Letter to the Editor

Enhanced magnetization and conductive phase in NiFe$_2$O$_4$

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ABSTRACT

Recent advances on nanometer films observed magnetization enhanced NiFe$_2$O$_4$ (NFO) in insulating phase as well as in conductive state with highly spin-polarized current which together can be integrated for potential applications in spintronics. In this brief report, we demonstrate, using density-functional-based calculations, how various cation distributions and magnetic orders can lead to a quadruple enhanced magnetization in NFO and the possible tuning of their electronic properties. The ground-state phase was identified as a structure having a tetragonal symmetry space group of $P4_{3}2_{1}$ which is consistent with the most recent experimental conclusion. The energetically most likely phase exhibiting enhanced magnetization is an insulating inverse spinel phase while the experimentally observed conductive phase likely originates from a phase with cation inversion.

Bulk nickel ferrite, NiFe$_2$O$_4$ (NFO), is a semiconductor with a room-temperature resistivity of 1 kΩ cm and shows soft ferrimagnetic order below 850 K with a relatively low magnetization of 2 μ$_B$ per formula unit (2 μ$_B$/fu), i.e. about 300 emu cm$^{-3}$ [1]. It is believed to have a completely inverse spinel structure in its bulk form. Recent advances on NFO nanometer films observed enhanced magnetic moments and succeeded in possible tuning of their electronic properties from insulating to conductive state possessing highly spin-polarized current [2–6]. These magnetization enhanced materials can hence be integrated for spintronics devices [6]. The enhanced magnetization and conductive property are commonly attributed to cation inversion in the experimental discussions [2,4,6]. The enhanced magnetization was observed experimentally to depend on the growth temperature, sizes, substrates, etc. [2,4,6]. The interface/surface states might contribute directly to the effect too. However, a double or quadruple enhancement of the magnetization in a 12-nm film which consists of 110 atomic layers (along the growth direction (001)) is beyond the effect of interface/surface as the enhanced magnetization of the film as a whole requires an even further enhancement in the interface/surface layers, considering the middle of the film retaining the bulk property. That is why the cation inversion is usually conjectured in the experimental papers and cation inversion is known to occur in spinel ferrite thin films [7,8] as well as in nanoparticles [9–11]. The present paper, by performing density-functional-based calculations, studies the possible origins of these interesting experimental observations from the bulk consideration. We demonstrate, through exploring various magnetic orders and cation distributions in this material, that the energetically most probable phase exhibiting enhanced magnetization is an insulating inverse spinel phase while the metallic property only exists in the normal spinel phases, i.e. due to the cation inversion.

The structure of spinel ferrites (AB$_2$O$_4$) is 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. In the inverse spinel structure of the bulk NFO, the Ni cations occupy the B site while the Fe cations distribute equally between the A and B sites. A normal spinel, which is considered as a structure with cation inversion in NFO, corresponds to the structure with Ni and Fe cations occupying A and B site respectively. In addition to the distinction between the inverse and normal spinel structures, there are several possible distributions for cations at B sites (divided into two groups and denoted as the B1 and B2 sites) as well as different magnetic orders for the cations at A, B1 and B2 sites [12]. The B-site cation distribution presented in this report corresponds to the SC3 in Ref. [12] as its energy is always found being the lowest among the four distributions (SC1-SC4) having the same magnetic order between the A-site, B1-site and B2-site cations. Table 1 lists all the phases considered in this study.

In the present study, the electronic calculations are based on the spin polarized density functional theory [13–15] implemented in the plane-wave-based Vienna ab initio simulation program (VASP) which was developed at the Institute fur Material Physik of the Universitat Wien [16,17]. The generalized gradient approximation (GGA) developed by Perdew et al. [18] is used for the exchange-correlation energy functional. In transition metals, the on-site Coulomb repulsion is included to account for the strong correlation of the d-orbital electrons [19,20]. The values of $U$ and $J$ for Fe, as generally adopted in iron spinel, are taken from the previous studies as 4.5 eV and 0.89 eV, respectively [19–21]. For
The space group of this phase, taking into account of both the U energy cutoffs (600 eV) and denser k-point sets (8 8 8) would i.e. 2m most stable phase is always the Ipnn phase and its magnetization, on-site Coulomb interactions considered in the present study, the not depend on the U Ni, the values of 2, 4, and 6 eV for Fig. 1. The calculated relative energies of all the studied phases in Table 1 relative to the lowest-energy phase of Ipnn at different U (Ni).

Ni, the values of 2, 4, and 6 eV for U, all with J=1.0 eV, are included in order to explore the U effect of Ni in this material which is not well established yet [22]. The interaction between ions and valence electrons is described by the projector augmented wave (PAW) method [23] which was implemented by Kresse and Joubert [24]. The valence electrons included are 10, 8, and 6 for Ni, Fe, and oxygen respectively. Throughout this study, the cubic unit cell consisting of eight formulas is used in order to examine the chemical and magnetic interactions between cations. The energy cutoff that determines the number of the plane waves is 500 eV and the k-point sampling according to Monkhorst–Pack [25] is (6 6 6) for the 8-formula cubic cell. Atomic and volume relaxations are implemented in turn until the atomic forces are smaller than 0.02 eV/Å and the total energy (per 8 formulas) is converged to 10^{-6} eV while keeping the cubic unit cell. The higher energy cutoffs (600 eV) and denser k-point sets (8 8 8) would change the total energy differences between different phases by no more than 1 meV/fu [12].

The calculated relative energies of all the studied phases in Table 1 are plotted in Fig. 1 and the magnetic moments, which do not depend on the U (Ni) values, are listed in Table 2. For all the on-site Coulomb interactions considered in the present study, the most stable phase is always the Ipnn phase and its magnetization, i.e. 2 μ_B/Ni, is consistent with the experimental value for the bulk NFO [1]. In this phase, the antiparallel moments of the Fe ions at A and B sites are cancelled out with each other and the net moment of the phase comes from the moment of the Ni ions at B site. The theoretical lattice constant is 8.40 Å, with less than 1% difference between results of all the considered U (Ni) cases, which compares closely to the experimental lattice constant of 8.34 Å [1]. The space group of this phase, taking into account of both the cation distribution and magnetic order, is P4_22 of the tetragonal space group. Note that the previously examined structure [26–30] is the SC1 of Ref. [12] which corresponds to the Imma in the orthorhombic space group. A recent experimental paper has reported evidence for a short-range B-site order in NiFe_{2}O_{4} with possible tetragonal P4_22/P4_22 symmetry, though the phase with Imma space group was not ruled out [31]. Our calculations always lead to an energetic preference of P4_22 over Imma, though by various amounts in different U cases, all within the range between 10 and 20 meV/fu. The different physical properties between these two phases also show up in the electronic structure. For example, in the case without including U (Ni) and U (Fe), the SC1 phase (Imma symmetry) is a conductor while the SC3 phase (P4_22 symmetry) has a band gap of 0.20 eV.

Of the four inverse spinel phases studied here which have the same cation distribution but different magnetic orders, two phases have magnetizations much more enhanced than the lowest-energy Ipnn phase, i.e. Ipnp and Ippp. The Ipnn phase has a magnetization which is four times that of the Ipnn. As both the parallel moment of the A-site and B-site Fe contribute 5 B/Fe, together with the antiparallel moment of Ni (2 μ_B/Ni) they lead to a total of 8 μ_B/fu. The Ipnn phase is the energetically most likely phase in the bulk form which might contribute to the much enhanced magnetization observed in the thin film or nanoparticles of NFO. This enhanced magnetization is achieved by having different magnetic orders from the lowest-energy Ipnn phase and accordingly involves no cation inversion, contrary to the popular proposal previously [2–6]. Its origin lies mainly on the much smaller magnetic moment of Ni cations (2 μ_B) than that of Fe cations (5 μ_B). Whenever the two Fe ions (per formula) have parallel moments, the system would results in a much enhanced magnetization. Similarly, of the three magnetic orders in the normal spinel structure, both the Npnn and Nppp phases exhibit enhanced magnetizations. However, the energies of Npnn and Nppp are larger than Ipnn (and Ippp too) and display a much stronger U (Ni) dependence than the Npnn and the inverse spinel phases. These results were found to come in parallel with the metallic property of the Npnn and Nppp phases.

The calculated electronic properties are summarized in Table 2. All the inverse spinel phases are insulators. As the bulk NFO has a room-temperature resistivity of 1 kΩ cm, the band gap is expected to be close to that of the bulk Si (1.22 eV at 0 K). This corresponds most closely to the ground state phase Ipnn at U (Ni)=2 eV case. The case with U (Ni)=2 eV is therefore expected to be the most likely physical picture for NFO. The two normal phases with much enhanced magnetization, i.e. Npnn and Nppp, are either half metals or metals. The Nppp phase is always found a half metal, irrespective of U (Ni) values. For the Npnn phase in the cases of U (Ni)=2 eV, the density of states (DOS) is close to a half metal except for a short tail (~0.2 eV) of low DOS in the minority-spin component extending below Fermi level (Fig. 2). The Npnn phase is therefore expected to be conductive with highly spin-polarized current. Including both the results in

### Table 1

<table>
<thead>
<tr>
<th>Site</th>
<th>Inverse spinel</th>
<th>Normal spinel</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ion Ipnn Ipnp Ippn Ippp</td>
<td>Ion Npnn Nppn Nppp</td>
</tr>
<tr>
<td>A</td>
<td>Fe + + + +</td>
<td>Ni + + +</td>
</tr>
<tr>
<td>B1</td>
<td>Fe − − − +</td>
<td>Fe − + +</td>
</tr>
<tr>
<td>B2</td>
<td>Ni − − + +</td>
<td>Fe − − +</td>
</tr>
</tbody>
</table>

### Table 2

The band gaps (in unit of eV) of the studied phases at different U cases. HM and M denote half metal and metal respectively. The notation of ~ HM indicates a nearly half metal (details in text). Also listed are the calculated saturation magnetic moments.

<table>
<thead>
<tr>
<th>U (Ni) (eV)</th>
<th>Ipnn</th>
<th>Ipnp</th>
<th>Ippn</th>
<th>Ippp</th>
<th>Npnn</th>
<th>Nppn</th>
<th>Nppp</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.47</td>
<td>1.47</td>
<td>0.92</td>
<td>0.77</td>
<td>~ HM</td>
<td>0.66</td>
<td>HM</td>
</tr>
<tr>
<td>4</td>
<td>1.76</td>
<td>1.77</td>
<td>1.29</td>
<td>1.08</td>
<td>M</td>
<td>1.46</td>
<td>HM</td>
</tr>
<tr>
<td>6</td>
<td>1.92</td>
<td>2.02</td>
<td>1.33</td>
<td>1.17</td>
<td>M</td>
<td>1.86</td>
<td>HM</td>
</tr>
</tbody>
</table>

μ_B/fu  

| 2     | 2    | 8    | 12   | 8    | 2    | 12   |
and Nppp phases. The magnetic and electronic properties of bulk NiFe$_2$O$_4$ with different cation distributions and magnetic orders are investigated by the density-functional-based methods. The energetically most likely phase exhibiting enhanced magnetization is the Ippn phase which is insulating and an inverse spinel structure. The experimentally observed conducting phase with highly spin-polarized current likely originates from the normal Npnn phase which is a nearly half metal.

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**Table 3**

The exchange interactions (in unit of meV) for the inverse and normal spinel NFO at different U (Ni). The negative sign represents an antiferromagnetic interaction.

<table>
<thead>
<tr>
<th>U (Ni) (eV)</th>
<th>Inverse spinel (meV)</th>
<th>Normal spinel (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_{AA}$</td>
<td>$J_{AB}$</td>
</tr>
<tr>
<td>2</td>
<td>−38.3</td>
<td>−23.6</td>
</tr>
<tr>
<td>4</td>
<td>−38.9</td>
<td>−19.4</td>
</tr>
<tr>
<td>6</td>
<td>−39.3</td>
<td>−15.5</td>
</tr>
</tbody>
</table>

energetics and magnetization, the energetically most likely isolating and conductive phase with much enhanced magnetization are the Ippn and Npnn phase respectively while the Npnn is a nearly half metal (Table 3).

Using the Heisenberg model to describe the magnetic interactions between cations, we can obtain the three nearest-neighbor interactions for the inverse spinel phases, i.e. $J_{AA}$, $J_{AB}$, and $J_{BB}$ from the calculated energies of the four inverse phases in Table I. Note that the cation distributions for the four inverse phases considered here are identical and their differences are solely from the different magnetic orders. The exchange interactions for all the considered U cases are in similar magnitude. All the three interactions are antiferromagnetic. However, the interactions between the B-site cations are one order in magnitude smaller than those between the A-site and B-site cations. This result is the main reason why the most stable phase Ippn has the magnetic order of pnn, a configuration sacrifices the weak antiferromagnetic interaction among B-site cations for the strong antiferromagnetic interaction between A-site and B-site cations. The strong A–B interactions are due to the around 120° A–O–B angle whose connecting structure provides the strong coupling between d orbitals of the A-site and B-site cations through the p orbital of oxygen anions while, on the other hand, the B–B interactions are connected through the around 90° B–O–B angle. The nearest-neighbor interactions in the normal spinel structures are also found to be antiferromagnetic. However, the $J_{BB}$ interaction is found stronger than the $J_{AB}$ interaction. The unexpected large size of $J_{BB}$ is likely due to the metallic properties of the Npnn and Nppp phases.

In conclusion, we show that the ground-state phase of NFO has a tetragonal symmetry space group of P4$_2$22. The energetics, magnetic and electronic properties of bulk NiFe$_2$O$_4$ with different

**References**