Electronic structure calculation of the structural and magnetic properties of the $MgFe_2O_4$. From bulk to surface

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ABSTRACT

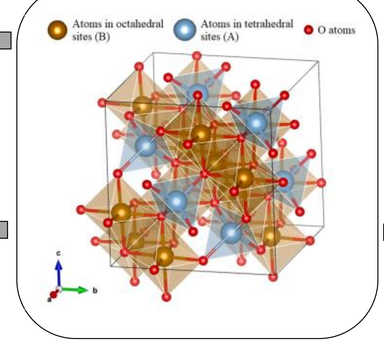
In this work we present an ab initio study of the structural, electronic, magnetic, and hyperfine properties of Magnesium ferrite, $MgFe_2O_4$ (spinel structure). This study was carried out within the framework of Density Functional Theory (DFT) using the FP-LAPW+LO and Pseudopotential methods, employing the Generalized Gradient Approximation (GGA) and the GGA+U for the potential term and exchange. The calculations show that the equilibrium structure corresponds to an inverted and antiferromagnetic configuration, where the magnetic moments of the Fe atoms at A sites are ferromagnetically ordered among themselves and antiferromagnetically with respect to the Fe in the sub lattice of B sites, while the magnesium atoms do not polarize. The GGA calculations underestimate the energy gap of the system, while GGA+U predicts a gap of 2.4 eV, value that agrees with what has been reported experimentally [1], and a magnetic moment of Fe atoms of ±4.1 μ_B, a characteristic value for this type of compounds and in accordance with the experimental values reported in the literature [2]. The hyperfine parameters calculated at the Fe sites (isomer shift, quadrupole splitting and hyperfine field) are in excellent agreement with those experimentally obtained by Mössbauer spectroscopy reported in the literature [3], supporting the equilibrium structure predicted by FP-LAPW+ LO. The surface of the $MgFe_2O_4$ ferrite was also studied, considering different terminations and considering structural reconstructions in all cases. The presented results predict that the most stable surface is inverted and exhibits a net magnetic moment, resulting in a ferrimagnetic system.

I. Introduction

Spinels Structure $MgFe_2O_4$

Spinel systems crystallize in space group Fd-3m (No. 227).

Two types of cationic sites: tetrahedral coordination A-sites and octahedral coordination B-sites.



General formula: $(Mg_{1-x}Fe_x)_A[Mg_x\ Fe_{2-x}]_BO_4$

Normal spinels: M^{2+} A-sites
Inversed spinels: M^{3+} A-sites

- $MgFe_2O_4$ presents an inversed structure.
- Experimentally, inversion degrees between 0.90-0.96 has been reported.
- On the surface, it has been reported that the inversion degree decreases to 0.7.

II. Theoretical and Computational Methods

- Density Functional Theory (DFT): using the Full-Potential Linearized Plane Waves method (FPLAPW) and the plane wave and pseudopotential method as implemented in Quantum-Espresso code.
- FPLAPW: The exchange and correlation effects were treated using Perdew-Burke-Ernzerhof (PBE) parameterization of the generalized gradient approximation plus the Hubbard U term (GGA+U) in the self-interaction correction (SIC) scheme. For the present calculations, U = 5eV for the Fe-3d orbitals
- Quantum expresso: The ionic cores were described using ultrasoft pseudo-potentials from the Standard Solid State pseudopotentials library (SSSP), where the converged kinetic energy cutoff for the wave function and charge density was set to 70 Ry and 500 Ry, respectively.
- $MgFe_2O_4$: 56-atoms cell ($Mg_8Fe_{16}O_{32}$) for bulk calculations and for the fully terminated at sites A, sites B and sites B reduced terminations contain 58, 68 and 60 atoms, respectively.

Stability determination on surfaces.

- Stoichiometric and antisymmetric system: $\gamma_1 = \frac{1}{2a^2}\left(E^{slab} - mE_{f.u}^{Volumen}\right)$

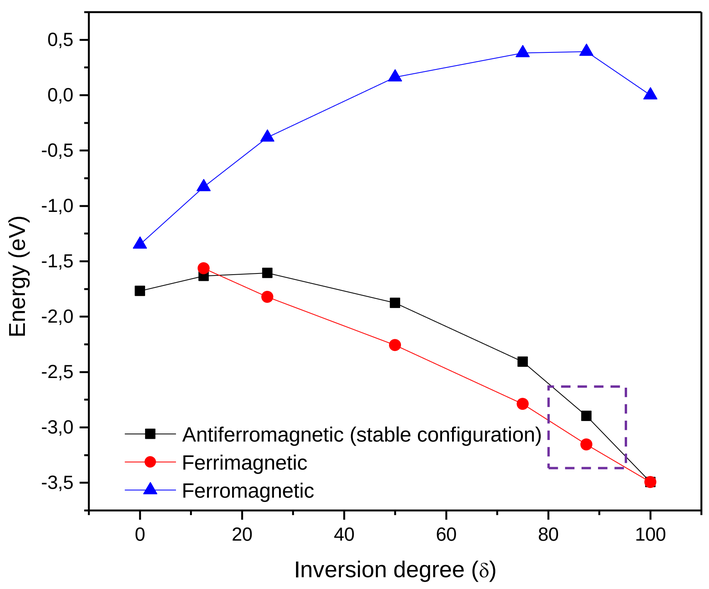
  m is the number of formula units that enter the slab

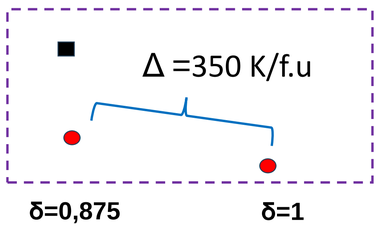
- Non-stoichiometric and symmetric system: $\gamma_2 = \frac{1}{2a^2}\left[E^{slab} - \left(mE_{f.u}^{Volumen} + \sum_i n_i E_i\right)\right]$

  n_i is the number of atoms of Zn, Fe or O needed to symmetrize the slab.
  E_i is the atomic energy that is referred to a model (isolated atom or an oxide).

III. Results and discussions

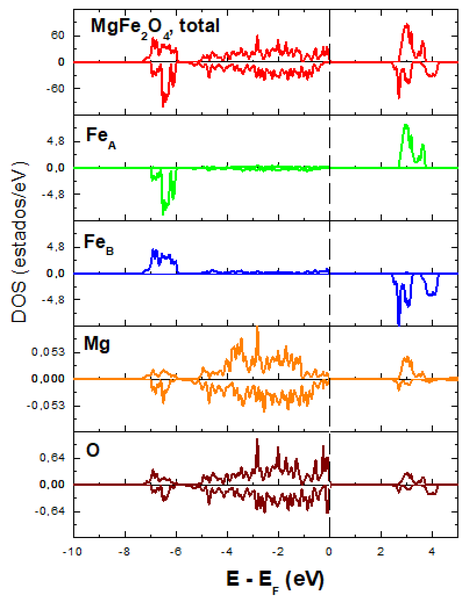
➢ **$MgFe_2O_4$** magnetic configuration in bulk

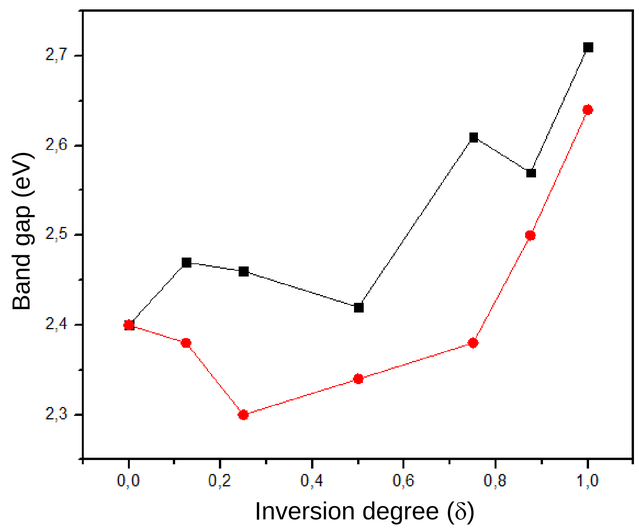




Site	μ(Fe) - GGA+U
(A)	+4.1 μ_B
[B]	-4.1 μ_B

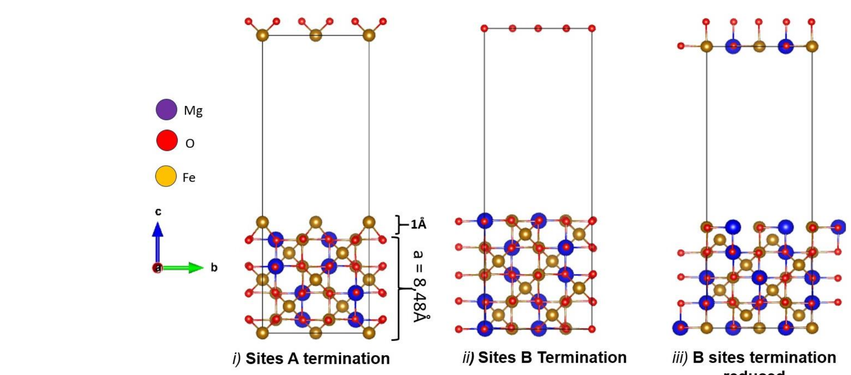
➢ **$MgFe_2O_4$** Density of states in bulk

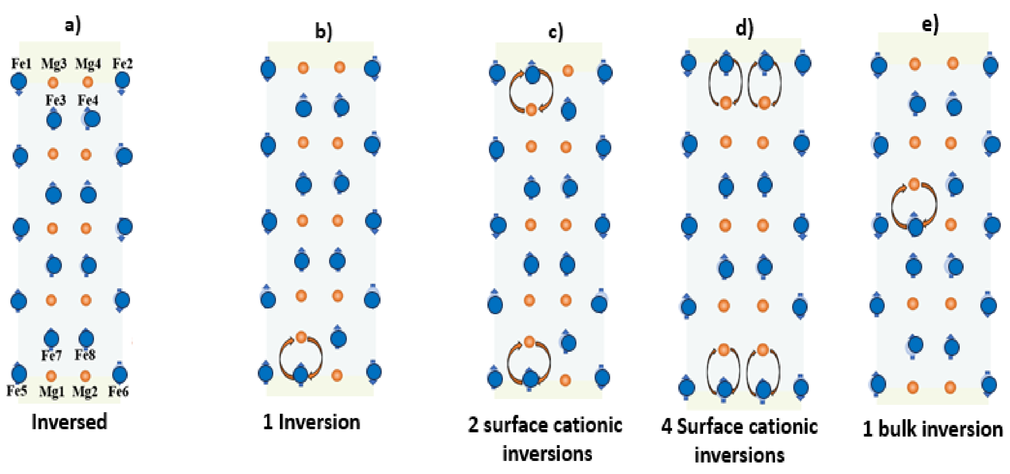


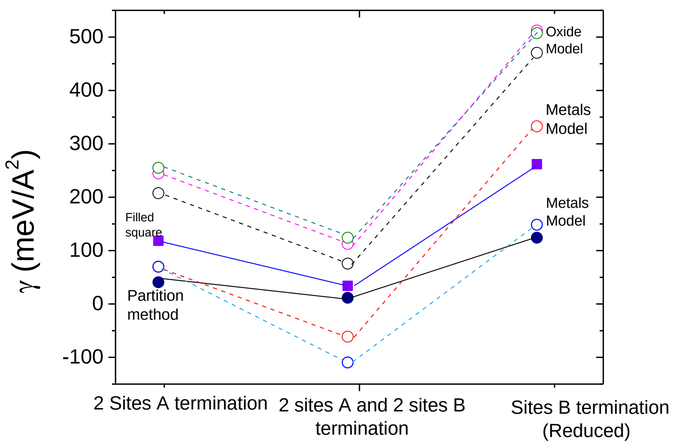


- Temperatures lower than 500 K are enough to reduce the inversion degree from 1 to 0.90, which explains the inversion degrees that are usually reported
- Ferrite with inversion degree of 0.875, the system transitions from antiferromagnetic to ferrimagnetic with a net magnetic moment of 10μ_B (0,625μ_B/Fe atom)
- Magnesium ferrite has a semiconductor character regardless of the inverted degree.

➢ **$MgFe_2O_4$**







Termination 4O-2Fe-2Mg-4O			
Structural Model	**Energy (meV)**	**Band gap (eV)**	**μ^{total} (μ_B)**
Inversed	0	Metallic	4,0
1 surf. Inversion	-290	0,3 / 0,3	6,0
2 surface cationic inversions	-300	1,1 / 0,7	8,0
4 Surf. cationic inversions	+80	Metallic	8,0
1 bulk inversion	+160	1,9 / 0,4	14,0
1 surf. Inversion Fe3: Inverted spin	-420	1,1 / 0,7	8,0
2 surf. cationic Inversions Fe3 and Fe4: inverted spin	-500	2,0 / 0,5	24,0

Conclusions

- ✓ The proposed theoretical model for $MgFe_2O_4$ agree with experimental studies, showing that the degree of surface inversion decreases, and the system has a magnetic response.
- ✓ Considering different structural models for surface and bulk inversion, was possible to determine that surface inversion requires lower formation energy than bulk inversion.
- ✓ The inversion degree on the ferrite surface is different that the volume.

References

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[3] V. Šepelák, D. Baabe, D. Mienert, F.J. Litterst, K.D.Becker. *Scripta Materialia. (2003) 48, 961-966.*