Epitaxial Zn$_{x}$Fe$_{3-x}$O$_{4}$ Thin Films: A Spintronic Material with Tunable Electrical and Magnetic Properties

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The ferrimagnetic spinel oxide Zn$_{x}$Fe$_{3-x}$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 Zn$_{x}$Fe$_{3-x}$O$_{4}$ thin films (0 ≤ x ≤ 0.9) on MgO(001) substrates with excellent structural properties both in pure Ar atmosphere and an Ar/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$^{2}$...10$^{7}$Ω$^{-1}$m$^{-1}$ and 1.0...3.2 $\mu$B/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 Zn$_{x}$Fe$_{3-x}$O$_{4}$ with antiparallel Fe moments on the A and B sublattice: (i) Zn substitution removes both Fe$^{3+}$ 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 is 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 Fe	extsuperscript{2+}/Fe	extsuperscript{3+} ions on the B sublattice. A decrease (increase) of charge carrier density results in a weakening (strengthening) of double exchange and thereby a decrease (increase) of 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 Zn$_{x}$Fe$_{3-x}$O$_{4}$ films with semiconductor materials such as ZnO in multi-functional heterostructures seems to be particularly appealing.

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1. INTRODUCTION

Spintronic materials and devices are in the focus of current research activities$^{1,2}$. 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$^{3}$ or spin transistors$^{4}$ 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 an applied electric field$^{5}$, elastic stress$^{6,7}$, or light$^{8}$. In this respect, Fe$_{3}$O$_{4}$ (magnetite) is a highly promising candidate. First, it has both a high Curie temperature of $T_{C}$ ≈ 860 K and according to band structure calculations is expected a half-metal$^{9}$ corroborated by spin-resolved photoelectron spectroscopy$^{10,11}$. Second, recent experiments indicated that both the electronic and magnetic properties of Fe$_{3}$O$_{4}$ thin films can be nicely tailored in solid solution systems of Fe$_{3-x}$M$_{x}$O$_{4}$ (M = Zn, Mn)$^{12,13}$. Third, it has been demonstrated that the magnetic anisotropy of Fe$_{3}$O$_{4}$ can be tuned by elastic stress imposed by a piezoelectric actuator$^{14}$. 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 Fe$^{3+}$/ion (3$d^{5}$, S = 5/2), whereas on the octahedrally coordinated B sites (16 per unit cell) there is an alternating arrangement of Fe$^{2+}$/B (3$d^{6}$, S = 2) and Fe$^{3+}$/B (3$d^{5}$, S = 5/2) ions. Therefore, the sum formula of magnetite can be expressed as [Fe$^{3+}$/A]Fe$^{3+}$/Fe$^{2+}$/B. 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 Fe$^{2+}$. 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 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 coupling, 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, in the simplest model ferrimagnetism in Fe$_3$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 Fe$^{3+}_A$ and Fe$^{3+}_B$ moments compensate each other, a saturation magnetization of $4\mu_B$/formula unit (f.u.) is expected from the remaining Fe$^{2+}_B$ ($S = 2$) moments. Later on, the simple Néel model has been extended by Yafet and Kittel. They proposed a more elaborate model in which the $B$ sublattice is subdivided into two Fe$^{2+}_B$ and Fe$^{3+}_B$ 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 of the saturation magnetization. More recent models show that a detailed modelling 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.

There are several possibilities to tailor the magnetic properties of magnetite. First, Fe$^{3+}_A$ 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 of the saturation magnetization is expected at low substitution level. However, on increasing the $A$ site substitution the dilution of the $A$ site moments reduces $J_{AB}$, whereas $J_{BB}$ stays about constant. Then the moments on the $A$ and $B$ site do no longer need to be rigidly antiparallel, resulting in a finite Yafet-Kittel angle (see Fig. 1(c) and (d)). This angle increases with increasing substitution, resulting in a reduction of the saturation magnetization. Due to the isovalent substitution the charge carrier density should stay unaffected. However, the hopping between the mixed-valent (Fe$^{2+}_B$/Fe$^{3+}_B$) 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 Fe$_3$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, Fe$^{3+}_A$ on the $A$ site can be replaced by a nonmagnetic divalent ion such as Zn$^{2+}$ (3d$^{10}, S = 0$). It is known that Zn$^{2+}$ preferably occupies the tetrahedrally coordinated $A$ site in the inverse spinel structure. Again some of the antiferromagnetically coupled moments on the $A$ sites are removed, leading to an initial increase of the saturation magnetization at low Zn substitution. However, in the same way as discussed before, a finite Yafet-Kittel angle and, in turn, a reduction of the saturation magnetization is expected going to larger substitution levels. Moreover, substitution of Fe$^{3+}_A$ by Zn$^{2+}$ on the $A$ site also reduces the amount of Fe$^{2+}_B$ 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. Thus, with increasing Zn substitution the electrical conductivity is reduced both by a reduction of 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. Since Fe vacancies are formally equivalent to the presence of excess O$^{2-}$ ions, charge neutrality again requires a reduced (increased) amount of Fe$^{2+}_B$ (Fe$^{3+}_B$) 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
FIG. 2: (color online) X-ray diffraction diagrams (ω-2θ scans) of the out-of-plane reflections from Zn$_{x}$Fe$_{3-x}$O$_{4}$ thin films deposited in different growth atmospheres of Ar/O$_{2}$ (99:1) (left panels) and pure Ar (right panels). With increasing $x$ the Zn$_{x}$Fe$_{3-x}$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 Zn$_{x}$Fe$_{3-x}$O$_{4}$ (004) reflection, except for (f) where the Zn$_{x}$Fe$_{3-x}$O$_{4}$ (008) reflection is displayed.

oxides with spinel structure are interesting materials. They do not only have high Curie temperature and high spin polarization but also offer various opportunities to tailor their electrical (charge carrier density, electrical conductivity) and magnetic properties (saturation magnetization, 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 Fe$_3$O$_4$/ZnO heterostructures has been demonstrated$^{27}$. Here, we report on the growth as well as the structural, magnetic and magnetotransport properties of epitaxial thin film samples of Zn$_x$Fe$_{3-x}$O$_4$ with $x = 0, 0.1, 0.33, 0.5, 0.9$ deposited in different oxygen partial pressure. 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 anti-phase boundaries (APBs) in the thin film samples which could affect both their electrical conductivity and their saturation magnetization$^{28,29}$. However,
we have clear evidence that APBs do not play a dominant role in this study. In particular, they cannot explain the change of 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.

2. THIN FILM GROWTH

Epitaxial thin films of Zn$_x$Fe$_{3-x}$O$_4$ with $x \leq 0.9$ and thicknesses between 40 nm and 60 nm were deposited from stoichiometric targets on single crystalline, (001) oriented MgO substrates by laser molecular beam epitaxy (laser-MBE)\(^3\). The exact film thickness was determined by x-ray reflectometry. Both bulk Fe$_3$O$_4$ having an inverse spinel structure ($Fd3m$) and MgO ($Fm3m$) are cubic with lattice constants of $a_{Fe_3O_4} = 8.394$ Å\(^4\) and $a_{MgO} = 4.212$ Å, respectively, resulting in a small lattice mismatch of $(a_{Fe_3O_4} - a_{MgO})/2a_{MgO} = -0.4\%$. The energy density of the KrF excimer laser ($\lambda = 248$ nm) at the target was $3.1 \text{J/cm}^2$ and the laser repetition rate $2 \text{Hz}$. 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 $320^\circ$C. In an Ar/O$_2$ (99:1) mixture, thin films with $x = 0.5$ were deposited at $320^\circ$C and with $x = 0, 0.33$, and 0.9 at $400^\circ$C. The growth process was monitored in situ by reflection high energy electron diffraction (RHEED)\(^3\). We observed four RHEED intensity oscillations per unit cell, indicating a block-by-block growth mode with four charge neutral blocks. There is already known for Fe$_3$O$_4$\(^3\),\(^4\),\(^3\) and also holds when substituting Zn up to Zn$_{0.9}$Fe$_{2.1}$O$_4$. A more detailed description of the thin film deposition for Fe$_3$O$_4$ on MgO is given elsewhere\(^3\),\(^3\),\(^3\).

3. STRUCTURAL PROPERTIES

The structural properties of the Zn$_x$Fe$_{3-x}$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 [001] 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 Fe$_3$O$_4$ and $\gamma$-Fe$_2$O$_3$ (maghemite) as they both share the same inverse spinel lattice.\(^3\). It is known that excess oxygen results in the formation of Fe vacancies and in the extreme case to formation of Fe$_2$O$_3/\gamma$-Fe$_2$O$_3$ solid solutions.\(^3\),\(^3\),\(^2\). The Fe$_2$O$_3/\gamma$-Fe$_2$O$_3$ thermodynamic equilibrium line was determined to log($p_{O_2}/p_0$) = $-24.634$ K/T with $p_0 = 9.1 \times 10^{13}$ bar.\(^2\). 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 to an effective growth temperature much larger than the substrate temperature favoring the stability of Fe$_3$O$_4$.\(^2\),\(^4\).\(^5\). Therefore, for the deposition temperature and oxygen partial pressure used in our experiments we are sufficiently far away from the Fe$_3$O$_4/\gamma$-Fe$_2$O$_3$ equilibrium line.\(^3\),\(^3\),\(^5\).

As shown by Fig. 2, the (004) reflection from Zn$_x$Fe$_{3-x}$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 Zn$_x$Fe$_{3-x}$O$_4$ thin film samples with very low mosaic spread, comparable to epitaxial Fe$_3$O$_4$ films.\(^3\),\(^3\),\(^3\). In the $\omega$-2$\theta$ scan, the (004) reflection from Fe$_3$O$_4$ is positioned at a slightly larger angle than the (002) reflection from the MgO substrate (see Fig. 2(a,b)), indicating $c_{Fe_3O_4} < 2c_{MgO}$. With increasing Zn concentration, the (004) reflection moves to lower angles and crosses the MgO(002) reflection at $x = 0.5$ (see Fig. 2(e,f)). At $x = 0.9$, the position of the (004) reflection from the Zn$_x$Fe$_{3-x}$O$_4$ film is shifted to an angle below the (002) reflection from MgO (see Fig. 2(g,h)). This corresponds to $c_{Zn_{0.9}Fe_{2.1}O_4} > 2c_{MgO}$.

The absolute value and variation of the $c$ axis lattice parameter of the Zn$_x$Fe$_{3-x}$O$_4$ films with Zn content $x$ are related to two effects, namely epitaxial coherency strain and the larger ionic radius of tetrahedrally coordinated
Zn$^{2+}$ of 0.6 Å compared to the radius of only 0.49 Å of Fe$^{3+}$ on the tetrahedrally coordinated A site\cite{12}. First, for $x = 0$ the lattice mismatch of $-0.4\%$ between Fe$_3$O$_4$ film and MgO substrate leads to a tensile in-plane epitaxial coherency strain and, in turn, to a slight reduction of the $c$ axis lattice parameter of the Fe$_3$O$_4$ film below the bulk value (cf. Fig. 3(a)). The fully coherent growth of the Zn$_x$Fe$_{3-x}$O$_4$ thin films is demonstrated by reciprocal space maps around the (204) reflection of the MgO substrate (see Fig. 3(b)). The (408) reflection of the film is located exactly at the same in-plane scattering vector $q_{||}$ 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 MgO substrate. Second, for $x > 0$ the unit cell volume of Zn$_x$Fe$_{3-x}$O$_4$ is expected to increase about linearly with increasing $x$ due to the larger ionic radius of Zn$^{2+}$. However, since the Zn$_x$Fe$_{3-x}$O$_4$ films grow coherently on the 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 [00$|$0] 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 Al$_2$O$_3$(0001) substrates\cite{12}. 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 Zn$_x$Fe$_{3-x}$O$_4$ films grown in pure Ar atmosphere are larger than those of the films grown in an Ar/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 results in a reduction of the unit cell volume most likely due to the formation of Fe vacancies. The latter most likely are partially compensated by additional Zn substitution.

4. MAGNETOTRANSPORT PROPERTIES

For magnetotransport measurements, the films were patterned into typically 45 µm wide and 350 µm long Hall bars directed in the (00$|$1) direction by photolithography and Ar ion beam milling\cite{43}. 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\cite{45,44} and are not discussed here.

4.1. 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$_2$ (99:1) mixture, $\rho_{xx}(T)$ increases by more than two orders of magnitude on decreasing $T$ from 375 K down to 90 K. Plotting...
log(ρ_xx) on a reciprocal T scale as shown in Fig. 4(b) results in about 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 ρ_xx(T) of the x = 0 sample results from the Verwey transition discussed below. Fig. 4(b) suggests that the longitudinal resistivity of the samples with x ≥ 0.1 follows a simple activated behavior ρ_xx(T) ≈ exp(E_a/k_BT) with the Boltzmann constant k_B = 1.38 × 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 ρ_xx(T) data also can be equally well fitted by small polaron hopping \[ ρ_xx(T) \propto T \exp(E_{pol}/k_BT) \], with the potential barrier for polaron hopping, E_{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_2 mixture. The derived activation energies are typical for zinc ferrites. 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 Mn^{3+} and Mn^{4+} ions.

We next discuss the observability of the Verwey transition in the measured ρ_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 Fe^{2+} and Fe^{3+} ions on the B sublattice in a process reminiscent to Wigner crystallization. Whereas at T > T_V the extra electrons from Fe^{3+} can hop to neighboring Fe^{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. However, in the recent past 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. It is evident from Fig. 4 that a pronounced change in the ρ_xx(T) curves due to the Verwey transition is observed only for the Fe_3O_4 film (x = 0) grown in pure Ar atmosphere. For this film there is no jump but a clear kink in the ρ_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 introducing Fe vacancies by growing the films in finite oxygen partial pressure results in deviations from equal numbers of Fe^{2+} and Fe^{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 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 Fe_3O_4 films substituted by Zn or grown in finite oxygen partial pressure provides evidence for the presence of an unequal number of Fe^{2+} and Fe^{3+} ions on the B sublattice.

We next discuss the ρ_xx values of the Zn_xFe_{3−x}O_4 (0 ≤ x ≤ 0.5) films grown in pure Ar atmosphere. The strong increase of resistivity with decreasing T can be un-
derstood 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 Fe$_3$O$_4$ thin films or single crystals. In this context, we note that the presence of anti-phase boundaries (APBs) in Fe$_3$O$_4$ thin film samples may have a significant influence on the measured longitudinal resistivity. However, this is not the case for our samples. First, our Fe$_3$O$_4$ thin film grown in Ar atmosphere has a room-temperature resistivity value close to that of Fe$_3$O$_4$ single crystals ($6.2 \times 10^{-5} \Omega \text{m}$) considered as APB-free. Second, comparing the resistivity value to those of Fe$_3$O$_4$ thin films with different APB density, we estimate that the volume fraction of the APB phase in our thin film is reduced, resulting in an increase of the resistivity.

That is, the density of 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 Fe$_3$O$_4$ thin films or single crystals. In this context, we note that the presence of anti-phase boundaries (APBs) in Fe$_3$O$_4$ thin film samples may have a significant influence on the measured longitudinal resistivity. However, this is not the case for our samples. First, our Fe$_3$O$_4$ thin film grown in Ar atmosphere has a room-temperature resistivity value close to that of Fe$_3$O$_4$ single crystals ($6.2 \times 10^{-5} \Omega \text{m}$) considered as APB-free. Second, comparing the resistivity value to those of Fe$_3$O$_4$ thin films with different APB density, we estimate that the volume fraction of the APB phase in our thin film is reduced, resulting in an increase of the resistivity.

$\rho_{xx}$ measurement using APB-free Fe$_3$O$_4$ thin films grown in pure Ar. Since growth of magnetite in excess oxygen is known to create Fe vacancies $X^0$, equivalent to two (three) missing electrons per Fe$^{2+}$ (Fe$^{3+}$) vacancy, the requirement of charge neutrality shifts the 1:1 balance between Fe$^{2+}$ and Fe$^{3+}$ towards Fe$^{3+}$ as $[\text{Fe}^{3+}]_A [\text{Fe}^{3+}\text{Fe}^{2+}]_B \text{O}^{2-} \Rightarrow \text{[Fe}^{3+}]_A [\text{Fe}^{1+2+}\text{Fe}^{1-3+}\text{X}^{2-}]_B \text{O}^{2-}$. (2) Evidently, Fe vacancies in the same way as Zn substitution result in a reduction of Fe$^{2+}$. 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 $^{20,63}$. Actually, for Zn$_x$Fe$_{3-x}$O$_4$ ($0 \leq x \leq 0.3$) single crystals Wang et al. $^1$ report a compositional correspondence $x = 3\delta$ regarding the resistivity data $^{20}$. Again, with the same arguments given above for the films grown in pure Ar, a reliable evaluation of the various mechanisms (localization, 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 $\gamma$-Fe$_2$O$_3$ (maghemite) phase in the extreme case of $\delta = 1/3$. $^64$

$\text{Zn}$ substitution in our magnetite films grown in an $\text{Ar}/\text{O}_2$ mixture results in a decrease of 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 Zn$^{2+}$ again preferentially occupies the tetrahedrally coordinated $A$ lattice sites, substituting Fe$^{3+}$ and thereby reducing carrier density. That is, one would expect an increase of 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 Zn$^{2+}$ compared to 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 Zn$^{2+}$ does not only remove an electron by substituting Fe$^{3+}$ on an $A$ site, but also adds two/three electrons by removing a vacancy on a Fe$^{2+}/\text{Fe}^{3+}$ site. That is, by Zn substitution also $X^0$ is replaced by Fe$^{2+}$ or Fe$^{3+}$. Evidently, in total this leads to an effective increase of the carrier density with increasing $x$ in agreement with our experimental data in the range 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 Zn$_x$Fe$_{3-x}$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 of 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 of 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 of 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.\textsuperscript{44}

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\(_2\) 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\textsuperscript{44}.

### 4.2. Magnetoresistance

In this subsection we address the magnetoresistance (MR) of the Zn\(_{x}\)Fe\(_{3−x}\)O\(_4\) films. The MR effect, \(\text{MR}_{xx} = \frac{\rho_{xx}(H) − \rho_{xx}(0)}{\rho_{xx}(0)}\) 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 two 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 \(E_{pol}\)) 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 \(E(H) = E_{a,pol} + E_s(H)\) is obtained. Then, no matter whether the transport is by thermally activated hopping, \(\rho_{xx} = \rho_{0,a} \exp[\frac{E(H)}{k_B T}]\), or small polaron hopping, \(\rho_{xx}/T = \rho_{0,pol} \exp[\frac{E(H)}{k_B T}]\), the MR effect is obtained as

\[
\text{MR}_{xx} = \frac{\exp\left(\frac{E_a(H)}{k_B T}\right) − \exp\left(\frac{E_a(0)}{k_B T}\right)}{\exp\left(\frac{E_a(0)}{k_B T}\right)} = \exp\left(-\frac{\Delta E_s(H)}{k_B T}\right) − 1.\tag{3}
\]

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 \(\rho_{0,pol}\)) and the activation energies (\(E_a\) or \(E_{pol}\)), 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 \(\Delta E_s(H)\) of the spin-dependent part of the activation energy is about the same for all samples.

Since the transport in Zn\(_{x}\)Fe\(_{3−x}\)O\(_4\) by hopping of the \(t_{2g}\) spin-down electrons between mixed-valent Fe\(_{2+}\)/Fe\(_{3+}\) ions is equivalent to the hopping of the \(e_g\) electrons between mixed-valent Mn\(_{3+}\)/Mn\(_{4+}\) ions in the doped manganites, we can adopt models developed for the MR effect in the perovskite manganites\textsuperscript{65,66,67}. According to these models the magnetic field dependent change of the acti-
viation energy for hopping between two lattice sites \( i \) and \( j \) can be expressed as

\[
\Delta E_s(H) = \alpha \left( \langle m_i \cdot m_j \rangle_H - \langle m_i \cdot m_j \rangle_{H=0} \right),
\]

(4)

where \( m_i \) and \( m_j \) are the local moments on the lattice sites \( i \) and \( j \), \( \langle ...)_{H=0} \) and \( \langle ...)_{H} \) denote the sample average at zero and finite magnetic fields, respectively, and \( \alpha \) is a constant that may depend on temperature. The local moments \( m_i \) and \( m_j \) 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 independent 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 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 structural 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 \( \mathcal{B} \) giving

\[
\Delta E_s(H) = \beta \mathcal{B} \left( \frac{\mu_\text{eff} \mu_0 H}{k_B T} \right),
\]

(5)

with the vacuum permeability \( \mu_0 = 4\pi \times 10^{-7} \text{Vs/Am} \). Here, \( \mu_\text{eff} \) is the average value of the local moments and \( \beta \) 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

\[
\text{MR}_{xx} \approx -\beta \frac{\mathcal{B} \left( \frac{\mu_\text{eff} \mu_0 H}{k_B T} \right)}{k_B T}.
\]

(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 15 to 30 and 15 to 18 \( \text{Fe}^{2+} \) ions, for the samples grown in pure Ar and an Ar/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 of 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 \( \text{Fe}^{2+}/\text{Fe}^{3+} \) 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, \( \text{MR}_{xx} \propto -\mathcal{B} \) 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 of the MR effect with increasing temperature are nicely reproduced.

5. MAGNETIC PROPERTIES

We have seen that \( \text{Zn} \) substitution and the creation of Fe vacancies in magnetite results in changes of the carrier density and hopping amplitudes of the itinerant charge carriers on the \( B \) sublattice. Following our discussion in the introduction, 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 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 \( \text{Zn} \) 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. 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 \( \text{Fe}_3^{3+} \) (3d\( ^{5} \), \( S = 5/2 \)) by \( \text{Zn}^{2+} \) (3d\( ^{10} \), \( S = 0 \)) results in a decrease of the magnetization on the \( A \) sublattice. That
Zn substitution. For $x = 0$, the Fe vacancies shift the Fe$_3^+$/Fe$_B^+$ 1:1 balance towards Fe$_3^+$, 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 are removed. This shifts the Fe$_B^+/Fe_B^{3+}$ ratio back towards a 1:1 balance. The related increase of 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 $0 < x < 0.5$ from $M_S = 1.05 \mu_B/f.u.$ up to $3.02 \mu_B/f.u.$ at $x = 0.5$. At 10K, $M_S$ increases from 1.26 $\mu_B/f.u.$ at $x = 0$ up to 3.92 $\mu_B/f.u.$ at $x = 0.5$. For even larger $x$, the Fe$_A^{3+}$ moments on the A sublattice are strongly diluted, resulting in a strong weakening of the antiferromagnetic

FIG. 6: (color online) Room temperature magnetization $M$ versus magnetic field $H$ applied in the film plane for Zn$_x$Fe$_{3-x}$O$_4$ thin films grown in (a) pure Ar atmosphere and (b) in an Ar/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 $\mu_B/f.u.$ as a function of the Zn substitution level $x$. The lines are guides to the eye.

is, since the compensating magnetization of the A sublattice is removed, one would expect an increase of the total magnetization of the ferrimagnet. However, Zn substitution also weakens $J_{AB}$ by diluting the A site moments. Furthermore, it converts Fe$_B^{2+}$ $(3d^6, S = 2)$ into Fe$_B^{3+}$ on the B sublattice, resulting in a reduction of the itinerant charge carrier density. This weakens the ferromagnetic double exchange, competing with antiferromagnetic superexchange interaction on the B sublattice. As discussed in the introduction, taken together this leads to an increase of the spin canting on the B sublattice with increasing $x$ (cf. Fig. 1), explaining the observed reduction of the total magnetization of the ferrimagnetic Zn$_x$Fe$_{3-x}$O$_4$ films. We note that recently Takaobushi et al. reported a monotonic increase of the saturation magnetization from about 0.5 $\mu_B/f.u.$ to 3.2 $\mu_B/f.u.$ at 10K in the range $0 < x < 0.9$ and explained this observation by 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 $\mu_B/f.u.$ when grown in Ar in our case, 0.5 $\mu_B/f.u.$ in Ref. 12) clearly shows that the samples can not 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 Zn$_x$Fe$_{3-x}$O$_4$ films grown in an Ar/O$_2$ (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 mT to 8 mT on 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 Fe$_B^{2+}$/Fe$_B^{3+}$ 1:1 balance towards 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 are removed. This shifts the Fe$_B^{2+}$/Fe$_B^{3+}$ ratio back towards a 1:1 balance. The related increase of 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 $0 < x < 0.5$ from $M_S = 1.05 \mu_B/f.u.$ up to $3.02 \mu_B/f.u.$ at $x = 0.5$. At 10K, $M_S$ increases from 1.26 $\mu_B/f.u.$ at $x = 0$ up to 3.92 $\mu_B/f.u.$ at $x = 0.5$. For even larger $x$, the Fe$_A^{3+}$ moments on the A sublattice are strongly diluted, resulting in a strong weakening of the antiferromagnetic

FIG. 7: (color online) Remanent magnetization $M_R$ plotted versus temperature $T$ for a Zn$_{0.5}$Fe$_{2.5}$O$_4$ film grown in an Ar/O$_2$ (99:1) mixture. The data were taken after field cooling at 7 T on 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.
superexchange $J_{AB}$ between the $A$ and $B$ sublattices. Furthermore, Zn substitution may overcompensate the Fe vacancies again shifting the Fe$^{2+}$/Fe$^{3+}$ balance towards Fe$^{3+}$. Taken together, this explains the decrease of $M_S$ 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 of $M_S$ with increasing $x$ for Zn$_{x}$Fe$_{3-x}$O$_4$ films grown in an Ar/O$_2$ mixture is consistent with the result of Takaobushi et al.\textsuperscript{12}, who reported an increase of $M_S$(10 K) from 0.5 $\mu_B$/f.u. to 3.2 $\mu_B$/f.u. on 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 Fe$^{2+}$ moments on the $A$ sites as argued in Ref.\textsuperscript{12}.

Figure 7 shows the temperature dependence of the remanent magnetization $M_R$ for a Zn$_{0.5}$Fe$_{0.5}$O$_4$ film grown in an Ar/O$_2$ 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 Fe$_3$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 a smearing or suppression of the Verwey transition by an amount of Zn substitution as small as $x = 0.01$.\textsuperscript{68}

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, then increases up to $T \approx 275$ K, before it decreases again towards room temperature. Such a behavior is often observed in ferrimagnets and can be explained on the basis of Néel’s two sublattice model.\textsuperscript{69} 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 Fe$^{3+}$ by nonmagnetic 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 Zn$^{2+}$ in the inverse spinel structure. 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 Zn$_x$Fe$_{3-x}$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 Fe$^{3+}$ 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 of 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 of 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$_2$ 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 $\sigma_{xx} \simeq 1/\rho_{xx}$\textsuperscript{14} for films with various $x$ and grown in Ar or Ar/O$_2$ (Fig. 8). Evidently, there is a 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 Fe$^{2+}$/Fe$^{3+}$ 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 anti-parallel 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 of the electrical conductivity.

6. 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 atmosphere and an Ar/O$_2$ mixture using laser molecular beam epitaxy. We show that the electrical conductivity and the saturation magnetization can be tuned over a wide range ($1.0 \ldots 3.2 \mu \Omega \cdot \text{cm}$ and $10^2 \ldots 10^4 \Omega^{-1} \text{m}^{-1}$ 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 the 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 $\text{Fe}^{3+}_{B}/\text{Fe}^{4+}_{B}$ ions, providing electrical conduction and mediating 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 fine oxygen partial pressure. First, Zn substitution removes both $\text{Fe}^{3+}_{A}$ 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 of the charge carrier density and a weakening of the ferromagnetic DE on the $B$ sublattice is obtained. This results in an increase of resistivity and a reduction of 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 multi-functional heterostructures will be particularly appealing.

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