Effects of cation distribution in ZnFe$_2$O$_4$ and CdFe$_2$O$_4$: ab initio studies

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Abstract. Two different distributions for the octahedral-site cations in ZnFe$_2$O$_4$ and CdFe$_2$O$_4$ are investigated by the first-principles method of density functional theory. Both the local density approximation (LDA) and the generalized gradient approximation (GGA) as well as the inclusion of the one-site Coulomb interaction (LDA+U and GGA+U) are considered for the exchange-correlation energy functional. It is shown that a different octahedral-site distribution can lead to considerably different density of states as well as band gaps in both the normal and inverse spinel configurations of these two materials.

1. Introduction

Both zinc and cadmium ferrites (ZnFe$_2$O$_4$ and CdFe$_2$O$_4$ shorted as ZFO and CFO hereafter) are well known as one type of the geometrically frustrated systems[1,2]. Experimentally there has been suggestion that no long-range order can be established down to 0.1K for CFO even with an applied field of up to 9T [3] and similarly ZFO was found remaining disordered even at the lowest observable temperature of 1.5K [4]. The Fe-Fe interactions in these two systems were studied and determined quantitatively in a previous presentation [5] by considering structures with different collinear magnetic distributions as well as cation distributions and using the first-principles methods of density functional theory [6]. The interactions up to third neighbours were found to be all antiferromagnetic for both materials in the approximation schemes of the GGA and GGA+U. In this article, we demonstrate through the first-principles calculations that the magnetic as well as cation distribution for the octahedral-site cations has effects on both energies as well as density of states, including the band gaps of the systems, no matter which approximation scheme is used for the exchange-correlation energy functional.

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. 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 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 [7]. There are two types of B-site cations corresponding to differently polarized Fe ions in the normal spinel and different cations, e.g. Fe and Zn, in the inverse

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spinel. In the previous studies the two types of B-site cations was assumed distributed as the SC1 in figure 1. However, that is not the only possible distribution and another possible choice of SC3 is presented in figure 1. Inclusion of the possible cation distribution on the A and B sites as well as the different magnetic orders of the Fe ions leads to the structures of nb1, nb3, ib1, and ib3 where the n and i denotes the normal and inverse spinel respectively and the 1 and 3 corresponds to the distributions of the two types of B-site cations as in SC1 and SC3 of figure 1. Note that we do not consider the ferromagnetic cases here.

**Figure 1.** The two 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 consisting of eight formulas (56 atoms). The B-site cations are divided into two groups, one denoted in green and the other in blue.

All electronic calculations in this study are based on the spin-polarized density functional theory [8]. The LDA [9] and GGA proposed by Perdew, Burke and Ernzerhof (PBE) [10] schemes are used for the exchange-correlation energy functional. The on-site Coulomb interaction $U$ [11] for Fe ions is also included with the values of 4.5 eV for $U$ [12] and 0.89 eV for $J$ [11] taken from the previous studies. The interactions between the ions and valence electrons are described by the projector augmented-wave method [13] in the implementation of Kresse and Joubert [14]. The single-particle Kohn-Sham equations [15] are solved using the plane-wave-based Vienna ab-initio simulation program[16]. The energy cutoffs used for the plane-wave basis is 500 eV and a set of (6 6 6) k-points sampling according to Monkhorst-Pack [17] is used for the integration over the first Brillouin zone. 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 results of the relative energies and density of states for these four studied configurations will be presented in the next section.

2. Results and Discussions

2.1. Relative energies

**Figure 2.** The relative energies (in unit of eV per 8 formulas) of the four studied configurations of ZFO obtained from using GGA(PBE) and LDA as well as the GGA(PBE)+U and LDA+U. The results calculated from two different values of $U$ are also presented.

The relative energies (relative to the corresponding lowest-energy one) of the four considered configurations, i.e. nb1, nb3, ib1 and ib3, for ZFO are presented in figure 2. In addition to LDA and GGA schemes, different values of $U$ for the LDA+U and GGA+U are also included for studying the effects of varying the values of $U$. The value of 4.5eV for $U$ taken from the previous studies [12] is expected to be the more appropriate one for the Fe ions in the spinel ferrites.
Firstly we notice that the different B-site distributions in the normal spinel systems, i.e. different magnetic distributions, lead to different energies. This is expected as there are interactions between the polarized magnetic Fe ions and our previous studies [5] show that these interactions extend up to third neighbours. Similarly, the different distributions of Fe and Zn (or Cd) cations in the B sites also lead to different energies. In the results of no U, the most stable configurations are nb1 in LDA but ib3 in GGA. However, the LDA calculations of the normal spinel configurations would result in a dominant ferromagnetic nearest-neighbour interaction between the B-site Fe ions (similar discussion as those in reference [5]). This is not consistent with the experimentally observed antiferromagnetic properties of the ZFO and therefore the LDA can not describe the ZFO system properly. The most stable configuration for both of the LDA and GGA results switches to nb3 when the on-site U of 4.5eV is included in the calculations. Note that nb3 is a different B-site distribution from the nb1 used in all the previous studies. At the value of U=2.5eV, the most stable structure is ib3 for both the LDA and GGA approach. We notice that different values of U would change the relative stability between the normal and inverse spinel configurations. However the SC3 configuration stays as the more stable configuration than SC1 no matter whether it is in the normal or inverse spinel (we exclude the LDA(U=0) case here). Similar conclusions were found for the CFO material.

2.2. Density of states
The total and partial density of states (DOS) for the nb1 and nb3 configurations in ZFO using GGA and GGA+U(4.5) are presented in figure 3. There are finite band gaps in the SC3 configurations for both normal and inverse spinel in the GGA and GGA+U scheme. For the SC1 configuration in the GGA scheme, the band gap is only about 0.05eV for nb1 while ib1 is not insulating. In the GGA+U scheme, the gaps are opened up for both nb1 and ib1, but they are still smaller than those of the corresponding SC3 configurations, i.e. nb3 and ib3. These results are consistent with the lower energy of the SC3 than that of the SC1 presented in the last section.

The total and partial DOS for the nb3 of CFO are presented in figure 4. The behaviour is similar to that of ZFO except that the ten strongly localized d electrons of Cd in the GGA scheme locate in a lower energy region than the rest of the valence electrons of the system. Inclusion of the on-site U interaction, as expected, would pushes five d electrons of the Fe ions down to the lower energy region as well as opens up the band gap. The difference between CFO and ZFO is that in ZFO the five d electrons...
electrons of the Fe ions are pushed down to a lower energy region than the d electrons of Zn while in CFO the five d electrons of the Fe ions are still mostly in the higher energy range than the d electrons of Cd.

![Density of States](image)

**Figure 4.** The total and partial density of states for the nb3 of CFO from the GGA and GGA+U(4.5) calculations.

3. Conclusion

We demonstrate through first-principles calculations that the different B-site distributions would lead to considerably different physical properties for both the normal and inverse spinel configurations in ZFO and CFO. The energies, DOS as well as band gaps can all depend on the B-site distributions of the cations. Its implication for the inverse spinel ferrites should not be overlooked.

Acknowledgements  This work was sponsored by the National Science Council of Taiwan. The computer resources were mainly provided by the National Center for High-Performance Computing in Hsin Chu of Taiwan.

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Highly Frustrated Magnetism 2008 (HFM 2008) IOP Publishing
Journal of Physics: Conference Series **145** (2009) 012028 doi:10.1088/1742-6596/145/1/012028

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Journal of Physics: Conference Series **145** (2009) 012028 doi:10.1088/1742-6596/145/1/012028