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Effects of inverse degree on electronic structure and electron energy-loss spectrum in zinc ferrites

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ABSTRACT

First-principles calculations were performed to study the effects of inverse degree in zinc ferrite on electronic structure and properties. The electron energy-loss near-edge fine structure (ELNES) were simulated, and the splitting of peak and intensities of the oxygen K-edges can be used to identify the inversion of zinc ferrite. More Fe³⁺ transferring from the octahedral sites to the tetrahedral sites lead to the changing of the ligand shells surrounding the absorbing atom, accounting for the observed changing in ELNES. The standard criterion for determining the reversal extent of the cations in zinc ferrite by ELNES was given.

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1. Introduction

Zinc ferrite, a well-characterized antiferromagnetic insulator, has attracted considerable attention due to its intriguing magnetic properties [1,2]. The spinel zinc ferrite has a general formula ZnFe₂O₄, where Zn ions and Fe ions are divalent and trivalent metal cations, respectively. The structure of ZnFe₂O₄ consists of a cubic close-packed array of oxygen ions, with metal cations distributed in one eighth of tetrahedral interstices (A sites) and half of the octahedral interstices (B sites) [3,4]. The ZnFe₂O₄ can be classified as normal or inverse structure, depending on the distribution of the metal ions over the tetrahedral and octahedral sites. In a normal spinel (Zn)^{tet}[Fe]₂^{oct}O₄, all of the occupied octahedral sites are Fe³⁺ ions. Whereas in a completely inverse spinel (Fe)^{tet}[Zn,Fe]^{oct}O₄, they are occupied by Zn²⁺ and Fe³⁺ ions with equal proportions. However, in an actual case, the spinel ZnFe₂O₄ is partially inverted and has cation distributions between these two extremes. The inversion parameter, δ ($0 \leq \delta \leq 1$), is defined as the fraction of the filled tetrahedral sites that are occupied by Fe³⁺ ions [5,6]. Using this parameter, the cation site occupation of ZnFe₂O₄ can be described with a general formula (Zn_{1- δ} Fe _{δ})^{tet}[Zn _{δ} Fe_{2- δ}]^{oct}O₄, where the round and the square brackets represent the elements in A and B sites, respectively [7,8]. ZnFe₂O₄ with different inversion parameter can be synthesized

experimentally with much nonequilibrium processing, including rapid quenching [9], changing the oxygen partial pressure [10], and adjusting the synthesis temperatures [3], etc. The change in atomic arrangement of Fe³⁺ ions and Zn²⁺ ions in zinc ferrites affect both its structural characteristics and physical properties that are sensitive to the crystalline structure, such as its lattice parameter, magnetic behavior, electronic structure, etc [10,11].

Consequently, scrutinizing the local atomic coordination environment of the ZnFe₂O₄ is extremely important in understanding its potentially applied properties. Many characterization techniques have been used to investigate the local atomic coordination environment of ZnFe₂O₄, including X-ray absorption fine structures [12], neutron diffraction [11,13], Mössbauer spectroscopy [14,15], and electron energy-loss spectrum (EELS) [3].

EELS attached to transmission electron microscopy (TEM) is a powerful analytical technique that can be utilized to obtain information on the structure, bonding and electronic properties of a material [16]. Especially, the electron energy-loss near-edge fine structure (ELNES) resolves electronic dipole transitions from the core states of a particular atom to unoccupied final states. ELNES is sensitive to variations of the chemical environment of a given element, reflecting directly the unoccupied states of the atoms. The experimental ELNES characterization for ZnFe₂O₄ has been performed to study the relation between the microstructure and magnetic properties [3]. Usually, information about the structure or bonding of the sample is determined from comparison between the acquired spectrum and the available reference spectrum. Unfortunately, there is no standard reference spectrum available

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for comparison in the literature. ELNES simulation based on the density functional theory (DFT) has become an established technique to predict and interpret EELS for materials [17]. It is needed to make a systematic study to clarify relationship between the electronic structure and the local atomic coordination with the help of the first principle calculations.

In this paper, we provide the theoretical ELNES data for the zinc ferrite with different cation distribution by the first-principle simulation. The changes in the splitting of peak and intensities of the oxygen K-edges can be used to identify the inversion degree of zinc ferrite. The determination on the reversal extent of the cations in experimented ELNES for zinc ferrite was realized.

2. Computational details

First-principles calculations based on density functional theory have been used for both geometry optimization and ELNES simulating with the CASTEP code [18]. The exchange-correlation energy is described by the Perdew–Burke–Ernzerhof (PBE) formalism of the generalized gradient approximation (GGA). Lorentz broadening function with a full width at maximum (FWHM) of 0.2 eV is used in the Brillouin zone spectral integration, and the spectra are further convolved with a Gaussian with a FWHM of 0.4 eV to take into account the spectral resolution. The valence electronic configurations for O, Zn, and Fe are $O\ 2s^2 2p^4$, $Zn\ 3d^{10} 4s^2$, and $Fe\ 3d^6 4s^2$, respectively. To ensure a good convergence of the DFT calculations, we carefully test the dependences of the total energy on the plane-wave cutoff energy and the k -point meshes. The wave functions were expanded in plane waves up to a cutoff energy of 500 eV, and a $2 \times 2 \times 2$ Monkhorst–Pack mesh as k -point sampling was used to sample the irreducible Brillouin zone. Geometry optimizations were performed to fully relax the atomic internal coordinates and the lattice parameters within the BFGS minimization algorithm. The

self-convergence thresholds for maximum stress and maximum displacement between optimization cycles are 0.02 GPa and 5×10^{-4} Å. The structures were fully relaxed until the Hellmann–Feynman force was less than 0.01 eV/Å and the energy convergence was better than 5×10^{-6} eV/atom.

3. Results and discussions

The crystal structure of $ZnFe_2O_4$ used in our calculations are taken from the neutron powder data with the cubic space group $Fd\bar{3}m$ and the lattice parameters $a=b=c=8.412$ Å [19]. The configurations with different inversion degrees were studied in our work as shown in Fig. 1. Fig. 1(a) shows the ideal normal spinel structure of $ZnFe_2O_4$ with 56 atoms (the inversion parameter $\delta=0$); Fig. 1(b) shows the structure of $(Zn_6Fe_2)[Zn_2Fe_{14}]O_{32}$, in which two Zn atoms in tetrahedral sites and two Fe atoms in octahedral sites are inverted with each other ($\delta=0.25$); Fig. 1(c) shows the structure of $(Zn_4Fe_4)[Zn_4Fe_{12}]O_{32}$, in which four Zn atoms in tetrahedral sites and four Fe atoms in octahedral sites are inverted ($\delta=0.5$); Fig. 1(d) shows the total inverse spinel structure $(Fe_8)[Zn_8Fe_8]O_{32}$ ($\delta=1$). The optimized lattice parameters and volumes for different inverse structures are shown in Table 1. The results show that the inversion between Zn and Fe does not deform the structure seriously after full relaxation, except a slight increase in the unit cell volume.

To get a further insight into the electronic structure and magnetic properties in zinc ferrite with different inverse degrees, the calculated total density of states (TDOS) and partial density of states (PDOS) for zinc ferrite with different inverse degrees are shown in Fig. 2. The TDOS of normal spinel $Zn_8Fe_{16}O_{32}$ is shown in Fig. 2(a), where the Fermi level is set at zero, and the system is an insulator, which is similar to previous calculations [10,20]. Fig. 2(b)–(d) shows the TDOS of zinc ferrite with different inversion parameters (i.e., $(Zn_6Fe_2)[Zn_2Fe_{14}]O_{32}$, $(Zn_4Fe_4)[Zn_4Fe_{12}]O_{32}$ and $(Fe_8)[Zn_8Fe_8]O_{32}$

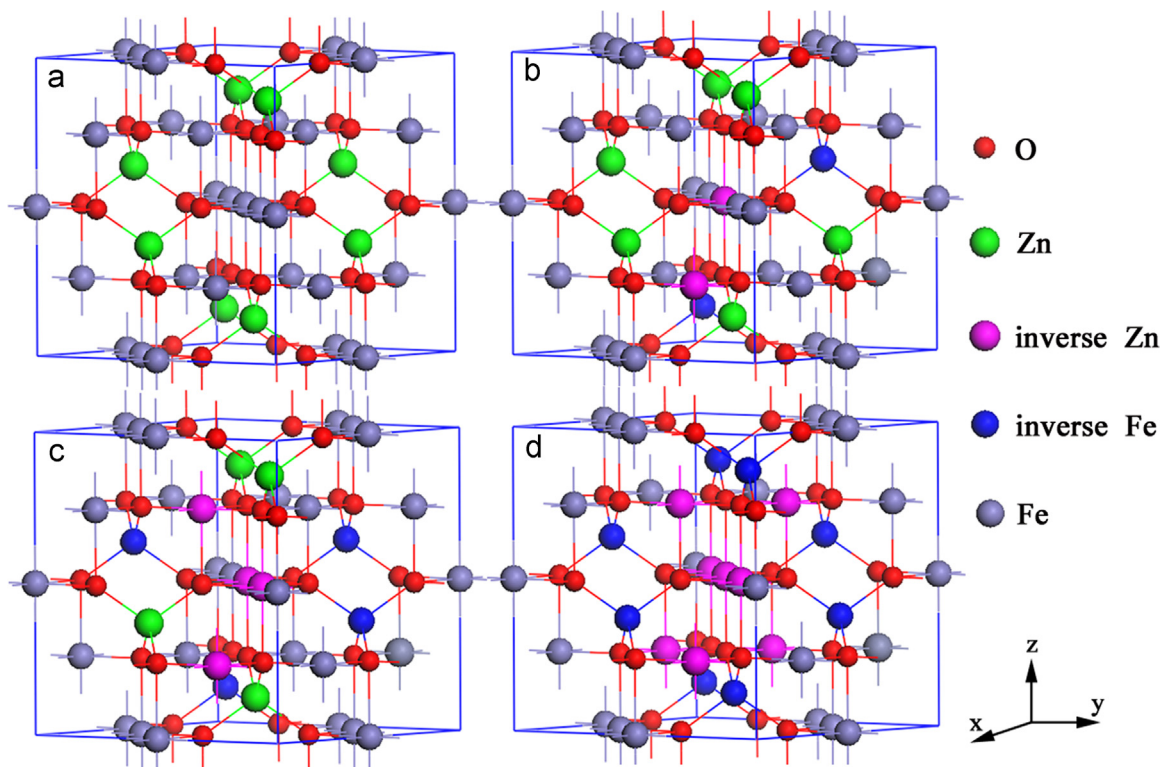


Fig. 1. (Color Online) Structural models for ELNES simulation: (a) $Zn_8Fe_{16}O_{32}$, (b) $(Zn_6Fe_2)[Zn_2Fe_{14}]O_{32}$, (c) $(Zn_4Fe_4)[Zn_4Fe_{12}]O_{32}$, (d) $(Fe_8)[Zn_8Fe_8]O_{32}$, respectively. The red, green, and purple spheres represent the oxygen, zinc, and iron atoms, respectively. The pink and blue atoms represent the inverted zinc and iron atoms, respectively.

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