

# Epitaxial $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ thin films: A spintronic material with tunable electrical and magnetic properties

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The ferrimagnetic spinel oxide  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  combines high Curie temperature and spin polarization with tunable electrical and magnetic properties, making it a promising functional material for spintronic devices. We have grown epitaxial  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  thin films ( $0 \leq x \leq 0.9$ ) on  $\text{MgO}(001)$  substrates with excellent structural properties both in pure Ar atmosphere and an  $\text{Ar}/\text{O}_2$  mixture by laser molecular beam epitaxy and systematically studied their structural, magnetotransport, and magnetic properties. We find that the electrical conductivity and the saturation magnetization can be tuned over a wide range ( $10^2 \dots 10^4 \text{ } \Omega^{-1} \text{ m}^{-1}$  and  $1.0 \dots 3.2 \text{ } \mu_B/\text{f.u.}$  at room temperature) by Zn substitution and/or finite oxygen partial pressure during growth. Our extensive characterization of the films provides a clear picture of the underlying physics of the spinel ferrimagnet  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  with antiparallel Fe moments on the *A* and *B* sublattices: (i) Zn substitution removes both  $\text{Fe}_A^{3+}$  moments from the *A* sublattice and itinerant charge carriers from the *B* sublattice; (ii) growth in finite oxygen partial pressure generates Fe vacancies on the *B* sublattice also removing itinerant charge carriers; and (iii) application of both Zn substitution and excess oxygen results in a compensation effect as Zn substitution partially removes the Fe vacancies. Both electrical conduction and magnetism are determined by the density and hopping amplitude of the itinerant charge carriers on the *B* sublattice, providing electrical conduction and ferromagnetic double exchange between the mixed-valent  $\text{Fe}_B^{2+}/\text{Fe}_B^{3+}$  ions on the *B* sublattice. A decrease (increase) in charge carrier density results in a weakening (strengthening) of double exchange and thereby a decrease (increase) in the conductivity and the saturation magnetization. This scenario is confirmed by the observation that the saturation magnetization scales with the longitudinal conductivity. The combination of tailored  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films with semiconductor materials such as ZnO in multifunctional heterostructures seems to be particularly appealing.

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## I. INTRODUCTION

Spintronic materials and devices are the focus of current research activities.<sup>1,2</sup> Regarding functional spintronic materials, transition-metal oxides are promising candidates since they show a rich variety of electrical and magnetic properties specifically interesting for applications in spintronics. Evidently, useful spintronic devices such as magnetoresistive elements based on the tunneling magnetoresistance<sup>3</sup> (TMR) or spin transistors<sup>4</sup> require ferromagnetic materials with high Curie temperature  $T_C$  well above room temperature and large spin polarization  $P$  of the charge carriers at the Fermi level  $E_F$ . Moreover, advanced applications often require materials with magnetic properties which can be deliberately tuned by external control parameters such as applied electric field,<sup>5</sup> elastic stress,<sup>6,7</sup> or light.<sup>8</sup> In this respect,  $\text{Fe}_3\text{O}_4$  (magnetite) is a highly promising candidate. First, it has a high Curie temperature of  $T_C \approx 860 \text{ K}$  and according to band-structure calculations is expected to be a half-metal<sup>9</sup> corroborated by spin-resolved photoelectron spectroscopy.<sup>10,11</sup> Second, recent experiments indicated that both the electronic and magnetic properties of  $\text{Fe}_3\text{O}_4$  thin films can be nicely tailored in solid solution systems of  $\text{Fe}_{3-x}\text{M}_x\text{O}_4$  ( $M = \text{Zn}, \text{Mn}$ ).<sup>12,13</sup> Third, it has been demonstrated that the magnetic anisotropy of  $\text{Fe}_3\text{O}_4$  can be tuned by elastic stress imposed by a piezoelectric

actuator.<sup>14</sup> Taken all together, due to their interesting, versatile, and tunable properties magnetite thin films and heterostructures became the focus of recent research activities.

Before discussing the various possibilities for tuning and tailoring the electronic and magnetic properties of magnetite, we briefly review its basic structural and magnetic properties. Magnetite is known to have an inverse spinel structure as shown in Fig. 1(a). The *A* sites (8 per unit cell), which are surrounded by oxygen tetrahedra, are occupied by trivalent  $\text{Fe}_A^{3+}$  ( $3d^5, S=5/2$ ), whereas on the octahedrally coordinated *B* sites (16 per unit cell) there is an alternating arrangement of  $\text{Fe}_B^{2+}$  ( $3d^6, S=2$ ) and  $\text{Fe}_B^{3+}$  ( $3d^5, S=5/2$ ) ions. Therefore, the sum formula of magnetite can be expressed as  $[\text{Fe}^{3+}]_A[\text{Fe}^{3+}\text{Fe}^{2+}]_B\text{O}_4$ . The density of itinerant charge carriers is determined by the density of the  $t_{2g}$  spin-down electron on the *B* site, i.e., by the density of  $\text{Fe}_B^{2+}$ . The magnetic exchange in magnetite is governed by a combination of antiferromagnetic superexchange (SE) and ferromagnetic double exchange (DE) interactions. There are three antiferromagnetic SE interactions  $J_{AA}(A-O-A)$ ,  $J_{BB}(B-O-B)$ , and  $J_{AB}(A-O-B)$  between the  $\text{Fe}^{3+}$  ions on the *A* and *B* sites, mediated by the oxygen (O) ions. In addition, there is a ferromagnetic DE interaction mediated by the itinerant spin-down  $t_{2g}$  electrons hopping between the mixed-valent Fe ions on the *B* sites (cf. Fig. 1). Owing to Hund's rule cou-

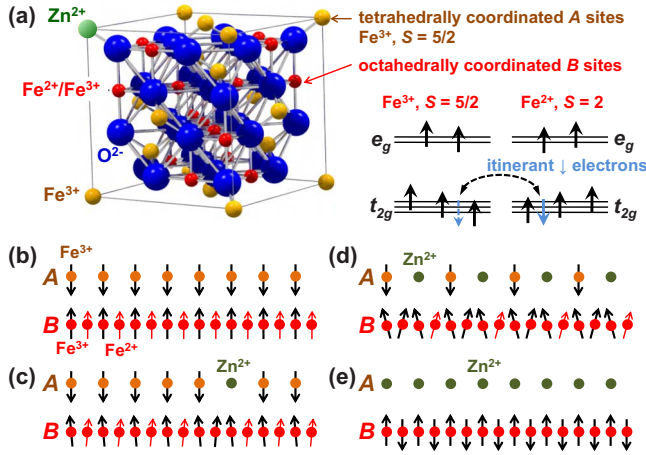


FIG. 1. (Color online) (a) Inverse spinel structure of magnetite with  $\text{Fe}_A^{3+}$  on the tetrahedrally coordinated  $A$  site and mixed-valent  $\text{Fe}_B^{2+}(3d^6, S=2)/\text{Fe}_B^{3+}(3d^5, S=5/2)$  ions on the octahedrally coordinated  $B$  site. Zn substitution replaces  $\text{Fe}_A^{3+}$  on the  $A$  site by nonmagnetic  $\text{Zn}^{2+}(3d^{10}, S=0)$  ions. Also shown is the occupation of the  $\text{Fe}_B^{2+}$  and  $\text{Fe}_B^{3+}$   $3d$  states with  $t_{2g}$  and  $e_g$  symmetry separated by the crystal-field splitting due to the octahedral oxygen surrounding. The  $t_{2g}$  spin-down electron can hop between  $\text{Fe}_B^{2+}$  and  $\text{Fe}_B^{3+}$  ions with its spin coupled antiparallel to the local moment formed by the spin-up electrons owing to Hund's rule coupling. (b)–(e) show the  $A$  and  $B$  sublattice configuration for  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  for (b)  $x=0$ , (c)  $x=1/8$ , (d)  $x=0.5$ , and (e)  $x=1$ .

pling, the spins of these itinerant electrons are antiferromagnetically coupled to the localized spins formed by the  $3d$  spin-up electrons. As pointed out by Néel,<sup>15</sup> in the simplest model ferrimagnetism in  $\text{Fe}_3\text{O}_4$  with high  $T_C$  is obtained without any DE interaction for large  $J_{AB} \gg J_{BB}, J_{AA}$  forcing an antiparallel alignment of the moments on the  $A$  and  $B$  sites [see Fig. 1(b)]. Since the antiparallel  $\text{Fe}_A^{3+}$  and  $\text{Fe}_B^{3+}$  moments compensate each other, a saturation magnetization of  $4\mu_B/\text{f.u.}$  (formula unit) is expected from the remaining  $\text{Fe}_B^{2+}(S=2)$  moments. Later on, the simple Néel model has been extended by Yafet and Kittel.<sup>16</sup> They proposed a more elaborate model in which the  $B$  sublattice is subdivided into two  $\text{Fe}_B^{2+}$  and  $\text{Fe}_B^{3+}$  sublattices. It was shown that on weakening  $J_{AB}$  and strengthening  $J_{BB}$ , the  $B$  site magnetic moments are no longer rigidly parallel to the  $A$  site moments. The stronger  $B$ - $O$ - $B$  SE interaction results in spin canting expressed by a finite Yafet-Kittel angle and thus a reduction in the saturation magnetization. More recent models show that a detailed modeling of the magnetic properties of magnetite is only possible by taking into account the ferromagnetic DE interaction of the  $B$  sublattice competing with the antiferromagnetic SE.<sup>17–19</sup>

There are several possibilities to tailor the magnetic properties of magnetite. First,  $\text{Fe}_A^{3+}$  on the  $A$  site can be replaced by an isovalent nonmagnetic ion. In this way antiferromagnetically coupled moments on the  $A$  sites are removed without affecting the magnetic exchange on the  $B$  sublattices. Hence, an increase in the saturation magnetization is expected at low substitution level. However, upon increasing the  $A$  site substitution the dilution of the  $A$  site moments reduces  $J_{AB}$ , whereas  $J_{BB}$  stays about constant. Then the mo-

ments on the  $A$  and  $B$  site no longer need to be rigidly antiparallel, resulting in a finite Yafet-Kittel angle [see Figs. 1(c) and 1(d)]. This angle increases with increasing substitution, resulting in a reduction in the saturation magnetization. Due to the isovalent substitution the charge carrier density should stay unaffected. However, the hopping between the mixed-valent ( $\text{Fe}_B^{2+}/\text{Fe}_B^{3+}$ ) ions on the  $B$  sublattice is reduced due to the spin canting, resulting in a lower electrical conductivity and reduced DE interaction. To our knowledge a nonmagnetic isovalent  $A$  site substitution in  $\text{Fe}_3\text{O}_4$  has not been reported so far. Most likely this can be attributed to the fact that suitable trivalent ions usually prefer the octahedral coordination on the  $B$  site and thus cannot be substituted solely on the tetrahedral  $A$  site. Second, as done in our work,  $\text{Fe}_A^{3+}$  on the  $A$  site can be replaced by a nonmagnetic divalent ion such as  $\text{Zn}^{2+}(3d^{10}, S=0)$ .<sup>20</sup> It is known that  $\text{Zn}^{2+}$  preferably occupies the tetrahedrally coordinated  $A$  site in the inverse spinel structure.<sup>21</sup> Again some of the antiferromagnetically coupled moments on the  $A$  sites are removed, leading to an initial increase in the saturation magnetization at low Zn substitution.<sup>12,22</sup> However, in the same way as discussed before, a finite Yafet-Kittel angle and, in turn, a reduction in the saturation magnetization are expected when going to larger substitution levels.<sup>22</sup> Moreover, substitution of  $\text{Fe}_A^{3+}$  by  $\text{Zn}^{2+}$  on the  $A$  site also reduces the amount of  $\text{Fe}_B^{2+}$  on the  $B$  site due to charge neutrality. That is, the amount of itinerant charge carriers mediating the DE on the  $B$  sublattice is reduced as shown by photoemission spectroscopy.<sup>13</sup> Thus, with increasing Zn substitution the electrical conductivity is reduced both by a reduction in the density of itinerant charge carriers and their hopping amplitude due to spin canting. Third, Fe vacancies can be introduced by preparing magnetite samples in excess oxygen.<sup>20,23–26</sup> Since Fe vacancies are formally equivalent to the presence of excess of  $\text{O}^{2-}$  ions, charge neutrality again requires a reduced (increased) amount of  $\text{Fe}_B^{2+}(\text{Fe}_B^{3+})$  ions on the  $B$  site. This strengthens antiferromagnetic SE and weakens ferromagnetic DE on the  $B$  sublattice. In turn, this results in a finite Yafet-Kittel angle and a reduced saturation magnetization. Furthermore, a reduced electrical conductivity is expected both by a reduced carrier density and hopping amplitude.

Our brief discussion shows that Fe based magnetic oxides with spinel structure are interesting materials. They not only have high Curie temperature and high spin polarization but also offer various opportunities to tailor their electrical (charge carrier density and electrical conductivity) and magnetic properties (saturation magnetization and Curie temperature). Such tunable ferromagnetic materials are desired for spintronic devices operating at room temperature. For example, tuning the electrical conductivity of ferromagnetic materials with high spin polarization is promising for spin injection devices as one can reduce and deliberately choose the conductivity mismatch between semiconductors and ferromagnetic spin injectors. To this end, recently the growth of epitaxial  $\text{Fe}_3\text{O}_4/\text{ZnO}$  heterostructures has been demonstrated.<sup>27</sup> Here, we report on the growth as well as the structural, magnetic, and magnetotransport properties of epitaxial thin-film samples of  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  with  $x=0, 0.1, 0.33, 0.5, 0.9$  deposited in different oxygen partial pressures. We show that their saturation magnetization and

electrical conductivity can be tuned over a wide range both by Zn substitution and varying oxygen partial pressure during growth. Furthermore, our systematic study provides clear evidence that their electrical conductivity is closely related to the overall magnetization. We also carefully consider the presence of antiphase boundaries (APBs) in the thin-film samples which could affect both their electrical conductivity and their saturation magnetization.<sup>28,29</sup> However, we have clear evidence that APBs do not play a dominant role in this study. In particular, they cannot explain the change in the magnetic and magnetotransport properties on varying the Zn content and the deposition atmosphere. In contrast, these properties can be consistently explained solely by disorder and spin canting on the *B* sublattice, tending to localize the itinerant charge carriers on the *B* sublattice.

## II. THIN-FILM GROWTH

Epitaxial thin films of  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  with  $x \leq 0.9$  and thicknesses between 40 and 60 nm were deposited from stoichiometric targets on single crystalline, (001)- oriented MgO substrates by laser molecular-beam epitaxy (laser MBE).<sup>30</sup> The exact film thickness was determined by x-ray reflectometry. Both bulk  $\text{Fe}_3\text{O}_4$  having an inverse spinel structure (*Fd3m*) and MgO (*Fm3m*) are cubic with lattice constants of  $a_{\text{Fe}_3\text{O}_4} = 8.394$  Å (Ref. 31) and  $a_{\text{MgO}} = 4.212$  Å, respectively, resulting in a small lattice mismatch of  $(a_{\text{Fe}_3\text{O}_4} - 2a_{\text{MgO}})/2a_{\text{MgO}} = -0.4\%$ . The energy density of the KrF excimer laser ( $\lambda = 248$  nm) at the target was  $3.1$  J/cm<sup>2</sup> and the laser repetition rate was 2 Hz. At the same total pressure of  $3.7 \times 10^{-3}$  mbar, two sets of samples were deposited in two different growth atmospheres. In pure Ar, thin films with  $x = 0, 0.1, 0.5,$  and  $0.9$  were grown at a substrate temperature of  $320$  °C. In an Ar/O<sub>2</sub> (99:1) mixture, thin films with  $x = 0.5$  were deposited at  $320$  °C and with  $x = 0, 0.33,$  and  $0.9$  at  $400$  °C. The growth process was monitored *in situ* by reflection high energy electron diffraction (RHEED).<sup>32</sup> We observed four RHEED intensity oscillations per unit cell, indicating a block-by-block growth mode with four charge neutral blocks. This is already known for  $\text{Fe}_3\text{O}_4$  (Refs. 33 and 34) and also holds when substituting Zn up to  $\text{Zn}_{0.9}\text{Fe}_{2.1}\text{O}_4$ . A more detailed description of the thin-film deposition for  $\text{Fe}_3\text{O}_4$  on MgO is given elsewhere.<sup>33,35</sup>

## III. STRUCTURAL PROPERTIES

The structural properties of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films were analyzed by high-resolution x-ray diffractometry using a Bruker AXS D8 Discover four-circle diffractometer. Our detailed analysis reveals a very high epitaxial quality of all thin-film samples. In the  $[00\ell]$  direction,  $\omega$ - $2\theta$  scans display no impurity phases, in particular from other iron or zinc oxides. We note that we may not be able to distinguish between  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite) as they both share the same inverse spinel lattice.<sup>36</sup> It is known that excess oxygen results in the formation of Fe vacancies and in the extreme case in the formation of  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  solid solutions.<sup>24,25</sup> The  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  thermodynamic equilibrium line was determined to  $\log(p_{\text{O}_2}/p_0) = -\frac{24634}{T} \text{ K}$  with  $p_0 = 9.1 \times 10^{13}$  bar.<sup>24</sup>

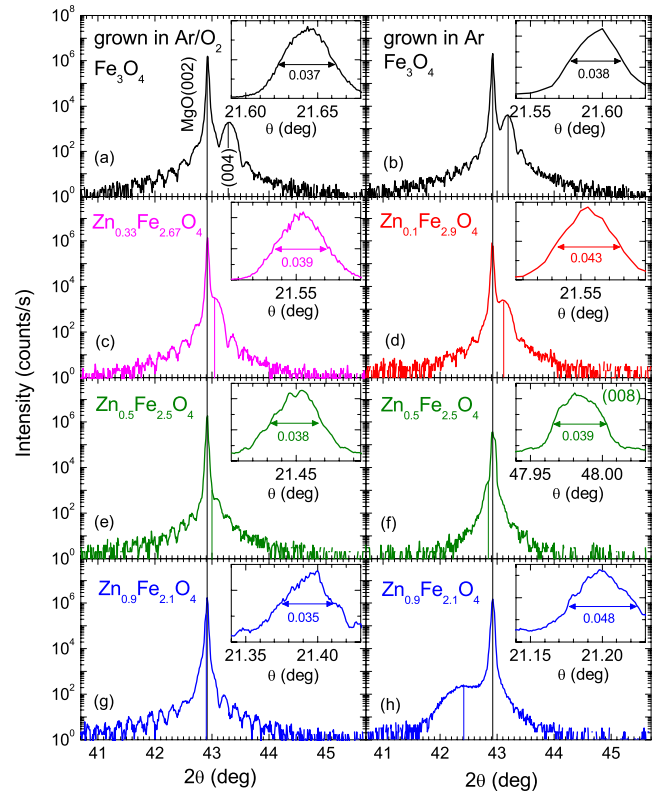


FIG. 2. (Color online) X-ray diffraction diagrams ( $\omega$ - $2\theta$  scans) of the out-of-plane reflections from  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  thin films deposited in different growth atmospheres of Ar/O<sub>2</sub> (99:1) (left panels) and pure Ar (right panels). With increasing  $x$  the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  (004) reflection shifts across the (002) reflection of the MgO substrates marked by the vertical line. The insets show the corresponding rocking curves of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  (004) reflection, except for (f) where the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  (008) reflection is displayed.

Unfortunately, both calculations and experimental studies of phase and point defect equilibria always apply to thermal equilibrium situations which certainly are not appropriate for the laser-MBE growth process occurring far from equilibrium. Nevertheless, the high energy of the particles in the laser plume can be associated with an effective growth temperature much larger than the substrate temperature favoring the stability of  $\text{Fe}_3\text{O}_4$ .<sup>24,25</sup> Therefore, for the deposition temperature and oxygen partial pressure used in our experiments we are sufficiently far away from the  $\text{Fe}_3\text{O}_4/\gamma\text{-Fe}_2\text{O}_3$  equilibrium line.<sup>37,38</sup>

As shown by Fig. 2, the (004) reflection from  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  can be clearly observed together with satellites due to Laue oscillations. These oscillations demonstrate that the thin films are coherently strained and have a small surface roughness. The rocking curves of the (004) or (008) reflections (insets of Fig. 2) show a full width at half maximum (FWHM) of  $\Delta\omega \leq 0.05^\circ$ . This demonstrates the excellent structural quality of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  thin-film samples with very low mosaic spread, comparable to epitaxial  $\text{Fe}_3\text{O}_4$  films.<sup>33,35</sup> In the  $\omega$ - $2\theta$  scan, the (004) reflection from  $\text{Fe}_3\text{O}_4$  is positioned at a slightly larger angle than the (002) reflection from the MgO substrate [see Figs. 2(a) and 2(b)], indicating  $c_{\text{Fe}_3\text{O}_4} < 2c_{\text{MgO}}$ . With increasing Zn concentration, the

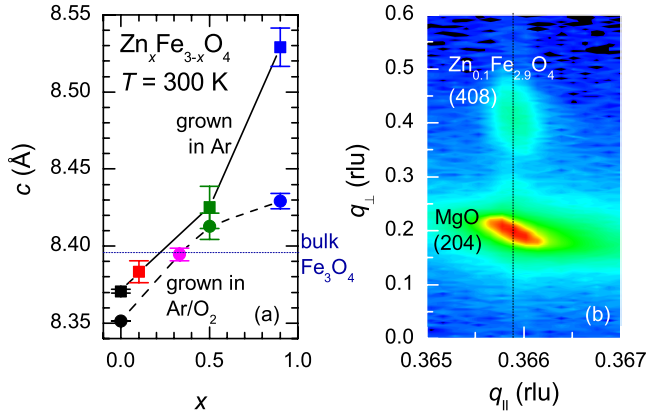


FIG. 3. (Color online) (a) Change in the  $c$ -axis lattice parameter of  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films grown on  $\text{MgO}(001)$  in pure Ar atmosphere (squares) and an  $\text{Ar}/\text{O}_2$  mixture (circles) with Zn content  $x$ . The bulk  $c$ -axis lattice constant of  $\text{Fe}_3\text{O}_4$  is marked by the dashed horizontal line. (b) Reciprocal space map around the (204) reflection of the  $\text{MgO}(001)$  substrate. The (408) reflection from the  $\text{Zn}_{0.1}\text{Fe}_{2.9}\text{O}_4$  film appears at the same in-plane scattering vector  $q_{\parallel}$  marked by the dashed vertical line.

(004) reflection moves to lower angles and crosses the  $\text{MgO}(002)$  reflection at  $x=0.5$  [see Figs. 2(e) and 2(f)]. At  $x=0.9$ , the position of the (004) reflection from the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  film is shifted to an angle below the (002) reflection from  $\text{MgO}$  [see Figs. 2(g) and 2(h)]. This corresponds to  $c_{\text{Zn}_{0.9}\text{Fe}_{2.1}\text{O}_4} > 2c_{\text{MgO}}$ .

The absolute value and variation in the  $c$ -axis lattice parameter of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films with Zn content  $x$  are related to two effects, namely, the epitaxial coherency strain and the larger ionic radius of tetrahedrally coordinated  $\text{Zn}^{2+}$  of 0.6 Å compared to the radius of only 0.49 Å of  $\text{Fe}^{3+}$  on the tetrahedrally coordinated  $A$  site.<sup>12</sup> First, for  $x=0$  the lattice mismatch of  $-0.4\%$  between  $\text{Fe}_3\text{O}_4$  film and  $\text{MgO}$  substrate leads to a tensile in-plane epitaxial coherency strain and, in turn, to a slight reduction in the  $c$ -axis lattice parameter of the  $\text{Fe}_3\text{O}_4$  film below the bulk value [cf. Fig. 3(a)]. The fully coherent growth of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  thin films is demonstrated by reciprocal space maps around the (204) reflection of the  $\text{MgO}$  substrate [see Fig. 3(b)]. The (408) reflection of the film is located exactly at the same in-plane scattering vector  $q_{\parallel}$  as the (204) reflection of the substrate. This clearly demonstrates that the in-plane lattice constant of the film perfectly matches twice the one of the  $\text{MgO}$  substrate. Second, for  $x > 0$  the unit cell volume of  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  is expected to increase about linearly with increasing  $x$  due to the larger ionic radius of  $\text{Zn}^{2+}$ . However, since the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films grow coherently on the  $\text{MgO}(001)$  substrate without any relaxation up to the maximal thickness of 60 nm studied in our experiments, the in-plane lattice constant stays unchanged. Only the out-of-plane lattice constant is found to vary with increasing  $x$ . Depending on whether the in-plane strain is tensile or compressive, a reduction or expansion of the unit cell in the  $[00\ell]$  direction, respectively, is found [Fig. 3(a)], resulting in a tetragonal distortion of the cubic lattice. The  $c$ -axis parameter increases from a value below ( $x=0$ , tensile strain) to a value above the bulk value ( $x \geq 0.3$ , compressive

strain). The expansion of the out-of-plane lattice parameter with increasing  $x$  has been reported also for (111)-oriented films grown on  $\text{Al}_2\text{O}_3(0001)$  substrates.<sup>12</sup> However, we note that those films are relaxed due to the very large lattice mismatch of 8% between film and substrate. Therefore, both results cannot be compared directly.

An interesting result shown in Fig. 3 is the fact that the  $c$ -axis lattice parameters of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films grown in pure Ar atmosphere are larger than those of the films grown in an  $\text{Ar}/\text{O}_2$  mixture and also show a slightly weaker increase with Zn content in the range  $0 \leq x \leq 0.5$ . This most likely is caused by the formation of Fe vacancies when growing the films in finite oxygen partial pressure.<sup>20,23–26</sup> The presence of Fe vacancies can be viewed as an internal negative pressure effect leading to a reduced cell volume. The weaker increase in the  $c$ -axis parameter for the films grown in  $\text{Ar}/\text{O}_2$  suggests a partial compensation of the Fe vacancies by Zn substitution. This is in agreement with the transport data discussed below. We note, however, that this result has to be considered with some care. The problem is that the close vicinity of film and substrate reflections in the  $\omega-2\theta$  scans does not allow an unambiguous derivation of the film  $c$ -axis parameter with small error bars.

In summary, the structural analysis demonstrates that our  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4(001)$  thin films are coherently strained and show a very small mosaic spread. Zn substitution results in an increase in the unit cell volume, causing the in-plane epitaxial strain to change from tensile to compressive upon increasing the Zn content  $x$ . Growth in excess oxygen results in a reduction in the unit cell volume most likely due to the formation of Fe vacancies. The latter most likely is partially compensated by additional Zn substitution.

#### IV. MAGNETOTRANSPORT PROPERTIES

For magnetite the electrical conduction above the Verwey transition is believed to be determined by the hopping of the spin-down electrons between the mixed-valent  $\text{Fe}_B^{2+}$  and  $\text{Fe}_B^{3+}$  ions on the  $B$  sublattice. From the hopping amplitude  $t \sim 0.1$  eV an electron conduction bandwidth  $D \sim 1$  eV is expected. However, experimental data cannot be explained within a simple band theory. They can be better ascribed to some thermally activated motion of charge carriers. The reason is that the bare hopping amplitude and bandwidth is strongly reduced due to the translation of a polaronic lattice deformation associated with electron motion.<sup>39,40</sup> If the reduced bandwidth is smaller than the energy of polarization phonons (typically 70 meV in magnetite), small polaron hopping is expected.<sup>41</sup> We note that the hopping takes place between  $\text{Fe}_B^{2+}$  and  $\text{Fe}_B^{3+}$  ions on the  $B$  sublattice. Below the Curie temperature, the spins of these ions are aligned parallel in the ideal case. However, as discussed above in reality there is some spin canting on the  $B$  sublattice. This has to be taken into account by an appropriate spin correlation factor<sup>42</sup> leading to a spin-dependent part of the activation energy. Since the spin alignment is improved by applying a magnetic field, this spin-dependent part of the activation energy can be reduced by the external field resulting in a large negative magnetoresistance as shown below.

For magnetotransport measurements, the films were patterned into typically 45- $\mu\text{m}$ -wide and 350- $\mu\text{m}$ -long Hall bars directed in the  $\langle 010 \rangle$  direction by photolithography and Ar ion beam milling.<sup>43</sup> The longitudinal resistivity  $\rho_{xx}$  has been measured as a function of temperature  $T$  and applied magnetic field  $H$  using a standard four-probe technique. The films with  $x=0.9$  were found to be insulating and are not further discussed in the following. We note that measurements of the anomalous and the ordinary Hall effect have been reported previously<sup>35,44</sup> and are not discussed here.

### A. Temperature dependence of resistivity

The  $\rho_{xx}(T)$  curves of representative samples with  $x \leq 0.5$  are shown in Fig. 4. Despite a similar shape of all  $\rho_{xx}(T)$  curves, it is evident that the absolute magnitude of  $\rho_{xx}$  sensitively depends on the Zn substitution  $x$  and the growth atmosphere. For both samples sets grown in pure Ar atmosphere and an Ar/O<sub>2</sub> (99:1) mixture,  $\rho_{xx}(T)$  increases by more than 2 orders of magnitude upon decreasing  $T$  from 375 down to 90 K. Plotting  $\log(\rho_{xx})$  on a reciprocal  $T$  scale as shown in Fig. 4(b) results in linear curves over a wide temperature range except for the  $x=0$  and  $x=0.1$  samples grown in pure Ar atmosphere. The kink in  $\rho_{xx}(T)$  of the  $x=0$  sample results from the Verwey transition discussed below. Figure 4(b) suggests that the longitudinal resistivity of the samples with  $x \geq 0.1$  follows a simple activated behavior  $\rho_{xx}(T) \propto \exp(E_a/k_B T)$  with the Boltzmann constant  $k_B = 1.38 \times 10^{-23}$  J/K and activation energies  $E_a$  ranging between 61 and 84 meV. However, an unambiguous determination of the detailed transport process is difficult. As indicated by Fig. 4(c), the  $\rho_{xx}(T)$  data also can be equally well fitted by small polaron hopping,<sup>41,45,46</sup>  $\rho_{xx}(T) \propto T \exp(E_{\text{pol}}/k_B T)$ , with the potential barrier for polaron hopping,  $E_{\text{pol}}$ , ranging between 64 and 95 meV. Actually, small polaron hopping yields a slightly better fit for the samples grown in pure Ar atmosphere, whereas the simple activated transport better fits the transport data of the samples grown in an Ar/O<sub>2</sub> mixture. The derived activation energies are typical for zinc ferrites.<sup>20,37,46–48</sup> We also note that a similar transport behavior with similar activation energies is reported for the mixed-valent manganites, where charge transport is determined by the hopping between mixed-valent  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions.<sup>49–52</sup>

We next discuss the observability of the Verwey<sup>53</sup> transition in the measured  $\rho_{xx}(T)$  curves. In bulk material, this metal-insulator transition, associated with a cubic to monoclinic structural phase transition, occurs at  $T_V = 123$  K and in the classic picture is argued to arise from a charge ordering of the  $\text{Fe}_B^{2+}$  and  $\text{Fe}_B^{3+}$  on the  $B$  sublattice in a process reminiscent to Wigner crystallization.<sup>54</sup> Whereas at  $T > T_V$  the extra electrons from  $\text{Fe}_B^{2+}$  ions can hop to neighboring  $\text{Fe}_B^{3+}$  ions on the corner sharing tetrahedral network on the  $B$  sublattice, giving rise to electrical conduction, this process is frozen in at  $T < T_V$  due to Coulomb repulsion.<sup>55</sup> However, more recently it became evident that also elastic and orbital interactions play a significant role. This leads to a renewed controversial discussion of the nature of the Verwey transition.<sup>18,56–59</sup> It is evident from Fig. 4 that a pronounced change in the  $\rho_{xx}(T)$  curves due to the Verwey transition is

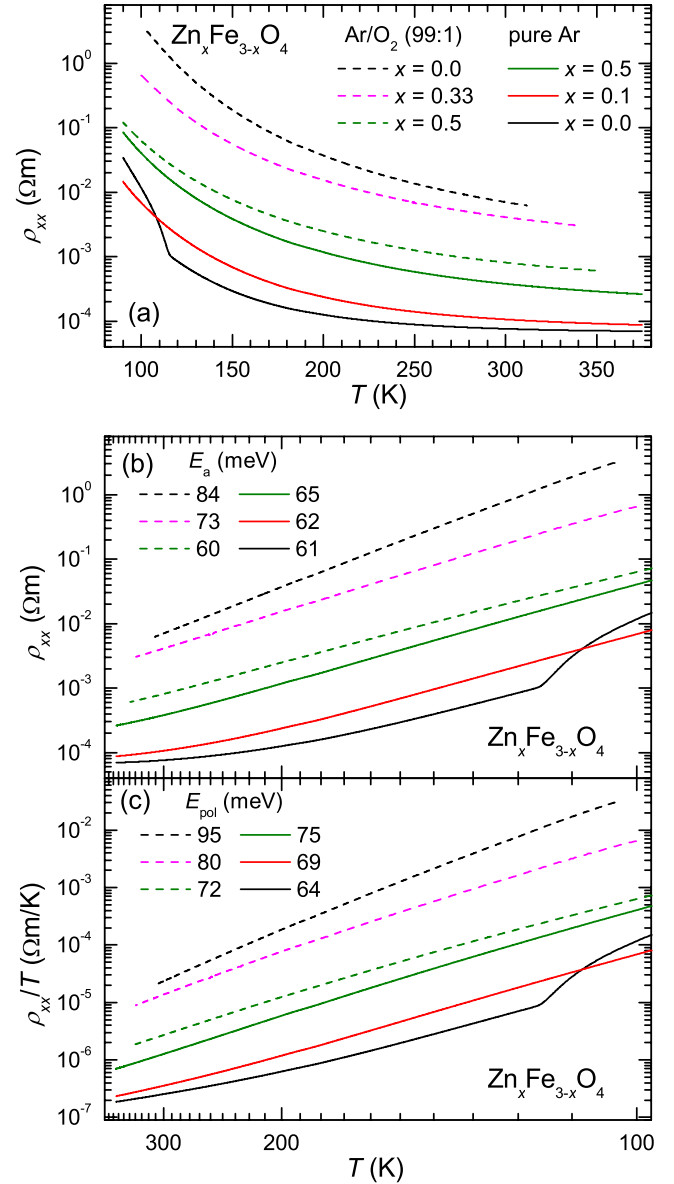


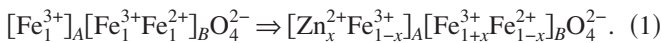
FIG. 4. (Color online) (a) Longitudinal resistivity  $\rho_{xx}$  as a function of temperature  $T$  for epitaxial  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  thin films, grown in pure Ar atmosphere (solid lines) or an Ar/O<sub>2</sub> (99:1) mixture (dashed lines) on MgO(001) substrates. In (b) and (c)  $\rho_{xx}$  and  $\rho_{xx}/T$  of the same samples are plotted versus a reciprocal temperature scale. Fitting the linear parts of the curves in (b) and (c) by  $\rho_{xx} \propto \exp(E_a/k_B T)$  and  $\rho_{xx}/T \propto \exp(E_{\text{pol}}/k_B T)$ , respectively, gives the listed activation energies  $E_a$  and  $E_{\text{pol}}$ .

observed only for the  $\text{Fe}_3\text{O}_4$  film ( $x=0$ ) grown in pure Ar atmosphere. For this film there is no jump but a clear kink in the  $\rho_{xx}(T)$  curve at a slightly reduced temperature of about 115 K. For all other samples no clear signature of the Verwey transition is observable. This can be understood in a straightforward way. As discussed above, both substitution of Zn and introduction of Fe vacancies by growing the films in finite oxygen partial pressure result in deviations from equal numbers of  $\text{Fe}_B^{2+}$  and  $\text{Fe}_B^{3+}$  on the  $B$  sublattice. This can be viewed as disorder on the  $B$  sublattice, tending to smear out the Verwey transition. The fact that the observability of the

Verwey transition seems to sensitively depend on deviations from perfect stoichiometry already has been reported in literature<sup>20,23,25,26,28</sup> and is further supported by our results. The other way round, we can argue that the absence of any clear signature of the Verwey transition for the  $\text{Fe}_3\text{O}_4$  films substituted by Zn or grown in finite oxygen partial pressure provides evidence for the presence of an unequal number of  $\text{Fe}_B^{2+}$  and  $\text{Fe}_B^{3+}$  ions on the  $B$  sublattice.

We next discuss the  $\rho_{xx}$  values of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  ( $0 \leq x \leq 0.5$ ) films grown in pure Ar atmosphere. The strong increase in resistivity with decreasing  $T$  can be understood in terms of a thermally activated hopping type transport mechanism of the itinerant electrons on the  $B$  sublattice. For  $x=0$ , the room-temperature  $\rho_{xx}$  value ( $7.6 \times 10^{-5} \Omega \text{ m}$ ) corresponds well with literature data for  $\text{Fe}_3\text{O}_4$  thin films<sup>35</sup> or single crystals.<sup>60</sup> In this context, we note that the presence of antiphase boundaries (APBs) in  $\text{Fe}_3\text{O}_4$  thin-film samples may have a significant influence on the measured longitudinal resistivity.<sup>61</sup> However, this is not the case for our samples. First, our  $\text{Fe}_3\text{O}_4$  thin film grown in Ar atmosphere has a room-temperature resistivity value close to that of  $\text{Fe}_3\text{O}_4$  single crystals ( $6.2 \times 10^{-5} \Omega \text{ m}$ ) considered as APB free.<sup>60</sup> Second, comparing the resistivity value to those of  $\text{Fe}_3\text{O}_4$  thin films with different APB density, we estimate that the volume fraction of the APB phase in our thin film is less than 20%.<sup>61</sup> Third, it is known that the formation and the density of APBs sensitively depend on the used substrates<sup>62</sup> or the film thickness.<sup>61</sup> However, in our study always the same substrate and film thickness is used. Since also Zn substitution is not expected to severely affect the APB density, we can safely assume that all samples grown in the same atmosphere have a similar APB density.

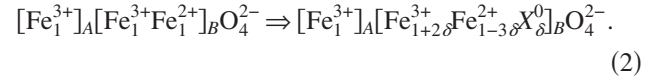
With increasing  $x$ , as discussed in Sec. I,  $\text{Zn}^{2+}$  preferably occupies the tetrahedrally coordinated  $A$  site in the inverse spinel structure.<sup>21</sup> Hence, the substitution of  $\text{Fe}_A^{3+}$  by  $\text{Zn}^{2+}$  reduces the amount of  $\text{Fe}_B^{2+}$  as



That is, the density of itinerant electrons on the  $B$  sublattice is reduced, resulting in an increase in the resistivity with increasing  $x$ . This is in perfect agreement with our observation and literature data.<sup>12,13</sup> We note however, that the increase in resistivity is not only caused by a reduction in the carrier density but also by several other effects. First, deviations from the 1:1 balance of  $\text{Fe}_B^{2+}$  and  $\text{Fe}_B^{3+}$  on the  $B$  sublattice cause disorder, tending to localize the itinerant charge carriers. Second, Zn substitution dilutes the  $A$  sublattice, thereby weakening the antiferromagnetic exchange  $J_{AB}$  between the  $A$  and  $B$  sublattices. As discussed above, this results in spin canting on the  $B$  sublattice, reducing the hopping amplitude. This amplitude is maximum for a parallel alignment of the local moments due to strong antiparallel Hund's rule coupling of the spins of the itinerant electrons. Both effects are expected to result in an increase in the activation energy for the hopping transport with increasing  $x$  in agreement with our observations.

The  $\rho_{xx}(T)$  curves of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  ( $0 \leq x \leq 0.5$ ) films grown in an Ar/ $\text{O}_2$  mixture show a similar overall temperature dependence but with resistivity values that are much

higher than those measured for the films grown in pure Ar atmosphere. Furthermore, the resistivity values decrease with increasing  $x$  in contrast to what is observed for the films grown in Ar. We first discuss the origin of the much higher resistivity value ( $\rho_{xx}=7 \times 10^{-3} \Omega \text{ m}$  at 300 K) of the  $\text{Fe}_3\text{O}_4$  ( $x=0$ ) film grown in finite oxygen partial pressure compared to that ( $\rho_{xx}=7.6 \times 10^{-5} \Omega \text{ m}$  at 300 K) of the film grown in pure Ar. Since growth of magnetite in excess oxygen is known to create Fe vacancies  $X^0$ ,<sup>23-26</sup> equivalent to two (three) missing electrons per  $\text{Fe}^{2+}$  ( $\text{Fe}^{3+}$ ) vacancy, the requirement of charge neutrality shifts the 1:1 balance between  $\text{Fe}_B^{2+}$  and  $\text{Fe}_B^{3+}$  toward  $\text{Fe}_B^{3+}$  as



Evidently, Fe vacancies in the same way as Zn substitution result in a reduction in  $\text{Fe}_B^{2+}$ . Hence, the density of itinerant electrons on the  $B$  sublattice decreases and, in turn, the resistivity increases with increasing  $\delta$ . This is exactly what is observed in our experiments and reported in literature.<sup>20,63</sup> Actually, for  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  ( $0 \leq x \leq 0.3$ ) single crystals Wang *et al.*<sup>20</sup> reported a compositional correspondence  $x=3\delta$  regarding the measured resistivity data. Again, with the same arguments given above for the films grown in pure Ar, a reliable evaluation of the various mechanisms (localization and spin canting) responsible for the increase in resistivity is not possible. We also note that according to Eq. (2) growth in high oxygen partial pressure (not the case in our experiments) may lead to the formation of the cubic  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite) phase in the extreme case of  $\delta=1/3$ .<sup>64</sup>

Zn substitution in our magnetite films grown in an Ar/ $\text{O}_2$  mixture results in a decrease in resistivity in contrast to what is observed for the films grown in pure Ar atmosphere. On first sight, this is astonishing and seems to be in conflict with the above discussion since  $\text{Zn}^{2+}$  again preferably occupies the tetrahedrally coordinated  $A$  lattice sites,<sup>21</sup> substituting  $\text{Fe}^{3+}$  and thereby reducing carrier density. That is, one would expect an increase in resistivity with increasing  $x$ . However, since Zn substitution also results in an increase of the unit cell volume due to the larger ionic radius of  $\text{Zn}^{2+}$  compared to  $\text{Fe}^{3+}$ , it is expected that Zn substitution removes part of the Fe vacancies. This is intuitive since now Fe can be more easily incorporated into the expanded lattice. Then, it is expected that  $\text{Zn}^{2+}$  does not only remove an electron by substituting  $\text{Fe}_A^{3+}$  on an  $A$  site but also adds two/three electrons by removing a vacancy on a  $\text{Fe}_B^{2+}/\text{Fe}_B^{3+}$  site. That is, by Zn substitution also  $X^0$  is replaced by  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$ . Evidently, in total this leads to an effective increase in the carrier density with increasing  $x$  in agreement with our experimental data in the range of up to  $x=0.5$ . The partial removal of the Fe vacancies by Zn substitution is in agreement with the  $x$ -ray data of Fig. 3(a).

In summary, the  $\rho_{xx}(T)$  curves of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films grown under different oxygen partial pressure show a similar shape, originating from a hopping-type transport mechanism but strongly differing absolute resistivity values. These differences can be consistently explained by the change in the itinerant charge carrier density on the  $B$  sublattice and their

hopping amplitude by either Zn substitution or the generation of Fe vacancies due to growth at finite oxygen partial pressure. However, applying both Zn substitution and excess oxygen results in an increase in the carrier density as Zn substitution is removing part of the Fe vacancies generated by excess oxygen. It would be interesting to directly check the change in the carrier density by measurements of the Hall effect. However, we cannot unambiguously separate the small ordinary from the large anomalous Hall contribution, and any attempt to do so would result in large errors of the derived carrier density.<sup>44</sup>

We note that the observed dependence of the resistivities on the Zn substitution levels  $x$  cannot be simply explained by the assumption of different APB densities in the different thin-film samples. It is unlikely that with increasing  $x$  the APB density increases for samples of the same thickness when grown in Ar atmosphere while it decreases for those prepared in the Ar/O<sub>2</sub> mixture. Moreover, the samples show a universal scaling relation of the anomalous Hall conductivity with the longitudinal conductivity indicating a negligibly small APB resistivity as already pointed out earlier.<sup>44</sup>

### B. Magnetoresistance

In this subsection we address the magnetoresistance (MR) of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films. The MR effect,  $\text{MR}_{xx} = [\rho_{xx}(H) - \rho_{xx}(0)]/\rho_{xx}(0)$  is shown in Fig. 5(a) at several temperatures for the  $x=0.1$  samples grown in pure Ar. As shown in Fig. 5(b), very similar  $\text{MR}_{xx}(H)$  curves with similar absolute values of  $\text{MR}_{xx}$  at room temperature are found for the other samples, although the absolute values of their resistivities vary by more than 2 orders of magnitude (cf. Fig. 4). This interesting observation can be consistently explained in the framework of thermally activated hopping of the itinerant electrons on the  $B$  sublattice. Due to the strong on-site Hund's rule coupling, the spins of the itinerant spin-down electrons are coupled antiparallel to the localized spins formed by the spin-up electrons. Therefore, the activation energy for the hopping process is given by the sum of a spin-independent energy ( $E_a$  or  $E_{\text{pol}}$ ) and a spin-dependent contribution  $E_s$ . The latter depends on the spin canting of the local moments on the  $B$  sublattice and disappears for a perfect parallel alignment. Since in the presence of a finite canting of the local moments an applied magnetic field tends to improve the alignment, a magnetic-field-dependent total activation energy  $E(H) = E_{a,\text{pol}} + E_s(H)$  is obtained. Then, no matter whether the transport is by thermally activated hopping,  $\rho_{xx} = \rho_{0,a} \exp[E(H)/k_B T]$ , or small polaron hopping,  $\rho_{xx}/T = \rho_{0,\text{pol}} \exp[E(H)/k_B T]$ , the MR effect is obtained as

$$\text{MR}_{xx} = \frac{\exp\left(\frac{E_s(H)}{k_B T}\right) - \exp\left(\frac{E_s(0)}{k_B T}\right)}{\exp\left(\frac{E_s(0)}{k_B T}\right)} = \exp\left(\frac{-\Delta E_s(H)}{k_B T}\right) - 1, \quad (3)$$

with  $\Delta E_s(H) = E_s(0) - E_s(H)$ . Evidently, with the assumptions made,  $\text{MR}_{xx}(H)$  is independent of the magnitude of the prefactors ( $\rho_{0,a}$  or  $\rho_{0,\text{pol}}$ ) and the activation energies ( $E_a$  or  $E_{\text{pol}}$ ),

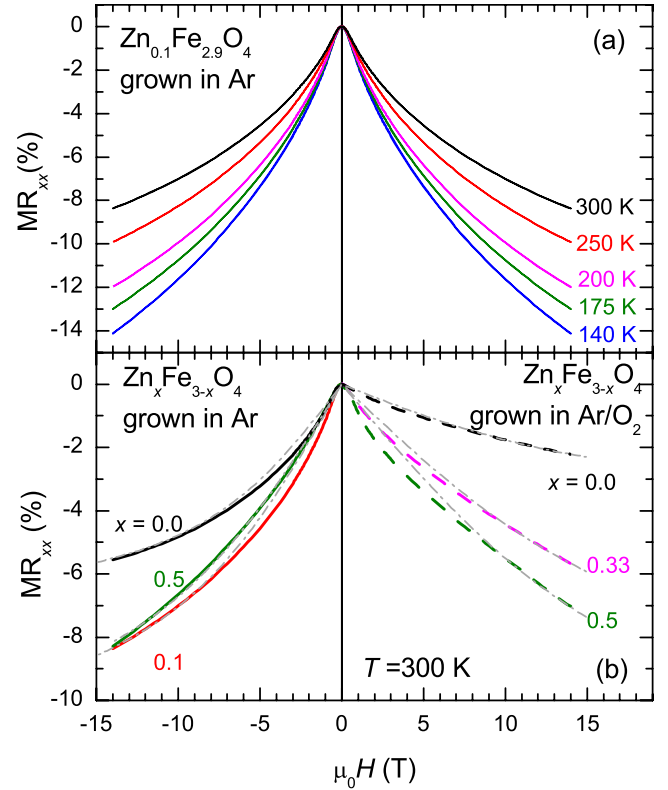


FIG. 5. (Color online) (a)  $\text{MR}_{xx}$  plotted versus the magnetic field  $H$  applied perpendicular to the film plane at different temperatures for  $\text{Zn}_{0.1}\text{Fe}_{2.9}\text{O}_4$  thin films grown in pure Ar atmosphere. (b)  $\text{MR}_{xx}(H)$  curves measured at 300 K for different  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  grown in pure Ar atmosphere (left) or an Ar/O<sub>2</sub> mixture (right). The dash-dotted gray lines are fits to the data according to Eq. (6).

which may strongly vary for samples with different  $x$  and grown in different atmosphere. Moreover, similar  $\text{MR}_{xx}(H)$  curves with comparable absolute values are obtained if the magnetic-field-induced change  $\Delta E_s(H)$  in the spin-dependent part of the activation energy is about the same for all samples.

Since the transport in  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  by hopping of the  $t_{2g}$  spin-down electrons between mixed-valent  $\text{Fe}_B^{2+}/\text{Fe}_B^{3+}$  ions is equivalent to the hopping of the  $e_g$  electrons between mixed-valent  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ions in the doped manganites, we can adopt models developed for the MR effect in the perovskite manganites.<sup>65–67</sup> According to these models the magnetic-field-dependent change in the activation energy for hopping between two lattice sites  $i$  and  $j$  can be expressed as

$$\Delta E_s(H) = \alpha(\langle \mathbf{m}_i \cdot \mathbf{m}_j \rangle_H - \langle \mathbf{m}_i \cdot \mathbf{m}_j \rangle_{H=0}), \quad (4)$$

where  $\mathbf{m}_i$  and  $\mathbf{m}_j$  are the local moments on the lattice sites  $i$  and  $j$ ,  $\langle \dots \rangle_{H=0}$  and  $\langle \dots \rangle_H$  denote the sample average at zero and finite magnetic fields, respectively, and  $\alpha$  is a constant that may depend on temperature. The local moments  $\mathbf{m}_i$  and  $\mathbf{m}_j$  can be associated either with the localized spins of the individual Fe ions or the moments of small spin clusters. Note that these spin clusters also can be considered as spin polarons, that is, itinerant electrons dressed by a small cloud of parallel aligned localized spins. Evidently,  $\Delta E_s = 0$  is inde-

pendent of  $H$  if the local moments are already perfectly aligned in zero magnetic field (ideal ferromagnet). In this case, no MR effect is expected. However, if there is a finite canting of the neighboring moments, applying a magnetic field results in a reduction in this spin canting and thereby in  $\Delta E_s > 0$ . According to Eq. (3) this results in a finite negative MR effect with a magnitude determined by the value of  $\Delta E_s/k_B T$ . The magnetic field dependence of  $\Delta E_s$  can be estimated by keeping in mind that in the ferromagnetic state both the molecular field and the applied magnetic field support a parallel alignment of the local moments. Since the molecular field is usually much larger than the applied field, the deviations of the directions of the local moments from the average direction are small. In this case  $\Delta E_s(H)$  is found to follow the Brillouin function  $\mathfrak{B}$  giving<sup>65–67</sup>

$$\Delta E_s(H) = \beta \mathfrak{B} \left( \frac{\mu_{\text{eff}} \mu_0 H}{k_B T} \right), \quad (5)$$

with the vacuum permeability  $\mu_0 = 4\pi \times 10^{-7}$  Vs/Am. Here,  $\mu_{\text{eff}}$  is the average value of the local moments and  $\beta$  is a constant, which may show a weak temperature dependence. Assuming  $\Delta E_s \ll k_B T$ , what certainly is a reasonable assumption at room temperature we can approximate Eq. (3) by

$$\text{MR}_{xx} \approx -\beta \frac{\mathfrak{B} \left( \frac{\mu_{\text{eff}} \mu_0 H}{k_B T} \right)}{k_B T}. \quad (6)$$

This shows that the magnetic field dependence of the MR effect measured at constant temperature should follow the Brillouin function. As shown in Fig. 5(b), this is indeed the case. The data of all samples can be well fitted by Eq. (6). Fitting the data gives the  $\mu_{\text{eff}}$  values of the local moments. They range between 70 to 120  $\mu_B$  and 60 to 70  $\mu_B$ , corresponding to about 18 to 30 and 15 to 18  $\text{Fe}^{2+}$  ions, for the samples grown in pure Ar and  $\text{Ar}/\text{O}_2$  mixture, respectively. Here,  $\mu_B$  is Bohr's magneton. Evidently, the derived moments are larger than the localized spins of the individual Fe ions. They can be considered as the moments of small ferromagnetic clusters with perfectly parallel spins in which the electrons can move freely but with small misalignment between neighboring clusters. Since there are eight  $\text{Fe}^{2+}$  ions per unit cell, their size ranges between about two and four unit cells. We also note that Eq. (6) does not only describe the magnetic field dependence of the MR effect but also nicely explains the decrease in the MR effect with increasing temperature.

In summary, the MR effect of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films in the same way as the  $\rho_{xx}(T)$  data can be well described within a model based on thermally activated hopping of itinerant charge carriers or small polarons between the mixed-valent  $\text{Fe}_B^{2+}/\text{Fe}_B^{3+}$  ions on the  $B$  sublattice. The activation energy contains a magnetic-field-dependent part, which depends on the misalignment of the neighboring spin moments. Within this model,  $\text{MR}_{xx} \propto -\mathfrak{B}(\text{const. } H/T)$  is expected in good agreement with the experimental data. In particular, the similar  $\text{MR}_{xx}(H)$  curves for samples with strongly different  $\rho_{xx}$  values and the decrease in the MR effect with increasing temperature are nicely reproduced.

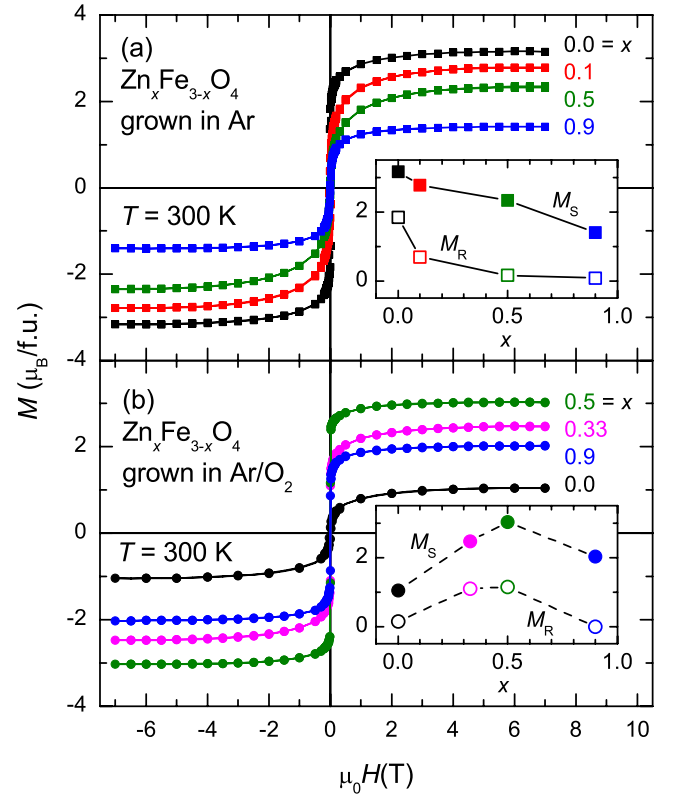


FIG. 6. (Color online) Room-temperature magnetization  $M$  versus magnetic field  $H$  applied in the film plane for  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  thin films grown in (a) pure Ar atmosphere and in (b)  $\text{Ar}/\text{O}_2$  (99:1) mixture. The insets show the saturation magnetization  $M_S$  (full symbols) and the remanence  $M_R$  (open symbols) in units of  $\mu_B/\text{f.u.}$  as a function of the Zn substitution level  $x$ . The lines are guides to the eyes.

## V. MAGNETIC PROPERTIES

We have seen that Zn substitution and the creation of Fe vacancies in magnetite result in changes in the carrier density and hopping amplitudes of the itinerant charge carriers on the  $B$  sublattice. Following our discussion in Sec. I, this is expected to have significant influence on the magnetic properties. Therefore, we also systematically analyzed the magnetic properties of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films. The magnetic characterization was performed with the unpatterned films using superconducting quantum interference device (SQUID) magnetometry with magnetic fields  $\mu_0 H$  up to 7 T applied in the film plane. At room temperature, the  $M(H)$  loops show ferromagnetic behavior for all samples (Fig. 6). However, the measured saturation magnetization  $M_S$ , as well as the remanent magnetization  $M_R$  and coercive field, was found to strongly depend on both the Zn substitution level  $x$  and the growth atmosphere.

We start our discussion with the stoichiometric  $\text{Fe}_3\text{O}_4$  film grown in pure Ar atmosphere, serving as a reference. Figure 6(a) shows that for this film the highest values for the room-temperature saturation magnetization ( $M_S = 3.16 \mu_B/\text{f.u.}$ ) and remanence ( $M_R = 1.83 \mu_B/\text{f.u.}$ ) are obtained. We note that we do not obtain the theoretically expected value of  $M_S = 4 \mu_B/\text{f.u.}$  This is typical for thin-film samples due to



the presence of APBs.<sup>28,29</sup> However, the value measured for our film is among the highest reported in literature and corresponds well with the volume fraction of the APB phase of 20% estimated above.

We next discuss the evolution of the saturation magnetization of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films grown in pure Ar atmosphere with increasing  $x$ . As shown in the inset of Fig. 6(a), both  $M_S$  and  $M_R$  were found to decrease with increasing  $x$ . Recalling Eq. (1), the substitution of  $\text{Fe}_A^{3+}$  ( $3d^5, S=5/2$ ) by  $\text{Zn}^{2+}$  ( $3d^{10}, S=0$ ) results in a decrease in the magnetization on the A sublattice. That is, since the compensating magnetization of the A sublattice is removed, one would expect an increase in the total magnetization of the ferrimagnet. However, Zn substitution also weakens  $J_{AB}$  by diluting the A site moments. Furthermore, it converts  $\text{Fe}_B^{2+}$  ( $3d^6, S=2$ ) into  $\text{Fe}_B^{3+}$  on the B sublattice, resulting in a reduction in the itinerant charge carrier density. This weakens the ferromagnetic double exchange, competing with antiferromagnetic superexchange interaction on the B sublattice. As discussed in Sec. I, taken together this leads to an increase in the spin canting on the B sublattice with increasing  $x$  (cf. Fig. 1), explaining the observed reduction in the total magnetization of the ferrimagnetic  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films. We note that recently Takao-bushi *et al.*<sup>12</sup> reported a monotonic increase in the saturation magnetization from about 0.5 to 3.2  $\mu_B/\text{f.u.}$  at 10 K in the range  $0 \leq x \leq 0.9$  and explained this observation through the assumption that the A sublattice magnetization is reduced by Zn substitution. Comparison of the low temperature saturation magnetization of the  $x=0$  films (3.31  $\mu_B/\text{f.u.}$  when grown in Ar in our case; 0.5  $\mu_B/\text{f.u.}$  in Ref. 12) clearly shows that the samples cannot be directly compared. The reason is that the films in Ref. 12 have been grown at finite oxygen partial pressure of  $1.0 \times 10^{-6}$  mbar. In this case, the effect of Fe vacancies has to be taken into consideration as follows.

The magnetic properties of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films grown in an Ar/O<sub>2</sub> (99:1) mixture are shown in Fig. 6(b). There are pronounced differences to the films grown in pure Ar atmosphere. First, for  $x=0$  both  $M_S$  and  $M_R$  are much lower than for the films grown in pure Ar. Second,  $M_S$  and  $M_R$  is found to increase with increasing  $x$  for  $0 \leq x \leq 0.5$  and then to decrease again for  $x=0.9$  as shown in the inset of Fig. 6(b). The coercive field decreases from about 55 to 8 mT upon increasing  $x$  from 0 to 0.9. The  $M_S(x)$  dependence can be straightforwardly explained by the presence of Fe vacancies in films grown in finite oxygen partial pressure and their removal by Zn substitution. For  $x=0$ , the Fe vacancies shift the  $\text{Fe}_B^{2+}/\text{Fe}_B^{3+}$  1:1 balance toward  $\text{Fe}_B^{3+}$ , removing itinerant charge carriers and weakening the ferromagnetic double exchange at the expense of antiferromagnetic superexchange on the B sublattice. This results in spin canting on the B sublattice, giving rise to a reduced saturation magnetization. On Zn substitution, part of the Fe vacancies is removed. This shifts the  $\text{Fe}_B^{2+}/\text{Fe}_B^{3+}$  ratio back toward a 1:1 balance. The related increase in the itinerant charge carrier density and DE interaction on the B sublattice reduces the spin canting with increasing  $x$ . This explains the increase of the room-temperature saturation magnetization in the range  $0 < x \leq 0.5$  from  $M_S=1.05$  up to 3.02  $\mu_B/\text{f.u.}$  at  $x=0.5$ . At 10 K,  $M_S$  increases from 1.26  $\mu_B/\text{f.u.}$  at  $x=0$  up to 3.92  $\mu_B/\text{f.u.}$  at

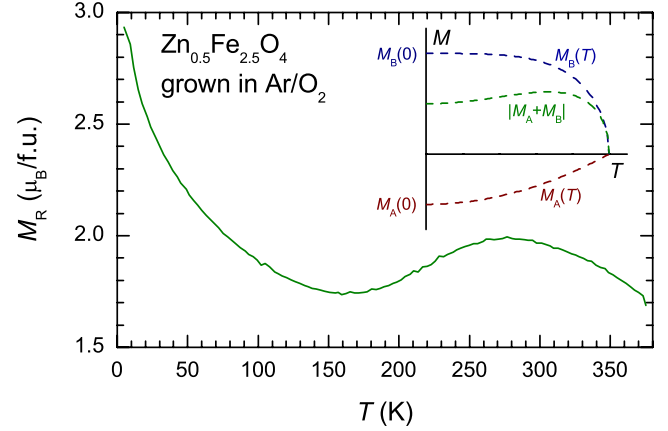


FIG. 7. (Color online) Remanent magnetization  $M_R$  plotted versus temperature  $T$  for a  $\text{Zn}_{0.5}\text{Fe}_{2.5}\text{O}_4$  film grown in an Ar/O<sub>2</sub> (99:1) mixture. The data were taken after field cooling at 7 T upon increasing the temperature at zero applied magnetic field. The inset schematically shows the hump in the  $M(T)$  curve as the result of two opposite sublattice magnetizations with different  $T$  dependence.

$x=0.5$ . For even larger  $x$ , the  $\text{Fe}_A^{3+}$  moments on the A sublattice are strongly diluted, resulting in a strong weakening of the antiferromagnetic superexchange  $J_{AB}$  between the A and B sublattices. Furthermore, Zn substitution may overcompensate the Fe vacancies, again shifting the  $\text{Fe}_B^{2+}/\text{Fe}_B^{3+}$  balance toward  $\text{Fe}_B^{3+}$ . Taken together, this explains the decrease in  $M_S$  above the critical value of  $x \approx 0.5$ , which of course depends on the oxygen partial pressure during growth and the corresponding amount of Fe vacancies. The observed increase in  $M_S$  with increasing  $x$  for  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films grown in an Ar/O<sub>2</sub> mixture is consistent with the result of Takao-bushi *et al.*,<sup>12</sup> who reported an increase in  $M_S(10\text{K})$  from 0.5 to 3.2  $\mu_B/\text{f.u.}$  upon increasing  $x$  from 0 to even 0.9. However, our systematic study strongly suggests that this increase is most likely caused by the removal of Fe vacancies rather than due to the removal of  $\text{Fe}_A^{3+}$  moments on the A sites as argued in Ref. 12.

Figure 7 shows the temperature dependence of the remanent magnetization  $M_R$  for a  $\text{Zn}_{0.5}\text{Fe}_{2.5}\text{O}_4$  film grown in an Ar/O<sub>2</sub> mixture. In agreement with the  $\rho_{xx}(T)$  data of Fig. 4, there is no indication for the Verwey transition in  $M_R(T)$  around 120 K. This is the case for all samples, except for the  $\text{Fe}_3\text{O}_4$  film grown in pure Ar. This observation is not only consistent with our transport data but also with magnetization data from other groups, indicating smearing or suppression of the Verwey transition by an amount of Zn substitution as small as  $x=0.01$ .<sup>68</sup> As shown in Fig. 7, the measured  $M_R(T)$  curve first decreases with increasing  $T$ , goes through a minimum at  $T \approx 150$  K, and then increases up to  $T \approx 275$  K before it decreases again toward room temperature. Such a behavior is often observed in ferrimagnets and can be explained on the basis of Néel's two sublattice model.<sup>69</sup> Within this model the origin of the hump at 275 K is a different  $T$  dependence of the two sublattice magnetizations  $M_A(T)$  and  $M_B(T)$  due to different effective molecular fields on the A and B sites. In our case the effective molecular field on the A sublattice is expected to be smaller due to the partial substitution of  $\text{Fe}_A^{3+}$  by nonmagnetic  $\text{Zn}^{2+}$ . As a result, the

combined magnetization  $M(T) = M_A(T) + M_B(T)$  should show an upward hump in agreement with the experimental result. Note that the observation of a hump, which is directed upwards, provides direct experimental evidence for A site substitution of  $\text{Zn}^{2+}$  in the inverse spinel structure.<sup>69</sup> For the  $x = 0.33$  sample, no hump could be observed, most likely due to a too small imbalance in the effective molecular fields at the smaller substitution level.

In conclusion, the magnetic properties of the  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  films grown under different oxygen partial pressure strongly depend on whether the films were grown in pure Ar atmosphere or at finite oxygen partial pressure. Fully consistent with the transport data these differences can be explained by the following effects. (i) For films grown in pure Ar, Zn substitution on the A site removes  $\text{Fe}_A^{3+}$  moments from the A sublattice and due to charge neutrality itinerant electrons from the B sublattice. The resulting weakening of both the antiferromagnetic A-O-B SE and the ferromagnetic DE on the B sublattice results in an increasing spin canting on the B sublattice with increasing  $x$ . This causes a reduction in the saturation magnetization with increasing  $x$ . (ii) For films grown in oxygen partial pressure, the magnetic properties are strongly influenced by the presence of Fe vacancies. They reduce the density of itinerant electrons on the B sublattice, thereby weakening the ferromagnetic DE at the expense of antiferromagnetic SE. This causes spin canting on the B sublattice and, in turn, a reduced saturation magnetization. The effect of additional Zn substitution is the partial removal of the Fe vacancies. This effectively increases the density of itinerant electrons on the B sublattice, thereby strengthening the ferromagnetic DE. The result is an increase in the saturation magnetization with increasing  $x$ . Again, the observed dependence of the saturation magnetization on the Zn substitution levels  $x$  cannot be simply explained by different APB densities in the different thin-film samples. It is very unlikely that the APB density increases with increasing  $x$  for samples of the same thickness when grown in Ar atmosphere, while for those prepared in the Ar/O<sub>2</sub> mixture it first decreases for  $x \leq 0.5$  and then increases again for  $x \geq 0.5$ .

We finally link the magnetic properties to the transport data by plotting the saturation magnetization  $M_S$  versus the electrical conductivity  $\sigma_{xx} \approx 1/\rho_{xx}$  (Ref. 44) for films with various  $x$  and grown in Ar or Ar/O<sub>2</sub> (Fig. 8). Evidently, there is clear correlation between  $M_S$  and  $\sigma_{xx}$ . Samples with high  $M_S$  have large  $\sigma_{xx}$  and vice versa. Again, this correlation can be straightforwardly explained within the scenario presented above. Charge transport is dominated by the hopping of the itinerant  $t_{2g}$  electrons between the mixed-valent  $\text{Fe}_B^{2+}/\text{Fe}_B^{3+}$  ions on the B sublattice. Due to the strong on-site Hund's rule coupling the spin of the hopping spin-down electron is aligned antiparallel to the local moment of the spin-up electrons (cf. Fig. 1). Therefore, the hopping amplitude is significantly suppressed if the moments of neighboring B sites are not parallel. That is, any spin canting on the B sublattice reducing the saturation magnetization also results in a reduction in the electrical conductivity.

## VI. CONCLUSION

We have grown epitaxial  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  thin films ( $0 \leq x \leq 0.9$ ) with excellent structural properties both in pure Ar

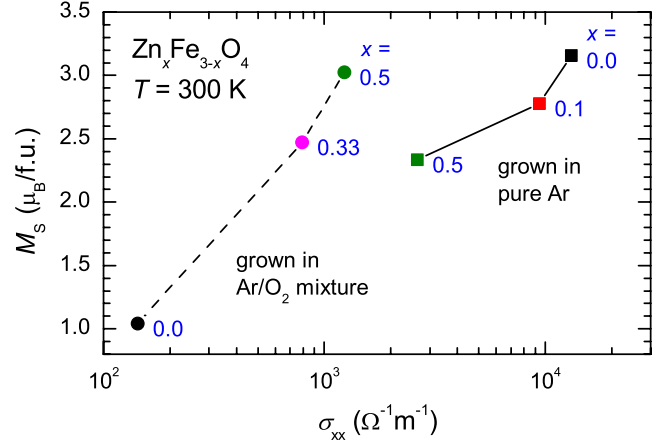


FIG. 8. (Color online) Saturation magnetization  $M_S$  plotted versus the longitudinal conductivity  $\sigma_{xx}$  for epitaxial  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  thin films with different Zn substitution  $x \leq 0.5$  grown in pure Ar atmosphere (squares) or Ar/O<sub>2</sub> (99:1) mixture (circles).

atmosphere and Ar/O<sub>2</sub> mixture using laser molecular-beam epitaxy. We show that the electrical conductivity and the saturation magnetization can be tuned over a wide range ( $1.0 \dots 3.2 \mu_B/\text{f.u.}$  and  $10^2 \dots 10^4 \Omega^{-1} \text{m}^{-1}$  at room temperature) by Zn substitution and/or finite oxygen partial pressure during growth. This demonstrates that  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  can be used as a material with tailored electrical and magnetic properties. Our comprehensive study shows that electrical conduction, magnetotransport, and magnetic properties of  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  are dominated by the density and thermally activated hopping of the itinerant  $t_{2g}$  electrons between the mixed-valent  $\text{Fe}_B^{2+}/\text{Fe}_B^{3+}$  ions, providing electrical conduction and mediation of a ferromagnetic DE interaction on the B sublattice. This scenario is confirmed by the observation that the saturation magnetization scales with the longitudinal conductivity and the field dependence of the MR effect. Our combined systematic analysis of the magnetotransport and magnetic properties also provides a clear picture of the effect of Zn substitution and growth in finite oxygen partial pressure. First, Zn substitution removes both  $\text{Fe}_A^{3+}$  moments from the A sublattice and itinerant charge carriers from the B sublattice. Second, growth in finite oxygen partial pressure generates Fe vacancies, also removing itinerant charge carriers from the B sublattice. Hence, in both cases a reduction in the charge carrier density and a weakening of the ferromagnetic DE on the B sublattice is obtained. This results in an increase in resistivity and a reduction in the saturation magnetization due to spin canting on the B sublattice. Third, applying both Zn substitution and growth in oxygen at the same time does not result in an additive effect. In contrast, a compensation effect is observed since Zn substitution removes part of the Fe vacancies. To sum up, one can say that the high Curie temperature together with the electrical and magnetic properties that can be tuned over a wide range make  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  a promising functional material for spintronic devices. The combination of  $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$  with semiconductor materials such as ZnO in multifunctional heterostructures<sup>27</sup> will be particularly appealing.

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