Long-range antiferromagnetic interactions in $ZnFe_2O_4$ and $CdFe_2O_4$: Density functional theory calculations

Ching Cheng

Department of Physics and National Center for Theoretical Sciences, National Cheng Kung University, Tainan 70101, Taiwan

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For the first time, the Fe-Fe interactions in the geometrically frustrated antiferromagnetic systems of zinc and cadmium ferrites are determined quantitatively by the first-principles methods of density functional theory. Both the generalized gradient approximation (GGA) and GGA plus the one-site Coulomb interaction (GGA +U) are considered for the exchange-correlation energy functional. The interactions up to third neighbors are found to be all antiferromagnetic for both materials, regardless of which approximation scheme (GGA or GGA+U) is used. Surprisingly, the third-neighbor interactions are estimated to be much stronger than the second-neighbor interactions and on the same order in magnitude as the first-neighbor interactions.

The geometrically frustrated antiferromagnets, distinct from other magnetic systems, exhibit a number of exceptional features whose formation, to a great extent, depends on the range as well as the nature of the interactions between the magnetic ions in the systems.[1–3] Both zinc and cadmium ferrites ($ZnFe_2O_4$ and $CdFe_2O_4$ shorted as ZFO and CFO hereafter) are well known as one type of the geometrically frustrated systems.[4,5] Magnetic neutron scattering measurements have been carried out on both ZFO and CFO to determine the interactions between the Fe ions. Surprisingly, it was concluded that the frustration in CFO (Ref. 6) is driven mainly by the strong nearest-neighbor antiferromagnetic interaction in contrast to the antiferromagnetically coupled third-neighbor interaction in ZFO.[7] In this Brief Report, we study the magnetic interactions between the Fe ions in these two compounds by considering structures with different collinear magnetic distributions, as well as cation distributions using *ab initio* methods.

The structure of spinel ferrites are constructed by filling one-eighth of the tetrahedral sites and half of the octahedral sites (denoted as A and B site, respectively, hereafter) in the fcc sublattice of oxygen. Spinel ferrites are usually categorized into two types, i.e., normal and inverse spinel, according to the distribution of the divalent and trivalent cations in the A and B sites. A normal spinel corresponds to the structure with all the A sites being occupied by the divalent cations, e.g., Zn (Cd) of ZFO (CFO) and the B sites by the trivalent cations, i.e., the Fe ions. In an inverse-spinel structure, the divalent cations occupy half of the B sites while the other half as well as all the A sites are occupied by the Fe ions. Both ZFO and CFO are considered forming normal spinel though coexistence of both phases has been reported.[8] To investigate the magnetic interactions between the Fe ions, we consider three different B-site cation distributions (named SC1, SC2, and SC3 as shown in Fig. 1) on the basis of a cubic cell consisting of eight formulas (56 atoms) of the materials. Inclusion of the possible cation distributions on the A and B sites, as well as the different magnetic orders of the Fe ions, leads to the structures summarized in Table I, i.e., four configurations for normal spinel and six configurations for inverse spinel. A fourth B-site cation distribution, i.e., SC4, is also included to estimate the magnitude of the more distant interactions between Fe cations in the normal

spinel as will be discussed later. There have been first-principles calculations for other spinel compounds, e.g., studies of $MnFe_2O_4$, Fe_3O_4, $CoFe_2O_4$, and $NiFe_2O_4$ by Szotek *et al.*[9] and ACr_2X_4 (A=Zn, Cd, and Hg; X=O, S, and Se) by Yaresko.[10] Note that the only configuration considered in the previous studies[4,11] corresponds to that of nb1 in Table I, i.e., the normal spinel phase with an equal number of oppositely polarized B-site Fe ions distributed as those in SC1 of Fig. 1. We shall show that the nb3 is a more stable structure compared to that of nb1 and similarly ib3 to ib1 for both ZFO and CFO.

To study the extent of the interactions between the cations in these systems, the distances and numbers of neighboring cations for the A- and B-site cations with neighboring distances up to around 6.7 Å are listed in Table II. If we assume that the interactions between the Fe ions in the normal spinel can be approximately modeled by the Ising model, i.e., $H=-(1/2)\Sigma_n\Sigma_i J_n S_i S_{i+n}$, the values of E_0, J_1, J_2, and J_3

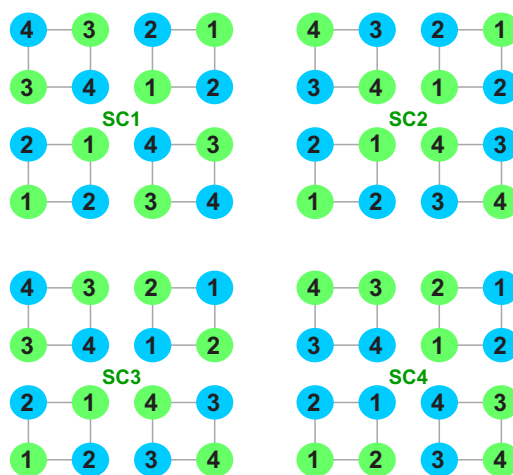FIG. 1. (Color online) The four B-site cation distributions considered in this study. The numbers denote the nth layer when one views along the (001) direction of the cubic cell. The B-site cations are divided into two groups (B1 and B2 in Table I), one denoted in green (light gray) and the other in blue (dark gray). The two types of B-site cations correspond to different cations, e.g., Fe and Zn, in the inverse spinel or oppositely polarized Fe ions in the normal spinel.

TABLE I. The ten configurations considered in the present study and their corresponding cation distributions on the A and B sites, as well as the magnetic orders of the Fe ions.

	Site	A	B1	B2	Configurations
Normal	Cation	Zn(Cd)	Fe	Fe	
Spinel	Magnetic	0	+	+	na1=na2=na3
	Configurations	0	+	−	nb1, nb2, nb3
Inverse	Cation	Fe	Zn(Cd)	Fe	
Spinel	Magnetic	+	0	+	ia1, ia2, ia3
	Configurations	+	0	−	ib1, ib2, ib3

of these materials can be obtained from the calculated total energies of the four configurations of na, nb1, nb2, and nb3. The approximations made by using this simple model to describe the interactions in these compounds and to obtain the corresponding interaction energies are supported by the fact that the moments on the Fe ions in ZFO and CFO are sizable and considerably localized. Similar approaches have been used previously to study the magnetism, e.g., in spinel MnO_2 (Ref. [12]) and $YCuO_{2.5}$.[13] Studies using first-principles calculations for these systems with collinear magnetic distributions should provide information on the size and the extent of the interactions between the magnetic cations in these systems. These pieces of information are, on the other hand, important references to further understand the possible phases of the materials through the studies of the corresponding classical three-dimensional Heisenberg model.

All electronic calculations in this study are based on the spin-polarized density functional theory.[14,15] The generalized gradient approximation (GGA) proposed by Perdew, Burke, and Ernzerhof[16] for the nonlocal correction to a purely local treatment of the exchange-correlation energy functional is used. The on-site Coulomb interaction U (Ref. [17]) for Fe ions is also included in the second stage of the investigation to study its effect on the physical properties of these systems. The values of U and J are taken from the previous studies as 4.5 eV (Ref. [18]) and 0.89 eV (Ref. [17]), respectively. The interactions between the ions and valence electrons are described by the projector augmented wave (PAW) method[19] in the implementation of Kresse and Joubert[20] and the numbers of the treated valence electrons are 12, 8, and 6 for Zn (Cd), Fe, and O atoms, respectively. The single-particle Kohn-Sham equations[21] are solved using the plane-wave-based Vienna *ab initio* simulation program (VASP) developed at the Institut für Material Physik of the Universität Wien.[22] The energy cutoffs used for the plane-wave basis is 500 eV and a set of (6 6 6) *k*-point sampling according to Monkhorst-Pack[23] is used for the integration over the first Brillouin zone, unless specified otherwise. Relaxation processes in optimizing static structures are accomplished by moving oxygen atoms to the positions at which the atomic forces are smaller than 0.02 eV/Å. The cell volumes are also relaxed under the constraint that the systems remain cubic.

The calculated energies (relative to the corresponding lowest-energy one), lattice constants, and magnetic moments of Fe ions of the studied configurations (Table I) for both

TABLE II. The distances (d) and numbers (N) of neighboring cations in the spinel systems are listed in the order of increasing distances. For example, the number of the nearest-neighbor B-site cations for an A-site cation is twelve as indicated in the second line. The distances are written in terms of the squared values (in unit of a_0, i.e., the cubic lattice constant) and the length (in unit of Å) assuming $a_0=8.5$ Å. They are further grouped according to the order of neighboring. The nth-neighbor interactions between the B-site Fe ions in normal spinel, i.e., J_n of the Ising model, are also denoted.

	$(d/a_0)^2$	d(Å) when $a_0=8.5$ Å	N
B(B) J_1	8/64	3.0	6
A(B)	11/64	3.5	12
B(A)	11/64	3.5	6
A(A)	12/64	3.7	4
B(B) J_2	24/64	5.2	12
A(B)	27/64	5.5	16
B(A)	27/64	5.5	8
A(A)	32/64	6.0	12
B(B) J_3	32/64	6.0	12
B(B) J_4	40/64	6.7	12

ZFO and CFO using either GGA or GGA+U approach are listed in Table III.

The experimental lattice constants for ZFO and CFO are around 8.52 Å (Ref. [7]) and 8.72 Å (Ref. [6]), respectively. The calculated lattice constants are all within 1% deviation from the experimental values except for the ia1, ia2, and ia3 of ZFO.[24] One also notices that the energies of these three ferromagnetic inverse-spinel configurations are significantly larger than the rest of the considered configurations. Therefore the effect of U is not applied to the ia1, ia2, and ia3 configurations. From now on we shall focus the discussions on the rest of the seven configurations.

The local magnetic moments for Fe ions in these configurations were found to be within the range of $3.7 \sim 3.9$ μ_0 and $4.1 \sim 4.2$ μ_0 for GGA and GGA+U calculations, respectively. The GGA+U results are closer to the experimental estimates of the magnetic moments, i.e., 4.22 (Ref. [25]) and 4.44^6 μ_0 for ZFO and CFO, respectively.

The orders in energy of these configurations are different for ZFO and CFO which demonstrates the underlying differences in the properties of these two compounds. However the lowest-energy configurations are identical for these two compounds; i.e., they are ib3 and nb3 in the GGA and GGA+U calculations, respectively. Although the lowest-energy configuration is an inverse spinel in the GGA calculations, it is a normal spinel in the GGA+U calculations. The on-site Coulomb interaction U is usually considered as essential for properly describing the electronic and magnetic properties of the Fe ions in spinel ferrites. Note that the lowest-energy configuration of the GGA+U results, i.e., nb3, is different from the configuration considered in all the previous studies, i.e., nb1.

The interaction energies between the B-site Fe ions up to third neighbors can be determined by applying the Ising model to the calculated energies of the four normal spinel configurations, i.e., nb1, nb2, nb3, and na, and the results are

TABLE III. The calculated energies (in unit of eV per eight formulas of the materials) relative to the corresponding lowest-energy configuration, the lattice constants (in Å), and the local magnetic moments of Fe ions (in unit of Bohr magneton) for the ten configurations of Table I using either GGA or GGA+U (data in parentheses) approach.

ZFO	na	nb1	nb2	nb3	ia1	ia2	ia3	ib1	ib2	ib3
ΔE	4.28(0.54)	2.21(0.18)	2.71(0.14)	1.98(0.00)	5.18	4.89	4.12	0.38(2.18)	0.90(2.68)	0.00(1.68)
a_0	8.52(8.53)	8.50(8.52)	8.51(8.52)	8.50(8.52)	8.35	8.36	8.35	8.45(8.49)	8.45(8.50)	8.45(8.49)
μ	3.9(4.2)	3.8(4.2)	3.9(4.2)	3.8(4.2)	3.7/1.5	3.7/14	3.7/15	3.7(4.1)	3.7(4.1)	3.7(4.1)
CFO	na	nb1	nb2	nb3	ia1	ia2	ia3	ib1	ib2	ib3
ΔE	3.50(0.76)	0.99(0.15)	1.74(0.27)	0.79(0.00)	8.32	7.71	6.89	1.91(4.94)	1.89(4.41)	0.00(2.81)
a_0	8.82(8.82)	8.78(8.81)	8.80(8.81)	8.79(8.81)	8.77	8.15	8.77	8.73(8.76)	8.75(8.78)	8.72(8.75)
μ	4.0(4.2)	3.8(4.2)	3.9(4.2)	3.8(4.2)	3.8	3.9	3.8	3.7(4.1)	3.7(4.1)	3.7(4.1)

presented in Table IV. They all turn out to be antiferromagnetic no matter whether the effect of U is included or not. The effect of U reduces the magnitudes of J_1 and J_2 substantially, but only halves the magnitudes of J_3. The universal reduction in magnitude of J_n after including U is implied in the density of states of these systems. The most prominent effect of U in ZFO is localizing the five d electrons of Fe ions, which are previously well hybridized with the other valence electrons, and therefore weakening the interactions between them while at the same time widening the band gap of the system. Similar results take place in CFO except that the strongly localized ten d electrons of the Cd ions locate at the lower energy range than the localized five d electrons of Fe ions even after the effect of U is included. That how the exchange interactions depend on the values of U has been studied previously, e.g., in $FeSbO_4$ (Ref. 26) and in $NiGa_2S_4$.[27] The variations in J due to U were shown being monotonically. Our results of using U=0 and U=4.5 suggest that for both ZFO and CFO with the on-site Coulomb interaction within the range of 0 to 4.5 all lead to having antiferromagnetic interactions up to third neighbors and stronger

third-neighbor interactions than the second-neighbor ones. These conclusions are consistent with the tested results of calculations using U=2.5 eV as shown in Table IV.

As the magnitude of J_2 in the GGA+U results is considerably smaller than those of J_1 and J_3, the numerical errors due to using finite basis sets and discrete k points are examined. The lower (400 eV) and higher (600 eV) energy cutoffs for the plane-wave basis are considered, as well as the sparser (4 4 4) and denser (8 8 8) sets of Monkhorst-Pack sampling. The results in Table IV indicate that the significant figure for the values of these interactions, i.e., $8J_n$ (eight is the number of formulas in the cubic cell used in the calculations), can be considered as in meV. The magnitude of J_3 is at least three (five) times larger than that of J_2 and about one third (sixth) of J_1 for ZFO (CFO) in the GGA+U calculations. This, i.e., the J_3 interaction, corresponds to an interaction between B-site Fe ions of at least 6 Å apart, which is a considerably long-range interaction. If the interactions beyond the second neighbors are negligible, the values for J_1 and J_2 can be readily obtained from merely considering the energies of nb1, nb2, and nb3. These results are also listed in

TABLE IV. The nth-neighbor interaction energy (in unit of meV) between the B-site Fe ions obtained from the energies of the normal spinel configurations of na, nb1, nb2, and nb3, unless specified otherwise. The J_1 and J_2 obtained from considering merely the energies of nb1, nb2, and nb3 are also listed for comparison. All the results presented here use the GGA (PBE) scheme with different values of U (in unit of eV). The corresponding values of energy cutoff and the Monkhorst-Pack mesh (k point) are also indicated.

ZFO	E_{cutoff}	k point	$4J_1$	$4J_2$	$4J_3$	$4J_1$ [a]	$4J_2$ [b]
U=0.0	500	(6 6 6)	−220.4	−19.0	−23.6	−126.2	+28.1
U=2.5	500	(6 6 6)	−97.7	−7.0	−16.5	−31.6	+26.0
U=4.5	400	(4 4 4)	−43.7	−3.2	−12.2	+5.0	+21.1
U=4.5	500	(6 6 6)	−39.6	−2.7	−12.3	+9.7	+22.0
U=4.5	600	(8 8 8)	−39.7	−2.6	−12.4	+9.8	+22.2
U=4.5[c]	500	(6 6 6)	−38.1	−3.5	−12.7		
U=4.5[d]	500	(6 6 6)	−40.2	−2.4	−12.5		
CFO	E_{cutoff}	k point	$4J_1$	$4J_2$	$4J_3$	$4J_1$ [a]	$4J_2$ [b]
U=0.0	500	(6 6 6)	−275.9	−18.7	−21.8	−188.8	+24.8
U=4.5	500	(6 6 6)	−71.1	−2.2	−10.6	−28.9	+18.9

[a]$J_1 = (nb1 - nb2)/2$.
[b]$J_2 = (nb1 - nb3)/4$.
[c]Obtained from na, nb1, nb2, nb4.
[d]Obtained from na, nb1, nb3, nb4.

Table IV. Under this assumption, both J_1 and J_2 of ZFO in the GGA+U calculations are switched to ferromagnetic interactions. This is not a plausible result when considering the experimentally identified antiferromagnetic phase for ZFO. To estimate the magnitude of the next distant interaction, i.e., J_4, which is not included in the previous discussion, the total energy of the SC4 configuration in the normal spinel, i.e., nb4, was also calculated. The magnitude of J_4 cannot be obtained from considering the five configurations of na, nb1, nb2, nb3, and nb4 as their energy formulas are linearly dependent. However, the magnitudes of the first three neighbor interactions can be evaluated from considering either na, nb1, nb2, and nb4 or na, nb1, nb3, and nb4, whose results are also listed in Table IV. It is obvious that the effect of the longer-distance interactions does not change the findings we shall conclude next, i.e., existing antiferromagnetic interactions up to the third neighbors, much weaker J_2 compared to those of J_1 and J_3 and that J_1 and J_3 are at the same order of magnitude. Similar characters take place in CFO except that the nearest-neighbor interaction, when compared to J_3, is much more dominant than that in ZFO, which is consistent with the experimental suggestions.[6,7]

There have been numerous theoretical studies for the geometrically frustrated antiferromagnetic systems using the classical three-dimensional Heisenberg model.[1–3] Studies including up to the second neighbor interactions suggested that with the present estimated values of J_1 and J_2, i.e., $J_1 < 0$ and $J_2/J_1 < 0.5$, the system remains paramagnetic down to 0 K.[2] A mean-field approach to magnetic ordering in the highly frustrated pyrochlores also concluded that no long-range order can be established for a system with antiferromagnetic J_1 and J_3 interactions but negligible J_2 and J_4 interactions.[3] Experimentally there has been suggestion that no long-range order can be established down to 0.1 K for CFO even with an applied field of up to 9 T (Ref. 6) and similarly ZFO was found remaining disordered even at the lowest observable temperature of 1.5 K.[7]

In summary, we have generated different configurations, in both cation distribution and magnetic order, to study quantitatively the Fe-Fe interactions in ZFO and CFO using GGA, as well as GGA+U approach. The interactions between the B-site Fe ions are found to extend up to third neighbors and all in antiferromagnetic nature. The second-neighbor interaction is estimated to be much smaller in magnitude than those of the first-neighbor and the third-neighbor interactions.

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