CrossMark

Experimental and *ab initio* study of the hyperfine parameters of ZnFe$_2$O$_4$ with defects

**J. Melo Quintero[1] · K. L. Salcedo Rodríguez[1] ·
G. A. Pasquevich[1] · P. Mendoza Zélis[1] · S. J. Stewart[1,2] ·
C. E. Rodríguez Torres[1] · L. A. Errico[1,3]**

Abstract We present a combined Mössbauer and *ab initio* study on the influence of oxygen-vacancies on the hyperfine and magnetic properties of the ZnFe$_2$O$_4$ spinel ferrite. Samples with different degree of oxygen-vacancies were obtained from zinc ferrite powder that was thermally treated at different temperatures up to 650 °C under vacuum.Theoretical calculations of the hyperfine parameters, magnetic moments and magnetic alignment have been carried out considering different defects such as oxygen vacancies and cation inversion. We show how theoretical and experimental approaches are complementary to characterize the local structure around Fe atoms and interpret the observed changes in the hyperfine parameters as the level of defects increases.

Keywords Ferrites · Zinc ferrite · Hyperfine parameters calculation · ZnFe$_2$O$_4$

1 Introduction

The spinel oxides AB$_2$O$_4$ are one of the most widely studied materials. Depending on the nature of A and B atoms these oxides can display semiconductor and magnetic properties,

✉ S. J. Stewart
  stewart@fisica.unlp.edu.ar

1   IFLP-CCT- La Plata-CONICET and Departamento de Física, Facultad de Ciencias Exactas, C. C. 67, Universidad Nacional de La Plata, 1900 La Plata, Argentina

2   Instituto Ciencias de la Salud, Universidad Nacional Arturo Jauretche, Av. Calchaquí N°, 6200, Florencio Varela, Argentina

3   Universidad Nacional del Noroeste de la Pcia. de Buenos Aires (UNNOBA), Monteagudo 2772, Pergamino, CP 2700 Buenos Aires, Argentina

⚛ Springer

which might become them suitable for applications in the field of spintronics. Zinc ferrite ($ZnFe_2O_4$, ZFO) is one of the spinel compounds that have attracted a considerable interest due to its versatility to change their magnetic properties depending on the fabrication conditions [1–3]. Indeed, the spin configuration of ZFO strongly depends on structural defects such as the presence of oxygen vacancies and cationic inversion. As a consequence, their electronic and magnetic properties can be tuned by selecting the synthesis conditions [4–6], in such a way to increase its magnetic moment and furthermore, to favour a ferrimagnetic long range ordering.

It is known that bulk $ZnFe_2O_4$ is an antiferromagnet (AF) with a Néel temperature (T_N) of 10.5 K [7]. It crystallizes in the space group *Fd3m* (a = 8.44 Å) and the magnetic moment per Fe atom is 4.2 μ_B. The Zn and Fe cations occupy some of the interstitial sites that result from the *fcc* oxygen packing. In its normal configuration, the Zn and Fe ions occupy sites of tetrahedral (A) and octahedral (B) symmetry, respectively. On the other side, nanostructured $ZnFe_2O_4$(nanoparticles and thin films) usually display a ferrimagnetic behavior at room temperature [5, 6, 8–12]. This feature is attributed to the distribution of Fe^{3+} and Zn^{2+} at both A and B sites. Besides, the oxygen concentration seems to be a crucial point in the inducement of ferrimagnetism. In a recent work [12], we demonstrated that the large magnetic moment observed in zinc ferrite thin films grown at low oxygen pressure is due to the ferromagnetic coupling between iron ions at the B sites. Hence, to understand the magnetism of this compound it is important to characterize the local environment of Fe and investigate how it changes when cation inversion and/or oxygen-vacancies take place.

^{57}Fe Mössbauer spectroscopy (MS) is perhaps the most straightforward way to determine the local nature of Fe sites and determine the electronic and structural Fe environments by the hyperfine parameters. The assignment of the observed interactions to a specific Fe site is usually based on empirical assumptions, geometrical considerations and simple models. Recently, we have demonstrated the capability of combining MS and *ab initio* calculations [12, 13] to clearly determine the localization and electronic structure of Fe probes in oxides. In this work, we report on the hyperfine characterization of Fe sites in ZFO powders that were annealed in vacuum at different temperatures. The experimental MS results are contrasted with *ab-initio* calculations performed considering the normal, inverted and oxygen-deficient ZFO. We show that this complementary study allows quantifying the changes in the hyperfine parameters induced by oxygen-vacancies and inversion.

2 Experimental

Bulk zinc ferrite was prepared by conventional solid state reaction from α-Fe_2O_3 and ZnO stoichiometric mixtures. Afterwards, the ZFO powders were thermally treated for 4 h in vacuum ($\sim$ 1.5 $\times$ 10^{-4} Torr) at different temperatures. These treatments were performed in a tubular furnace where a spatial gradient of temperature can be established from a minimum T_{min} up to a maximum T_{max} temperature. This set-up allows annealing several samples simultaneously at different temperatures under the same atmosphere. Two sample batches were prepared: Series I with T_{min} = 100 °C and T_{max} = 450 °C and Series II with T_{min} = 240 ° C and T_{max} = 685 °C. All treated samples were characterized by X-ray diffraction (XRD) and MS. The MS spectra were recorded in transmission geometry at room temperature with a ^{57}Co source in an Rh matrix. The isomer shifts (IS) are referred to α-Fe.

Fig. 1 Mössbauer spectra of
as-cast ZFO (*upper*) and ZFO
annealed at $T_A = 619\,°C$
(*bottom*). *Solid lines* are the
result of the fitting
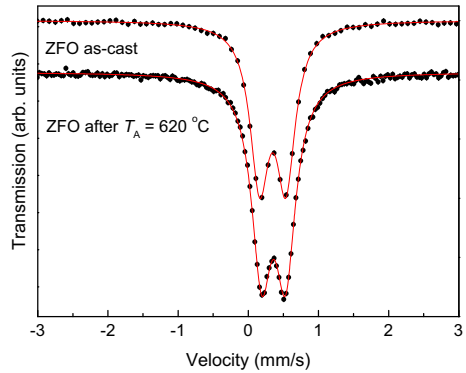
3 Calculation details

The *ab initio* spin-polarized electronic-structure calculations were performed using the *ab initio* code Wien2K [14], an implementation of the full-potential augmented plane waves plus local orbitals (APW+lo) method [15, 16]. The parameter RK_{MAX}, which controls the size of the basis set, was set to 6.0 (R is the smallest muffin tin radius and RK_{MAX} the largest wave number of the basis set). Integration in the reciprocal space was performed using the tetrahedron method taking 100 k-points in the first Brillouin zone. The muffin tin radius (RMT) was chosen 1.05 Å for Zn and Fe, and 0.79 Å for O. In order to obtain the atomic displacements, once self-consistency of the potential was achieved, quantum-mechanically derived forces were obtained, the ions were displaced according to a Newton damped scheme and the new atoms positions were obtained. This procedure was repeated until the forces on the ions were below a tolerance value of 0.05 eV/Å. The exchange and correlation effects were treated using the generalized gradient approximation (GGA [17]) plus an external Hubbard U term in the self-interaction-corrected scheme [18]. For the present calculations we use U= 5.0 eV. With this parameter value we correctly reproduce the magnetic moments, hyperfine parameters and band gaps of pristine ZFO and Fe oxides (FeO, Fe_2O_3, Fe_3O_4, $FeTiO_3$).

4 Results and discussion

XRD patterns (not shown here) showed that all samples are single-phase with the spinel structure. MS spectra consist in all cases in a symmetric doublet. As an example, in Fig. 1 the MS spectra for the as-cast ZFO and ZFO treated at 650 °C are shown. All spectra were fitted assuming a single quadrupolar site with Lorentzian line-shapes. The IS and quadrupole splitting (QS) of the as-cast sample were IS = 0.347_1 mm/s and QS= 0.375_1 mm/s. The hyperfine values reported for pristine ZFO are IS = 0.350_6 mm/s and QS= 0.333_1 m/s) [19].

Figure 2 shows the variation of IS and QS as a function of annealing temperature (T_A). It can be observed that, considering that the annealing temperatures of series I and II overlap between 250 and 475 °C, there is a very good agreement between the hyperfine parameters obtained for both series. This reproducibility allows us to consider T_A as the parameter that identifies the calcinations. We observe that for samples annealed below 250 °C both IS and QS are nearly constant. When T_A varies between 250 and 320 °C, QS presents a sharp decrease and IS slowly increases (Fig. 2). At 325 °C both parameters are close to the
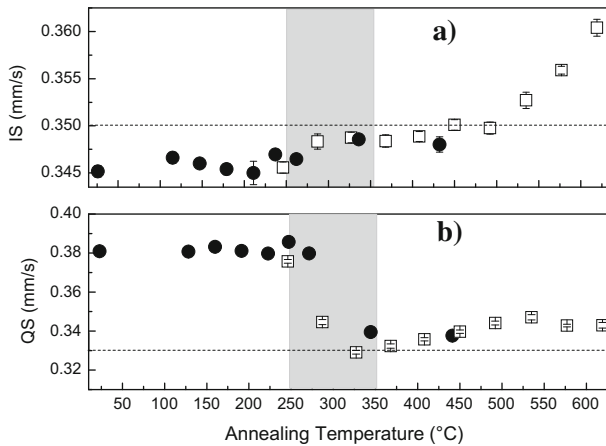
Fig. 2 Isomer shift (IS) and quadrupole splitting (QS) obtained from the fitting of the Mössbauer spectra the annealing temperature T_A. *Dashed lines* show the values reported for pristine ZFO [19]. The *shaded* region indicates the temperature range where the degree of inversion changes

reported values for pristine ZFO (ref. [19], see dashed lines in Fig. 2). Finally, for T_A higher than 325 °C, both IS and QS increase. The increment is more noticeable for IS.

Additional results from x-ray absorption spectroscopy and magnetic measurements (not shown here) showed evidences of a slight degree of inversion in the as-cast ZFO. Such inversion begins to disappear when the sample is annealed at around 250 °C. This could explain the different IS and QS values for the as-cast ZFO when compared to the pristine sample. In order to check this hypothesis and understand the changes in the hyperfine parameters that occur at higher T_A, we have performed *ab-initio* calculations for Fe in ZFO for the pristine structure and also considering cation inversion and oxygen vacancies.

The type of antiferromagnetic arrangement displayed by pristine ZFO is an open question [7]. For that reason, we also explore different local spin configurations to find that one that minimizes the energy of the system. The lowest energy case corresponds to a pair of ferromagnetic Fe atoms aligned antiferromagnetically to another pair. Then, this spin arrangement can be seen as local ferromagnetic clusters surrounded by similar ferromagnetic clusters but with opposite spin orientation (see Fig. 3a). For this equilibrium structure we found a magnetic moment μ of 4.2 μ_B/Fe, a hyperfine field (HF) of 51.4 T and a band gap of 2.2 eV, in excellent agreement with the experimental results ($\mu_{exp} = 4.2\,\mu_B$/Fe, HF= 51.5 T obtained by extrapolating to 0 K the reported value of 50.2 T measured at 4.2 K, energy gap of 1.923 eV (see refs. [7, 19–21]). The IS and QS values (Table 1) show some differences but they are not far from those obtained experimentally. In the following, we will only consider the relative changes of these parameters.

In order to study the inversion effects, we exchange one Fe (with spin-up) by one of its eight Zn nearest-neighbours (no spin). This configuration corresponds to an inversion degree $c = 1/16$. After the refinement of the structure, we find that the Fe atom at the A-site (Fe^A) presents a spin polarization of about 4.1 μ_B/Fe the Zn atom located at the B-site. The spin orientation of the Fe^A remains up, then the magnetic moment of the cell is null (antiferromagnetic configuration). Concerning the hyperfine parameters, the IS corresponding to the fifteen atoms at B sites (Fe^B) is the same that those of pristine ZFO (0.38 mm/s) while Fe^A present a smaller IS (0.30 mm/s) (see Table 1). This result, i. e. IS of Fe^A is 0.08 mm/s

Fig. 3 Structure and magnetic arrangement of **a** normal ZFO. O^{Vac} indicates the location of the oxygen vacancy site, and I, II, III denotes the first-neighbors Fe atoms of the vacancy site. **b** Inverted ZFO (degree of inversion: 1/16). Fe^A and Zn^B denote the Fe atom at sites A and the Zn atom at site B of the structure. In both cases *blue*, *dark grey* and *red* balls represent Fe, Zn, and O atoms, respectively
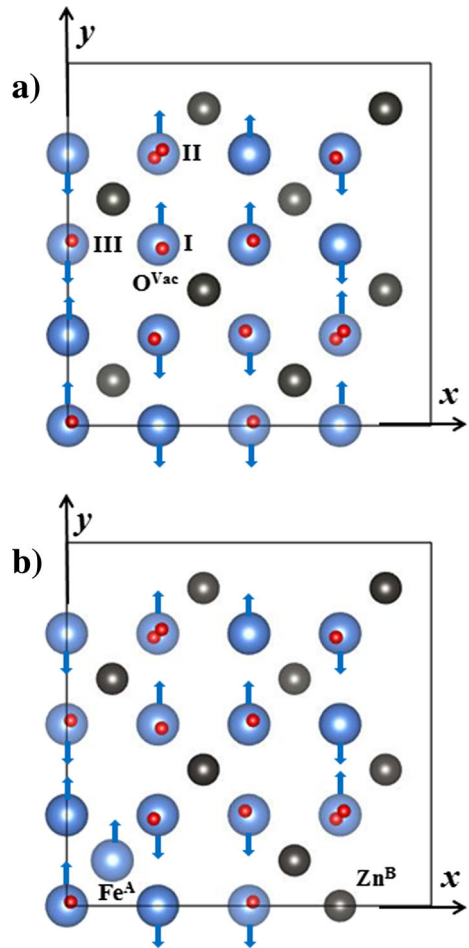
smaller than that of Fe^B, does not depend on the inversion degree. This means that the average IS over the entire supercell (SC) will be 0.375 mm/s (in the case of one inversion in the SC). In the case of QS, Fe^A is characterized by QS=0.19 mm/s meanwhile a QS distribution was found for the QS of Fe at sites B (the QS averaged value is 0.33 mm/s) (see Table 1). It means that the average QS over the entire supercell will be 0.32 mm/s. From these we conclude that the effect of inversion is to reduce IS and increase QS with respect to the pristine one. This is in agreement with our previous observation concerning the slight degree of inversion that presents the as-cast sample, which disappears when T_A ranges between 250 and 325 °C (see Fig. 2).

The presence of the oxygen-vacancy in ZFO induces large structural distortions. After computing these distortions, the lowest energy case corresponds to a ZFO system in which one of the Fe atoms close to the oxygen vacancy changes its spin orientation, giving rise to a system with a net magnetic moment of 8.0 μ_B. The IS of two of the three neighbours of the oxygen-vacancy increases up to 0.83 mm/s (interaction B_1 in Table 1). As a result, the average IS increases up to 0.44 mm/s. In addition, the structural distortion triggered by the vacancy, causes an increment of the QS at the Fe atoms nearest-neighbours to the vacancy

Table 1 *Ab-initio* predictions for IS and QS for the different systems studied

System	Fe at site	IS (mm/s)	QS (mm/s)
ZFO*	B	0.350_6	0.333_1
Normal	B	0.38	0.25
ZFO+cation inversion	A	0.30	0.19
	B (average value)	0.38	0.33
ZFO + one oxygen vacancy	B_1 (near O vacancy)	0.83	2.20
	B_2 (far O vacancy)	0.38	0.32

B_1 and B_2 correspond to the average IS and QS obtained considering the fifteen Fe atoms nearest-neighbours of the oxygen-vacancy site (B_1) and the other Fe in the cell (B_2). *Experimental values at 300 K [19] are included for comparison

(B_1 in Table 1). On the other side, the QS for the Fe atoms far away from the oxygen-vacancy (B_2 in Table 1) are similar to those predicted for the pristine system. Then, the effect of oxygen-vacancies on the hyperfine parameters is to increment both the IS and the QS with respect to pristine ZFO. This explains the observed increase of IS and QS in samples treated at T_A higher that 400 °C due to the formation of oxygen vacancies. Finally, our preliminary calculations considering both cation inversion and oxygen vacancies simultaneously confirm the results presented here.

5 Conclusion

By combining experimental and theoretical results we found that the as-cast zinc ferrite presents some degree of inversion, which disappears after annealing at temperatures higher than 325 °C. The evolution of the hyperfine parameters afterannealing treatments at temperatures higher than 400 °C can be interpreted in terms of the formation of oxygen- vacancies. Our results show the capability offered by the use of the Mössbauer spectroscopy jointly with calculation to determine the local structure and the role played by defects on the electronic and hyperfine properties at Fe sites in spinel oxides.

References

1. Liang, Y.-C., Hsia, H.-Y.: Growth and crystallographic feature-dependent characterization of spinel zinc ferrite thin films by RF sputtering. Nanoscale Res. Lett. **8**, 537–544 (2013)
2. Salcedo Rodríguez, K.L., Golmar, F., Rodríguez Torres, C.E.: Magnetic properties of Zn-ferrites obtained from multilayer film deposited by sputtering. IEEE Trans. Magn. **49**, 4559–4561 (2013)
3. Kundu, A., et al.: Magnetic properties of a partially inverted zinc ferrite synthesized by a new coprecipitation technique using urea. Phys. Lett. A **311**, 410–415 (2003)
4. Chen, Y.F., Spoddig, D., Ziese, M.: Epitaxial thin film $ZnFe_2O_4$: a semi-transparent magnetic semiconductor with high Curie temperature. J. Phys. D: Appl. Phys **41**, 205004–205004 (2008)
5. Ayyappan, S., Venkateswaran, C., Philip, J., Raj, B.: Magnetic properties of Zn-Ferrites obtained from multilayer film deposited by sputtering. Appl. Phys. Lett. **96**, 143106–143106-3 (2010)
6. Nakashima, S., et al.: High magnetization and the high-temperature superparamagnetic transition with intercluster interaction in disordered zinc ferrite thin film. J. Phys.: Condens. Matter **17**, 137–149 (2005)

7. Schiessl, W., Potzel, W., Karzel, H., Steiner, M., Kalvius, G.M., Martin, A., Krause, M.K., Halevy, I., Gal, J., Schäfer, W., Will, G., Hillberg, M., Wäppling, R.: Magnetic properties of the $ZnFe_2O_4$ spinel. Phys. Rev. B **53**, 9143–9151 (1996)

8. RaeisiShahraki, R., et al.: Structural characterization and magnetic properties of superparamagnetic zinc ferrite nanoparticles synthesized by the coprecipitation method. J. Magn. Magn. Mat **324**, 3762–3765 (2012)

9. Mozaffari, M., et al.: The effect of cation distribution on magnetization of $ZnFe_2O_4$ nanoparticles. J. Magn. Magn. Mat **322**, 3240–3244 (2010)

10. Takaobushi, J., et al.: Fe3−xZnxO4 thin film as tunable high Curie temperature ferromagnetic semiconductor. Appl. Phys. Lett **89**, 242507–242509 (2006). doi:10.1063/1.2405389

11. Raghavender, A.T.: Room temperature ferromagnetism in laser ablated Zn ferrite thin films. Mater. Lett. **65**, 3636–3638 (2011)

12. Rodríguez Torres, C.E., et al.: Oxygen-vacancy-induced local ferromagnetism as a driving mechanism in enhancing the magnetic response of ferrites. Phys. Rev. B **89**, 104411–104411-7 (2014)

13. Mudarra Navarro, A.M., Rodríguez Torres, C.E., Bilovol, V., Cabrera, A.F., Errico, L.A., Weissmann, M.: Study of the relation between oxygen vacancies and ferromagnetism in Fe-doped TiO2 nano-powders. J. Appl. Phys **115**, 223908–223908-8 (2014)

14. Blaha, P., Schwarz, K., Madsen, G., Kvasnicka, D., Luitz, J.: WIEN2k: an Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties. Vienna University of Technology, Vienna, Austria (2012)

15. Sjöostedt, L.N., Singh, D.J.: Solid State Commun. **114**, 15 (2000)

16. Madsen, G.K.H., Blaha, P., Schwarz, K., Sjöstedt, E., Nordström, L.: Phys. Rev. B **64**, 195134 (2001). See also S. Cottenier, Density Functional Theory and the Family of (L)APW-Methods: A Step-by-Step Introduction, KU Leuven, Leuven, Belgium, (2002)

17. Wu, Z., Cohen, R.E.: More accurate generalized gradient approximation for solids. Phys. Rev. B **73**, 235116–235121 (2006)

18. Anisimov, V.I., Zaanen, J., Andersen, O.K.: Phys. Rev. B **44**, 943–954 (1991). doi:10.1103/PhysRevB.44.943

19. Evans, B.J., Hafner, S.S., Weber, H.P.: Electric field gradients at 57 Fe in $ZnFe_2O_4$ and $CdFe_2O_4$. J. Chem. Phys. **55**, 5282–5288 (1971)

20. Dickof, P.A., Schurer, P.J., Morrish, A.H.: Magnetic structure of zinc-substituted magnetite at T=4.2 K. Phys. Rev. B **22**, 115–127 (1980)

21. Valenzuela, M.A., Bosch, P., Jiménez-Becerrill, J., Quiroz, O., Páez, A.I.: Preparation, characterization and photocatalytic activity of ZnO, Fe_2O_3 and $ZnFe_2O_4$. J. Photochem. Photobiol. A Chem. **148**, 177–182 (2002)