Impact of Defects on Magnetic Properties of Spinel Zinc Ferrite Thin Films
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This article explores recent developments in the study of magnetic properties in spinel zinc ferrite system. Engineering of ionic valence and site distribution allows tailoring of the magnetic interactions. We review recent literature and present own investigations for a conclusive understanding of the mechanisms responsible for the magnetic behavior in this material system. By varying the Zn-to-Fe ratio, the deposition as well as thermal annealing conditions, ZnFe₂O₄ thin films with a wide range of crystalline quality were produced. In particular, we focus on the magnetic structure in relation to spectroscopic properties of disordered ZnFe₂O₄ thin films. Comparing the cation distribution in film bulk (optical transitions in the dielectric function) and near-surface region (X-ray absorption), it is found that an inhomogeneous cation distribution leads to a weaker magnetic response in films of inverse configuration, whereas defects in normal spinel are likely to be found at the film surface. The results presented show that it is possible to engineer the defect distribution in the magnetic spinel ferrite film structure and to tailor their magnetic properties on demand. It is demonstrated that these properties can be read out optically, which allows a controlled growth of the material, and applications in future magneto-optical devices.

1 Introduction

The wide range of tunable properties in spinel iron oxides can be realized through the optimization of synthetic fabrication[1]. The diversity of ion configurations makes transition metal oxides, MFe₂O₄ (where M is the divalent cation), uniquely suitable for a vast scope of applications. For example, remarkable optoelectronic tunability, and high thermal as well as chemical stability enables photoanode application for solar water oxidation[2,3,4,5]. Excellent electrochemical properties and reversible magnetization has advanced the design of novel Li-ion controlled electronic devices[6,7,8,9]. Recently, simultaneous detection and treatment of cancer cells by magnetic hyperthermia has been realized through drug delivery and heat generation by

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utilizing surface adsorption and superparamagnetic nature of biocompatible franklinite (ZnFe₂O₄) nanoparticles[10,11,12,13,14]. Furthermore, the predicted 100% spin polarization of the conduction electrons at the Fermi level makes magnetite an outstanding candidate for design of next-generation complex spintronic devices[15,16,17,18,19,20]. While the magnetic properties of magnetite have been theoretically and experimentally investigated, the mechanisms behind the magnetic order in zinc ferrite remain controversial. Efforts to precisely fabricate and probe the defect contribution to the physical properties remain technologically challenging.

In this work, we examine the crystalline structure of spinel ferrite thin films in dependence on deposition and thermal treatment temperature and atmosphere as well as Zn-to-Fe ratio. The magnetic behavior of spinel ferrite thin films shows a strong dependence on cation disorder and local defects as well as their distribution within the thin film. Based on the cation contribution to the (magneto-) optical properties as well as X-ray absorption spectra, the main mechanisms behind ferrimagnetic behavior are identified. The results, examined in this study, demonstrate the possibility of engineering and optical determination thin film ionic valence and site distribution in order to tailor the magnetic properties that are necessary for device applications.

2 Basic Principles

Spinel ferrite oxides, MFe₂O₄ (where M is the divalent cation), crystallize in a cubic close packed oxygen superlattice, belonging to the Fd3m space group. The cations are located on interstitial sites of either tetrahedral (Td) or octahedral (Oh) coordination. Based on their allocation, a lattice of either normal or inverse configuration is formed. Magnetite (Fe₃O₄) crystallizes in an inverse spinel configuration, where the divalent Fe cations are of octahedral coordination and trivalent Fe cations are distributed evenly over both sublattices. Franklinite (ZnFe₂O₄), on the other hand, crystallizes in a normal spinel configuration, where divalent Zn cations are of tetrahedral coordination and trivalent Fe cations are located on octahedral lattice sites only. Therefore, the equilibrium state of the spinel lattice, as a function of Zn concentration (x), is expected to assemble in the following cation configuration:

\[(\text{Zn}^{2+}\text{Fe}_{1-x}^{3+}) \text{Td}(\text{Fe}_{1-x}^{3+}\text{Fe}_{x}^{2+}) \text{OhO}_{4}^{2-}\]  

where \(x = 0\) and \(1\) would correspond to the inverse Fe₃O₄ and normal spinel ZnFe₂O₄ structure, respectively. Deviation from the equilibrium and thus the formation of a disordered cation state will be discussed within the framework of this investigation.

2.1 Identification of Optical Transitions Related to Magnetic Effects

Although the optical properties of magnetite have been widely investigated, a controversy over the assignment of the electronic transitions is found in literature. Following the initial photoelectron and spin polarization investigations by Alvarado et al. (Ref. [21]), Schlegel et al.[22] conducted Kramers-Kronig consistent reflectivity measurements. It was postulated that the optical spectra of magnetite is dominated by an overlap of interband transitions, namely O 2p → Fe 4s transitions and Fe 3d⁰ → 3d⁻¹ 4s orbital promotion processes[22]. Analysis of the off-diagonal dielectric tensor elements (magneto-optical spectra) was conducted in order to clarify the nature of the assigned transitions by Fontijn et al.[23] and Zaag et al.[24]. Through
partial substitution of Fe$^{2+}$ and Fe$^{3+}$ in magnetite by nonmagnetic ions, namely by Mg$^{2+}$ and Al$^{3+}$, they were able to distinguish transitions due to cations on various sites. Upon substitution and based on the observed trends, two types of transitions were experimentally determined to be active in magnetite, namely inter-valence and inter-sublattice charge transfer transitions[23,24]. Later theoretical work by Antonov et al.[25] showed reasonable agreement with the experimental results. The optical spectra of Fe$_3$O$_4$ was determined to be sorted in three groups of inter-band transitions: between Fe 3d bands below 2.5 eV, transitions from O 2p to Fe 3d bands in the spectral range 2.5 - 9 eV and Fe 3d → 4p and O 2p → Fe 4s inter-band transitions above 9 eV[25]. Upon substitution of Fe$^{2+}$ by Mg$^{2+}$ in magnetite, strong hybridization of Mg 3p and O 2p states occurs. As a result, the optical spectra was dominated by O 2p to Fe$^{3+}_{3z}$ and Fe$^{3+}_{3z,y}$ inter-band transitions and a lack of low energy absorption (at ~ 0.9 eV) was observed[25].

A lack of information on the optical properties of magnetite substituted by Zn$^{2+}$ and ZnFe$_2$O$_4$ serves as a motivation for this work. Recent theoretical investigation by Fritsch et al.[26] has compared calculation approaches for normal and inverse spinel configurations of ZnFe$_2$O$_4$. It was found that the antiferromagnetically coupled normal spinel is energetically favored and the hybrid functional calculations yield a better agreement with the experimental results[26]. Ziaei et al.[27] claim that the optical absorption is due to intra-atomic p → p and d → d transitions at the $\Gamma$-point, Fig. 1. Their transition assignment, however, contradicts the previously discussed studies on magnetite and do not distinguish between valence and site specific Fe cations. Determination of the optical absorption for ZnFe$_2$O$_4$ over a wide range of fabrication temperatures was initially conducted by Böntgen et al.[28]. Magneto-optical (MO) properties were determined by Liskova-Jakubisova et al.[29] to show a strong response for low temperature grown ZnFe$_2$O$_4$ thin film. In combination with the diagonal elements of the dielectric tensor ($\epsilon_{zz}$), the off-diagonal elements ($\epsilon_{z}\parallel$) were analyzed in order to determine the nature of magnetically active transitions in ZnFe$_2$O$_4$[30].

![Figure 1: Orbital contributions to the density of states at the $\Gamma$-point. (Reproduced with permission, Copyright 2017, Springer Nature.)](image)

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Fig. 2 shows a comparison of the diagonal ($\varepsilon_{xx}$) and off-diagonal ($\varepsilon_{xy}$) dielectric tensor elements for high (HT) and low (LT) fabrication temperature of ZnFe$_2$O$_4$ thin films. Details about the modeling procedure of the MO response as well as the thin film fabrication can be found in the original paper, Ref.[30]. By comparing the off-diagonal dielectric tensor elements of spinel ferrites and cobaltites, it was found that the ferrites of inverse or disordered normal spinel configuration showed the strongest MO response. For ZnFe$_2$O$_4$, the MO transitions exhibit a red-shift with decrease in deposition temperature, consistent with the increase in crystal lattice parameter. The increase in the strength of MO features with decrease in deposition temperature indicates cations which are most affected by the applied magnetic field and thus can be related to disordered cations[31, 32]. Consistent with transition energies found in literature for Fe$_3$O$_4$ (Refs. [33, 24, 25]) and correlated to MO active cation transitions, the numerically determined dielectric function (B-Spline approximation[34, 35]) was parametrized by the procedure described in Ref. [36]. The dielectric function line-shape is approximated by a series of Lorentzian (L), Gaussian (G) and Critical Point Model (CPM) functions, as exemplary depicted for disordered ZnFe$_2$O$_4$ thin film grown at low oxygen partial pressure and substrate temperature, Fig. 3. Electronic transition resonance energies of Fe$_3$O$_4$ and disordered ZnFe$_2$O$_4$ thin film are listed in Table 1.
Figure 3: Parametric diagonal elements of the dielectric tensor ($\varepsilon_{ij}$) for disordered ZnFe$_2$O$_4$ thin film grown at low oxygen partial pressure (LP) and substrate temperature. Contributions of the Lorentzian (L), Gaussian (G) and Critical Point Model (CPM) approximation functions to the dielectric function line-shape are depicted by solid lines[37].

Table 1: Resonance energies of the assigned electronic transitions. Corresponding cations and anions involved are indicated for each Lorentzian (L), Gaussian (G) and Critical Point Model (CPM) approximation function. The estimated error for the specified energy values is in the order of the last digit. Resonance energies for Fe$_3$O$_4$ were taken from [24, 25], unless specified otherwise.

<table>
<thead>
<tr>
<th>Osc.</th>
<th>Transition</th>
<th>Fe$_3$O$_4$ (eV)</th>
<th>LP ZFO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$_0$</td>
<td>(Fe$<em>{3+}$) $a</em>{1g}$ - (Fe$<em>{3+}$) $t</em>{2g}$</td>
<td>0.91</td>
<td>0.84</td>
</tr>
<tr>
<td>G$_1$</td>
<td>(Fe$<em>{3+}$) $a</em>{1g}$ - (Fe$_{3+}$) $e_g$</td>
<td>1.94</td>
<td>2.05</td>
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<tr>
<td>G$_2$</td>
<td>O 2p - (Fe$<em>{3+}$) $t</em>{2g}$</td>
<td>2.61[38]</td>
<td>2.58</td>
</tr>
<tr>
<td>CPM$_0$</td>
<td>(Zn$_{2+}$)4s [39]</td>
<td></td>
<td>2.91</td>
</tr>
<tr>
<td>G$_3$</td>
<td>(Fe$<em>{3+}$) $e_g$ - (Fe$</em>{3+}$) $e$</td>
<td>3.20</td>
<td>3.21</td>
</tr>
<tr>
<td>G$_4$</td>
<td>O 2p - (Fe$_{3+}$) $e_g$</td>
<td>4.30</td>
<td>3.76</td>
</tr>
<tr>
<td>G$_5$</td>
<td>O 2p - (Fe$_{3+}$)4s</td>
<td>4.50[40]</td>
<td>4.87</td>
</tr>
<tr>
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<td>O 2p - (Fe$_{3+}$)4s</td>
<td>5.57[36]</td>
<td>5.72</td>
</tr>
<tr>
<td>G$_7$</td>
<td>O 2p - (Zn$_{2+}$) &gt; 4s [41]</td>
<td></td>
<td>6.48</td>
</tr>
<tr>
<td>G$_8$</td>
<td>O 2p - (Fe$_{3+}$)4s</td>
<td>6.85</td>
<td>7.41</td>
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</table>

2.2 Magnetic Cation Exchange Interactions

Magnetic ground state of iron oxides in spinel configuration is governed mainly by indirect magnetic exchange interactions between Fe cations, mediated by oxygen anions. Individual divalent ($3d^6$, $S = 2$) and trivalent ($3d^5$, $S = 5/2$) Fe cations have a net magnetic moment of 4$\mu_B$ and 5$\mu_B$, respectively. Depending on their allocation within the lattice structure, a combination of ferromagnetic (FM) double-exchange (DE) and antiferromagnetic (AF) super-exchange (SE) interactions between Fe cations of the $Td$ (spin down) and $Oh$ (spin up) site occupation give rise to the overall magnetic order.

Ideally, normal spinel ZnFe$_2$O$_4$ has an antiferromagnetic order below the Neél temperature of 10 K. However, neutron scattering experiments have shown that long-range magnetic order is not attained in a single crystal normal spinel ZnFe$_2$O$_4$ even at temperatures as low as 1.5 K due to three-dimensional geometrical spin frustration[42, 43]. The presence of structural disorder would suppress the intrinsic spin frustration, leading to the finite-range magnetic order[44]. Consequently, the possible cases are schematically depicted in Fig. 4 (Refs. [45, 46]), and listed below with respect to the increase in disorder from the normal spinel

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\( \text{ZnFe}_2\text{O}_4 \) towards the inverse spinel magnetite:

- **Case 1:** AF ordered normal \( \text{ZnFe}_2\text{O}_4 \). The AF oxygen mediated SE interaction between two octahedrally coordinated \( \text{Fe}^{3+} \) cations[44, 26].

- **Case 2:** Disordered \( \text{ZnFe}_2\text{O}_4 \), where \( \text{Fe}^{3+} \) and \( \text{Zn}^{2+} \) are displaced to occupy \( Td \) and \( Oh \) lattice sites, due to the inversion mechanism. The strong oxygen mediated SE interaction between \( \text{Fe}^{3+} \), located on \( Td \) and \( Oh \) lattice sites gives rise to the overall ferrimagnetic behavior[47].

- **Case 3:** Disordered \( \text{ZnFe}_2\text{O}_4 \) with \( \text{Fe}^{3+} \) on nominally unoccupied tetrahedral lattice site. This gives rise to the weak FM oxygen mediated SE interaction between the two \( Oh \) \( \text{Fe}^{3+} \) and a strong oxygen mediated AF SE interaction between \( \text{Fe}^{3+} \), located on \( Td \) and \( Oh \) lattice sites[48, 46].

- **Case 4:** Disordered \( \text{ZnFe}_2\text{O}_4 \) with the presence of an oxygen vacancy ( \( \text{O}_{\text{vac}}^{2-} \)). The AF SE interaction becomes FM interaction between \( \text{Fe}^{3+} \) cations[46, 49].

- **Case 5:** Mixed \( Td \) occupation, due to the presence of \( Td \) coordinated, non-magnetic, \( \text{Zn} \) cations as well as \( \text{Fe} \) cations. The magnetic interactions \( Td-O-Oh \) become uncompensated and result in a FM DE interaction. The spins on the \( Oh \) sublattice are canted with respect to each other by an angle known as the Yafet-Kittel angle[50, 45, 51].

- **Case 6:** The case of \( \text{Fe}_3\text{O}_4 \), where FM DE \( Oh-O-Oh \) and AF SE \( Td-O-Oh \) interactions are exhibited[52, 53].

The initial model for ferromagnetism in \( \text{Fe}_3\text{O}_4 \) was proposed by Néel, where the antiparallel alignment of \( Td-Oh \) moments of \( \text{Fe}^{3+} \) cations would compensate each other and the net magnetic moment of 4 \( \mu_\text{B} \) f.u. would originate from the remaining \( \text{Fe}^{2+} \) cations[52]. However, this model does not take the FM DE interaction between \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) cations into account. Yafet et al.[50] proposed a more elaborate model where the \( Oh \) lattice site would be divided into \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) sublattices, Case 6 in Fig. 4. Due to the strengthening of the FM DE \( Oh-O-Oh \) interaction, the spins would no longer be strictly parallel to one another, but rather canted by a finite Yafet-Kittel angle. This mechanism is particularly important when the AF SE \( Td-O-Oh \) becomes weakened due to \( \text{Zn}^{2+} \) substitution, Case 5 in Figure 4. As a result, magnetization saturation would originate from the competing AF SE between the two sites and the FM DE between \( \text{Fe}^{3+} \) and \( \text{Fe}^{2+} \) cations.

Theoretical approximation of the exchange integrals in magnetite has been described by Uhl et al.[53]. The inter-sublattice AF SE was calculated to be the strongest nearest-neighbor magnetic coupling with \( J_{td-Oh} = -2.88 \) meV. The FM DE coupling, due to mixed valence state on the \( Oh \) site, was the second strongest with \( J_{Oh-Oh} = 0.83 \) meV. Lastly, the AF SE coupling between two \( Td \) \( \text{Fe}^{3+} \) cations on adjacent sublattices was the weakest, with \( J_{td-td} = -0.18 \) meV. Although the values, calculated in this approximation, were slightly larger than those determined experimentally, a distinctive strength of the \( Td-O-Oh \) magnetic exchange interaction is evident.
Furthermore, the importance of oxygen vacancies has been only recently considered and predicted to strongly influence the net magnetic moment of $\text{ZnFe}_2\text{O}_4$ [46]. The lack of an anion between the two AF coupled $\text{Oh}$ Fe cations would result in a FM exchange interaction instead, Case 4 in Fig. 4. Theoretical calculations by Rodriguez Torres et al. [46] showed a contribution of 8 $\mu_B$ per oxygen vacancy per supercell due to the flipping of the spins, while a contribution of 6 and 10 $\mu_B$ per additional $Td$ Fe cation per supercell was predicted for Case 2 and Case 3 in Fig. 4, respectively. Not only would the length of the bonds be locally affected by the oxygen vacancy, but the lack of oxygen could be responsible for creating Fe$^{2+}$ cations. This effect was considered to explain room temperature ferrimagnetic order in $\text{ZnFe}_2\text{O}_4$ in dependence on oxygen pressure during fabrication [48]. However, as the detection of the Fe$^{2+}$ cation by X-ray magnetic circular dichroism (XMCD) remains challenging, its direct contribution to the net magnetic moment of $\text{ZnFe}_2\text{O}_4$ is yet to be carefully examined [47].

The presence of Fe$^{3+}$ due to oxygen vacancy formation can be demonstrated indirectly. The FM DE interaction is mediated by the itinerant spin down $t_{2g}$ electron hopping between Fe$^{3+}$ and Fe$^{4+}$ cations on the $\text{Oh}$ sites. Owing to Hund’s coupling rule, the spin of the itinerant electron is AF coupled to the local 3d spin up electrons [54]. As a result, the density of itinerant charge carriers is directly related to the electrical conductivity in spinel ferrite [55, 56]. This has been shown by Brachwitz et al. [57] in $\text{ZnFe}_2\text{O}_4$ thin films, grown in a wide range of oxygen partial pressures. Electrical conductivity was also found to be significantly lower in $\text{ZnFe}_{1-x}\text{O}_4$ films grown in finite Ar/$\text{O}_2$ (99:1) mixed atmosphere, as compared to those grown in Ar [45]. Venkateshvaran et al. [45] attributed this effect to the presence of octahedral Fe$^{3+}$ cation vacancies, which would weaken the density of thermally activated itinerant electron hopping between the mixed-valent octahedral Fe$^{2+}$/Fe$^{3+}$ cations. The deficiency of the octahedral Fe$^{3+}$ cations would decrease the strength of the $Td$-$O$-$\text{Oh}$ AF SE interaction and would further contribute to a weakened magnetic response in magnetite [45]. The effects of cation vacancies on the geometric and electronic structures of normal $\text{ZnFe}_2\text{O}_4$, have been theoretically predicted by Yao et al. [58] to show a change from semiconducting to metallic band structure, depending on the vacancy defect.

![Figure 4: Schematic representation of main magnetic configurations and interactions between the neighboring cations, ordered from Case 1 normal spinel ($\text{ZnFe}_2\text{O}_4$) to Case 6 inverse spinel ($\text{Fe}_3\text{O}_4$). The cations are color-coded and the antiferromagnetic (AF) or ferromagnetic (FM) alignment of the magnetic moment is depicted by the red arrows for each case, see text for details.](image)

### 3 Order Through Fabrication Parameters

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Ferrimagnetic order in ZnFe$_2$O$_4$ thin films can be obtained by varying the fabrication method as well as growth parameters. Apart from particle size[59] and thin film thickness, cation inversion and defects show a strong dependence on oxygen partial pressure and substrate temperature during deposition. Further details on ZnFe$_2$O$_4$ thin films prepared by pulsed laser deposition can be found in Ref. [60] and the references within.

Substrate temperature during thin film deposition was shown to have a strong effect on the electronic structure and magnetic properties of ZnFe$_2$O$_4$ thin films, Fig. 5 (a) and (b)[36]. First and foremost, the crystalline quality improves with the increase in growth temperature, with the lowest lattice constant for the film grown at the highest substrate temperature as reported by Böntgen et al.[28] as well as Brachwitz et al.[57]. The change in both optical and MO spectra manifests itself by a general red-shift of the main absorption features with the decrease in substrate temperature[28, 29]. Important to note, the choice of highest deposition partial pressure allows the production of films free of oxygen vacancies and Fe$^{3+}$-$\text{Fe}^{2+}$ exchange, consistent with a lack of low energy absorption[29]. A decrease in the high energy absorption peak (at $\sim$ 6 eV) corresponds well to a more disordered structure with the decrease in substrate temperature. Simultaneously, an increase in the oscillator amplitude of $G_3$ is observed with the decrease in deposition temperature and was previously correlated to an increase in the saturation and remnant magnetization, measured at 5 K, Fig. 5 (c)[36]. Consistent with the transition assignment in Section 2.1, this would indicate an increase in Fe$^{3+}_{\text{ml}}$ cation concentration, due to either cation inversion (Case 2 in Fig. 4) or Fe$^{3+}$ on nominally unoccupied tetrahedral lattice sites (Case 3 in Fig. 4)[36]. Theoretical work by Soliman et al.[61] predicted that the cation disorder would affect the oxygen parameter and the disordered state was found to be energetically favorable as it tends to decrease stress of the octahedral sites and reduce the point group symmetry from O$_h$ to C$_{4v}$.

![Figure 5: Magnetization as a function of applied magnetic field at room temperature (a) and at 5 K (b) with deposition temperature indicated. Saturation and twice of remanent magnetization](image)

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measured at 5 K as well as the amplitude of the transition involving $\text{Fe}^{2+}$ cations, discussed in Section 2.1, as a function of growth temperature (c). (Reproduced with permission.[36] Copyright 2016, AIP Publishing.)

A detailed study on the ferrimagnetic order in ZnFe$_2$O$_4$ thin films in dependence on oxygen partial pressure was conducted by Rodriguez Torres et al.[48]. Magnetic moment as a function of applied field for films prepared at different partial pressures is depicted in Fig. 6 (a) and (b).[62] The disorder in cation distribution was revealed by examining the Zn and Fe K-edge X-ray absorption near-edge structure (XANES) spectra. While the Zn ions were determined to be of tetrahedral coordination, the Fe ions were allocated on both sites[48]. In this case, $\text{Fe}^{3+}$ of tetrahedral coordination were not due to Zn and Fe ion inversion, but rather due to $\text{Fe}^{3+}$ situated on nominally unoccupied tetrahedral lattice sties, Case 3 in Fig. 4. However, the main mechanism responsible for the increase in magnetic response with the decrease in oxygen partial pressure was attributed to the production of oxygen vacancies and thus the reduction of $\text{Fe}^{3+}$ ions into $\text{Fe}^{2+}$ ions on octahedral lattice sites. Similar behavior was reported by Sultan et al.[63] for ZnFe$_2$O$_4$ thin films prepared by rf-magnetron sputtering. A combination of experimental and first principles studies was conducted by Jin et al.[64] to show that under cation disordering, presence of oxygen vacancies would make ZnFe$_2$O$_4$ to a half-metal semiconductor, while ZnFe$_2$O$_4$ with no oxygen vacancies is an insulator, suitable for spintronic device application as a spin filter layer.

In their later work, Rodriguez Torres et al.[46] demonstrated the influence of an oxygen vacancy on the magnetic structure. Fig. 6 (c) shows the isosurfaces and the difference in the magnetization density $\Delta m(r)$, induced by an oxygen vacancy. As mentioned in the previous section, the presence of an oxygen vacancy would affect the bond lengths at the Fe cations, forcing a fluctuation between 0 and 4%. The abrupt change in the charge density at the oxygen vacancy site forces the neighboring iron ion to flip its moment, Case 4 in Fig. 4. Therefore the nominally AF oxygen mediated interaction becomes FM and contributes to the total moment of 8 $\mu_0$ per unit cell[46].

The model dielectric function for two thin films grown at low substrate temperature, but at two different oxygen partial pressures is depicted in Fig. 6 (d)[37]. A clear difference in the low energy absorption (below 2.5 eV) is observed. Based on the assigned electronic transitions, Section 2.1, the film grown at low oxygen partial pressure contains $\text{Fe}^{2+}$ cations, which are likely induced by oxygen vacancy formation. The difference in the experimentally determined magnetic response, in this case, is difficult to attribute to one type of defect. However, remnant magnetization measured at 5 K is in fact higher for the low oxygen partial pressure (205 emu/cm$^3$) than for the high pressure (147 emu/cm$^3$) grown thin film. Similarly, an increase in ferrimagnetic order was reported by Chen et al.[65] with the decrease in deposition oxygen partial pressure. Therefore, the control of magnetic properties and electronic structure of ZnFe$_2$O$_4$ thin films is shown to be possible through control of oxygen partial pressure during deposition.

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Figure 6: Magnetic moment as a function of applied field at room temperature (a) and 5 K (b) for films prepared at different partial pressures [48]. (c) Isosurfaces and the difference in the magnetization density $\Delta m(r)$, induced by an oxygen vacancy (sphere with the white cross), with respect to the ideal structure. Gold and blue spheres are $\text{Fe}^{3+}_{\text{Oh}}$ and $\text{Fe}^{3+}_{\text{Td}}$, respectively. The right-hand side graph shows magnetization density integrated over x-y plane (blue line) and along the z direction (red line) [46]. (d) Imaginary component of the parametric model dielectric function for $\text{ZnFe}_2\text{O}_4$ films deposited at two different oxygen partial pressures. Contributions of the approximation functions to the dielectric function line-shape are depicted for the high pressure grown $\text{ZnFe}_2\text{O}_4$ by dashed lines. (Reproduced with permission. [48, 46] Copyright 2011 and 2014, American Physical Society.)

4 Cation Normalization by Thermal Treatment

An alternative way to alter the magnetic behavior of $\text{ZnFe}_2\text{O}_4$ is by thermal treatment. Static and dynamic magnetic response in combination with XANES and XMCD experiments was recently analyzed as a function of annealing temperature by Salcedo Rodríguez et al. [66]. Polycrystalline $\text{ZnFe}_2\text{O}_4$ was obtained by conventional solid state reaction with repeated vacuum annealing steps with intermediate grinding. Magnetization as a function of applied field was found to consist of two contributions, namely the paramagnetic and ferromagnetic components. To account for their superposition, the following equation was used to model the magnetic response at high fields:

$$M(H) = M_s \left[1 - (\alpha H^2) - (\beta H^2)\right] + \chi_r H$$

(2)
where $M_s$ is the saturation magnetization and $\chi_h$ is the high-field paramagnetic differential susceptibility, due to non-collinear spins in the magnetic structure[67]. Both parameters exhibit a sharp increase for annealing temperatures above 370°C, Fig. 7 (a) and (b). The cation distribution was examined based on the positive (A1) and negative (B1 and B2) XMCD signals of Fe L-edge spectra, which correspond to tetrahedral and octahedral site occupation by Fe$^{3+}$ cations, respectively. Upon annealing the samples at 370°C, a decrease in cation inversion was observed, Fig. 7 (c)[66]. Interestingly, the ZFO-620 spectrum indicates a reoccupation of the tetrahedral as well as the octahedral lattice sites, indicative by the strength of the A1, B1 and B2 XMCD signals. Consistent with dynamic magnetic measurements, the decrease in magnetic response was attributed to cation redistribution toward normal spinel structure and a cluster-glass behavior was reported for annealing temperatures above 250°C. Above 450°C, oxygen deficiency strengthens the $Oh$-$O_{vac}$-$Oh$ FM interaction and dominates over cation inversion, which was found at the surface regions[66].

![Figure 7: (a) Parametric susceptibility $\chi_p$ and (b) saturation magnetization $M_s$ as a function of annealing temperature. (c) XANES spectra at Fe L$_3$-edge for ZFO-620 and XMCD signals for ZFO, ZFO-370 and ZFO-620 samples. (Reproduced with permission.[66] Copyright 2018, Elsevier.)](image)

After annealing ZnFe$_2$O$_4$ under oxygen atmosphere, a similar effect was determined by Figueroa et al.[68] by examining the Zn K-edge of the XANES spectra. It was determined that the activation of the disorder-order transition takes place above 312°C and the transference of Zn cations follows the first-order kinetic process. The decrease in ferrimagnetic order was attributed to cation redistribution toward an equilibrium state, namely Zn and Fe to tetrahedral and octahedral lattice sites, respectively[68]. Kumar et al.[69] reported a systematic decrease in the magnetic response, first attributed to possible recrystallization upon annealing in Ar (500-600°C).
and then due to oxygen vacancy reduction after consequent annealing in oxygen. At sufficiently high annealing temperature (1000 °C), Ayyappan et al.[70] determined an increase in the paramagnetic response upon annealing ZnFe₂O₄ nanoparticles in oxygen, while a ferromagnetic behavior was exhibited after annealing in vacuum. Similarly, while Mendonca et al.[71] reported a decrease in magnetic response after oxygen treatment, Philip et al.[72] reported a significant increase after annealing ZnFe₂O₄ nanoparticles in vacuum.

Theoretical calculations of XANES and extended X-ray absorption fine structures (EXAFS) spectra were conducted by Nakashima et al.[44] and compared to the experimental findings. The Fourier transform of the Zn-K EXAFS spectra is depicted in Fig. 8. While a single peak located at 3.1 Å would correspond to the tetrahedral occupation of Zn cations, a double peak (as-deposited film) indicates contributions from Zn²⁺-Zn²⁺ and Zn²⁺-Fe³⁺ pairs. Based on the theoretical simulations, the as-deposited ZnFe₂O₄ thin film was found to contain 60% of Zn²⁺ cations on the octahedral lattice site. As a result, the Fe³⁺ cations would be displaced, yielding a strong ferrimagnetic behavior due to the Td-O-Oh interaction. The competing Td-O-Oh and Oh-O-Oh interactions would give rise to frustration and the as-deposited film would exhibit a magnetic transition above room temperature. Below this transition temperature, known as the spin freezing or blocking temperature, irreversibility between magnetic moment measured after cooling with (field cooled) and without (zero field cooled) an applied field is exhibited. This behavior is consistent with either cluster spin-glass, superparamagnetism, or diluted antiferromagnetic behavior[73]. Upon annealing the as-deposited thin film in air, the frustration is relieved and the cation configuration exhibits a redistribution toward a normal spinel structure[44]. With a low degree of cation disorder, the AF superexchange interaction between Fe³⁺ cations becomes dominant and an antiferromagnetic behavior is observed (Case 1 in Fig. 4).
In order to investigate the effects of annealing in individual atmospheres, high (10⁻² mbar) and low (10⁻⁵ mbar) pressure films, presented in Fig. 6 (d), were annealed in argon and oxygen atmospheres, respectively, at temperatures between 250 and 375 °C [62]. Upon annealing in argon at 250 °C, the film exhibited a decrease in the spin freezing temperature (T_{SF}), depicted in Fig. 9 (a). As postulated by Nakashima et al. [44], the decrease in T_{SF} corresponds to a weakening of the Td-O-Oh magnetic interaction and thus a diminishing concentration of Fe_{Td}³⁺ cations. The inversion recovery is consistent with a decrease and increase in the amplitude of G₃ and G₅ functions, which correspond to transitions involving Fe_{Td}³⁺ and Fe_{Oh}³⁺ cations, respectively, Section 2.1. However, an increase in remnant magnetization is observed, Fig. 9 (b). Simultaneously, low energy absorption due to Fe²⁺ cations becomes apparent, Fig. 9 (c). Therefore, the likely mechanism to cause an increase in magnetization is the production of oxygen vacancies thereby strengthening the FM Oh-O_{Oh} -Oh interaction. On the other hand, upon annealing in oxygen at 250 °C, the increase in remnant magnetization can be explained by the elimination of oxygen vacancies, which would strengthen the dominant Td-O-Oh interaction. This is consistent with a decrease in L₀, depicted in Fig. 9 (d)[37, 62].

Contrary to Tanaka et al. [74], who reported an increase in magnetization upon annealing ZnFe₂O₄ thin films in air at 300 °C, a decrease in magnetic moment is observed after annealing at 300 °C in both atmospheres. The diminished magnetic response can be explained by the cation redistribution toward a normal spinel structure, consistent with the decrease and increase in Fe_{Td}³⁺.
and Fe\textsuperscript{3+} cation transition amplitudes, respectively. This comes to show that individual defect type and therefore the dominant magnetic interaction can be induced or eliminated by an appropriate choice of fabrication as well as thermal treatment parameters.

![Image](image.png)

**Figure 9:** Spin freezing temperature (a) and remnant magnetization, measured at 5 K, (b) as a function of annealing temperature in argon (red) and oxygen (blue) atmosphere. Imaginary component of the model dielectric function for films annealed argon (c) and oxygen (d) atmosphere. Contributions of the $L_0$, $G_3$, and $G_6$ approximation functions to the dielectric function are depicted by dashed lines in (c) and (d)\cite{62}.

## 5 Inverse to Normal Structure by Zn Doping

Doping of Fe\textsubscript{3}O\textsubscript{4} by non-magnetic Zn ion allows tailoring of magnetic and electronic properties from a ferrimagnetic half-metal to an antiferromagnetic insulator, making the Zn\textsubscript{y}Fe\textsubscript{3-x}O\textsubscript{4} compound particularly attractive for spintronic applications. The magnetic moment per Zn\textsubscript{y}Fe\textsubscript{3-x}O\textsubscript{4} formula unit (f.u.) is expected to increase monotonically with the increase in Zn concentration (x), following $m = (4 + 6x)\mu_s$ relation proposed by Néel\cite{52}. While both theoretical and experimental studies demonstrate a deviation from this relation, the interpretation of the diminishing magnetic response with increasing x remains unclear.

As it is thoroughly described by Venkateshvaran *et al.*\cite{45} and references within, the magnetic moment in magnetite is due to competing AF Td-O-Oh and FM Oh-O-Oh, Case 6 in Fig. 4. The latter is a DE interaction mediated by the itinerant spin down $t_{sz}$ electron hopping...
between mixed-valent octahedrally coordinated Fe cations. While this interaction remains unchanged with low concentration of dopant Zn ions, the AF interaction weakens and an increase in magnetization is expected. This behavior has been experimentally demonstrated by Yuan et al.[75, 76] up to Zn concentration of x = 0.1. However, upon further increase in Zn concentration, spins of Fe cations on Td and Oh lattice sites are no longer parallel, Case 5 in Fig. 4. The Yafet-Kittel canting angle increases with increasing substitution and a decrease in magnetic order is expected. As Zn $^{2+}$ preferentially occupy the tetrahedral lattice sites, concentration of Fe$^{3+}_{\text{Oh}}$ decreases. In order to maintain neutrality of charge, this substitution reduces the amount of Fe$^{2+}$ on octahedral sites. Therefore, through Zn substitution the AF and mixed-valent FM interaction is weakened and the AF interaction between Oh-O-Oh isovalent Fe cations is strengthened.

Theoretical calculations by Cheng et al.[77] show an increase in magnetic moment up to 8.3 $\mu_B$/f.u. for x = 0.75, followed by a decrease to 3.2 $\mu_B$/f.u. for x = 1. Takaobushi et al.[55] were able to achieve an increase in low temperature (10 K) magnetic moment from 0.5 to 3.2 $\mu_B$/f.u. with the increase in Zn concentration from 0 to 0.9. They explain this observation on the basis of the substitution mechanism on the Td sites, thereby weakening the AF Td-O-Oh coupling and strengthening the FM Oh-O-Oh interaction[55, 56]. This has been demonstrated in their later work by XMCD and hard X-ray photoemission spectroscopy[78]. Venkateshvaran et al.[45] report an increase in saturation magnetization up to x = 0.5 and then a decrease for x = 0.9, Fig. 10 (b). As the thin films were deposited in a finite oxygen partial pressure (Ar/O$_2$ and O$_2$) in both cases, Venkateshvaran et al.[45] argue that the magnetization increase is likely caused by the removal of Fe vacancies, rather than Fe$^{2+}_{\text{Td}}$ moments. They suggest that upon Zn substitution, the existing Fe vacancy concentration decreases, consequently decreasing the spin canting angle on the Oh sites. For larger Zn concentration, the moments of the Fe$^{3+}_{\text{Td}}$ become strongly diluted, thereby weakening the AF Td-O-Oh interaction as well as the magnetic response.
For Zn$_{x}$Fe$_{3-x}$O$_4$ thin films deposited in Ar atmosphere, Venkateshvaran et al. [45] report a decrease in magnetization with increase in Zn concentration, depicted in Fig. 10 (a). Such behavior was attributed to the weakening of both the AF SE $Td$-$O\cdot Oh$ and the FM DE $Oh$-$O\cdot Oh$ interactions and giving rise to spin canting and the AF SE interaction between $Oh$-$O\cdot Oh$ isovalent Fe cations. In order to investigate this phenomena further, Zn$_{x}$Fe$_{3-x}$O$_4$ thin films were deposited on previously optimized TiN/(100)MgO [79] substrates and at same conditions as those reported by Venkateshvaran et al. [45, 37]. The magnetization values, depicted in Fig. 12 (b), were found to be lower than those reported by Venkateshvaran et al. [45], but higher than those reported by Takaobushi et al. [55] for $x \leq 0.57$.

Figure 10: Room temperature magnetization as a function of magnetic field applied in film plane for Zn$_{x}$Fe$_{3-x}$O$_4$ films grown in pure Ar (a) and in Ar/O$_2$ (99:1) mixed atmosphere (b). Insets show saturation magnetization ($M_s$) and remanence ($M_r$) as a function of Zn concentration ($x$). (Reproduced with permission.[45] Copyright 2009, American Physical Society.)

Based on the approach proposed by Fujii et al. [80] and Yamashita et al. [81], the relative composition of individual Fe cations in the near-surface region was estimated by analysis of the X-ray photoelectron (XPS) Fe 2p and 3p core level spectra. The individual contribution of site- and valence-specific Fe cations to the Fe 2p and 3p core level surface spectra, with the Shirley background subtracted, is depicted in Fig. 11 (a) for the $x = 0$ thin film. A clear difference in the surface electronic structure with the increase in Zn concentration manifests itself by an increase in the Fe 2p satellite peak (719 eV) as well as the decrease in the low energy shoulder for both Fe

Figure 11: (a) Model fit to the measured surface XPS Fe 2p and 3p core level spectra without the Shirley background and (b) the bulk model dielectric function for the $x = 0$, 0.57 and 1.26 films. XPS intensity of the resulting fit and $\varepsilon_{ap}$ approximation line-shapes are multiplied by a factor of two for clarity. The individual cation contribution to the modeled spectra are depicted by dashed lines for the $x = 0$ thin film, Section 2.1. The satellite contribution between Fe 2p$_{3/2}$ and 2p$_{1/2}$ is indicated by an arrow [37].
As discussed in Section 2.1, the transition functions involving only the 3d and 4s orbitals of individual Fe cations to the x = 0 thin film model dielectric function are depicted in Fig. 11 (b). The relative cation composition in the bulk of the thin film was estimated from their contribution to the dielectric function line-shape. By comparing the cation composition in the near-surface (XPS) and bulk (dielectric function) regions, the relative surface to bulk cation ratio as a function of Zn concentration is derived as depicted in Fig. 12 (a)[37].

The weakened magnetic moment for films with predominantly inverse spinel configuration (x ≤ 0.57) can be explained by a deficiency of Fe^{3+} in the film bulk, in comparison to the near-surface region. The uneven distribution of Fe^{3+} cations throughout the film would weaken the AF SE Td-O-Oh and the FM DE Oh-O-Oh interactions in the bulk of the film. Similarly, Jedrecy et al.[82] investigated Zn_{x}Fe_{3-x}O_{4} thin films grown on different substrates to show a strong dependence of magnetic properties on microstructure and chemical composition distribution within the film.

The highest degree of inversion as well as the critical value between the inverse and normal spinel structure, according to the O’Neil-Navrotsky model[83], is predicted to occur at x = 0.67, vertical line in Fig. 12 (b). Therefore, it is likely that two films of x ≥ 0.87 are of predominantly normal spinel configuration. The saturation magnetization as a function of temperature for x = 0.87 film was found to follow the Bloch law, indicating formation of homogeneous ferromagnetic layers, coincident with a smooth surface morphology and nearly homogeneous cation distribution. Furthermore, the Td to Oh Fe bulk cation ratio of 0.5 indicates a high degree of cation disorder in the x = 0.87 thin film, yielding a strong room temperature saturation magnetization (1.48 μB/f.u.). A more detailed discussion of the magnetic behavior with respect to the cation composition distribution in inverse and normal spinel ferrite thin films will be presented in our future work [37].
Figure 12: (a) Relative surface to bulk Fe cation concentration ratio, obtained from XPS and dielectric function analysis, respectively, as a function of Zn$^{2+}$ concentration obtained from energy dispersive X-ray spectroscopy analysis. The horizontal dashed line represents the ratio value for a homogeneous cation distribution, when the cation ratio is equal to 1. (b) Room temperature saturation magnetization ($M_s$) and ratio of remnant ($M_{rem}$) to $M_s$ as a function of bulk Zn$^{2+}$ concentration. The critical value, between the inverse and normal spinel structure according to the O’Neil-(Neil)Navrotsky model[83], is depicted by the dashed vertical line[37].

The x = 1.26 film exhibits a low magnetization saturation as well as superparamagnetic behavior at room temperature. Interestingly, the concentration of Fe$^{3+}_{Td}$ cations in this film is higher in the surface than in the bulk. This is consistent with previous studies that claim that cation inversion is likely found in the surface of the ZnFe$_2$O$_4$ film. By the analysis of XANES spectrum at the Zn K-edge, Salcedo Rodríguez et al.[73] reported cation inversion at the film surface to induce magnetic order and cause a spin glass behavior. Due to a high surface concentration of Zn$^{2+}_{oh}$, Steward et al.[84] have suggested that inhomogeneously distributed inversion would cause high density regions where both Td-O-Oh and Oh-O-Oh interactions could coexist. XMCD intensity as a function of magnetic field was examined by Mendoza Zélis et al.[85] to show antiparallel alignment of Td and Oh Fe cations in the near-surface region. Recent ab-initio study by Salcedo Rodríguez et al.[49] on the stability of (001) ZnFe$_2$O$_4$ surface termination predicts that the cationic inversion and defect formation become energetically favorable in the surface, making disordered nanostructures with dominant AF SE Td-O-Oh interaction particularly interesting for device applications.

6 Conclusions

In summary, we have demonstrated that engineering of ionic valence and site distribution
is possible through variation of Zn concentration, fabrication as well as thermal annealing temperature and atmosphere. The defects, responsible for the magnetic properties, were identified and can be determined based on the transitions active in optical absorption. Considering the technological interest in nanostructured functional materials, the inhomogeneous cation (defect) distribution in structure of predominantly normal or inverse spinel configuration would affect the cation magnetic interactions and therefore either enhance or diminish the magnetic response, respectively.

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References


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BIO

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Recent developments in the understanding of the magnetic interactions, responsible for the magnetic behavior in normal spinel zinc ferrite system. Spectroscopic determination of the type and concentration of individual defects allows the possibility to engineer the defect distribution in the thin film structure and to tailor the desired magnetic properties.