

## Electronic structure calculations for $\text{ZnFe}_2\text{O}_4$

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Local density approximation was applied to scrutinize the electronic structure and magnetic properties of the spinel ferrite  $\text{ZnFe}_2\text{O}_4$ . Various cation distributions were established to obtain the ground state for the system. In magnetic crystals, the position of the atoms is not enough for symmetry determination. A structure prediction by decreasing the octahedral point group symmetry  $O_h$  of Fe to  $D_{4h}$ ,  $C_{4v}$ , and  $C_{3v}$  was carried out. The effect of the exchange and correlation terms on the band structure of  $\text{ZnFe}_2\text{O}_4$  was studied by the generalized gradient approximation + the Hubbard correlation parameter  $U$ . The optimized structure parameters, which are in good agreement with the experimental values, were used as the input parameters for the calculations. In agreement with experimental studies, the semiconducting behavior for the studied compound, taking the effect of spin arrangement on symmetry into account, was obtained.

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### I. INTRODUCTION

Ferrites are certainly one of the most extensively studied families of magnetic materials. Since ferrites behave as low gap semiconductors and as insulators at low temperatures they have been used in a number of technologically important applications. Among these are microwave devices, magnetic and magneto-optic recording, and electronic information mass storage.

The spinel ferrite has  $AB_2O_4$  structure with a cubic close-packed arrangement of oxygen ions, with  $A^{2+}$  and  $B^{3+}$  ions at two different crystallographic sites. These sites have  $AO_4$  tetrahedral and  $BO_6$  octahedral oxygen coordination ( $A$  and  $B$  sites, respectively). Accordingly, the resulting local symmetries of both sites are different. In this regard the spinel structure can be defined and described by three parameters: the lattice parameter  $a$ , the oxygen positional parameter  $u$ , and the cation inversion parameter  $i$ . Consequently the ideal chemical formula of spinel takes the form  $A^{2+}OB_2^{3+}O_3$ , where  $A^{2+} = \text{Mg, Mn, Fe, Co, Ni, Cu, or Zn}$ , and  $B^{3+} = \text{Al, V, Cr, Mn, Fe, Co, or any closely related structure}$ . When  $A$  is a magnetic ion, the total magnetic moment of the eight blocks that form the unit cell in  $AB_2O_4$  is due to uncompensated magnetic moments of the  $A$  and/or  $B$  magnetic sublattice. According to the strength of  $A$ - $A$  or  $A$ - $B$  interaction the materials behave as either ferromagnetic or antiferromagnetic, respectively. Transition metal spinel oxides provide various properties such as superconductivity as in  $\text{LiTi}_2\text{O}_4$ , heavy fermions behavior as in  $\text{LiV}_2\text{O}_4$ , charge order as in  $\text{AlV}_2\text{O}_4$ , unusual magnetic transition as in  $\text{ZnV}_2\text{O}_4$  and  $\text{ZnCr}_2\text{O}_4$  (Ref. 1), charge order as in  $\text{Fe}_3\text{O}_4$  (Ref. 2), and geometrical frustration.<sup>3</sup> It is well known that the properties of ferrite materials strongly depend on the preparation conditions;<sup>4</sup> for example, the cation distribution of Zn and Mn ferrite in bulk form differs from that for the nanosize powder.<sup>5</sup>

$\text{ZnFe}_2\text{O}_4$  is well known as an antiferromagnetic insulator, with a low ordering temperature of  $T_N = 10.5$  K and an energy gap of about 0.2 eV.<sup>6</sup> It has a complex spin structure, where the spin structure becomes simpler with higher ordering temperatures in samples with intersite cation disorder.<sup>7</sup> Cation disorder for  $\text{ZnFe}_2\text{O}_4$  was experimentally observed.<sup>4,8</sup> In

addition the magnetic moment of Fe in  $\text{ZnFe}_2\text{O}_4$  is around  $4.2\mu_B$  (Refs. 9 and 10) and the experimental lattice parameter is about 8.52 Å (Ref. 11).

Previous studies utilizing the generalized gradient approximation (GGA) and the local spin density approximation (LSDA), without Hubbard correlations, indicated that normal  $\text{ZnFe}_2\text{O}_4$  shows metallic behavior either for the ferromagnetic state or for the antiferromagnetic state.<sup>6</sup>

In this work we aim to describe the effect of symmetry on the properties of  $\text{ZnFe}_2\text{O}_4$  spinel ferrite. Calculations are carried out for different allowed symmetries and cation distributions. In addition the deviation of the oxygen positional parameter from the ideal value is calculated. The on-site  $3d$ -electron Coulomb interaction for Zn and Fe is also included.

### II. CRYSTAL STRUCTURE AND CALCULATION DETAILS

It is obvious that the physical properties of solids considerably depend on the local configuration and arrangement of the constituent atoms or ions. For spinel ferrite two types of oxygen interstices were recognized: 64 have fourfold coordination, 8 of which ( $A$  sites or tetrahedral sites) may be occupied by divalent cations; on the other hand 32 have sixfold coordination, 16 of which ( $B$  sites or octahedral sites) may be occupied by the trivalent cations. Site symmetries and overall symmetry of spinels are then conventionally assumed to correspond to the crystallographic  $Fd\bar{3}m$  space group.<sup>12</sup> The conventional choices for the unit cell origin in spinels are either  $\bar{4}3m$  on an  $A$ -site cation or  $\bar{3}m$  on an octahedral vacancy. The spinel structure is centrosymmetrical around the  $B$  site; the positions of cations are determined according to the symmetry of the structure, while the anion position is adjusted by the so-called oxygen position parameter  $u$ . For an ideal spinel  $u$  has the value of 0.375 for origin  $\bar{4}3m$  while  $u$  has a value of 0.25 for  $\bar{3}m$ . Practically  $u$  is often found to be higher than the above values. It should be mentioned that the increase in the value of  $u$  is inevitably associated with moving the anions in the  $[111]$  direction outward from the nearest  $A$  site. Accordingly, the  $B$  site volume will be compressed and consequently its symmetry

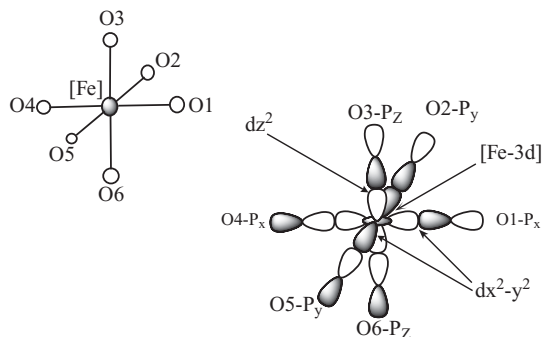


FIG. 1. Schematic representation for the octahedral structural unit of spinel  $\text{ZnFe}_2\text{O}_4$  and the atomic orbitals that contribute to covalent bonding. The three distinct oxygen atoms in the unit cell are labeled O1, O2, and O3 (shown as open circles in the structural unit). The six oxygen atoms form an octahedron centered by an Fe atom. Lines between the oxygen atoms and the Fe atom represent the covalent bonds in the structural unit. The Px, Py, and Pz orbitals of the O1, O2, and O3 atoms and the  $dx^2-y^2$  and  $dz^2$  orbitals of the Fe atom that participate in the formation of covalent bonds in the octahedron are shown.

might be changed. Figure 1 shows the tetrahedral unit and the atomic orbitals that contribute to the covalent bonding. From Fig. 1, the magnetic symmetry difference between oxygen atoms around the Fe atom in the octahedral site can be easily noticed. Figure 2 shows the point groups considered for the sixfold symmetry position ( $B$  site). A lattice parameter of  $8.53 \text{ \AA}$  was obtained from the optimization of Zn ferrite as a normal spinel with space group 227 ( $Fd3m$ ). In addition, since spinel properties are sensitive to the oxygen parameter,<sup>13</sup> optimization of the oxygen parameter  $u$  was performed until a reasonable value was obtained. The energy dependence of the oxygen parameter is shown in Fig. 3. The reasonable value of the oxygen parameter corresponding to the lowest energy per formula unit  $2\text{ZnFe}_2\text{O}_4$  is 0.2586 as shown in Fig. 3. The values of the optimized oxygen and lattice parameters seem likely to be in agreement with the experimental values [0.258 (Ref. 14) and  $8.52 \text{ \AA}$  (Ref. 11), respectively].

For self-consistent calculations of the electronic structure of atoms and solids, a proper potential function for a single electron is needed. This can be divided into two parts. One is the Coulomb potential due to the nuclear charge and the electron charge distribution; this was calculated with density functional theory by using full linearized augmented plane wave and local orbital extensions (FLAPW + Lo). The other part of the potential, which is the exchange correlation poten-

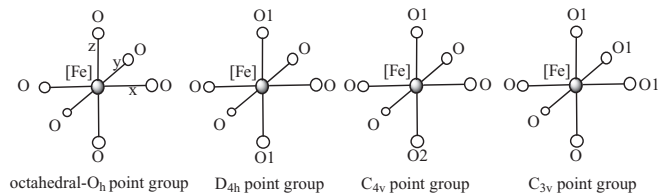


FIG. 2. The distribution of the six oxygen atoms for the studied point groups  $O_h$ ,  $D_{4h}$ ,  $C_{4v}$ , and  $C_{3v}$  on an octahedron centered by an Fe ion.

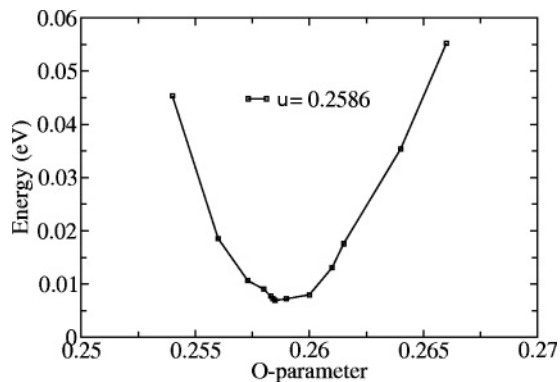


FIG. 3. The energy dependence on the oxygen parameter.

tial, has been taken as the generalized gradient approximation GGA (Ref. 15) for the band structure calculation. On the other hand the local density approximation (LDA) was applied for exchange correlation on structure optimization. Self-consistent calculations were performed with the aid of a computer-program called WIEN2k (Refs. 16 and 17). The self-consistent calculation is considered to be converged when the maximum value of the absolute difference between the new and the old charge density is put to be less than  $10^{-2}e$  and the relative difference of the new and the old energy eigenvalues of each state is less than  $10^{-3}$  Ry. To have convergence for the basis of the wave function, the cutoff parameter  $R_{MT} * K_{MAX} = 7$  was used for the number of plane waves. The expansion of the partial wave functions was set to  $\ell = 10$  inside the muffin tin atomic spheres while the charge density was Fourier expanded up to  $G = 12$ . In the self-consistent calculations a grid of 3000  $k$  points was employed in the irreducible Brillouin zone that results in  $14^3$  mesh with 735 points. The energy threshold between the core and the valence states was set at  $-9.5 \text{ eV}$ . The muffin tin radii (MTR) were chosen to ensure nearly touching spheres and to minimize the interstitial space. These (MTR) were found to be 1.97, 2.05, and  $1.74 \text{ \AA}$  for Zn, Fe, and O, respectively.

### III. RESULTS AND DISCUSSION

The 230 space groups are adequate for describing the structure of a nonmagnetic crystal in which it is just necessary to specify the positions of all atoms or ions in the crystal. The importance of considering the operation of antisymmetry becomes clear if one requires the description of the structure of a magnetically ordered crystal, in which not only the positions of the atoms but also the orientations of the magnetic moments of the atoms need to be specified. From this point of view, a different symmetry, shown in Fig. 2, will be considered in the calculation of the magnetic  $\text{ZnFe}_2\text{O}_4$  compound. In the normal spinel arrangement of  $\text{ZnFe}_2\text{O}_4$ , considering the ionic model,  $\text{Zn}^{2+}$  is located at the  $A$  site and  $\text{Fe}^{3+}$  is located at the  $B$  site (with  $3d^5$  or  $5\mu_B$  in a high spin state). Since the crystal field of  $\text{ZnFe}_2\text{O}_4$  is produced by Fe ions, Zn has an induced magnetic field due to the crystal field of Fe ions. That induced field should have the same direction as that for Fe. Accordingly in normal spinel  $\text{ZnFe}_2\text{O}_4$ , the  $A$ - $B$  interaction should be omitted. In the following, many techniques are implemented to

scrutinize the semiconducting and antiferromagnetic behavior of ZnFe<sub>2</sub>O<sub>4</sub> ferrite.

### A. The effect of symmetry

Breaking the symmetry of the magnetic system results in additional contributions to the magnetic anisotropy, which alters the net magnetization direction and decreases the degree of freedom of the electrons. Such freedom decreasing restricts the electron motion and might lead to obtaining the insulating properties for the spinel as obtained experimentally.

Now, in spinels, as  $u$  increases above the ideal value, anions move away from the tetrahedrally coordinated  $A$ -site cations along the  $[111]$  direction. This in turn will increase the volume of  $A$ -site interstices while the octahedral  $B$  site becomes correspondingly smaller. Thus, for the given spinel compound, the anion sublattices  $A$  and  $B$  expand or contract, by varying  $u$ , until the  $A$ - and  $B$ -site volumes match the radii of the constituent cations. The symmetry of the regular tetrahedral sites that is associated with the  $A$  site is unchanged by the anion-lattice dilation, but the  $B$  site suffers symmetry reduction. Such distortion of the octahedral symmetry was detected experimentally by Ying *et al.*<sup>18</sup> for MgAl<sub>2</sub>O<sub>4</sub> and ZnAl<sub>2</sub>O<sub>4</sub>.

For decreasing symmetry, first, Fe layers are suggested. Accordingly the spinel crystal has antiferromagnetic layers of Fe ions along the  $[001]$  axis, at intervals of one-fourth of the unit cell dimension ( $a/4$ ) regarding the origin is located at  $\bar{3}m$ . For such an arrangement, a semiconducting trend has been observed as shown in Fig. 4. The corresponding magnetic moment takes the value of  $4.2\mu_B$  for Fe ions but with energy, per formula unit, a little bit higher than that of the other studied techniques as will be shown later. Such estimated value of moment is consistent with the experimental reported value.<sup>9,10</sup> Second, decreasing the octahedral point group symmetry from  $O_h$  to  $D_{4h}$ ,  $C_{4v}$  and  $C_{3v}$  as shown in Fig. 2, can predict the octahedral distortion. Despite the  $D_{4h}$  point group symmetry,  $C_{4v}$  and  $C_{3v}$  point group symmetries produce half metallic behavior and nearly similar densities of state (DOS); however,  $C_{4v}$  has the lowest energy (as shown in Table I). Figure 5 shows the DOS and band structure for  $C_{4v}$  in which the lower channel shows zero indirect gap but the upper channel shows 0.4 eV indirect gap.

GGA calculations for  $C_{4v}$  yielded magnetization of  $9.99\mu_B$  which is physically in good agreement considering the Fe ions per  $2\text{ZnFe}_2\text{O}_4$  formula as shown in Table I. Considering the distribution of the Fe ions in the octahedral symmetry as

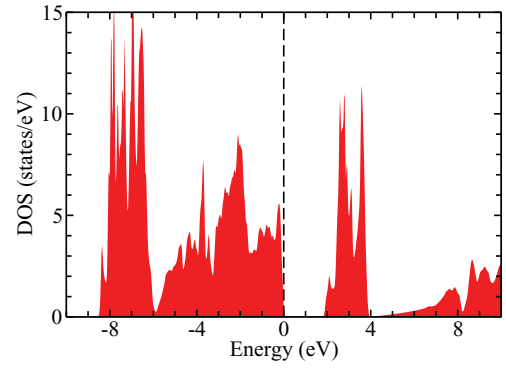


FIG. 4. (Color online) DOS for the antiferromagnetically layered configuration for Fe<sup>3+</sup>.

$[3\text{Fe}\uparrow + \text{Fe}\downarrow]$  (as shown in the first column of Table I), the net magnetic moment calculated for Fe becomes  $3 \times 3.93 - 3.4 = 8.39\mu_B$ . The difference between the net magnetic moment ( $8.39\mu_B$ ) and the unit cell moment ( $9.99\mu_B$ ) reveals the contribution of the oxygen sphere and the interstitials of the unit cell.

It has been found, in the present calculations, that the decrease of the octahedral symmetry from  $O_h$  to  $D_{4h}$  to  $C_{4v}$  to  $C_{3v}$  tends to shift the states from the metallic case to the zero gap case for the minority channel. Meanwhile the majority channel has a semiconducting trend for all studied octahedral point group symmetry. Regarding the energies of the previous octahedral point group symmetry,  $C_{4v}$  has been found to be the lowest state as depicted in Table I. For creating the energy gap, the Hubbard correlation parameter  $U$  has been applied to the  $C_{4v}$  symmetry. Figure 6 represents the GGA +  $U$  calculations with  $U = 1$  eV. The corresponding energy gaps of the up and down channels were found to be 0.4 and 0.7 eV, respectively. In addition the corresponding unit cell magnetic moment has been increased by  $0.01\mu_B$  and becomes  $10\mu_B$ . At the same time the magnetic moment of Fe has increased and becomes  $4\mu_B$ . Such values of magnetic moment are in good agreement with the experimental results for Fe in ZnFe<sub>2</sub>O<sub>4</sub> (Refs. 9 and 10).

### B. The effect of cation distribution

The experimental evidence for the misplacement of the Fe<sup>3+</sup> ions at the  $A$  site and the formation of the partial inverse spinel for ZnFe<sub>2</sub>O<sub>4</sub> (Refs. 4 and 8) give the possibility of a mixed or an inverse structure for ZnFe<sub>2</sub>O<sub>4</sub>. Accordingly it is

TABLE I. The ground state energy for each studied configuration and the magnetic moment produced by the Fe ion and also that for the cell,  $E_0 = -18571.137637$  Ry.

Cation distribution	Structure	$\Delta E(\text{Ry}) = E - E_0$	Fe moment ( $\mu_B$ )	Cell moment
2(Zn)[Fe <sub>2</sub> ]O <sub>4</sub>	Normal-ferro	0.021028	3.96	19.5
2(Zn)[Fe $\uparrow$ Fe $\downarrow$ ]O <sub>4</sub>	Fe layers	1.330577	4.22, 4.22	0.0
(Zn <sub>2</sub> )[Fe <sub>3</sub> $\uparrow$ Fe $\downarrow$ ]O <sub>8</sub>	$D_{4h}$	0.095298	3.92, 3.72	9.99
(Zn <sub>2</sub> )[Fe <sub>3</sub> $\uparrow$ Fe $\downarrow$ ]O <sub>8</sub>	$C_{4v}$	0.00668	3.93, 3.74	9.99
(Zn <sub>2</sub> )[Fe <sub>3</sub> $\uparrow$ Fe $\downarrow$ ]O <sub>8</sub>	$C_{3v}$	0.068837	3.94, 3.75	9.99
(Zn <sub>2</sub> )[Fe <sub>3</sub> $\uparrow$ Fe $\downarrow$ ]O <sub>8</sub>	$C_{4v} + 1$ eV	0.230192	4.007, 3.913	10.003
(Fe $\downarrow$ Zn)[Fe <sub>3</sub> $\uparrow$ Zn]O <sub>8</sub>	Mixed	0.083938	[3.85], (3.58)	9.96
2(Fe $\downarrow$ )[Fe $\uparrow$ Zn]O <sub>4</sub>	Inverse	0.000000	[3.75], (3.64)	0.0

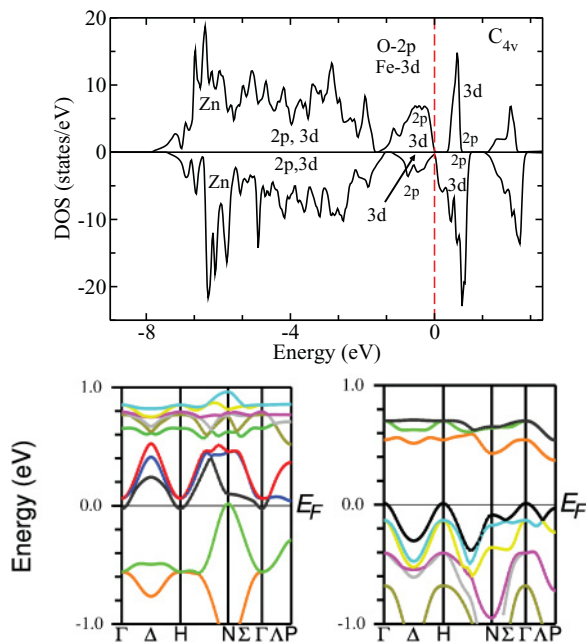


FIG. 5. (Color online) DOS and down-up channel band structure for  $C_{4v}$  symmetry.

wise to study the effect of cation distribution of  $Zn^{2+}$  and  $Fe^{3+}$  between  $A$  and  $B$  sites on the electrical and magnetic properties of  $ZnFe_2O_4$ .

The procedure of calculations is to exchange the Zn Wyckoff positions with the Fe positions, according to which the Zn ion migrates from the tetra to replace the Fe ion in the octa according to the proposed formula  $(Zn_2)[Fe_4]O_8$ . For a partially inverse spinel,  $(ZnFe)[ZnFe_3]O_8$ , the DOS still have half metallic behavior as shown in Fig. 7. For an inverse spinel, the calculations show not only the creation of an energy gap but also a decrease in the energy to become a bit lower than that obtained before in the case of  $C_{4v}$ .

The variation of  $u$  (oxygen parameter) from the ideal value 0.25 (for origin  $\bar{3}m$ ) to become 0.2586 tends to compress the contained 6 legend of the octahedral site. Consequently the  $e_{2g}$  of Fe 3d shifts to high energy above the Fermi level, revealing the metallic behavior. Such behavior has been obtained even for the exchange of one of the tetra Zn ions by an Fe ion.

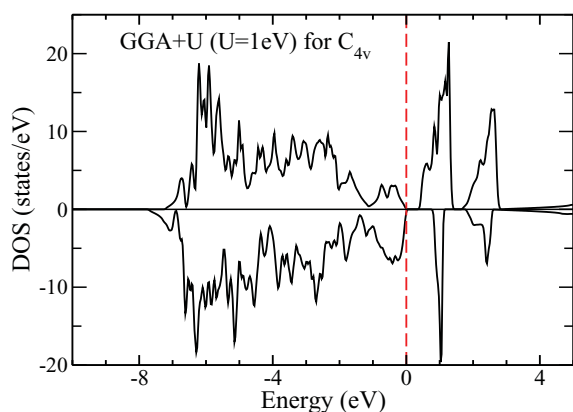


FIG. 6. (Color online) DOS from GGA +  $U$  calculation for  $C_{4v}$  symmetry with  $U = 1$  eV.

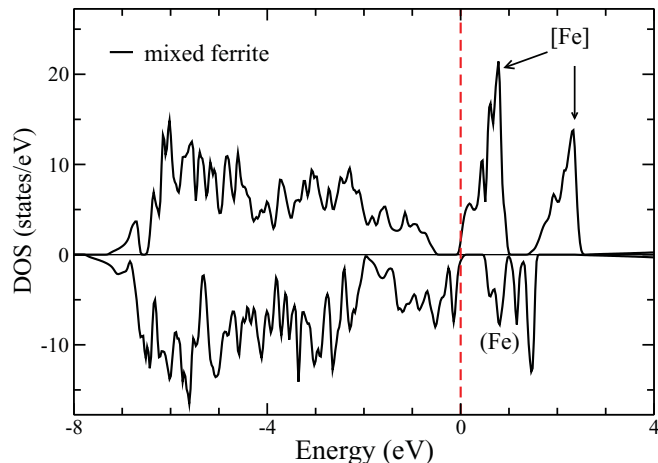


FIG. 7. (Color online) Mixed structure  $(ZnFe)[ZnFe_3]O_8$  still shows the metallic behavior. [Fe] stands for octahedral states, and (Fe) stands for tetrahedral states.

However in the inverse spinel, half of the octahedral sites are occupied by Zn ions and the rest are occupied by Fe ions. Since Zn has an ionic radius smaller than that of Fe, accordingly the octahedral sites occupied by the Zn ions shrink and those occupied by Fe ions expand. Such relaxation tends to decrease the crystal energy as shown in Table I. In turn, the energy of the octahedral site containing Fe decreases and the energy states for  $e_{2g}$  Fe and O-2p shift downward in Fermi level. This is the cause of semiconducting behavior as shown in Fig. 8.

It is worth noting that the semiconducting behavior occurs likely in the inverse state. However such behavior may be obtained for inversion more than 50%.

Energy gaps recognized for the inverse structure were found to be about 0.46 and 0.54 eV for the upper and lower channels, respectively. Moreover the Fe magnetic moment in the octahedral state is higher than that of the tetrahedral state by  $0.1\mu_B$  as shown in Table I.

### C. The effect of the Hubbard parameter $U$

One of the problems of the normal electronic structure framework is the absence of orbital energy dependence in the exchange correlation potential. For systems containing partial

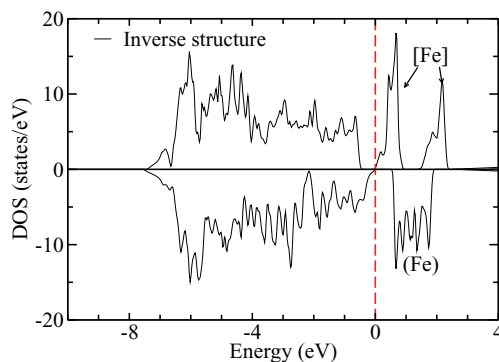


FIG. 8. (Color online) Inverse structure  $(Fe)[ZnFe]O_4$  shows the semiconductor behavior. The octahedral iron produces these two majority peaks above the Fermi level and the minority one is due to iron in the tetrahedral level.

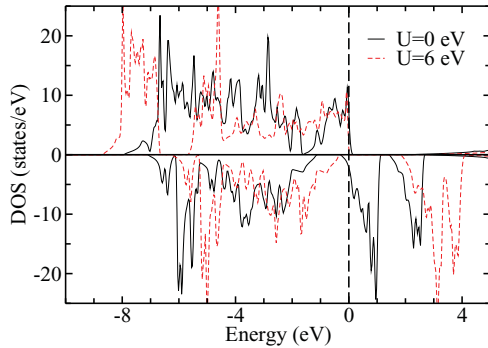


FIG. 9. (Color online) Spin polarization dependent on the Hubbard parameter with  $U = 0.0$  and  $6$  eV for Fe  $3d$ .

or total  $d$  or  $f$  shell, the method of potential calculation does not distinguish between orbitals with different  $m$  quantum numbers. Metallic behavior will be expected for such totally or partially filled states unless the exchange and crystal field splitting create a gap. Thus, the transition metal oxides, which are insulators, are predicted to be metals by the LDA or GGA method. An orbital-dependent potential has to be incorporated on top of the potential of the above framework methods. Such a potential, named the Hubbard parameter  $U$ , is acting only on the localized  $d$  states. This in turn splits the  $d$  bands forming the upper and lower Hubbard bands; accordingly this additional potential may work successfully.

For a complete view of the  $\text{ZnFe}_2\text{O}_4$  spinel, the gap dependence on  $U$  for Fe  $3d$  is calculated with GGA +  $U$ , where  $U = 0, 1, \dots, 6$  eV. It has been found that the value of  $U = 2$  eV is enough to obtain a gap for the minority channel. However for the majority channel the states of O  $2p$  still touch the Fermi level even for  $U = 6$  eV. Thus the metallic behavior is associated with those states of O  $2p$  touching the Fermi level. In most of the previous works for  $\text{ZnFe}_2\text{O}_4$  (Ref. 6), it was believed that the Hubbard parameter should be added to the  $d$  states of transition metals in order to obtain semiconducting behavior. According to our calculations  $U$  should also be added to the O  $2p$  potential. However the calculations showed that the O  $2p$  extends from just below the Fermi level deeply to about  $-7$  eV. Accordingly the addition of the extra potential  $U$  to the O  $2p$  physically seems unlogical. Consequently the system  $\text{ZnFe}_2\text{O}_4$  should not be treated as a correlated system only, but it should consider the octahedral deformation as proved before in Sec. A.

It has been found that the change of the unit cell energy is about  $0.11$  Ry per each  $1$  eV, where  $\Delta E = E_{U_0} - E_{U_6} = -0.675$  Ry. The DOS for both  $U_0 = 0$  and  $U_6 = 6$  is shown in Fig. 9. The magnetic moment produced by Fe ion changes from  $3.96$  eV for  $U_0$  to  $4.27$  eV for  $U_6$ . This means that the increase in  $U$  does not yield the semiconducting behavior but it adjusts the Fe magnetic moment with the experimental value in addition to the splitting of the  $d$  bands.

#### IV. SUMMARY AND CONCLUSIONS

*Ab initio* calculations have been used to examine the electronic structure of the  $\text{ZnFe}_2\text{O}_4$  spinel compound that exhibits semiconducting antiferromagnetic behavior. Employing GGA +  $U$  to  $\text{ZnFe}_2\text{O}_4$  where  $U$  is applied to the Fe  $3d$  electron (with  $U$  from  $1$  to  $6$  eV) does not give a significant energy gap. Due to the domination of the O  $2p$  states touching the Fermi level, the half metallic behavior still found. Consequently an increase of the Hubbard parameter to the Fe  $3d$  electron will not be effective. On the other hand to obtain semiconducting behavior by adding  $U$  to the O  $2p$  electrons is physically unreasonable. Consequently the application of Hubbard parameters only is not enough to demonstrate the Zn ferrite.

The effect of symmetry and cation distribution was achieved. The deviation of the oxygen parameter,  $u = 0.2586$ , from the ideal value,  $u = 0.25$ , tends to decrease the stress of the octahedral site by forcing the structure to increase its degree of inversion. Such an increase of inversion inevitably reduces the point group symmetry of the octahedral site from  $O_h$  to  $C_{4v}$  and tends to minimize the unit cell energy. In accordance, the energy gap is created by applying a small exchange correlation potential for Fe  $3d$  electrons.

Finally it is concluded that  $\text{ZnFe}_2\text{O}_4$  cannot be treated as a correlated system only and that the degree of inversion in addition to deformation of the octahedral site should be taken into consideration and this is the real case.

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