Structural, electronic and magnetic properties of partially inverse spinel CoFe$_2$O$_4$: a first-principles study

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Abstract
Partially inverse spinel CoFe$_2$O$_4$, which may be prepared through various heat treatments, differs remarkably from the ideal inverse spinel in many properties. The structure of partially inverse spinel CoFe$_2$O$_4$ as well as its electronic and magnetic properties through a systemic theoretical calculation of (Co$_{1-x}$Fe$_x$)$_{Tet}$(Co$_x$Fe$_{2-x}$)$_{Oct}$O$_4$ ($x = 0, 0.25, 0.5, 0.75$ and $1.0$) have been investigated by the generalized gradient approximation (GGA) + $U$ approach. It is found that the Co and Fe ions prefer their high spin configurations with higher spin moments at octahedral sites in all the studied cases, in line with experimental observations. The Co ions at the octahedral sites favour being far away from each other in the partial inverse spinels, which also show half metallicity at certain inversion degrees.

(Some figures in this article are in colour only in the electronic version)

1. Introduction
The spinel $AB_2X_4$ is one of the most interesting and important families of crystalline compounds, with applications in magnetic materials, ceramics, catalysis, etc [1]. $A$, $B$ and $X$ denote a divalent cation, a trivalent cation and a divalent anion, respectively, in the stoichiometric formula of $AB_2X_4$, including oxides, sulfides, selenides and tellurides [2–4]. Spinel ferrites [5] have been studied for many years due to their performance in high-frequency devices. In particular, the spinel cobalt ferrite (CoFe$_2$O$_4$) has covered a wide range of applications including electronic devices, ferrofluids, magnetic delivery microwave devices and high density information storage due to its wealth of magnetic and electronic properties, such as high magnetostriiction and high rate of change of strain with magnetic field, cubic magnetocrystalline anisotropy, high coercivity, moderate saturation magnetization, high Curie temperature $T_C$, photomagnetism, high chemical stability and good electrical insulation [6–18].

The cations $A$ and $B$ can occupy two different sites in a spinel structure, i.e. octahedral ($O_h$) and tetrahedral ($T_d$) sites within the fcc oxygen sublattices. The occupations of metals at $O_h$ and $T_d$ sites have an important effect on the properties of spinels, such as colour, diffusivity, magnetic behaviour, conductivity and catalytic activity [19–21]. The actual distribution of cations $A$ and $B$ in spinels is influenced by the heat treatment process and chemical environment [22]. The cation distribution can be distinctly characterized by the so-called degree of inversion $x$, which is defined as the fraction of the divalent metal cations in octahedral sites as follows:

\[(Co_{1-x}Fe_x)_{Tet}[Co_xFe_{2-x}]_{Oct}O_4\]

In normal spinels ($x = 0$), the tetrahedral and octahedral sites are occupied by divalent and trivalent cations, respectively, while in the inverse spinels ($x = 1$) all the divalent cations occupy the octahedral sites and trivalent cations occupy tetrahedral and octahedral sites evenly. When it is a partial inverse structure, the spinel is called disordered since the di- and trivalent cations may be distributed at both tetrahedral and octahedral sites. The numbers of trivalent and divalent ions are required to remain at 2:1 in a stable $AB_2X_4$. Typical
normal spinels at room temperature are MgAl2O4, FeAl2O4, ZnAl2O4 and FeCr2O4, while Fe2O4, MgFe2O4 and NiFe2O4 are typical inverse spinels [23]. The structure of spinel oxides can accommodate various cations, some of which may have multiple oxidation states, distributing at the tetrahedral and octahedral sites in different ways. For instance, Co ions of both 2+ and 3+ oxidation state can co-exist in the Co2FeO4 ferrites, and so do Fe ions in the Fe3O4 ferrites. Determination of the cation distribution is a crucial issue since it plays an important role in the properties of spinels [24].

Many researchers have reported that the actual cation distribution of cobalt ferrite depends on heat treatments [24–30]. Part of the Co2+ may be located at the octahedral sites under different heat treatment processes, and a range of 0.62–0.93 for the inverse parameter x is reported. Mössbauer spectroscopy measurements have suggested x ≈ 0.76 when samples annealed at 1520 K if they are water quenched, and x ≈ 0.93 if slowly cooled [25, 26]. Meanwhile, x ≈ 0.62 was measured when the samples annealed at 1320 K and quenched in water [27, 28], and x ≈ 0.80 was reported for CoFe2O4 prepared at 870 K [29]. A synchrotron x-ray diffraction study, making use of anomalous x-ray scattering, suggested x ≈ 0.78 when a sample annealed at 1073 K, though no details were given about the cooling conditions [30]. Analysis of the powder XRD data of CoFe2O4 samples annealed at 1170 K suggested x ≈ 0.75 [24].

Theoretical studies [8, 31–34] have focused on ideal inverse and normal spinels of CoFe2O4 by the local spin density approximation (LSDA) [8, 31] and beyond, for example, by invoking the on-site Coulomb repulsion energy (U) through the LSDA + U [32] and GGA + U (generalized gradient approximation +U) approaches [33] or using the self-interaction corrected (SIC)-LSDA method [34]. The LSDA approach usually describes these materials to be half-metallic or metallic, if no distortions are included. The transition metal (TM) d electrons in oxides (as well as f electrons in rare earth compounds) are generally strongly correlated and cannot be adequately described within the standard band theory framework with such approximations as LSDA or GGA, which place them too close to the Fermi level. The LDA + U or GGA + U approach, treating the Hubbard U as an adjustable parameter, has correctly described CoFe2O4 as insulators. The SIC-LSDA method, which is parameter free, may provide a better description of correlations than LSDA, but requires a much heavier computing resources than LDA + U or GGA + U.

In this paper we mainly apply the GGA + U approximation to study the optimal electronic structure of CoFe2O4 at different degrees of inversion. The electronic and magnetic properties of these systems were investigated by systematically varying cation distributions (x = 0.0, 0.25, 0.50, 0.75 and 1.0). This contributes to the understanding of the global behaviour exhibited by the known (observed) and new (expected) (Co1−xFe2+x)2O4 spinels in terms of local and microscopic properties. Our results show that the Co ions strongly prefer the octahedral sites, and the temperature effect-induced tetrahedral site Co ions like to be far away from the octahedral site Co. It also indicates that the Co and Fe ions always prefer the high spin configurations in the studied normal, inverse and partial inverse spinel CoFe2O4.

Figure 1. The cubic cell of spinel structure. The tetrahedral and octahedral cation sites are denoted by blue and dark gray spheres, respectively, while the oxygen atoms are represented by the small red spheres.

2. Computational details

2.1. Crystal modelling

The conventional unit cell of the spinel structure contains eight formula units as shown in figure 1, and it belongs to the Fd3m space group (227). Cations occupy 8a and 16d special Wyckoff positions of Td and Oh symmetries at (0, 0, 0) and (5/8, 5/8, 5/8), respectively, whereas oxygen ions occupy the 32e positions at (u, u, u) [35]. Here u is the positional parameter of oxygen. It should be noted that the spinel is a relatively open structure since cations only occupy around 33% volume of the octahedral and tetrahedral voids [36].

According to various occupations of Co and Fe ions, we calculated two types of structures for x = 0.25, three types of structures for both x = 0.5 and x = 0.75 considered in a 28-atom cell, and one type of structure for x = 0 and 1 in a 14-atom cell. For the convenience of description, different structures with the same x are denoted by their symmetry. For example, when the Co ion at the fractional coordinates (1, 1, 1) in a cubic cell of the normal spinel structure exchanges with the Fe ion at (5/8, 7/8, 7/8), the symmetry reduces to CM, and thus we identify this structure as 0.25(CM). Analogous notations are adopted for other structures.

2.2. Computational method

We performed the electronic structure calculation and structure optimization through the Vienna Ab initio Simulation Package (VASP) [37, 38], with Perdew–Burke–Ernzerhof parametrized GGA [39] and the projector augmented-wave (PAW) method [40, 41]. The plane-wave expansion was truncated at a cutoff energy of 450 eV in all of our calculations. The optimizations were performed with a 3 × 3 × 3 k-mesh for the partial inverse structure unit cells consisting of 28 atoms and with a 7 × 7 × 7 k-mesh for the normal and inverse structure unit cells consisting of 14 atoms. The relaxations of lattices are stopped until the forces on each ion are converged to...
less than 1 meV Å⁻¹. For the final total energy calculations, the tetrahedron method of a 7 × 7 × 7 k-mesh for the 28-atom cell and a 9 × 9 × 9 k-mesh for the 14-atom cell are used. The convergence was tested for x = 1 and x = 0.75 cases, which indicates that the total energy changes within 1 meV when the k-mesh is increased from 7 × 7 × 7 to 9 × 9 × 9 for a 28-atom cell, and within 10 meV/formula when the energy cutoff is increased from 450 to 550 eV. In both the structure optimization and electronic structure calculation, the Néel configuration is chosen as the initial magnetic configuration, where the magnetic moments on tetrahedral and octahedral sites are antiparallel to each other.

The density functional theory GGA + U methodology [42–44] has been employed for the final calculations on total energy, electronic structure and magnetic properties. Here we use the simple formulation by Liechtenstein et al [42] and Dudarev et al [43], where a single parameter Uₜₐₜₜ determines the orbital-dependent correction to the DFT energy. Uₜₐₜₜ is generally expressed as the difference between parameters U and J. The Hubbard U is the Coulomb-energetic cost to place two electrons at the same site, and J is an approximation to the Stoner exchange parameter. For the inverse cobalt ferrite, a series of calculations with Uₜₐₜₜ varying from 2 to 6 eV for Fe and Co 3d orbital have been conducted. It is found that the total magnetic moment and local moment for the cations change within 0.04µₜₐₜₜ/formula and 0.28µₜₐₜₜ/cation, respectively. Meanwhile, the value of the energy gap strongly depends on the choice of Uₜₐₜₜ. In order to be consistent with experimental reported magnetic moments and theoretical gap values in the earlier literature, we finally employed U = 4.22 eV (as in [44]) and J = 0.80 eV for Fe, and U = 4.08 eV (as in [44]) and J = 0.79 eV for Co in this work.

3. Results and discussion

3.1. Energetics of CoFe₂O₄

The calculated energies of various CoFe₂O₄ configurations relative to its ideal inversion spinel are listed in table 1, and illustrated in figure 2. It shows that the most stable structure is the inverse spinel structure with all the Co ions located at the octahedral sites, while the normal spinel structure is the most unstable. The total energy of CoFe₂O₄ increases as the inversion degree decreases.

For x = 0.25, Co ions can be located at the octahedral site at (0.0625, 0.0625, 0.5625) or (0.3125, 0.3125, 0.3125), and denoted for CM and R₃M, respectively, in a 28-atom cell. It is found that the CM configuration is more stable than R₃M by 0.1 eV/Co, indicating that Co (O₂⁻) prefers to be far away from Co (T₉). For x = 0.50, we considered three structures, namely C₂M, CM and P-1. It is found that the C₂M configuration with Co ions located at (0.0625, 0.0625, 0.5625) and (0.5625, 0.0625, 0.0625) is energetically favoured. It also shows the two Co (O₂⁻) atoms favour being far away from each other and also far away from Co (T₉) respectively.

For x = 0.75, we considered three structures, CM, P1 and R₃M. It is found that the configuration with space group of CM with Co ions located at the (0.0625, 0.5625, 0.5625), (0.5625, 0.0625, 0.0625) and (0.3125, 0.3125, 0.3125) is preferred energetically. It also indicates that Co (O₂⁻) prefer to be away from each other in the octahedral surrounding. Therefore, Co ions will be distributed rather uniformly in the experimentally prepared partially inversed samples. This also indicates that the relatively small unit cells adopted in this work for various inverse spinels are reasonable.

The site preference of Co and Fe ions at the spinel structure is determined by their corresponding Gibbs free energies, which are dominated by their size effect, Coulomb interaction with oxygen lattice, as well as the temperature dependent entropy contribution. In CoFe₂O₄, there are six surrounding oxygen ions at the octahedral site, which will have a stronger Coulomb attraction with Fe³⁺ ions than the tetrahedral site.

<table>
<thead>
<tr>
<th>x</th>
<th>u</th>
<th>A(Å)</th>
<th>ΔE (eV/Co)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.380</td>
<td>8.308</td>
<td>0.339(0.20⁴)</td>
</tr>
<tr>
<td>0.25</td>
<td>0.380</td>
<td>8.325</td>
<td>0.382</td>
</tr>
<tr>
<td>0.50</td>
<td>0.381</td>
<td>8.334</td>
<td>0.281</td>
</tr>
<tr>
<td>0.75</td>
<td>0.381</td>
<td>8.337</td>
<td>0.190</td>
</tr>
<tr>
<td>1.0</td>
<td>0.378</td>
<td>8.384(8.40⁰, 8.37⁹)</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: ΔE is relative to the total energy of the inverse spinel.

[42-44] from [33].
[43] from [34].
[44] from [24].
[45] from [45].
[46] from [35].
with four surrounding oxygen ions. Meanwhile, the interstitial octahedral site has a larger space than that of the tetrahedral site, and thus Co$^{2+}$ ions prefer the octahedral site from the size effect aspect since it has a radius of 0.72 Å, which is greater than that of Fe$^{3+}$ ions, 0.64 Å [46]. As a result, the site preference will be a competition between the size effect and Coulomb interaction under low temperature, where the entropy contribution is negligible. Our calculation indicates that the size effect prevails over the Coulomb effect, as the normal spinel structure is energetically higher than that of the ideal inverse spinel by 0.339 eV/Co. As the temperature increases, the entropy contribution has a remarkable influence on the distribution of Co and Fe ions, as the various partial inverse spinel structures reported in experiments. Although we have investigated several partial inverse spinel structures, it is clear that the inversion parameter $x$ depends on the heat treatments since our calculated energy for the configurations increases as $x$ decreases. However, the direct correlation between the heat treatments (mainly temperature) requires Monte Carlo simulation with more energy information for various configurations, which needs great computational effort. It is worth noting that the inverse degree of CoFe$_2$O$_4$ will not be smaller than 0.5 at the limit of high temperature, although the structures of $x = 0.25$ and $0$ are studied in this work.

The optimized structural parameters are also summarized in table 1, in comparison with available experimental and theoretical data in the literature. The equilibrium structural parameters of CoFe$_2$O$_4$ in the inverse spinel configuration ($x = 1$) is found to be $a = 8.384$ Å and $u = 0.378$, which is in excellent agreement with the experimental values of $a = 8.390$ Å and $u = 0.380$. As the inverse parameter $x$ decreases from 1 to 0, the lattice parameter increases slightly by less than 1%, with little changes for the internal coordinates of oxygen.

The calculated bond lengths of both Co–O and Fe–O at the tetrahedral sites are about 1.86 Å, while those at the octahedral sites are around 2.02 Å. There is no remarkable difference between the bond length of Co–O and Fe–O when they are at the same type of interstitial sites, in line with the negligible lattice change as $x$ changes from 1 to 0. We note that the bond length of Co–O and Fe–O at the tetrahedral sites for the ideal inverse spinel obtained by Walsh et al [33] is longer than ours by about 0.1 Å, while those at the octahedral sites are in good agreement. This could result from the incorrect spin configuration obtained in [33] for cations at the tetrahedral sites, which will be discussed in detail in the next section.

### 3.2. Magnetic properties and electronic structures

The spin configurations of various spinel structures ($x = 0$ to 1) are investigated to illustrate the nature of the magnetic properties of the CoFe$_2$O$_4$ spinels. Fe ions and Co ions are possessed of different local symmetries at different lattice sites. According to the crystal field (CF) theory, the $e_g$ levels are lower than the $t_{2g}$ levels in a tetrahedral CF due to the direct electrostatic repulsion between the $d_{xy}$, $d_{yz}$ and $d_{zx}$ orbitals and surrounding anion orbitals, while the order is reversed in the octahedral environment as the $d_{z^2}$ and $d_{x^2−y^2}$ orbitals are repelled directly. The electronic configuration depends on the relative strength of the CF and intra-atomic exchange field (EF), which results in possible high spin (CF $<$ EF) or low spin (CF $>$ EF) configurations [19].
Figure 3. The atom-projected DOS and TDOS of CoFe₂O₄ with the normal spinel structure. The minority DOS is set to negative, while the majority part is set to positive. VBM is set to 0.

The calculated magnetic moments (\(\mu_B\)) of Co and Fe ions, and their total magnetic moment are listed in table 2 for the considered cases. It shows that the total magnetic moment decreases with increasing \(x\), in line with the experimental observation in [47], which found that the saturation magnetization increases with increasing heat treatment temperature, implying that there is a net exchange of Co ions at octahedral sites with the Fe ions at tetrahedral sites.

The total and projected densities of states (DOS) of normal cobalt ferrite given by GGA and GGA+U are compared in figure 3. From table 2 and figure 3, it is clear that our calculated results correspond to a typical high spin (relative strong exchange splitting) configuration for both Co and Fe ions at the tetrahedral and octahedral sites, where three and five unpaired electrons are expected per Co²⁺ and Fe³⁺, respectively, leading to a final magnetic moment of \(7\mu_B\) per CoFe₂O₄ formula for the ideal normal spinel structure. The \(e_g\) levels of Co ion are completely filled at the tetrahedral sites, while the \(t_{2g}\) levels are half filled by the unpaired electrons for Co²⁺ ion. Meanwhile both the \(t_{2g}\) and \(e_g\) levels of Fe³⁺ at both tetrahedral and octahedral sites are half occupied by the unpaired electrons, as schematically shown in figure 4. Figure 3 also shows that cobalt ferrite in the normal spinel structure is metallic in GGA calculation and becomes insulating with a small band gap of 0.09 eV when \(U = 4.22\) eV and \(J = 0.80\) eV for Co and \(U = 4.08\) eV and \(J = 0.79\) eV for Fe is applied. It is noted here that low spin configuration of Co³⁺ ion at the octahedral site is reported in the theoretical work by Walsh et al [33], while our results show that CoFe₂O₄ for \(x = 0.00\) favours high spin configuration and the valence of Co at the octahedral site is 2+. To clarify the spin configuration of Co (Oh), we have also studied the case of low spin for Co ion, which indicates that the energy of low spin case is 0.71 eV per Co higher than that of high spin case. On the other hand, the high spin configuration of Co ion in Cobalt ferrite is in agreement with most theoretical and experimental results in the literature [24, 47].

For \(x = 0.25\), there are three tetrahedral ions and one octahedral Co²⁺ ion, and one tetrahedral and seven octahedral Fe³⁺ ions in the adopted 28-atom unit cell. The spins at tetrahedral sites are antiparallel to those at octahedral sites in the spinel structure. The favourite electronic configuration is calculated to be as follows. Each tetrahedral Co²⁺ ion contains three unpaired electrons at the \(t_{2g}\) levels, while the octahedral Co²⁺ ion contains one unpaired electron at \(t_{2g}\) and two unpaired electrons at \(e_g\) levels, respectively. Each tetrahedral or octahedral Fe³⁺ ion contains five unpaired electrons at \(e_g\) and \(t_{2g}\) levels, as schematically shown in figure 4, resulting in a final spin configuration of \(6\mu_B\) per CoFe₂O₄ unit. The same explanation can be applied to the spinel with \(x = 0.5\) and \(x = 0.75\), exhibiting a final spin configuration of \(5\mu_B\) and \(4\mu_B\) per CoFe₂O₄ unit, respectively. In [49], the authors gave only the average magnetic moment of Co and Fe at the corresponding sites, which are \(-3.08\mu_B\) for the A site and \(3.21\mu_B\) for the B site. Actually, our calculated magnetic moment at both A and B sites depends on the type of cations strongly, although the calculated average magnetic moments
Figure 5. TDOS of \((\text{Co}_{1-x}\text{Fe}_x)_{\text{Tet}}(\text{Co}_x\text{Fe}_{2-x})_{\text{Oct}}\text{O}_4\) at \(x = 0.75\) considered spinel structure. The minority DOS is set to negative, while the majority part is set to positive. VBM is set to 0.

Figure 6. The atom-projected DOS and TDOS of CoFe2O4 with the inverse spinel structure. The minority DOS is set to negative, while the majority part is set to positive. VBM is set to 0.

for A and B sites are consistent with the experimental values \((-3.19\) and \(3.36\mu_B\) versus \(-3.08\) and \(3.21\mu_B\)). There is no remarkable difference between the two studied structures \((CM\) and \(R3M\) of \(x = 0.25\)) on their magnetic moment, but clearly different on the electronic structure. The system of \(0.25(CM)\) is insulating with a band gap of \(0.08\) eV, while \(0.25(R3M)\) is a half-metal. For \(0.25(R3M)\), a sharp peak in the vicinity of Fermi energy in the minority spins implies the configuration is unstable, in line with its relatively higher energy. A similar situation is found in the spinels \((C2M, CM\) and \(P−1)\) at \(x = 0.50\) and \((CM, P1\) and \(R3M)\) at \(x = 0.75\). In the \(x = 0.50\) case, it shows that \(0.50(C2M)\) and \(0.50(CM)\) are insulating with band gaps of \(0.16\) eV and \(0.24\) eV, respectively, while the \(0.50(P−1)\) structure is a half-metal. In the case of \(x = 0.75\), it shows that the \(0.75(CM)\) structure is insulating with a band gap of \(0.30\) eV, while both \(0.75(P1)\) and \(0.75(R3M)\) spinel structures are half-metallic as shown in figure 5. It is worth noting that the systems are always insulating for the configurations of the lowest energy for a given \(x\).

In the case of ideal inverse spinel at \(x = 1.0\), the PDOS (cf figure 6) indicates that Co is in the 2+ state, and Fe is in its 3+ state at both tetrahedral and octahedral sites. Since the spin in the tetrahedral sites is always antiparallel to that in the octahedral sites, the magnetic moment of \(\text{Fe}^{3+}\) are cancelled out, leaving the only net contribution from \(\text{Co}^{2+}\), which gives a final magnetic moment of \(3\mu_B\) per CoFe2O4 formula. Figure 6 compares the DOS of inverse cobalt ferrite given by GGA and GGA + \(U\) calculations. It shows that cobalt ferrite in the inverse spinel structure is a half-metal in GGA calculation and becomes insulating with a band gap of \(0.72\) eV when GGA + \(U\)
is applied. The result given by GGA + U calculation is in
reasonable agreement with the earlier reported self-interaction
corrected DFT [34] value of 0.8 eV, LDA + U [32] value of
0.63 eV and GGA + U [33] value of 0.52 eV. To the best of our
knowledge no experimental reports of the band gap of CoFe₂O₄
have been available. However, conductivity measurements
indicate an electronic gap in the region of 0.5–0.6 eV for
stoichiometric CoFe₂O₄ [48].

4. Conclusions

In this study, the CoFe₂O₄ spinel was systematically
investigated by GGA and GGA+U calculations. Our
results show that CoFe₂O₄ energetically favours inverse
spinel (x = 1) and both Fe and Co always prefer high spin
configuration, no matter whether in octahedral or tetrahedral
sites in the partial inverse spinels. As x increases, the
total magnetic moment of CoFe₂O₄ decreases. The lattice
parameter of the spinel increases slightly with increasing
inversion parameter x. The Co ions in the partial inverse spinel
favour being far away from each other, allowing a reasonable
study of the system with relatively small unit cells.

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References

University Press)
4 317
126 273
(Amsterdam: Elsevier Science)
274 1139
12 1986
12 1986
and Winter H 2006 Phys. Rev. B 74 744431
Wiley-Interscience)
Phys. Rev. B 66 224414
and Winter H 2006 Phys. Rev. B 74 744431
Wiley-Interscience)