Ab-initio approach to the structural, electronic and magnetic properties of the (001) ZnFe$_2$O$_4$ surface terminations

K.L. Salcedo Rodríguez$^a$, J.J. Melo Quintero$^a$, H.H. Medina Chanduvi$^a$, A.V. Gil Rebaza$^{a,b}$, R. Faccio$^c$, W.A. Adeagbo$^d$, W. Hergert$^d$, C.E. Rodríguez Torres$^a$, L.A. Errico$^{a,e,*}$

$^a$ Instituto de Física La Plata (IFLP) and Departamento Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP)-CCT La Plata CONICET, C.C. 67, CP 1900 La Plata, Argentina
$^b$ Grupo de Estudio de Materiales y Dispositivos Electrónicos (GEMyDE), Dpto. de Electrotecnia, Fac. de Ingeniería, UNLP, Argentina
$^c$ Centro NanoMat-DETEMA, Facultad de Química, Universidad de la República, Uruguay
$^d$ Institut of Physik, Martin-Luther-Universität Halle-Wittenberg, Von-Seckendorff-Platz 1, 06120 Halle, Germany
$^e$ Universidad Nacional del Noroeste de la Provincia de Buenos Aires (UNNOBA), Monteagudo 2772, Pergamino CP 2700, Buenos Aires, Argentina

**Article Info**

**Keywords:**
- Zn-ferrite
- Surface termination
- Electronic structure
- Magnetic response
- Ab initio

**Abstract**

We present a Density Functional Theory (DFT) based study of the structural and magnetic properties of the (001) surface of the semiconducting oxide ZnFe$_2$O$_4$ (spinel structure). The calculations were performed using the DFT based ab initio plane wave and pseudopotential method as implemented in the Quantum Espresso code. The all electron Full-potential linearized-augmented-plane-wave method (FP-LAPW) was also employed to check the reproducibility of the plane wave method. In both calculations the DFT + $U$ methodology was employed and different (001) surface terminations of ZnFe$_2$O$_4$ were studied. We find that the surface terminated in Zn is the stable one. For all the (001) surface terminations our calculations predict that the Zn-Fe cationic inversion (anti-sites), which are defects in bulk ZnFe$_2$O$_4$, becomes stable and an integral part of the surface. Also, a ferromagnetic behavior is predicted for the case of anti-sites in the superficial layer. Our results for different properties of the surface of ZnFe$_2$O$_4$ are compared with those obtained in bulk samples and those reported in the literature.

**1. Introduction**

Due to their electronic, optical and magnetic properties, ferrites (XFe$_2$O$_4$ X: Zn, Co, Ni, Al, Mg, Ti, among others [1]) are very interesting materials both from a fundamental and application point of view. In the last decades, progress in synthesis process renews the interest in this kind of insulating oxides and improves their physical properties, expanding their applications to new areas [2–4]. Particularly, zinc ferrite (ZnFe$_2$O$_4$) is of interest not only in basic research due to its intriguing magnetic behavior [5–11] but also has great potential in technological applications [12–15].

ZnFe$_2$O$_4$ crystalize in the spinel-type structure in which the cations occupy tetrahedral and octahedral sites (A and B sites, respectively) [1]. In terms of the sites, the cation distribution can be described by the formula $\left(\text{Zn}_{1-\alpha}\text{Fe}_\alpha\right)\left[\text{Zn}_{\alpha}\text{Fe}_{2-\alpha}\right]\text{O}_4$ where round and square brackets denote A and B sites and $\alpha$ is the inversion parameter. For $\alpha = 0$ the Zn atoms occupy the A sites and the Fe atoms the B ones (normal ZnFe$_2$O$_4$).

For $0 < \alpha < 1$ some percentage of the Zn atoms are located at the B sites instead of the A sites and corresponding concentration of Fe then occupies A sites (partially inverted structure). In the case of $\alpha = 1$, all the A sites are occupied by Fe atoms. ZnFe$_2$O$_4$ belongs to the class of normal ferrites, but, depending on the sample preparation method and on the thermal treatment, some degree of inversion could appear. In defective bulk ZnFe$_2$O$_4$, the absence of Fe atoms at A sites (populated by non-magnetic Zn atoms) results in weak antiferromagnetic exchange interactions between the Fe atoms via intermediate oxygen anions (Fe$_B$–O–Fe$_A$ interactions, being Fe$_B$ iron cations located at the B sites), making ZFO a strongly paramagnetic oxide with antiferromagnetic coupling only below about 10 K [16] and a quite complex ground state ([17,18] and Refs. therein). However, when particle size is reduced to the nanoscale some degree of inversion that may scale with the surface area of the samples is observed [19–21]. The presence of inversion gives rise to Fe$_B$–O–Fe$_B$ and Fe$_A$–O–Fe$_A$ couplings, enhancing the magnetic interactions and the ferrimagnetic behavior at high temperatures [20].

*Corresponding author at: Universidad Nacional del Noroeste de la Provincia de Buenos Aires (UNNOBA), Monteagudo 2772, Pergamino CP 2700, Buenos Aires, Argentina.

E-mail address: errico@fisica.unlp.edu.ar (L.A. Errico).

https://doi.org/10.1016/j.apsusc.2019.143859

Received 5 March 2019; Received in revised form 23 July 2019; Accepted 2 September 2019

Available online 03 September 2019

0169-4332/ © 2019 Elsevier B.V. All rights reserved.
In this work, our aim is to understand, by means of ab initio calculations, the structure at the atomic scale (which has remained unsolved) and the stable termination of the (001) surface of ZnFe₂O₄. Additionally, it is relevant to know how the surface termination affects the structural and electronic properties of the near surface layers, the cation inversion degree and the magnetic response of the system.

2. Calculations details

The spinel structure, Fd3m (Oh7), of ZnFe₂O₄ is characterized by two parameters, the lattice constant \(a\) (8.43–8.46 Å, see Refs. [8,22–25]) and the oxygen position parameter \(u\) (0.258, Ref. [25]). The unit cell contains eight formula units (56 atoms). More details of the structure can be found in Reference [17]. Our aim here is to study the (001) surface of ZnFe₂O₄ and how the surface affects the formation of defects (cationic inversion and oxygen vacancies in the present case).

Two types of (001) surface terminations can be obtained from a bulk truncation of ZnFe₂O₄: the fully Zn-terminated surface (Zn₂) or an \(O_4\)-Fe₄-O₄ termination that “exposes” O and Fe atoms. In order to study the effect of a reducing atmosphere, a \(O_4\)-Fe₄ termination was studied. This termination was obtained by removing the four external oxygen atoms from the \(O_4\)-Fe₄-O₄ termination. These surface terminations are shown in Fig. 1. In order to study these (001) surface terminations ab initio calculations have been performed on the basis of Density Functional Theory (DFT) using two different methods of calculation, the Full-Potential Linearized Plane Waves method (FP-LAPW) [26–28] as implemented in Wien2k code [28] and the plane wave and pseudopotential method as implemented in Quantum-Espresso code (QE, Refs. [30] and [31]). The first method is recognized as one of the more accurate for the determination of the electronic structure of solids but is computationally expensive and time consuming when large systems or systems that present low symmetries or reduced dimensions (as in the case of surfaces). The plane wave and pseudo-potential methods is more flexible to study structural and electronic properties of complex systems. To be on the safe side, however, we need to verify first whether this fast and more approximative method correctly reproduces some key properties predicted by the more accurate FP-LAPW method.

In the case of the ab initio plane wave and pseudopotential calculations the exchange and correlation effects were treated within density-functional theory using Perdew-Burke-Ernzerhof (PBE) [32] parameterization of the generalized gradient approximation plus the Hubbard U term (GGA+U) in the self-interaction correction (SIC) scheme [33] with \(U = 5\) eV [17] for the Fe-3d orbitals. The ionic cores were described using ultrasoft pseudo-potentials from the Standard Solid State Pseudopotentials library (SSSP, Ref. [34]), where the converged kinetic energy cutoff for the wavefunction and charge density were set to 70 Ry and 500 Ry, respectively. For the electronic integration, the irreducible Brillouin zone was described according to the Monkhorst-Pack scheme [35] using a \(2 \times 2 \times 1\) k-point grid.

To validate whether it is legitimate to use QE results, we examine whether they correctly reproduce FP-LAPW calculations. Exchange and correlation effects were also treated within density-functional theory using the GGA+U in the SIC formalism [33] with \(U = 5\) eV for the Fe-3d orbitals [17,36]. A \(2 \times 2 \times 1\) k-point mesh was employed to sample the first Brillouin zone. The basis set size and muffin-tin radii were taken as in the case of the bulk system (Refs. [17] and [36]).

In both QE and FP-LAPW calculations atomic positions were optimized until obtain forces acting on all ion were smaller than 0.05 eV/Å. This tolerance value was taken because atomic displacements produced by forces smaller than 0.05 eV/Å results in changes in energies differences, magnetic moments or bond-lengths that are below our convergence error.

To check the precision of our calculations, we performed several additional calculations, following the procedure described by some of us in reference 17. By examining the effect of different basis sets and \(k\)-point grids (we considered \(1 \times 1 \times 1, 2 \times 2 \times 1, 3 \times 3 \times 1\) and \(4 \times 4 \times 2\) \(k\)-point grids) we conclude that for the parameters employed in the present ab initio study our results are very well converged, being these parameters an optimal compromise precision-computational times.

In contrast to a regular functional as PBE, the GGA+U method is not implemented in exactly the same way in the two employed codes. In the case of Wien2k the \(U\) correction is applied within the muffin tin spheres. A pseudopotential method as QE does not have this concept of muffin tin spheres. In consequence, differences between both methods are expected. We not pretend here to perform a deep comparison as
3. Results and discussion

We will start the discussion of the results obtained for the (001) surface terminations of ZnFe₂O₄ by the QE and FP-LAPW results obtained for the cases of the 8.5 Å thickness slab. QE and FP-LAPW predict the same results for the surface structure: in the cases of the Zn₂ and O₄-Fe₄-O₄ a strong surface reconstruction occurs. For the Zn₂ surface termination the superficial Zn atoms relax inward the sub-surface layer, being the magnitude of the Zn atoms displacement of about 1 Å (see Fig. 1d). In the case of the O₄-Fe₄-O₄ termination, the Zn atoms located in the sub-surface layer (1 Å below the O₄-Fe₄-O₄ superficial layer) relax outwards to the surface. The magnitude of the Zn atoms displacement along the z-direction is c.a. ~0.5 Å (see Fig. 1e). As a conclusion, we can point out that our ab initio calculations predict that, after the surface reconstruction, both terminations yield a similar structure with a O₄-Fe₄-Zn₂-O₄ superficial layer. In the case of the reduced O₄-Fe₄ surface termination, the surface reconstruction is less pronounced (see Fig. 1f).

QE calculations predict very similar results for the structural properties of the (001) surface terminations of ZnFe₂O₄ when a slab of 17 Å thickness is considered.

It is important to mention that the structural reconstruction of the different (001) surface terminations of ZnFe₂O₄ implies a nearly vertical movement (z direction in Figs. 1 and 2) of the superficial and sub-superficial layers. More complex reconstructions (in which the two-dimensional symmetry of the surface in the x-y plane is altered) can be realized in a real sample. These reconstructions cannot be described with the slab used in the present work to simulate the surface terminations. In order to study these complex reconstructions the dimensions of the slab must be duplicated (at least) in the x and y directions. These slabs contain > 224 atoms plus the vacuum and requires extremely large computational times and resources.

In order to determine the stability of each surface termination we study the surface energy formation that was calculated as [38,39]:

\[
\gamma = \frac{E_{\text{slab}} - \left[ N_{\text{Zn}} \mu(\text{Zn}) + N_{\text{Fe}} \mu(\text{Fe}) + N_{\text{O}} \mu(\text{O}) \right]}{2A}
\]

(1)
to take into account the different stoichiometries of each termination. In the above equation \(E_{\text{slab}}\) is the total energy of the slab structure considered, \(N_{\text{Zn}}, N_{\text{Fe}},\) and \(N_{\text{O}}\) are the number of Zn, Fe, and O atoms in the slab (the number of Zn, Fe, and O atoms for each slab configuration is shown in Table 1). \(\mu(\text{Zn}), \mu(\text{Fe})\) and \(\mu(\text{O})\) are the chemical potentials of Zn, Fe, and O that must satisfy:

\[
E(\text{ZFO}) = \mu(\text{Zn}) + 2\mu(\text{Fe}) + 4\mu(\text{O})
\]

(2)

and

\[
E(\text{ZnO}) = \mu(\text{Zn}) + \mu(\text{O})
\]

(3)

being \(E(\text{ZFO})\) and \(E(\text{ZnO})\) the total energies of one unit-formula of bulk

### Table 1

| Number of Zn, Fe, and O atoms (\(N_{\text{Zn}}, N_{\text{Fe}},\) \(N_{\text{O}}\)) in the slabs used for the simulation of the different (001) surface terminations of ZnFe₂O₄. |
|---|---|---|---|
| & \(N_{\text{Zn}}\) & \(N_{\text{Fe}}\) & \(N_{\text{O}}\) |
| 8.5 Å thickness slab | Zn₂ termination | 10 | 16 | 32 |
| | O₄-Fe₄ termination | 8 | 20 | 32 |
| | Zn₂,Fe₄-O₄ termination | 8 | 20 | 40 |
| | O₄-Fe₄-Zn₂-O₄ termination | 18 | 36 | 64 |
| | O₄-Fe₄-Zn₂-O₄ termination | 16 | 36 | 64 |
| 17 Å thickness slab | Zn₂ termination | 18 | 36 | 72 |
ZnFe$_2$O$_4$ and ZnO, respectively.

The chemical potentials vary depending on the experimental environments in which the surface is growth, but there are upper and lower limits that define a range for the chemical potentials. The upper limit of $\mu(O)$ is the chemical potential of an oxygen molecule, $\mu(O_2)$. For $\mu(O)$ larger than $\mu(O_2)/2$ vaporization of oxygen as molecules from the ZnFe$_2$O$_4$ surfaces will occur. In the following we call this upper limit "O-rich environment." In this situation, $\mu(O^{\text{rich}}) = \mu(O_2)/2$. The lower limit of $\mu(O)$ correspond to the upper limits of $\mu(Zn)$ and $\mu(Fe)$ which is the Zn and Fe chemical potentials in metallic Zn and Fe. For larger values of $\mu(Zn)$ and $\mu(Fe)$ segregation of metallic Zn and Fe will occur. This is the "oxygen-poor environment".

In order to obtain the required chemical potentials FP-LAPW and QE calculations (with the same precision than those corresponding to the slab structures and bulk ZnFe$_2$O$_4$) for a O$_2$ molecule and metallic Zn, metallic Fe and ZnO were performed. It was found that $\mu(O^{\text{poor}})$, $\mu(O^{\text{rich}}) = -5.4$ eV for the present calculations. By using Eqs. (1)-(3) and the surface energy for the O-rich environment ($\Gamma_{\text{O-rich}}$) we can write the surface energy as a linear function of the oxygen chemical potential:

$$\gamma = \frac{\mu(O^{\text{rich}})}{2A} + \left[\frac{1}{2}N_{Fe} + N_{Zn} - N_{O}\right] \mu(O) - \frac{\Delta \mu}{2A}$$

(4)

with $\Delta \mu = (\mu(O) - \mu(O^{\text{rich}}))$. From detailed convergence studies we determine that our precision error in $\gamma$ is in the order of 10 meV/Å$^2$.

In a first stage we will analyse the stability of the normal (001) terminations. Fig. 3 shows the calculated surface energies $\gamma$ as a function of the oxygen chemical potential for the case of the FP-LAPW calculations. The QE predictions for $\gamma$ follow the same trend and predict that the Zn$_2$ surface termination has the lowest surface energy formation for the possible range of the oxygen chemical potential. In Table 2, the values of $\gamma$ for the extreme oxygen potential range (O-rich and O-poor) are shown. We must point out here that the WIEN2k calculations predict negative values for $\gamma$ in the case of the Zn$_2$ surface termination. This negative value, that do not appear for the case of the QE calculations, would indicate a qualitatively different prediction and this is not what one expects for two equivalent DFT methods. As can be seen in Table 2 the differences in the surface energy values between WIEN2k and QE roughly correspond to a rigid shift. The (unphysical) negative sign predicted by the Wien2k calculations is related to the model used for the calculation of the atomic energies used in Eqs. (1)-(3) systems for the calculation of $\gamma$ (most probably the O$_2$-molecule), resulting in the rigid shift of the surface energies between both methods. For this reason, physical information is contained in the difference in the surface formation energies between terminations and not in its sign.

When the 17 Å thickness slabs are considered as a model for the simulation of the (001) terminations of ZnFe$_2$O$_4$ the QE calculations predict a similar trend, i.e., Zn$_2$ is the stable termination. Calculations performed using as a model for the surface a 25.5 Å thickness slab and 16 Å of vacuum confirm all the discussed results for the surface stability and confirms that even for the 8.5 Å slab thickness the spurious interaction between the upper and lower layers of the slab is negligible. As can be seen in Fig. 3, the O$_x$Fe$_{1-x}$O$_y$ termination is more stable than the O$_x$Fe$_{1-x}$O$_y$ in the O-poor environment. The inverse situation is observed, as expected, for the O-rich condition.

In Reference 40 it was shown that the surface energies obtained in PBE calculations overestimates the experimental values by about 12% and even after correcting for this bias there is a remaining $\pm \, 15$ meV/Å$^2$ uncertainty on the resulting surface energy. From our convergence tests an estimate uncertainty of 10 meV/Å$^2$ in $\gamma$ was derived. Even when the mentioned 12% overestimation correction, the convergence error and the remaining uncertainty are considered, the phase stability presented in Fig. 3 is not changed.

In Fig. 4 we present the QE results for the magnetic moments at the Fe sites for the case of the 17 Å thickness slab as a function of the distance of the Fe atom to the surface for the three terminations studied. As a general result we can see that Fe atoms in the surface present magnetic moments smaller than those located in the bulk. For the case of the O$_x$Fe$_{1-x}$ and the O$_x$Fe$_{1-x}$O$_y$ terminations, the magnitude of the magnetic moment of the Fe atoms located in the superficial layer are 3.95 and 3.60 $\mu_B$, respectively. This reduction of the magnetic moments of the Fe atoms located in the superficial layers of both terminations is associated to the change in the O-coordination of these Fe atoms and the subsequent changes in the charge in the atomic spheres of these Fe atoms (the reduction of the oxygen coordination of the Fe atoms at the surface induces an increment in the charge in this Fe atoms from 23.7e up to 23.9e). A similar effect was found in reduced bulk ZnFe$_2$O$_4$. In this case, the formation of an oxygen vacancy reduce the magnitude of the magnetic moments of the three Fe atoms nearest neighbors to the vacancy sites to from 4.2 $\mu_B$ [17] to 4.0 $\mu_B$ (two Fe atoms) and $\sim 3.6$ $\mu_B$ for the remaining one [36]. The Fe atoms located in layers 2.3 Å (at least) below the surface present magnetic moments in the order of 4.1–4.2 $\mu_B$. For both O$_x$Fe$_{1-x}$ and O$_x$Fe$_{1-x}$O terminations no spin-polarization was found at the Zn-sites while spin-polarization in the order of 0.15 $\mu_B$ was found for some oxygen atoms (a similar result was obtained in reduced ZnFe$_2$O$_4$, see Ref. [36]).

In the case of the Zn$_2$ surface termination, a different behavior was found. Similar to the previous cases, the Fe atoms located 1.3 Å below the surface present a spin-polarization of 4.0 $\mu_B$, an expected reduction due to the smaller oxygen coordination of these Fe atoms compared to the case of bulk ZnFe$_2$O$_4$. But, the Fe atoms located 3.4 Å below the surface present even smaller magnetic moments, 3.6 $\mu_B$. This result can be explained in terms of the superficial reconstruction and the charge rearrangement that induces: when the unreconstructed Zn$_2$ surface is inspected magnetic moments of $\pm \, 4.2$ $\mu_B$ are predicted for Fe-atoms located at 3.4 Å from the surface. After the structural reconstruction (that implies a large displacement of the superficial Zn$_2$ atoms to the O$_x$Fe$_{1-x}$O$_y$ sub-surface layer) the magnetic moment of the Fe atoms of the sub-surface layers drops to $\pm \, 3.6$ $\mu_B$. For this Zn$_2$ termination, no magnetic moments were found at the Zn sites and some oxygen atoms present magnetic moments in the order of 0.10 $\mu_B$. It is important to mention here that QE and FP-LAPW calculations performed in the 8.5 Å thickness slab predicts the same behavior for the magnetic moments (differences in the order of 0.2 $\mu_B$ between both methods).

After the study of the slabs with a normal distribution of Zn and Fe cations in the A and B sites of ZnFe$_2$O$_4$, we have considered the Zn-Fe anti-site defect formed by cation inversion between Zn and Fe atoms at superficial and deep layers. Our DFT-based calculations show that, independently of the surface termination considered, the normal structure and those with a superficial anti-site have the same energy (differences smaller than the convergence error), see Table 2. This result is
contrary to those found in bulk ZnFe$_2$O$_4$, for which the inversion process is strongly endothermic: the normal structure has the lowest-energy, being the energy difference between the normal and partially inverted structure $\sim 85$ meV per unit formula (f.u.) (Ref. [36]).

The superficial cation inversion is promoted by the rearrangement of the electronic structure in the surface layer in order to compensate the changes originated by the surface. As we discussed in a previous work, a similar effect is observed in volumetric and reduced ZnFe$_2$O$_4$: when an oxygen vacancy and one anti-site in the bulk structure is considered the energy necessary to produce a Zn-Fe anti-site is in the order of $\sim 30$ meV/f.u., 60% smaller than those required in the case of stoichiometric ZnFe$_2$O$_4$ [36]. These results show that the formation of oxygen vacancies or reduced coordination at the surfaces favours the cationic inversion in ZnFe$_2$O$_4$.

Based in our results we can conclude that Zn-Fe inversion is not a trapped defect (as in the bulk case) but also an integral component of the surface of ZnFe$_2$O$_4$. This conclusion is in agreement with experimental results that shown that the degree of cation inversion may scale with the surface area in MgAl$_2$O$_4$, ZnFe$_2$O$_4$, and NiFe$_2$O$_4$ ferrites spinel powders [21] or thin films [41]. In other works, it was shown that ZnFe$_2$O$_4$ nanoparticles of 6 nm diameter present a high degree of inversion that is associated to surface effects, i.e., involves cations allocated at the surface layer [42,43]. A similar result was obtained by Rasmussen et al. [38] in MgAlO$_4$ spinel, suggesting that surface-induced inversion could a general phenomenon in spinel-type oxides.

Concerning magnetic moments at the Fe sites, the same results previously discussed for normal ZnFe$_2$O$_4$ were found. The only difference is that the magnetic moments of the Fe atoms now allocated at the A-sites are 0.1–0.2 $\mu_B$ smaller than those of the Fe atoms that remain at the B-sites. This diminution is observed for Fe atoms allocated at the A sites in the surface layer or even in deep layers. For the case of the 17 Å slab, the Fe atoms located at A sites in deep layers (8.5 Å from the surfaces) present magnetic moments close to 4.2 $\mu_B$, the same value predicted for Fe at the B-sites.

There is a last point to discuss: the ferrimagnetic response experimentally observed in nano-size zinc ferrite [20,43]. In this case we take the Zn$_2$ terminated reconstructed slab with one superficial anti-site and we study different ferromagnetic spin configurations in addition to the antiferromagnetic ones. We found that the lowest-energy magnetic configuration corresponds to a ferrimagnetic system with a net magnetic moment of 1.2 $\mu_B$/Fe atom. For the case of the normal slab the lowest-energy solution is the antiferromagnetic one. This result shows

| Table 2 | Predicted surface energy formations $\gamma$ (in meV/A$^2$) for the different terminations and slabs studied here by means of FP-LAPW and QE calculations. |
|--------|-------------------------------------------------|
|        | $\gamma$ (meV/A$^2$) | $\gamma$ (meV/A$^2$) | $\gamma$ (meV/A$^2$) |
|        | O$_4$-Fe$_4$-O$_4$ termination | O$_2$-Fe$_2$ termination | Zn$_2$ termination |
| O-rich condition | | | |
| FP-LAPW, 8.5 Å thickness slab | Normal | 310 | 490 | $-120$ |
| | Superficial anti-site | 310 | 490 | $-120$ |
| | Deep anti-site | 310 | 500 | $-100$ |
| QE, 8.5 Å thickness slab | Normal | 218 | 386 | 155 |
| | Superficial anti-site | 218 | 386 | 158 |
| | Deep anti-site | 216 | 395 | 202 |
| QE, 17 Å thickness slab | Normal | 222 | 390 | 158 |
| | Superficial anti-site | 223 | 390 | 161 |
| | Deep anti-site | 222 | 400 | 204 |
| O-poor condition | | | |
| FP-LAPW, 8.5 Å thickness slab | Normal | 380 | 260 | $-190$ |
| | Superficial anti-site | 380 | 260 | $-190$ |
| | Deep anti-site | 380 | 270 | $-170$ |
| QE, 8.5 Å thickness slab | Normal | 293 | 159 | 80 |
| | Superficial anti-site | 293 | 159 | 83 |
| | Deep anti-site | 292 | 167 | 127 |
| QE, 17 Å thickness slab | Normal | 298 | 163 | 83 |
| | Superficial anti-site | 297 | 163 | 86 |
| | Deep anti-site | 298 | 172 | 128 |

Fig. 4. Magnetic moment $\mu$ at the Fe sites as a function of the distance (in Å) to the surface ($Z$) for the three (001) surface terminations studied here. In all cases the results correspond to the normal structures. $Z = 0$ correspond to the lower layer of the slabs showed in Fig. 1. Magnetic moments at the Fe sites in bulk ZnFe$_2$O$_4$ are 4.2 $\mu_B$. The superficial cation inversion is promoted by the rearrangement of the electronic structure in the surface layer in order to compensate the changes originated by the surface. As we discussed in a previous work, a similar effect is observed in volumetric and reduced ZnFe$_2$O$_4$: when an oxygen vacancy and one anti-site in the bulk structure is considered the energy necessary to produce a Zn-Fe anti-site is in the order of $\sim 30$ meV/f.u., 60% smaller than those required in the case of stoichiometric ZnFe$_2$O$_4$ [36]. These results show that the formation of oxygen vacancies or reduced coordination at the surfaces favours the cationic inversion in ZnFe$_2$O$_4$. Based in our results we can conclude that Zn-Fe inversion is not a trapped defect (as in the bulk case) but also an integral component of the surface of ZnFe$_2$O$_4$. This conclusion is in agreement with experimental results that shown that the degree of cation inversion may scale with the surface area in MgAl$_2$O$_4$, ZnFe$_2$O$_4$, and NiFe$_2$O$_4$ ferrites spinel powders [21] or thin films [41]. In other works, it was shown that ZnFe$_2$O$_4$ nanoparticles of 6 nm diameter present a high degree of inversion that is associated to surface effects, i.e., involves cations allocated at the surface layer [42,43]. A similar result was obtained by Rasmussen et al. [38] in MgAlO$_4$ spinel, suggesting that surface-induced inversion could a general phenomenon in spinel-type oxides. Concerning magnetic moments at the Fe sites, the same results previously discussed for normal ZnFe$_2$O$_4$ were found. The only difference is that the magnetic moments of the Fe atoms now allocated at the A-sites are 0.1–0.2 $\mu_B$ smaller than those of the Fe atoms that remain at the B-sites. This diminution is observed for Fe atoms allocated at the A sites in the surface layer or even in deep layers. For the case of the 17 Å slab, the Fe atoms located at A sites in deep layers (8.5 Å from the surfaces) present magnetic moments close to 4.2 $\mu_B$, the same value predicted for Fe at the B-sites.

There is a last point to discuss: the ferrimagnetic response experimentally observed in nano-size zinc ferrite [20,43]. In this case we take the Zn$_2$ terminated reconstructed slab with one superficial anti-site and we study different ferromagnetic spin configurations in addition to the antiferromagnetic ones. We found that the lowest-energy magnetic configuration corresponds to a ferrimagnetic system with a net magnetic moment of 1.2 $\mu_B$/Fe atom. For the case of the normal slab the lowest-energy solution is the antiferromagnetic one. This result shows
that the surface (reduced Fe-coordination) favours the cationic inversion and in turns the cationic inversion favours ferrimagnetic configurations. A systematic study of the magnetic behavior of the surface terminations of ZnFe₂O₄ is now in progress.

4. Conclusions

In this work we have studied, by using two different DFT-based methods (all electron FP-LAPW and plane wave and pseudopotentials method as implemented in the Quantum Espresso code) the stability of the Zn₂O₄·Fe₄ and O₄·Fe₄·O₄ terminations of the (001) surface of ZnFe₂O₄, considering slabs of 8.5 Å and 17 Å thickness. We found that, after the surface reconstruction, the Zn2 terminal is the stable one. We also found that cationic inversion, a defect in volumetric ZnFe₂O₄, become energetically favourable in the surface. This result explains the high degree of inversion observed in nano-sized and thin films of ZnFe₂O₄. The presence of some inversion degree in the samples gives rise to Fe₅₋₇-OFe⁷⁺ couplings that strengthen the magnetic interactions and the ferrimagnetic behavior at high temperatures. Calculations of the magnetic coupling constants in normal and inverted bulk and thin films of ZnFe₂O₄ are now in progress in order to correlate the degree of inversion with the magnetic behavior of this semiconductor oxide.

Acknowledgments

This research was partially supported by CONICET (Grant No. PIP0747, PIP0720), UNLP (Grant No. 11/X678, 11/X680, 11/X708, 11/X788, 11/X792), ANPCyT (Grant No. SIB 0176-2017), and “Proyecto Acelerado de Cálculo 2017”, Red Nacional de Computación de Alto Desempeño (SNCAD-MINCYT) – HPC Cluster, Rosario, Argentina. Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)–Projektnummer 31047525-SFB 762, Projects A4 and B1.

References

[1] J. Smit, H.P.J. Wijn, Ferrites, Philips Technical Library, Eindhoven, 1959.
[2] Chao Jin, Peng Li, Wenbo Mi, Haili Bai, Structure, magnetic, and transport properties of epitaxial ZnFe₂O₄ films: an experimental and first-principles study, J. Phys. 115 (2015) 213908.
[3] V. Rajkumar, K. Haris, S. Takahashi, J. Obre, K. Uchida, M. Mizuguchi, H. Umezawa, H. Kawai, K. Ando, K. Takahashi, S. Maekawa, E. Saitoh, Transmission of electrical signals by spin-interaction in a metal-insulator semiconductor, Nature 464 (2010) 262-266.
[4] C.E. Rodríguez Torres, F. Golmár, M. Ziese, P. Esquinazi, S.P. Hulsenau, Evidence of defect-induced ferromagnetism in ZnFe₂O₄ thin films, Phys. Rev. B 84 (2011) 064404.
[5] K. Kamaevaya, Y. Tsonouda, H. Kadowski, K. Kohn, Magnetic neutron scattering measurements on a single crystal of frustrated ZnFe₂O₄, Phys. Rev. B 68 (2003) 024412 and references there in.
[6] Y. Yamada, K. Kamaevaya, Y. Tsonouda, Interspin interactions in ZnFe₂O₄: theoretical analysis of neutron scattering study, Phys. Rev. B 66 (2002) 024401.
[7] K. Kamaevaya, Y. Tsonouda, K. Odaka, K. Kohn, Spin liquid state in ZnFe₂O₄, J. Phys. Chem. Solids 60 (1999) 1261-1264.
[8] W. Schiesell, W. Potzel, H. Karzel, M. Steiner, G.M. Kalvius, A. Martin, M.K. Krause, L. Cademartiri, J. Gal, W. Schäfer, G. Will, M. Hillberg, R. Wöll, Magnetic properties of the ZnFe₂O₄ spinel, Phys. Rev. B 53 (1996) 9143-9152.
[9] T. Ueda, K. Kamaevaya, H. Sekiya, S. Nakamura, Y. Tsonouda, K. Kohn, M. Tanaka, Magnetic properties of ZnFe₂O₄ as a 3-D geometrical spin frustration system, J. Phys. Soc. Jpn. 73 (2004) 2834-2840.
[10] K. Tomiyama, K. Kamaevaya, A spin molecule model for geometrically frustrated spinel ZnFe₂O₄, J. Phys. Soc. Jpn. 80 (2011) S8024.
[11] M.A. Hakim, M. Manjurul Haque, M. Hug, P. Nordblad, Spin-glass-like ordering in the spinel ZnFe₂O₄ ferrite, Physica B 406 (2001) 48-51.
[12] J.G. Fierro, Metal Oxides—Chemistry and Applications, Taylor and Francis, Boca Raton, Fl, 2006.
[13] R.E. Vandenbergh, E. De Grave, Mösbauer Spectroscopy Applied to Inorganic Chemistry, vol. 3, Plenum, New York, 1989.
[14] M. Niyasir, Effect of preparation on structure and magnetic properties of ZnFe₂O₄, J. Magn. 19 (2014) 101-105.
[15] S.D. Jackson, Metal Oxide Catalysis, vol. 2, Wiley-VCH Verlag GmbH & Co, Weinheim, 2009.
[16] G.A. Pettit, D.W. Forester, Mösbauer study of cobalt-zinc ferrites, Phys. Rev. B 4
W. Hergert, C.E. Rodriguez Torres, Producing ZnFe₂O₄ thin films from ZnO/FeO multilayers, Appl. Surf. Sci. 393 (2017) 256–261.

J.M. Ramallo López, S.G. Marchetti, J.F. Bengoa, R.J. Prado, F.G. Requejo, S.J. Stewart, S.J.A. Figueroa, Cationic exchange in nanosized ZnFe₂O₄ spinel revealed by experimental and simulated near-edge absorption structure, Phys. Rev. B 75 (2007) 073408.

S.J. Stewart, S.J.A. Figueroa, M.B. Sturla, R.B. Scorzelli, F. García, F.G. Requejo, Magnetic ZnFe₂O₄ nanoferrites studied by X-ray magnetic circular dichroism and Mössbauer spectroscopy, Physica B 389 (2007) 155–158.