Ab initio study on copper ferrite

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The impact of cation distribution on electronic structure and magnetic properties is investigated by the first-principle calculation. The structure optimization is based on generalized gradient approximation (GGA) exchange-correlation and projector augmented wave method. The optimized structures of inverse and normal copper ferrite are tetragonal (c/a=1.06) and cubic, respectively. The optimized structure of partial inverse copper ferrites can be cubic, tetragonal, or triclinic depending on the distribution of copper ions. The calculation of electronic structure is based on full potential linear augmented plane wave method and GGA+U exchange-correlation. The calculated density of states shows that the distribution of Cu ions impacts the electronic structure significantly. The normal and inverse copper ferrite are half-metallic and semiconducting, respectively. The partial inverse copper ferrites are metallic or half-metallic. © 2010 American Institute of Physics. [doi:10.1063/1.3338905]

Copper ferrite, characterized by the cubic-to-tetragonal phase transition induced by Jahn–Teller distortion, has been studied for decades.1–9 It has been established that the magnitude of the tetragonal distortion, characterized by the c/a ratio as referred to the cubic cell, can be modified by changing the distribution of copper ions on the A and B sublattices. The modifications of the tetragonal distortion of copper ferrite also lead to significant changes in magnetic properties, such as coercive force and saturation magnetization.10,11 Recently, copper ferrite was revisited as an example of artificial ferrite in which the electronic structure and magnetic properties can be tuned by redistributing the cations, Cu and Fe ions, on A and B sublattices.12

The cation distribution in copper ferrite can be represented as Cu1−xFe2−x[Fe2−x]O4 in which square brackets denote octahedral sites and x is the degree of inversion between 0 and 1. Due to the low migration energy of copper ions in the spinel lattice, copper ferrite in its bulk equilibrium form is a partial inverse spinel, with about 85% of copper ions on B sites. Hence, most of previous researches are based on powder or film samples with various cation distributions. As far as we know, the electronic properties of copper ferrite have been rarely discussed, and few detailed calculation studies of copper ferrite have been published.13 In this research, we investigate copper ferrite using ab initio calculation to explore the impact of cation distribution on the electronic structure and magnetic properties.

We performed the structure optimization followed by the calculation of electronic structure and magnetic properties. We construct the unit cells with different values of degree of inversion (x=0.0, 0.25, 0.5, 0.75, 1). Due to the different locations of Cu ions, there are two structures with x=0.25, three structures with x=0.5, and one structure for x=0.0, 0.75, 1. For the convenience of description, different structures with the same x are identified by their symmetry before optimization. For example, when the Cu ion at the fractional coordinates (1/1,1/1,1/1) in the cubic cell of the normal spinel structure exchanges its position with the Fe ion at (5/8,7/8,7/8), the symmetry reduces to CM (international space group number: 8). Thus, we identify this structure as 0.25CM. In the first step of the calculation, we optimize both the lattice constants and the positions of ions simultaneously using quasi-Newton method. The total energy is calculated using Perdew–Burke–Ernzerhof parameterization of generalized gradient approximation (GGA)14,15 and projector augmented wave method.16,17 The calculation is accomplished by using the VASP code.18–21 The optimizations were performed on a 3 × 3 × 3 k-mesh for the partial inverse structure unit cells consisting of 28 atoms and on a 9 × 9 × 9 k-mesh for the normal and inverse structure unit cells consisting of 14 atoms. The breaking conditions for the electronic and ionic loops are 10−4 and 10−3 eV, respectively. In both the structure optimization and the following electronic structure calculation, we assume the Néel configuration as the initial magnetic structure, where the magnetic moments on A and B sublattices are antiparallel to each other. In the second step, we calculate the electronic structure and magnetic properties using GGA+U exchange-correlation and full potential linear augmented plane wave method. The additional on-site Coulomb repulsion energy (U) is applied to the d-orbital of Fe atoms. This step is accomplished by using both the VASP code and the WIEN2K code. We first performed the electronic structure calculation using VASP with different values of U on a 7 × 7 × 7 k-mesh for the 28 atom cell and on a 9 × 9 × 9 k-mesh for the 14 atom cell. Then, we calculated the electronic structure and magnetic properties with U=4 eV using the WIEN2K code on 11 × 11 × 11 and 21 × 21 × 21 k-meshes. The accuracy of WIEN2K calculation is up to 10−6 Ry.

For the convenience of comparison, the lattice parameters of all structures will be referred to the cubic cell in the same x.
The optimized structure of inverse spinel copper ferrite is tetragonal \((a=b=8.136 \, \text{Å}, \text{and } c =8.669 \, \text{Å})\), and \(c/a\) ratio is 1.065. This result is in a good agreement with the experimental results.\(^1\),\(^2\) The Cu–O bond lengths in CuO\(_6\) octahedron are 2.287 Å out of the basal plane and 1.98 Å in the plane, respectively, due to the Jahn–Teller distortion of Cu\(^{2+}\) ions. The optimized structure of normal spinel copper ferrite is cubic \((a=b=c=8.062 \, \text{Å})\). When \(x=0.25\), the structure 0.25R3M is trigonally distorted \((a=b=c=8.068 \, \text{Å})\), while the other structure 0.25CM is slightly distorted \((a=b=8.093 \, \text{Å}, \, c=8.029 \, \text{Å}, \, c/a =0.991)\). As for structures with 50% Cu ions on \(B\) sites, 0.5CM is tetragonally distorted \((a=b=7.923 \, \text{Å}, \, c =8.449 \, \text{Å}, \, c/a=1.066)\), 0.5R3M is triclinically distorted \((a=b=c=8.148 \, \text{Å}, \, \alpha=92.69^\circ, \, \gamma=87.32^\circ)\), and 0.5CC is also triclinically distorted. We also studied one structure with \(x=75\%\), which is triclinically distorted.

Figure 1 compares the density of states (DOS) of inverse and normal copper ferrite given by GGA and GGA+U calculations using VASP. Similar results with \(U=0\) and 4 eV are also given by the calculations using WIEN2K. It shows that copper ferrite in inverse spinel structure is metallic in GGA calculation and becomes semiconducting when \(U\) is applied. For inverse copper ferrite, we perform a series of calculations with \(U\) varying from 0 to 8 eV. We find that the band gap increases to 0.23 eV when \(U=4\) eV, and its variation becomes flat when \(U\) increases further (Table I). The calculated effective Coulomb repulsion energy between the \(d\) electrons of the \(B\)-site Fe ion in inverse copper ferrite is about 4 eV when \(U\) is not applied and increases to 10 eV when \(U =4\) eV, which is the experimental value in Fe\(_2\)O\(_3\).\(^2\) The GGA result of DOS indicates that normal copper ferrite is half-metallic, where the majority spin Fe–d \(t_{2g}\) bands extend across the Fermi level \((E_F)\). When \(U\) increases to 2 eV, normal copper ferrite becomes metallic. When \(U\) increases to 4 eV, normal copper ferrite becomes half-metallic again. This is due to the shift in majority spin Fe–d \(t_{2g}\) bands toward higher energy when \(U\) increases. However, the minority spin Cu–d \(t_{2g}\) bands stay across the \(E_F\), and normal copper ferrite remains half-metallic when \(U\) increases to 6 eV. This indicates that normal copper ferrite may be half-metallic.

Following above discussion, we choose \(U=4\) eV as the optimal value for the calculations of copper ferrite systems. Figures 2(a)–2(h) show the total and projected DOS of all structures with \(U=4\) eV, which are given by GGA+U calculations using WIEN2K. The calculations show that the electronic structure of copper ferrite is not only sensitive to the concentration of Cu ion on \(B\) sites but also impacted by the specific location of Cu ions on \(B\) sites. The total DOS results show that normal copper ferrite is half-metallic and that the copper ferrite systems labeled as 0.25R3M and 0.50CM are

**TABLE I.** Calculated band gap of inverse copper ferrite with different Coulomb repulsion energy \(U\) on Fe.

<table>
<thead>
<tr>
<th>(U) (eV)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap (eV)</td>
<td>0.016</td>
<td>0.13</td>
<td>0.216</td>
<td>0.232</td>
<td>0.232</td>
<td>0.232</td>
<td>0.232</td>
<td></td>
</tr>
</tbody>
</table>

FIG. 1. (Color online) Calculated DOS of inverse and normal copper ferrite by VASP. The dashed line indicates the \(E_F\).
also half-metallic, while 0.25CM, 0.50CC, and 0.50R3M are metallic. The copper ferrite system with 75% Cu ions in B sites is metallic, and inverse spinel copper ferrite \((x = 1)\) is semiconducting. For inverse spinel copper ferrite, which is close to the experiment samples, we performed an improved calculation and applied \(U_{\text{Cu}} = 4.5 \) eV and \(U_{\text{Fe}} = 4 \) eV on Cu and Fe ions, respectively. The result is shown in Fig. 2(i) in which the band gap increases to 1.2 eV. This agrees with the measured activation energy of conduction in copper ferrite, which is in the range of 0.16–0.41 eV. Due to the deep impurity states in the band gap induced by the oxygen vacancies, the activation energy of conduction is usually smaller than the band gap in ferrites.

The dependence of the electronic structure of copper ferrite on cation distribution can be explained by the projected DOS of cations. As shown in Figs. 2(a)–2(h), the projected DOS in copper ferrite system is strongly related to the position of cation. If we focus on the electronic structure near the \(E_F\), we can find that the DOS contributed by A-site Fe-\(d\) orbital is dominant in the range of 1–3 eV above the \(E_F\) and highly polarized only with minority spin, while the DOS contributed by B-site Fe-\(d\) orbital is dominant in the range of 0.5–4 eV above the \(E_F\) and highly polarized only with majority spin. This projected DOS feature of Fe ions is found in almost all studied structures besides that B-site Fe-\(d\) orbital slightly contributes to the DOS at the \(E_F\) in the structures with \(x < 0.5\). Thus, the projected DOS of Fe ions has little impact on the electronic structure at the \(E_F\). In fact, the projected DOS of Cu ions plays an important role in the electronic structure of copper ferrite system at the \(E_F\). Similar to the case of Fe ions, projected DOS of Cu ions also shows a clear feature related to the cation distribution. A-site Cu-\(d\) orbitals only contributed to the minority spin DOS at the \(E_F\), and this is independent of \(x\). B-site Cu-\(d\) orbitals only contribute to the majority spin DOS at \(E_F\). As a result, normal copper ferrite is half-metallic. As \(x\) increases, more Cu ions are located on B sites, and the majority spin DOS at the \(E_F\) increases. As a result, the partial inverse copper ferrite systems (0 < \(x < 1\)) are mostly metallic. There are, however, some half-metals in partial inverse copper ferrites, 0.5 and 0.25R3M, where the density of B-site Cu-\(d\) band vanishes at the \(E_F\). In inverse copper ferrite, there is no Cu ion on A sites, and the minority spin vanishes at \(E_F\). Thus, the system is semiconducting due to the band gap at the \(E_F\).

The calculated magnetic structures are the same as the initial ferrimagnetic structure. The magnetization of A sites are antiparallel to that of B sites, whereas the magnetic order inside A or B sublattice is ferromagnetic. The mean magnetic moments of A-site and B-site Fe ion are 3.83\(\mu_B\) and 3.96\(\mu_B\), respectively. As more Fe ions occupy A sites and their magnetic moments are antiparallel to those on B sites, the magnetization per unit cell decreases as \(x\) increases (Table II). The magnetic moment of inverse copper ferrite per 28 atom cell is 4\(\mu_B\), and the saturation magnetization \((M_s)\) is 162 G. This result is lower than the experimental values ranging from 225 to 290 G (Ref. 26) since the copper ferrite samples are partially inverse and the degree of inverse ranges from 83% to 90%. In conclusion, the lattice parameters of inverse copper ferrite given by first-principle calculation are in a good agreement with the values given by the experiments. The electronic structure results given by GGA+U calculation show that Cu ions on A sites and B sites contribute to the DOS in opposite spin directions at the \(E_F\), and the contribution of Fe ion distribution to the electronic structure at the \(E_F\) is negligible. The distribution of copper ions however determines the electronic structure at the \(E_F\). Normal copper ferrite and inverse copper ferrite are half-metallic and semiconducting, respectively. The partial inverse copper ferrite systems are mostly metallic since Cu ions distribute on both A and B sites.

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### Table II. Calculated magnetic moment per cell with 28 atoms of all studied structures.

<table>
<thead>
<tr>
<th>(x)</th>
<th>0</th>
<th>0.25</th>
<th>0.5</th>
<th>0.5</th>
<th>0.75</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>CM</td>
<td>R3M</td>
<td>CM</td>
<td>R3M</td>
<td>CC</td>
<td>P1</td>
</tr>
<tr>
<td>(M_{\text{tot}}(\mu_B))</td>
<td>36</td>
<td>27.77</td>
<td>26</td>
<td>20</td>
<td>19.87</td>
<td>15.96</td>
</tr>
</tbody>
</table>