Oxygen-vacancy-induced local ferromagnetism as a driving mechanism in enhancing the magnetic response of ferrites

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I. INTRODUCTION

The observation of room-temperature ferromagnetism in nonmagnetic solids has been controversially related to the role of extrinsic or intrinsic defects [1–3]. Understanding the origin of the magnetic order and its coupling mechanism is essential for the development of new technological strategies to design materials suitable for spintronics applications. Extrinsic defects can be created by doping nonmagnetic oxide hosts with magnetic or nonmagnetic transition-metal ions, a research topic that has attracted considerable interest in recent decades [4]. On the other hand, the ferromagnetism displayed by some undoped nonmagnetic oxides has been linked to defects such as lattice vacancies or local disorder that is generated, for instance, by the reallocation of ions [5]. Both phenomena are known as defect-induced magnetism (DIM) [1–3]. The potential role of these defects in triggering or enhancing the ferromagnetic (FM) order in certain magnetic oxides has not yet been studied systematically.

One group of magnetic oxides, the spinel ferrites $MFe_2O_4$ ($M$: divalent transition-metal cation), has been widely studied for years due to its diversity of ion configurations. Despite the relevance of the cationic distribution between the tetrahedral A and the octahedral B sites that determines the physical properties of spinels [6], there is still no consensus on the nature of the interactions responsible for the preferred ground-state structure [7,8]. Furthermore, the cation arrangement can be modified either by applying thermal treatments [9,10], by using fabrication methods that make the formation of nonequilibrium phases easier [11–13], or by reducing the characteristic lengths of the specimen to the nanoscale [14].

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It is well known that the disordered distribution of zinc and iron ions in ZnFe$_2$O$_4$ leads to a drastic change in its magnetic order. This phenomenon makes ZnFe$_2$O$_4$ one of the most studied ferrites in the area. Normal ZnFe$_2$O$_4$ has an antiferromagnetic order below the Neél temperature $T_N = 10.5$ K, which is driven by an oxygen-mediated superexchange between the Fe$^{3+}$ ions located at the B sites (case I in Fig. 1) [16]. However, some authors claim that ZnFe$_2$O$_4$ is intrinsically a frustrated system with a ferromagnetic first-neighbor exchange interaction $J_{AB} > 0$ (between two B sites) [17]. Anyway, all nanosized ZnFe$_2$O$_4$ samples, whether as nanoparticles (NPs) obtained by mechanical milling or by chemical routes [11,18], or as thin films prepared by sputtering [19] or by pulsed laser deposition (PLD) [8,12,20], display ferrimagnetic behavior at room temperature. This ferrimagnetic feature is attributed to the distribution of Fe$^{3+}$ and Zn$^{2+}$ at both the A and B sites (case II in Fig. 1), which gives rise to strong negative $J_{AB}$ interactions. The oxygen concentration also seems to be crucial for the cationic configuration since samples prepared under low oxygen pressure show a large magnetic response at room temperature [17,21,22]. It is likely that the disorder involving a cation swap is influenced by an oxygen displacement in the spinel structure [7,22]. The open question is whether the magnetization enhancement in ZnFe$_2$O$_4$ can be attributed only to a partial inversion, or also to local defects such as vacancies, or to interface effects in the case of thin films [23]. Since the knowledge of the structure of spinels at the microscopic level is still limited, the spin configuration and the origin of ferrimagnetism at room temperature in ZnFe$_2$O$_4$ remains unclear. Therefore, we use x-ray magnetic circular dichroism (XMCD) measurements and complementary $ab$ initio density-functional-theory (DFT) calculations to prove that the enhanced magnetic response observed in nominally nonmagnetic or antiferromagnetic ferrites arises not only from cation inversion, but also from the existence of oxygen vacancies.
II. EXPERIMENT

A. Sample description

The investigated ferrites were (i) a thin film grown under low oxygen pressure conditions (ZFO1) of thickness \( t = 57 \text{ nm} \), (ii) milled hydrothermally prepared ZnFe\(_2\)O\(_4\) nanoparticles (2ZF10H) with an average grain size of \( D = 13 \text{ nm} \), and (iii) zinc ferrite nanoparticles obtained by mechanically grinding bulk ZnFe\(_2\)O\(_4\) (BZF10H) with \( D = 14 \text{ nm} \). The details of sample preparation and characterization can be found elsewhere \([11,12]\). All samples show a large saturation magnetization \( M_s \) (see Table I).

TABLE I. \( M_s \) is the macroscopic saturation magnetization measured with vibrating sample magnetometry (VSM) at 5 K with a maximum applied field \( \mu_0 H = 5 \text{T} \). \( I_{B2}/I_k \) is the intensity ratio between the peaks \( B_2 \) and \( A \) of the XMCD signal [see Fig. 2(b)]. \( x_B/x_A \) is the relative Fe\(^{3+}\) and Fe\(^{2+}\) magnetic contribution ratio to the XMCD signal for each sample. \( m_{\text{XMCD}} \) and \( m_{\text{VSM}} \) are the magnetic moments per iron atom at room temperature determined either from the XMCD signals or \( M_s \) (measured by VSM), respectively.

| Sample     | \( M_s \) (A m\(^2\)/kg) | \( I_{B2}/I_k \) | \( x_B/x_A \) | \( m_{\text{XMCD}} \) \( \mu_B/\mu_F \) | \( m_{\text{VSM}} \) \( \mu_B/\mu_F \) |
|------------|-----------------|-----------------|-------------|----------------|----------------|
| ZFO1       | 360             | 3.3             | 2.2         | 0.93           | 0.93           |
| 2ZF10H     | 68              | 2.3             | 1.9         | 0.59           | 0.58           |
| BZF10H     | 72              | 2.2             | 1.9         | 0.57           | 0.57           |
| \( \gamma \)-Fe\(_2\)O\(_3\) NPs | 1.5             | 1.6             | 0.80        | 0.84           | 0.84           |
| Fe\(_2\)O\(_3\) bulk | 1.20             |                | 1.20        |                |                |

\( ^a \text{For the film, the units are A/m.} \)

B. XMCD experiments

XMCD experiments at the L\(_{2,3}\) edges of iron were performed at the PGM beam line at the Laboratorio Nacional de Luz Sincrotron, (LNLS, Campinas, Brazil), using an 80\% circularly polarized light beam. The absorption data were collected at room temperature in total electron yield (TEY) mode. The samples were placed perpendicular to the photon beam and a magnetic field \( \mu_0 H_m = 0.6 \text{T} \) was applied perpendicular to the sample plane. The absorption cross section of the circularly polarized x rays is labeled \( \mu^{\alpha\beta} \), where \( \alpha \) denotes the helicity of the photons \( \alpha = \uparrow (\downarrow) \) when the photons are right-hand (left-hand) polarized and \( \beta \) denotes the direction of \( H_m \) \( \beta = \uparrow (\downarrow) \) when the field is parallel (antiparallel) to the beam direction. The x-ray absorption spectra (XAS) are \( \mu^+ = (\mu^\uparrow + \mu^\downarrow)/2 \) and \( \mu^- = (\mu^\uparrow - \mu^\downarrow)/2 \). The XMCD spectra were obtained as \( \mu_{\text{XMCD}} = \mu^+ - \mu^- \).

III. THEORY

First-principles calculations have been performed with the Vienna \textit{ab initio} simulation package (VASP) code \([24,25]\) in order to prove that particular local arrangements (see Fig. 1) are energetically favorable and contribute ferromagnetically. The total-energy calculations are done in a cubic supercell configuration (including \( 56 \) atoms). The ground-state antiferromagnetic structure of Refs. \([26,27]\) is used as a reference structure in our calculations. All calculations were performed with a plane-wave energy cutoff of 600 eV. For the Brillouin-zone integration, we used a \( \Gamma \)-centered Monkhorst-Pack \( k \)-space grid with \( 112 k \) points. The exchange and correlation were treated by the generalized gradient approximation plus \( U \) (GGA + \( U \)) to describe the insulating and antiferromagnetic nature of ZnFe\(_2\)O\(_4\) correctly. The correlation correction \( (U = 3.5 \text{ eV}) \) is applied to the \( d \) orbitals of iron. The minimum-electricity parameters obtained are \( a = 8.53 \text{ Å} \) and \( u = 0.381 \), which are in good agreement with the experimental values and other calculations \([28]\). The positions of the ions in the supercell were relaxed by means of the conjugate gradient method until the forces on each atom converged to \( 7 \text{ meV/Å} \).

Using this supercell, we studied the magnetic interactions under the influence of the local defects given in Fig. 1. The magnetic interaction is characterized by the energy difference between an antiparallel arrangement of the moments to that of a parallel moment arrangement on the corresponding atoms and is written as \( \Delta E = E_{\text{AFM}} - E_{\text{FM}} \). A positive value of \( \Delta E \) implies a local ferromagnetic (FM) order, while a negative value of \( \Delta E \) demonstrates that antiferromagnetic (AFM) order is preferred. In order to validate our DFT calculation setup, we investigated the stability of the ideal antiferromagnetic (AFM) structure (case I in Fig. 1) with total-energy calculations. A local parallel arrangement of the magnetic moments of two Fe\(^{3+}\) atoms leads to an increase of the energy by \(~32 \text{ meV}\) as compared to the AFM ground state and, therefore, is more unlikely (see Table II).

IV. RESULTS AND DISCUSSION

The x-ray absorption spectra (XAS) of our three samples present the typical features \([29]\) corresponding to the \( 2p \) to \( 3d \) electronic transitions [see Fig. 2(a) for ZFO1 film; the
TABLE II. Total-energy difference $\Delta E = E_{\rm FM} - E_{\rm AFM}$ ($E_{\rm FM}, E_{\rm AFM} < 0$) and resulting magnetic moment $m$ from the theoretical calculations. The four cases correspond to the classification of Fig. 1. Case II is reached in a two-step model. S2 is the final result. See text for details.

| Property | Case I | Case II | Case III | Case IV |
|----------|--------|---------|----------|---------|
| $\Delta E$ (meV) | -31.80 | -65.27 (S1) | 49.72 | 27.5 |
| $m$ ($\mu_B$/supercell) | 0.0 | 0.0 (S1) | 6.0 | 8.0 |

spectra for 2ZF10H and BZF10H are not shown]. For all of the studied samples, we obtained detailed information about the magnetic moment of the absorbing atom and its projection onto the direction of the applied field by XMCD measurements [see Fig. 2(b)]. For comparison purposes, we registered the XMCD signals of samples ZFO1, 2ZF10H, and BZF10H (see Table I). From this intensity ratio, we can estimate the relative magnetic contributions of the Fe 3 $^+$ ions at the B and A sites that contribute to the XMCD signal ($x_B/x_A$). Comparing $(I_{B1}/I_{A1})$ ratios for our three samples with each other, the ZFO1 film has the highest one [orange line in Fig. 2(b)]. This value is 44% larger for ZFO1 than those of the samples 2ZF10H and BZF10H (see Table I). From this intensity ratio, we can estimate the relative magnetic contributions of the Fe 3 $^+$ at the XMCD signal ($x_B/x_A$; see Refs. [30,34]). To this end, we have taken into account the results published by Brice-Profeta et al. [30]. These authors simulated, using ligand field multiplet calculations developed by De Groot et al. [34], the contribution of Fe 3 $^+$ placed at A sites relative to Fe 3 $^+$ placed at B sites. Using the simulated XMCD signals (at the L3 edge of Fe) corresponding to Fe 3 $^+$ placed at A sites ($I_2$ symmetry) and to Fe 3 $^+$ placed at B sites ($O_b$ symmetry) (see bottom of Fig. 3 of Ref. [30]), we simulated the XMCD signals for different $x_A$ and $x_B$ values (see Fig. 3).

From these simulated signals, we extracted the values of the $I_{B1}/I_{A1}$ ratio for different $x_B/x_A$. Figure 4 shows the $x_B/x_A$ ratio for different $x_B/x_A$.
ratio versus $I_B/I_A$. Therefore, the $I_B/I_A$ ratios taken from our experimental results allow one to estimate the $x_B/x_A$ fraction for each sample (see Table I). Uncertainties of $I_B/I_A$ and $x_B/x_A$ are 0.05 and 0.02, respectively. Again, for ZFO1, $x_B/x_A$ is higher than for the nanoparticles 2ZF10H and BZF10H (see Table I). It is worth mentioning that the $x_B/x_A$ value obtained for γ-Fe₂O₃ NPs is close to the $Fe^{3+}/Fe^{2+}$ ratio of about 1.67 expected for maghemite, since the whole $Fe^{3+}$ moment aligns along the field direction and the $Fe^{2+}$ ones orient in the opposite direction. From the XAS and XMCD spectra, we also estimate the total magnetic moment per iron atom, $m_{XMCD} = m_1 + m_s$, with the orbital ($m_1$) and spin ($m_s$) contributions, by using sum rules and integrating over the energy of the spectra [35]:

$$m_1 = \frac{2}{3} \frac{n_h}{P_c \cos \theta} \frac{\Delta W_3 + \Delta W_2}{W_3 + W_2},$$

$$m_s = -\frac{n_h}{P_c \cos \theta} \Delta W_3 - \frac{2}{3} \frac{\Delta W_2}{W_3 + W_2} - \frac{7}{8} \langle T_z \rangle \langle S_z \rangle,$$

where

$$\Delta W_l = \int_{L_1} (\mu^+ - \mu^-)dE,$$

$$W_l = \frac{1}{2} \int_{L_1} (\mu^+ + \mu^-)dE.$$

$P_c$ is the degree of circular polarization, $\theta$ is the angle between the x-ray beam and the magnetization of the sample, $n_h$ is the number of d holes, and $\langle T_z \rangle$ and $\langle S_z \rangle$ are the expectation values of the magnetic dipole and spin component operators, respectively.

The total magnetic moment per iron atom is

$$m = m_1 + m_s = -\frac{n_h}{P_c \cos \theta} \frac{1}{W_3 + W_2} \left( \frac{5}{3} \Delta W_3 - \frac{4}{3} \Delta W_2 \right).$$

Here we have supposed that the relative dipolar contribution, i.e., $\langle T_z \rangle \langle S_z \rangle$, is negligible. This assumption is usually valid for ions having $d^5$ configuration in $O_h$ or lower symmetries and $d^6$ in $O_b$ symmetry [36,37]. Also, the fact that the XAS were registered at room temperature reduces its contribution [36].

XAS registered in TEY mode are typically affected by saturation effects [38], leading to an inaccurate quantitative analysis of $m_1$. Also, $m_1$ and $m_s$ values are sensible to the normalization procedure and to the way the continuum spectrum is subtracted. Being aware of these problems, we have also determined $m$ for the reference samples γ-Fe₂O₃ NPs and bulk Fe₂O₃ (see Table I). The $m$ values obtained for the ferrites were divided by the $m$ value obtained for Fe₂O₃, and then multiplied by the moment of 1.20 $\mu_B$, as expected per iron atom for Fe₂O₃. In order to check the reliability of this procedure, we also applied this procedure to γ-Fe₂O₃ NPs (Table I).

Also, the magnetic moments ($m_{VSM}$) were estimated from magnetization measurements at room temperature using a vibrating sample magnetometer (VSM). The average magnetic moment per iron atom for each powder sample was obtained dividing the total moment obtained at an applied magnetic field of 0.6 T (i.e., under the same condition as the XMCD measurements) by the number of magnetic atoms from saturation magnetization values. For all samples, both moments, $m_{XMCD}$ and $m_{VSM}$, agree very well (see Table I).

These experimental results for the magnetic moments and the ion distribution can be combined with two former investigations [11,12] to discuss the local structure of our samples and the magnetic response in more detail. From the XMCD experiments, we confirmed that both $Fe^{3+}$ and $Fe^{2+}$ ions contribute to the dichroic signal. In particular, for the two nanoparticle samples 2ZF10H and BZF10H, this quantitative contribution to the magnetic signal is $x_B/x_A \sim 2$. Since both samples are partially inverted ferrites (iron and zinc ions occupy both A and B sites; see Ref. [11]), they display the local magnetic configuration of case II (in Fig. 1). Furthermore, the same $x_B/x_A$ for 2ZF10H and BZF10H is consistent with their quite similar magnetic response, microstructure, and configuration of cations [11,39].

From the theoretical point of view, the AFM local rearrangement of case II also appeared energetically favorable [see Table II (S2)]. This local configuration was modeled in two steps. In the first step (S1), starting from the ground-state structure, a B-site Fe atom (represented as Fe₂ in Fig. 5) was swapped with a Zn atom at an A site. A strong antiferromagnetic interaction is found between Fe₁ and Fe₂ because of the interaction $J_{AB}$, which is strongly negative. In the second step (S2), keeping the alignment of moments of Fe₁ and Fe₂ fixed, the magnetic interaction between another Fe at a B site (Fe₃ in Fig. 5) and Fe₁ is investigated. The parallel arrangement of the Fe₁ and Fe₃ moment is found to be lower in energy, implying $J_{AB} > 0$. Thus, we have a positive energy difference for S2 in Table II and this situation leads to local ferromagnetic order with 10 $\mu_B$ per supercell.

For the zinc ferrite film ZFO1, the XMCD results showed the same iron occupation at the A and B sites, with a larger contribution from the octahedral sites, characterized by markedly more intense $B_1$ and $B_2$ peaks [see Fig. 2(b)] and
out that ZnFe$_2$O$_4$ is one of many compounds, where oxygen vacancies play an important role in the discussions of DIM [1–3,40,41].

In order to quantify the effects of a single vacancy as local defect in ZnFe$_2$O$_4$ and to complement the macroscopic experimental results, we investigated the local relaxation and the magnetic structure around this defect in more detail with the VASP code. The calculation supports the experimental conclusions that an oxygen vacancy between two Fe$^{3+}$ ions mediates a FM coupling. The AFM coupling in the ideal AFM structure mediated through the O site, represented by a negative $J_{BB}$ interaction, is now cut and the FM coupling of the two magnetic moments becomes more favorable, resulting in a magnetic moment of 8 $\mu_B$ per supercell (i.e., 8 $\mu_B$ per oxygen vacancy).

We compare the local changes in the lattice structure with the ideal AFM structure of case I (see Fig. 1), which corresponds to the perfect ZnFe$_2$O$_4$ in which all Fe-O and Zn-O bond lengths in the local environment are equivalent, as in the entire ferrite cell (see Table III). By introducing an oxygen vacancy, only the local surrounding as shown in Fig. 6 is affected. Due to the free space, the bond Zn$_1$-O$_1$ becomes elongated by about 0.3% (see Table III). The tetrahedral symmetry of the Zn atoms is broken and they show a tendency to form a dimer with the neighboring Zn atoms by moving away from V$_{O}$. So, the distance of Zn$_2$ from the ideal V$_O$ position (the oxygen position inside an ideal

![FIG. 5. (Color online) Figure depicting the situation of case II where the model is approached in two steps (see text). Rearrangement of atoms is achieved by swapping one Fe atom at the B site with that of one Zn atom at the A site (represented as black arrow). The most stable magnetic configuration with local ferromagnetic arrangement between Fe$_1$ and Fe$_3$ is shown, which were originally antiparallel in the ground-state cubic starting structure. Zn atoms are represented as gray, O as red, up-spin Fe as golden, and down-spin Fe as blue spheres, respectively.](Image 51x534 to 290x739)

![FIG. 6. (Color online) Local structure of ZnFe$_2$O$_4$ with labels used in Table III to explain the relaxation effect in the local environment of the oxygen vacancy [O (red), Fe site (golden), Zn site (gray), oxygen vacancy (black with white cross)].](Image 340x108 to 531x256)

| Bonding sites | Rel. distance | Bonding sites | Rel. distance |
|---------------|---------------|---------------|---------------|
| Zn$_1$-O$_1$  | 0.304         | Fe$_2$-V$_{O}$| 2.340         |
| Zn$_2$-V$_{O}$| 23.880        | Fe$_1$-O$_2$  | 1.162         |
| Fe$_1$-O$_1$  | −0.214        | Fe$_1$-O$_2$  | 3.692         |
| Fe$_1$-V$_{O}$| 0.970         | Fe$_2$-O$_3$  | 1.145         |
| Fe$_2$-O$_1$  | −2.733        | Fe$_2$-O$_3$  | −0.047        |

![TABLE III. Relaxation data near the oxygen vacancy, corresponding to case IV. Distances between bonding sites are given in % change with respect to the ideal structure with bonds Zn-O = 2.0023 Å and Fe-O = 2.0467 Å (see Fig. 6 for the labels).](Image 104411-5)
Zn dimer has a bond length of 3.13 Å, which is comparable to 3.22 Å of the Zn-Zn separation in the neighborhood of VO. The relaxation of the bond between Zn2 and its nearest Zn neighbor is −12.7%. In this case, a complete free dimer formation is hindered by other Zn-O bonds associated with the Zn atoms. VO is also responsible for an imbalance of bond lengths at the Fe1 and Fe2 sites. Fe2-O1 is elongated by about 2.0%, while Fe1-O1 remains nearly unchanged (contracted by about 0.2%). The three Fe atoms connected to VO are no longer equivalent and relax outwards with varying bond lengths of 1% and 2.3% for Fe1-VO and Fe2-VO, respectively, and 2.5% for the Fe atom above VO (which is not shown). Away from the vacancy site, the bond lengths at Fe sites fluctuate between 0 and 4%, which shows that the octahedral environment response to any defects in the tetrahedral region might be important. Furthermore, the calculations have been performed with different cell geometries leading to the same results.

In order to visualize the role of missing oxygen, the charge and magnetization densities in the supercell are calculated with an oxygen vacancy and compared to the ideal structure [shown in Fig. 7(a)]. The charge density changes abruptly at the vacancy site, but it also manifests a change in the oxygen atoms surrounding the iron ion that flips the moment; see Fig. 7(b). Due to this moment flip, the change in magnetization density reaches its highest value at the iron atom, while the oxygen atoms are also polarized and so contribute to the total moment of 8 μB per unit cell [see Fig. 7(c)]. Thus, the double Fe3+−O−Fe3+ superexchange paths are broken by the oxygen vacancies (case IV in Fig. 1) and contribute, therefore, to the Fe3+−Fe3+ FM configuration, which is different from the AFM configuration displayed in normal ferrites (case I in Fig. 1).

V. CONCLUSION

We can conclude that even though samples ZFO1, 2ZF10H, and BZF10H are all ferrimagnetic with relatively high saturation magnetizations, differences appear when exploring the distribution of cations that affect the local magnetic configuration. Our results demonstrate 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 occupying octahedral B sites. The reason for this is based on three main mechanisms that break the original antiferromagnetic interaction between B sites, namely, the A-site overpopulation, the consequent generation of octahedral cation vacancies, and the existence of an oxygen vacancy between two Fe ions.

So, the enhanced ferrimagnetic response observed in some nominally nonmagnetic or antiferromagnetic ferrites can be taken as a further example of the DIM phenomenon. By focusing on the defects-induced effects, our findings open up paths for applied research as well as attempts to further understand the nonequilibrium cation configuration, which gives rise to drastic changes in the magnetic behavior of certain ferrites.

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