933,1.868	102,101.3
J_{2b}	4.929	1.878,3.864,1.878	103.8,103.8
		1.878,3.864,1.878	103.8,103.8
		1.878,3.864,1.878	103.8,103.8
J_3	5.064	1.872, 2.362, 1.869	163.2, 102.7
J_4	5.074	1.872, 2.386, 1.877	143.0, 102.2
J_5	5.121	1.877, 2.384, 1.869	151.7, 103.5

^a The lengths are in Å, and the angles in degrees.

Table 2. Relative energies (in meV) of the eight ordered spin states obtained from GGA+U calculations (for the whole supercell adopted in our calculations).

U(eV)	FM	AF1	AF2	AF3	AF4	AF5	AF6	AF7
0	0	-664.4	-408.9	-661.6	-250.8	-625.1	-449.3	-141.8
2.5	0	-440.0	-272.8	-438.7	-161.2	-417.5	-297.1	-90.1
4.5	0	-321.8	-200.5	-321.2	-116.1	-306.9	-217.2	-64.6

Table 3. Spin exchange parameters $J_1 - J_5$ (in meV) obtained from GGA+U calculations ^a

U(eV)	J_{1a}	J_{1b}	J_{2a}	J_{2b}	J_3	J_4	J_5
0	-50.06	-48.46	-0.91	-1.22	-0.84	-0.90	-0.56
2.5	-34.15	-32.58	-0.28	-0.31	-0.48	-0.51	-0.34
4.5	-25.29	-24.01	-0.13	-0.10	-0.31	-0.33	-0.24

Figure captions

Figure 1. Crystal structure of $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$: (a) Projection view in ab plane in which the FeO_4 tetrahedra are connected with each other through the BO_3 triangles and surrounding by K^+ ions. (b) Side view of the layers alternating with layers of K^+ ions. The numbers 1a, 1b, 2a, 2b, 3-5 represent the spin exchanges J_{1a} , J_{1b} , J_{2a} , J_{2b} and J_3 - J_5 , respectively. J_{1a} , J_{1b} and J_{2a} , J_{2b} are the inter-layer spin exchange interactions and the J_3 - J_5 are the intra-layer interactions. The green, blue, red, yellow, cyan and pink circles represent the Fe1, Fe2, Fe3, K, B and O atoms, respectively.

Figure 2. Plots of the total DOS and the PDOS for the Fe 3d states obtained for the FM state of $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ (a) from the GGA calculations and (b) from the GGA+U calculations with $U = 2.5$ eV on Fe.

Figure 3. Six ordered spin states of $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$ employed to extract the spin exchanges J_1

– J_5 by mapping analysis based on density functional calculations, where the unshaded and shaded circles represent the Fe^{3+} ions with up-spin and down-spin, respectively.

Figure 4. (a) Shapes of the two magnetic orbitals of the FeO_4 tetrahedra obtained from extended Hückel tight-binding calculations. (b) Arrangement of two FeO_4 octahedra in the intra-layer spin exchange J_3 .

Figure 5. Network of the Fe^{3+} ions in the structure of $\text{K}_2\text{Fe}_2\text{B}_2\text{O}_7$. The J_{1a} and J_{1b} are the intra-dimer interactions.