Magnetic structure of Fe-doped CoFe₂O₄ probed by x-ray magnetic spectroscopies

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The magnetic properties of iron-doped cobalt ferrite ($Co_{1-x}Fe_{2+x}O_4$) (001) thin films grown epitaxially on MgO (001) substrates are investigated by superconducting quantum interference device magnetometry and soft x-ray magnetic linear and circular dichroisms. All $Co_{1-x}Fe_{2+x}O_4$ (0.01 $\leq x \leq 0.63$) samples have out-of-plane magnetic easy axes and large coercive fields, unlike Fe_3O_4 , due to a large Co^{2+} orbital moment. The magnetic moments for those samples are significantly reduced from their bulk values; however, as *x* increases, the magnetic moment is attributed to spin canting among the Co^{2+} cations, owing to a small in-plane tensile strain in the film and to an increased antiferromagnetic alignment among all the cations caused by a partially inverse spinel cubic structure and the likely presence of antiphase boundaries. Our results show that small changes in stoichiometry can lead to significant changes in the magnetic moment of $Co_{1-x}Fe_{2+x}O_4$, especially at large values of *x*.

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I. INTRODUCTION

The search for new, functional spintronic materials and the goal of designing devices that utilize both the charge and spin of the electron to realize novel functionalities is the driving force behind much current research.^{1,2} One class of materials that is promising for use in spintronic devices is the 3d transition-metal complex oxides, which, owing to their highly correlated d electrons, exhibit a wide variety of electronic and magnetic properties.^{3,4} These properties can often be tuned through small changes in strain or doping, such as the ferroelectric phase transition of SrTiO₃ upon application of strain⁵ and the antiferromagnetic/ferromagnetic⁶ and metal/insulator⁷ phase transitions of $La_{1-x}Sr_xMnO_3$ (LSMO) upon change in doping. Examples of novel behavior in complex oxides include room temperature tunneling magnetoresistance of LSMO/SrTiO₃/LSMO⁸ and Fe₃O₄/CoCr₂O₄/LSMO⁹ magnetic tunnel junctions, the spin filter effect of CoFe₂O₄¹⁰ and NiFe₂O₄,¹¹ and electric field control of ferromagnetism through strain-driven magnetoelectric coupling of CoFe₂O₄/BaTiO₃ nanostructures¹² and LSMO/BaTiO₃ multilayers¹³ and charge-driven magnetoelectric coupling in PbZr_xTi_{1-x}O₃/LSMO heterostructures.^{14,15}

One class of these complex oxides that has received much interest is the 3*d* transition-metal spinel ferrites, MFe_2O_4 (M = 3d transitional metal cation). These materials have the spinel crystal structure [see Fig. 1(a)] in which 1/3 of the cations are tetrahedrally coordinated, and 2/3 of the cations are octahedrally coordinated. The crystal structure is normal spinel if all the 2+ cations are located in tetrahedral sites, and inverse spinel if the 2+ cations occupy octahedral sites. The spinel ferrites are environmentally stable with widely varying magnetic properties, magnetic critical temperatures (T_c) much higher than room temperature, and large predicted spin polarizations.^{16–21} Of the stoichiometric spinel ferrites, only magnetite (Fe₃O₄) is electrically conducting with a conductivity up to 10 orders of magnitude larger than the other 3*d* spinel ferrites (M = Mn, Co, Ni, and Zn).^{16,22} However, upon Fe doping ($M_{1-x}Fe_{2+x}O_4$), the insulating ferrites become electrically conducting.^{23–28} Although the resistivity and density of states near the Fermi energy of $M_{1-x}Fe_{2+x}O_4$ thin films behave systematically upon Fe doping, recent studies on the magnetic structure of $Zn_{1-x}Fe_{2+x}O_4$ have shown that the magnetic moment behaves nonlinearly with Fe doping and does not obey Néel's theory of ferrimagnetism.^{26–28} This has been attributed to changes in the strength of the magnetic interactions among the different cations. This nonlinear behavior has also recently been seen in the magnetic moment of $Co_{1-x}Fe_{2+x}O_4$ as measured by superconducting quantum interference device (SQUID) magnetometry.²⁴

In this study, we report a detailed investigation into the nature of the magnetic structure of $Co_{1-x}Fe_{2+x}O_4$ over a doping range of $0.01 \le x \le 1$. SQUID magnetometry is used to determine the magnetic easy axes, while site-specific xray magnetic linear dichroism (XMLD) and x-ray magnetic circular dichroism (XMCD) allow for investigations into the magnetic properties of the individual cations. We find that the magnetic properties of $Co_{1-x}Fe_{2+x}O_4$ change markedly as x is increased from 0.01 to 1, as manifest most strikingly in a magnetic moment that is drastically reduced from its bulk value for CoFe₂O₄, and which increases nonlinearly up to a nearly bulk value magnetic moment for Fe₃O₄. Three factors are responsible for these unique magnetic properties: strain, a partially inverse spinel crystal structure, and the likely presence of antiphase boundaries. Our results and analysis show that a highly Fe-doped $Co_{1-x}Fe_{2+x}O_4$ thin film has unique magnetic properties that should make it an exciting candidate material for use in future spintronic devices.

To understand the magnetic structure of $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$, it is helpful to begin with the magnetic structure of Fe_3O_4 . Fe_3O_4 has a completely inverse spinel crystal structure with the Fe^{3+} cations on the octahedral and tetrahedral sites coupled antiferromagnetically via the magnetic superexchange interaction,



FIG. 1. (Color online) (a) Schematic of the spinel crystal structure, which is based on an oxygen FCC sublattice with the cations occupying interstitial sites: 1/3 of the cations are located in 1/8 of the available tetrahedral sites, and 2/3 of the cations are located in 1/2 of the available octahedral sites. (b) Illustration of the magnetic interactions in Fe₃O₄. The Fe³⁺ octahedral and tetrahedral cations are coupled antiferromagnetically via the superexchange (SE) interaction, and the Fe³⁺ and Fe²⁺ octahedral cations are coupled ferromagnetically via the double exchange (DE) interaction. Arrows located on cations represent sizes of magnetic moments. (c) Illustration of the magnetic interactions in CoFe₂O₄. Magnetic interactions are the same as Fe₃O₄, with Fe²⁺ cation replaced by Co²⁺.

and the Fe²⁺ and Fe³⁺ cations on the octahedral sites coupled ferromagnetically through the magnetic double exchange interaction [Fig. 1(b)].²⁹ This ferrimagnetic alignment results in a measured bulk magnetic moment of 4.1 μ_B /formula unit (f.u.),¹⁶ while theoretical calculations predict a magnetic moment varying between 3.65 and 4.43 μ_B /f.u., depending on the theoretical model.^{17–21,30} The coexistence of these two magnetic interactions gives Fe₃O₄ a high *T_c* of 858 K.¹⁶

 $CoFe_2O_4$ is similar to magnetite, except that the Fe²⁺ cations are replaced by Co²⁺ cations. The crystal structure is no longer fully inverse like magnetite; while the majority of Co²⁺ cations occupy octahedral sites, a small fraction (2-24%, depending strongly on the thermal history of the sample)³¹ are located on the tetrahedral sites.^{24,31,32} The Fe^{3+} cations on the octahedral and tetrahedral sublattices are still antiferromagnetically coupled, while the Fe³⁺ and Co²⁺ cations are ferromagnetically coupled, resulting in a ferrimagnet [Fig. 1(c)]. In a perfectly inverse crystal, CoFe₂O₄ has been predicted by different theoretical models to have a spin magnetic moment between 2.73 and 3 $\mu_B/f.u$, ^{17,18,21} whereas bulk CoFe₂O₄ has an experimentally determined magnetic moment of 3.7 $\mu_B/f.u.^{16}$ Here, T_c of the bulk has been measured to be 793 K.¹⁶ However, thin films grown on higher symmetry substrates, such as MgO and SrTiO₃, show a reduced saturation magnetization of 25-60% of bulk values.^{24,33–36} $CoFe_2O_4$ is unique among the ferrites in that it has a large magnetic anisotropy owing to a spin-orbit stabilized ground state (with unquenched orbital momentum $l_{z} = \pm 1$) caused by a trigonal crystal field on the Co^{2+} octahedral cations.^{33,37–42} This results in a cubic magnetocrystalline anisotropy constant, K_1 , that has a different sign and is over an order of magnitude larger than that of the other 3*d* transitionmetal spinel ferrites, and a magnetostriction constant, λ_s , of opposite sign and nearly three times as large as that of Fe₃O₄.¹⁶ Owing to this large magnetostriction, CoFe₂O₄ has been used extensively in strain-driven multiferroic ferroelectric-CoFe₂O₄ nanostructures, where a change in the polarization of the ferroelectric induces a lattice distortion on the CoFe₂O₄, resulting in a magnetization change. This has been realized with both CoFe₂O₄ nanopillars grown within a ferroelectric matrix^{12,43} and CoFe₂O₄ thin films grown epitaxially on ferroelectrics.^{44,45}

When $CoFe_2O_4$ is doped with extra iron to form $Co_{1-x}Fe_{2+x}O_4$, Fe^{2+} cations substitute solely for the Co^{2+} cations on the octahedral site, which results in a crystal structure that is more nearly inverse than $CoFe_2O_4$. Even though it has been shown that the resistivity and density of states near the Fermi energy vary smoothly with doping, the magnetic properties do not change in a predictable manner.²⁴ In particular, measurements on $Co_{0.1}Fe_{2.9}O_4$ particles show only small changes in K_1 from $CoFe_2O_4$ values, but large changes in λ_s .⁴⁶ Determination of the magnetic structure of $Co_{1-x}Fe_{2+x}O_4$ could lead to exciting possibilities for the field of spintronics and should help ascertain the cause for the reduced magnetic moment of thin-film $CoFe_2O_4$.

II. EXPERIMENTAL DETAILS

 $Co_{1-x}Fe_{2+x}O_4$ (001) thin films (x = 0.01, 0.18, 0.39, 0.63, and 1) were grown epitaxially on MgO (001) substrates using molecular beam epitaxy (MBE), with film thicknesses of \sim 20 nm. All samples were capped with 1 nm of MgO to prevent surface oxidation after removal from ultra-high vacuum. A previous analysis of the structural properties, along with details on the thin film growth, determination of stoichiometry, and electronic structure, has been published elsewhere.²⁴ Xray diffraction measurements (Cu $K\alpha$ line), using a Shimadzu diffractometer set in the parallel beam geometry, of 20 nm and 200 nm $Co_{1-x}Fe_{2+x}O_4$ (001) thin films had previously determined that all stoichiometries ($0 \le x \le 1$) are likely to have a small in-plane tensile strain due to a lattice mismatch of -0.3% between MgO and $Co_{1-x}Fe_{2+x}O_4$. Bulk magnetic properties were measured using a SQUID magnetometer (Quantum Design MPMS), while cation specific magnetic properties were investigated using XMLD and XMCD. XMLD and XMCD measurements were performed on beamline U4B at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (spectra measured in total electron yield mode) with energy resolutions of $\sim 0.3 (0.4) \text{ eV}$ for the XMLD (XMCD) measurements, respectively. The XMLD measurements were conducted with the samples at remnant magnetization and rotated with respect to the x-ray beam; x-ray absorption (XAS) measurements were taken at angles of 30° , 45° , 60° , 75° , and 90° between the E field of the x-rays and the [001] crystal direction. The degree of circular polarization for the XMCD measurements was 70% with the incident photons aligned parallel to the magnetic field and the [001] crystal direction, hence measuring the out-of-plane magnetic moments. The XMCD spectra were



FIG. 2. (Color online) In-plane *M*-*H* loops of $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ samples with 0.01 $\leq x \leq 1$ at (a) 100 K and (b) 300 K with the magnetic field aligned along the [010] direction, and out-of-plane *M*-*H* loops at (c) 100 K and (d) 300 K with the magnetic field aligned along the [001] direction.

obtained by using a fixed helicity of light and reversing the applied magnetic field by pulsing it to 9.5 kOe and holding it at 3.5 kOe during the measurement. The XMCD measurements were conducted at 300 K, while the SQUID and XMLD measurements were conducted at both 100 and 300 K.

III. RESULTS

A. Bulk magnetic properties

The bulk magnetic properties were determined by measuring the magnetic response of each sample using a SOUID magnetometer. Figure 2 shows the in-plane and out-of-plane M-H loops measured at both 100 and 300 K for five samples with $0.01 \leq x \leq 1$. A diamagnetic substrate contribution, similar for all samples, was removed from the data. It is clear from the *M*-*H* loops that the magnetic properties of the $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ (0.01 $\leq x \leq 0.63$) samples are drastically different than the Fe₃O₄ (x = 1) sample, with the Co_{1-x}Fe_{2+x}O₄ $(0.01 \le x \le 0.63)$ samples having notably larger coercive fields and smaller saturation magnetizations than the Fe₃O₄ sample. The magnetic easy axes are determined by comparing the in-plane and out-of-plane coercive fields [Figs. 3(a) and 3(b)]. The coercive fields of the $Co_{1-x}Fe_{2+x}O_4$ (0.01 $\leq x$ \leq 0.63) samples are larger for the out-of-plane direction, while the coercive field of the Fe₃O₄ sample is larger in the in-plane direction, leading to the conclusion that the magnetic easy axes for the $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ (0.01 $\leq x \leq 0.63$) samples are out of plane, while the magnetic easy axis of the Fe₃O₄ sample is in plane. This determination of the magnetic easy axes is in agreement with magnetoelastic anisotropy



FIG. 3. (Color online) Comparison of in-plane and out-of-plane coercive fields at (a) 100 K and (b) 300 K, and in-plane and out-of-plane saturation and remnant magnetizations at (c) 100 K and (d) 300 K vs stoichiometry.

energy calculations for films under a slight in-plane tensile strain. 47,48

The in-plane and out-of-plane saturation and remnant magnetizations for all samples are compared at 100 K [Fig. 3(c)] and 300 K [Fig. 3(d)]. At both 100 and 300 K, the in-plane saturation magnetization of Fe₃O₄ is larger than the out-of-plane magnetization with an in-plane value at 100 K of 495 emu/cm³, which is slightly lower than the bulk value of 514 emu/cm^{3.16} This slight reduction in magnetic moment has been attributed to the presence of antiphase boundaries in Fe₃O₄ thin films grown on higher symmetry substrates.⁴⁹ For the $Co_{1-x}Fe_{2+x}O_4$ (0.01 $\leq x \leq$ (0.63) samples, there is no discernable difference between the in-plane and out-of-plane magnetizations at both 100 and 300 K with the out-of-plane saturation magnetizations at 100 K increasing from 154 to 228 emu/cm^3 as x increases from 0.01 to 0.63. These values are significantly less than the bulk values, which, assuming a ferrimagnetic alignment between the octahedral and tetrahedral sites for all values of x, should increase linearly from 464 to 514 emu/cm^3 as x increases from 0 to 1.¹⁶ However, the saturation magnetizations tend closer to the bulk values with increased x. This reduced magnetization has been extensively reported for $CoFe_2O_4^{33-36}$ and $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ (x < 1)²⁴ films grown on higher symmetry substrates.

B. X-ray magnetic linear dichroism

Information on the direction of the spin axes for the individual cations has been obtained using XMLD, which is dependent on $\langle M^2 \rangle$ of the cations.⁵⁰ XAS measurements were taken with the samples in an out-of-plane remnant magnetization state and for different angles between the **E** field of the x-rays and the [001] crystal direction (30°, 45°,



FIG. 4. (Color online) (a) Interpolated Co 2p XAS spectra for Co_{0.61}Fe_{2.39}O₄ with electric field perpendicular and parallel to the [001] crystal direction, and the corresponding XMLD spectrum. (b) Co 2p XMLD spectra for Co_{1-x}Fe_{2+x}O₄ samples with x = 0.01, 0.18, 0.39, and 0.63. (c) Comparison between the measured Co 2p XMLD spectrum, the calculated LFM spectrum, and the individual LFM spectra for the Co²⁺ octahedral and tetrahedral cations.

 60° , 75° , and 90°). All measurements were normalized to the Fe doping level of the sample so that spectra of the same samples measured with different orientations between the **E** field of the x-rays and the [001] crystal direction have the same integrated intensities. This allowed for a qualitative analysis of the relative changes between the different XMLD spectra, while eliminating any reduction in signal due to the angle of the incident x-rays relative to the surface normal (i.e. saturation effects). The spectra with the x-ray **E** field perpendicular and parallel to the [001] crystal direction were determined by fitting the five measured spectra with the angle-dependent XAS equation:²⁹

$$I(\theta) = I_{\parallel} \cos^2 \theta + I_{\perp} \sin^2 \theta, \qquad (1)$$

from which I_{\parallel} and I_{\perp} are interpolated.

Figure 4(a) shows the interpolated Co $L_{2,3}$ XAS spectra for the **E** field perpendicular and parallel to the [001]



FIG. 5. (Color online) (a) Interpolated Fe 2p XAS spectra for Co_{0.61}Fe_{2.39}O₄ with electric field perpendicular and parallel to the [001] crystal direction, and the corresponding XMLD spectrum. (b) Fe 2p XMLD spectra for Co_{1-x}Fe_{2+x}O₄ samples with x = 0.01, 0.18, 0.39, and 0.63. (c) Comparison between the measured Fe 2p XMLD spectrum, the calculated LFM spectrum, and the individual LFM spectra for the Fe²⁺ octahedral, Fe³⁺ octahedral, and Fe³⁺ tetrahedral cations.

crystal direction, along with the difference spectrum for the $Co_{0.61}Fe_{2.39}O_4$ sample, while Fig. 4(b) compares the XMLD spectra for the four samples with x < 1, taken at 300 K. The L_3 edge is characterized by a large negative peak at 776.3 eV, two positive peaks at 777.2 and 778.3 eV, and a negative high energy shoulder, while the L_2 edge has a large positive peak at 792.9 eV and a small negative peak at 794.4 eV. The peaks of the $Co_{1-x}Fe_{2+x}O_4$ (0.01 $\leq x \leq 0.39$) samples all have similar intensities except for the low energy L_3 positive peak and L₂ positive peak of the Co_{0.99}Fe_{2.01}O₄ sample, which are larger. All peaks of the $Co_{0.37}Fe_{2.63}O_4$ sample have larger intensity compared with the other samples; the physical origin of this increased intensity will be discussed later. The interpolated Fe $L_{2,3}$ XAS spectra and the XMLD spectrum for the $Co_{0.61}Fe_{2.39}O_4$ sample are shown in Fig. 5(a), with a comparison of the XMLD spectra of the samples with x < 1shown in Fig. 5(b), taken at 300 K. Regions of interest are, in the L_3 region, four negative peaks at 706, 707.5, 708, and 710.2 eV and two positive peaks at 706.7 and 708.8 eV; and in the L_2 region, two negative peaks 718.7 and 720.5 eV and the two positive peaks at 719.8 and 722.3 eV. As x increases from 0.01 to 0.63, the four negative L_3 peaks all vary in amplitude, while the two positive peaks remain constant; in the L_2 region, the two low-energy peaks increase in size, while the two high-energy peaks remain constant. The changes in peak size increase markedly for the x = 0.63 sample. Measurements at 100 K yielded XMLD spectra almost identical to those in Figs. 4 and 5.

The dichroic effects in XMLD arise from charge anisotropies, which are caused by either a crystal field symmetry lower than cubic or the presence of a magnetic spin axis. Because of the high T_c of $Co_{1-x}Fe_{2+x}O_4$, it is not possible to separate these two effects by measuring the XMLD above T_c ; instead, XMLD spectra were calculated using the ligand field multiplet (LFM) model and compared with the experimental spectra.^{51–53} The LFM model calculates the spectra for a cation in a given ligand field with a magnetic exchange field oriented along the [001] crystal direction. By calculating the spectra of the relevant cationic states, the total LFM spectrum for the $Co_{1-x}Fe_{2+x}O_4$ sample is obtained from a weighted superposition of the individual spectra of each cation; this can then be compared with the measured XMLD spectrum to determine which cation is responsible for which peak in the experimental spectrum. LFM calculations were performed using the CTM4XAS 5.0 program,⁵⁴ including spin-orbit coupling, crystal field effects, and reduction of the Slater integrals F(dd), F(pd), and G(pd) to include the interatomic configuration interaction.55 The following parameters were obtained by comparing the LFM calculated spectrum with the experimental spectrum. The 2p and 3d spin-orbit interactions were reduced by multiplying by a factor of 0.98 and 0.75, respectively, for the cobalt cations, while full spin-orbit interactions were used for the iron cations. The F(dd), F(pd), and G(pd) integrals were taken to be 70%, 80%, and 75% of the Hartree-Fock values, respectively, for the cobalt cations and 70%, 80%, and 80%, respectively, for the iron cations. Octahedral crystals fields of 1.2 and 1.6 eV were used for the cobalt and iron cations, respectively, while tetrahedral crystals fields of 0.6 eV were used for both cobalt and iron cations. All Slater integral reductions and crystal field values are consistent with previous results on Fe₂O₃, Fe₃O₄, and CoFe₂O₄.⁵⁶⁻⁵⁹ The cation site occupancies were taken from analysis of the XAS spectra.²⁴ All spectra were broadened by a Lorentzian with a half-width of 0.1 (0.3) eV for the L_3 (L_2) edge to account for core-hole lifetime broadening and by a Gaussian with a half-width of 0.34 eV to account for instrumental broadening.

Figures 4(c) and 5(c) show the LFM calculation for the $Co_{0.61}Fe_{2.39}O_4$ sample with cubic symmetry and an additional magnetic exchange field oriented along the [001] crystal direction. The experimental and LFM calculated spectra match quite well. Attempts to calculate spectra using a tetragonal distortion due to a tensile strain could not reproduce the experimental spectra. This modeling of the spectra thus allowed us to determine that the majority of the dichroic effects seen in the XMLD spectra result from the magnetic spin axes and not from the small tensile strain; therefore, all interpretations of the XMLD spectra will neglect any effects due to noncubic crystal symmetries.

Since prior analysis of the XAS spectra of these samples concluded that there are only minor variations in the Co^{2+} tetrahedral/octahedral ratio with doping,²⁴ we conclude that the increase in peak intensity for the Co_{0.61}Fe_{2.39}O₄ sample is not caused by changes in the site occupancies, but by an increased alignment of the magnetic spin axes with the [001] crystal direction for the Co²⁺ cations. For the Fe cations, we know that increased doping causes an increase in number of Fe²⁺ octahedral cations. Examination of the individual iron cation LFM spectra in Fig. 5(c) shows that the peaks in Fig. 5(b) that do not change in intensity with increased xare caused solely by the Fe³⁺ cations, whereas the change in intensity in the other peaks is due to an increase in the number of Fe²⁺ octahedral cations. However, it has been noted that the intensity of these peaks does not change linearly with increasing x. Hence, we conclude from the XMLD data that the alignment of the spin axes for the Fe³⁺ cations does not change, whereas there is an enhanced alignment of the spin axes of the Fe^{2+} cations with the [001] crystal direction with increasing x.

C. X-ray magnetic circular dichroism

XMCD measurements were carried out to obtain information on the magnetic properties of the individual cations in our samples. Figure 6(a) shows the Co 2p XAS spectra with the magnetic field aligned in opposite directions and the corresponding XMCD spectrum for the $Co_{0.99}Fe_{2.01}O_4$ sample. All XMCD spectra are corrected to account for the degree of polarization of the x-rays, the Fe doping level, and the nonsaturated magnetic moments through comparison with SQUID measurements, resulting in spectra that correspond to fully magnetized samples. Comparison of the Co XMCD $L_{2,3}$ spectra for the four different $Co_{1-x}Fe_{2+x}O_4$ samples with x < 1 are displayed in Fig. 6(b). The L_3 edge is characterized by a main peak at 778 eV and a small low-energy peak at 776 eV, while the L_2 edge contains only one very broad peak spanning 792-796 eV. There is very little change in the spectra as x increases from 0.01 to 0.39 with only a slight increase occurring at the main L_3 peak; however, there is a large increase in dichroism for all three peaks for the Co_{0.37}Fe_{2.63}O₄ sample.

The Fe 2p XAS and XMCD spectra for the Fe₃O₄ sample are shown in Fig. 7(a); the Fe XMCD spectra were corrected in the same manner as the Co XMCD spectra. Figure 7(b)displays the Co_{1-x}Fe_{2+x}O₄ (0.01 $\leq x \leq 1$) Fe XMCD L_{2.3} spectra. The Fe XMCD spectra contain much more structure than the Co spectra with the L_3 region being the main region of interest; here, there is a low-energy shoulder around 705 eV, a low-energy negative peak at 707 eV, a positive peak at 708 eV, a high-energy negative peak at 708.9 eV, and a high-energy shoulder spanning 710–714.5 eV. The L_2 region for the Fe₃O₄ sample also contains a great deal of structure, but the peaks are much smaller for the samples with x < 1, and the structure is mostly indistinguishable for these samples; thus, only the L_3 region will be used for analysis. Like the Co XMCD spectra, there is little change in the Fe L_3 XMCD spectra as x increases from 0.01 to 0.39 with the intensity of the low energy negative peak increasing slightly, while the intensities of the positive and high-energy negative peaks both decrease. Then for the x



FIG. 6. (Color online) (a) Experimental Co 2*p* XAS spectra for $Co_{0.99}Fe_{2.01}O_4$ with a positive (μ^+) and negative (μ^+) magnetic field, and the corresponding XMCD spectrum. (b) Experimental Co 2*p* XMCD spectra for $Co_{1-x}Fe_{2+x}O_4$ samples with x = 0.01, 0.18, 0.39, and 0.63. (c) Comparison between the experimental Co 2*p* XMCD spectrum, the calculated LFM spectrum, and the individual LFM spectra for the Co²⁺ octahedral and tetrahedral cations.

= 0.63 and x = 1 samples, all peaks, except for the positive L_3 peak, show a substantial increase.

LFM calculations were performed for the XMCD spectra and compared with the experimental data. The same parameters were used for the XMCD spectra as in the XMLD spectra, except that the magnetic exchange fields for each cation were adjusted to match the main L_3 peak intensities of the experimental spectra, and the instrumental broadening was accounted for by a Gaussian with a half-width of 0.45 (0.40) eV for the Co (Fe) spectra. Figure 6(c) shows the Co_{0.99}Fe_{2.01}O₄ experimental spectrum along with the individual Co²⁺ octahedral and tetrahedral LFM spectra and the Co_{0.99}Fe_{2.01}O₄ LFM spectrum. The Co²⁺ octahedral cation LFM spectrum has two peaks in the L_3 and a single, broad peak in the L_2 region, which correspond well with the experimental spectrum, as well as a high-energy L_3 shoulder that is absent from the experimental spectrum. The tetrahedral cation has only one peak in both the L_3 and L_2 regions which reduces the intensities of the LFM main L_3 and L_2 peaks. Table I contains the exchange field energies used for the calculations; owing to the small peak intensity arising from the Co²⁺ tetrahedral cations, large



FIG. 7. (Color online) (a) Experimental Fe 2*p* XAS spectra for Fe₃O₄ with a positive (μ^+) and negative (μ^+) magnetic field, and the corresponding XMCD spectrum. (b) Experimental Fe 2*p* XMCD spectra for Co_{1-x}Fe_{2+x}O₄ samples with *x* = 0.01, 0.18, 0.39, 0.63, and 1. (c) Comparison between the experimental Fe 2*p* XMCD spectrum, the calculated LFM spectrum, and the individual LFM spectra for the Fe²⁺ octahedral, Fe³⁺ octahedral, and Fe³⁺ tetrahedral cations.

changes in the exchange field energies produced only small changes in the spectrum, and we thus set the exchange field energies equal for both Co²⁺ cations. The exchange field energies used in the modeling represent the average exchange field energy per cation oriented along the [001] direction. These energies show that there is a small, approximately linear increase in the average exchange field with increasing doping for the $Co_{1-x}Fe_{2+x}O_4$ (0.01 $\leq x \leq 0.39$) samples and a large increase in average exchange field for the Co_{0.37}Fe_{2.63}O₄ sample. This is in agreement with the XMLD data, since an enhanced alignment of the spin axes with the [001] direction, as determined for the Co_{0.37}Fe_{2.63}O₄ sample from the XMLD analysis, will result in a greater alignment of the exchange field axis with the [001] direction, resulting in the need for a larger average exchange field energy in the LFM calculation.

The results of the LFM calculations for the Fe²⁺ octahedral, Fe³⁺ octahedral, and Fe³⁺ tetrahedral cations, along with the Fe₃O₄ experimental and LFM spectra, are shown in Fig. 7(c). The L_3 region is characterized by three sharp

TABLE I. Average magnetic exchange field energies, $g\mu H$, used in calculating the LFM XMCD spectra given in units of meV.

Sample	Co ²⁺ oct and tet	Fe ²⁺ oct	Fe ³⁺ oct	Fe ³⁺ tet
$\overline{Co_{0.99}Fe_{2.01}O_4}$	6.2	6.4	6.7	5.9
$Co_{0.82}Fe_{2.18}O_4$	6.7	6.2	6.5	5.9
Co _{0.61} Fe _{2.39} O ₄	7.1	5.1	6.3	5.2
Co _{0.37} Fe _{2.63} O ₄	12.9	8.3	11.3	8.2
Fe ₃ O ₄		27.4	27.4	19.4

peaks and low- and high-energy shoulders; comparison with the LFM calculations allows us to determine which cations contribute to which peak. The Fe²⁺ octahedral cations are responsible for the low-energy shoulder, a majority of the negative low-energy peak, and a small fraction of the negative high-energy peak; the Fe³⁺ octahedral cations are responsible for the a small part of the negative low-energy peak and the majority of the negative high-energy peak; and the Fe^{3+} tetrahedral cations are responsible for the positive central peak. All three cations contribute intensity to the high-energy shoulder. The increase in Fe²⁺ cations can be seen clearly in the increase in the low-energy shoulder and an increase in the ratio between the intensities of the two negative peaks. The exchange field energies used for the calculations are listed in Table I. The behavior of the average exchange fields for the Fe cations is similar to that of the Co cations. The average exchange fields remain roughly constant for the $Co_{1-x}Fe_{2+x}O_4$ $(0.01 \le x \le 0.39)$ samples with a slightly decreasing trend, but increasing by large amounts for the $Co_{0.37}Fe_{2.63}O_4$ and Fe₃O₄ samples. It is important to note that the exchange field energy of each cation used in the LFM model is an average of all the exchange field energies of that cation throughout the sample. When two cations of the same type (i.e. Fe³⁺ tetrahedral cations) are antiferromagnetically aligned, the average exchange field of these two cations will be zero since their exchange field energies will be of opposite sign. Hence, even a small fraction of antiferromagnetically aligned cations of the same type will result in a significantly reduced average exchange field energy. This reasoning can be used to explain that the very large increase in the average exchange field energies for the Fe₃O₄ sample is likely caused by an enhanced ferromagnetic alignment of the Fe cations within both the octahedral and tetrahedral sublattices compared with the $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ (0.01 $\leq x \leq 0.63$) samples (the physical origin of the antiferromagnetic alignment will be discussed later). Using the same reasoning, the smaller average exchange field energy of the Fe³⁺ tetrahedral cations compared with the Fe³⁺ octahedral cations can be explained by the likely presence of antiphase boundaries in our films. Antiphase boundaries increase the probability of Fe³⁺ tetrahedral cations being next-nearest neighbors, which causes these Fe³⁺ tetrahedral cations to be antiferromagnetically coupled via superexchange interactions,⁴⁹ resulting in a smaller average exchange field compared with the average exchange field of the Fe^{3+} octahedral cations.

Quantitative information can be obtained from the XMCD data by using well-defined sum rules that relate the integration

of the XAS and XMCD spectra with the orbital⁶⁰ and spin⁶¹ magnetic moments by the equations:⁶²

$$m_{\rm orb} = -\frac{4\int_{L_3+L_2} (\mu_+ - \mu_-)d\omega}{3\int_{L_3+L_2} (\mu_+ + \mu_-)d\omega} (10 - n_{3d}), \qquad (2)$$

$$m_{\rm spin} = -\frac{6\int_{L_3} (\mu_+ - \mu_-)d\omega - 4\int_{L_3 + L_2} (\mu_+ - \mu_-)d\omega}{\int_{L_3 + L_2} (\mu_+ + \mu_-)d\omega} \times (10 - n_{3d}) \left(1 + \frac{7\langle T_z \rangle}{2\langle S_z \rangle}\right)^{-1},$$
(3)

where $m_{\rm orb}$ and $m_{\rm spin}$ are given in $\mu_B/{\rm cation}$, and n_{3d} is the 3d electron occupation number per specific cation. The n_{3d} values were estimated to be 5.3 and 6.1 for Fe³⁺ and Fe²⁺ cations, respectively, from Fe 2p core-level photoemission⁶³ and 7.21 for Co²⁺, which is expected for CoO.⁵⁹ $\langle T_z \rangle$ is the expectation value of the magnetic dipole operator and is only nonzero for systems of less than cubic symmetry.⁶⁴ In single-crystal Fe₃O₄ samples, $\langle T_z \rangle$ has been found to be negligible, ⁶⁵ and since the in-plane and out-of-plane saturation magnetizations of all the samples only differ slightly, we have neglected $\langle T_z \rangle$ in our calculations.

The magnetic moments per formula unit calculated with the XMCD sum rules are compared to the magnetic moments measured with SQUID magnetometry in Fig. 8(a), along with the cobalt and iron contributions to the magnetic moment. For the $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ (0.39 $\leq x \leq 1$) samples, the agreement between XMCD and SQUID is very good, differing by no more than 12%; however, the agreement gets progressively worse as x decreases. The reason for the poor agreement for the x =0.01 and 0.18 samples may be due to an overestimation of the Co^{2+} magnetic moments. Figure 8(b) shows the average orbital and spin magnetic moments per cobalt and iron cation. First considering the orbital moments, the cobalt cations have large orbital moments that increase with increasing x from 0.42 to 0.74 μ_B /cation. The largeness of the orbital moment is easily understood by examining the electron orbital occupations (the increase of the orbital moment with increased Fe doping will be discussed later). A $3d^7$ cation in an octahedral crystal field has two electrons to fill the three spin-down t_{2g} orbitals, while all the spin-up orbitals are already filled. Due to the tensile strain, a small tetragonal field is added, resulting in a filled d_{xy} orbital and either the d_{xz} or d_{yz} orbital being half filled, giving rise to an expected orbital magnetic moment of 1 μ_B . Likewise, a $3d^7$ cation in a tetrahedral crystal field will have no orbital moment since the two e_g orbitals will be full. The iron orbital moments are much smaller, increasing roughly linearly with x from 0.03 to 0.12 μ_B .

The spin moments for the cobalt and iron cations behave similarly in that they increase slightly with *x* for the $Co_{1-x}Fe_{2+x}O_4$ ($0.01 \le x \le 0.39$) samples before increasing rapidly for the $Co_{0.37}Fe_{2.63}O_4$ and Fe_3O_4 samples; however, their magnitudes differ markedly, with the iron spin moments being near zero for $x \le 0.39$. For $CoFe_2O_4$, all the iron cations are Fe^{3+} , and in a perfectly inverse spinel crystal, they do not contribute to the total magnetic moment due to the antiferromagnetic alignment of the octahedral and tetrahedral cations. This is consistent with our sum rule calculations and reveals that the majority of the magnetic moment for the



FIG. 8. (Color online) (a) Comparison of out-of-plane magnetic moments per f.u. as determined by SQUID and XMCD sum rules vs stoichiometry. Also included are the cobalt and iron contributions to the magnetic moment as determined by XMCD. (b) Comparison of the average orbital and spin magnetic moments per cobalt and iron cation vs stoichiometry as determined by XMCD sum rules.

 $Co_{1-x}Fe_{2+x}O_4$ (0.01 $\leq x \leq$ 0.39) samples is owing to the Co^{2+} cations.

IV. DISCUSSION

By using the information gained from SOUID magnetometry, XMLD, and XMCD measurements, we obtain a complete picture of the magnetic structure of $Co_{1-x}Fe_{2+x}O_4$ and the cause behind the reduced magnetization of CoFe₂O₄ grown on higher symmetry substrates. All samples with x < 1 have an out-of-plane easy magnetization axis, which is caused by the large orbital moments on the Co^{2+} octahedral cations, as measured by XMCD. These orbital moments point in the out-of-plane direction owing to the small in-plane tensile strain of the samples; hence, the spins of the Co²⁺ octahedral cations will also be aligned out of plane because of spin-orbit coupling. However, if these spins were aligned completely in the out-of-plane direction, $m_{\rm orb}$ should be determined by the percentage of Co^{2+} cations that are in octahedral sites. Previous modeling of isotropic XAS spectra of the same samples determined the percentage of Co²⁺ octahedral and tetrahedral cations to be \sim 88% and \sim 12%, respectively, for all samples with x < 1;²⁴ this would result in $m_{\rm orb} \sim 0.88 \,\mu_B$. This is much higher than the measured Co²⁺ orbital moments for the $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ (0.01 $\leq x \leq 0.39$) samples and slightly higher than the Co^{2+} orbital moment for the $\text{Co}_{0.37}\text{Fe}_{2.63}\text{O}_4$ sample, implying that the Co²⁺ cations have orbital moments that point away from and/or oppose the [001] direction. It has been shown in CoFe₂O₄/MgO (001) thin films that there is competition between an in-plane shape anisotropy and an out-of-plane strain-induced anisotropy.⁴⁷ Dislocations, caused by the inplane tensile strain of the film, can induce local strains, which, because of this energy competition, may result in some of the orbital moments favoring other crystal directions. This, as a consequence, may cause a canting of the spin moments due to spin-orbit coupling. The XMLD spectra support a spin-canting model since they show an increased spin alignment along the [001] crystal direction for the Co_{0.37}Fe_{2.63}O₄ compared with the $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ (0.01 $\leq x \leq 0.39$) samples, mimicking the behavior of the orbital moments. This increased spin alignment is also seen in the Fe XMLD spectra for the Fe^{2+} cations, suggesting a ferromagnetic coupling between the Fe^{2+} and Co^{2+} cations, resulting in spin canting of the Fe²⁺ cations as well.

In addition, there are two factors that support a model in which the cobalt and iron cations are also aligned antiferromagnetically within the octahedral and tetrahedral sublattices. The mixed spinel nature of $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ results in the Fe³⁺ octahedral/tetrahedral site occupancy ratio being > 1. The larger this ratio, the larger the probability that two Fe³⁺ cations will be next-nearest neighbors in the octahedral sublattice and have a Co^{2+} cation as their next-nearest neighbor in the tetrahedral sublattice. In this scenario, the Fe³⁺ octahedral cations will be antiferromagnetically aligned via superexchange since there is no Fe³⁺ tetrahedral cation to keep them both aligned ferromagnetically. This antiferromagnetic alignment will result in a reduced magnetic moment that will change nonlinearly as the Fe³⁺ octahedral/tetrahedral ratio decreases nonlinearly with increasing *x*.²⁴

The reduced magnetic moment is also attributed to the likelihood of antiphase boundaries existing in our samples, as evidenced by the smaller average exchange field energy of Fe^{3+} tetrahedral cations compared with the Fe^{3+} octahedral cations. As mentioned above, antiphase boundaries result in Fe³⁺ tetrahedral cations being coupled antiferromagnetically across the boundary. When the Fe^{2+}/Co^{2+} ratio is large, the double exchange interaction between the Fe^{2+} and Fe^{3+} octahedral cations is strong enough to keep the majority of the octahedral cations at the antiphase boundary ferromagnetically aligned and not affected by the antiferromagnetic alignment of the Fe³⁺ tetrahedral cations. Because the double exchange interaction between Co^{2+} and Fe^{3+} cations is weaker than the Fe²⁺/Fe³⁺ double exchange interaction, an increase in the number of Co^{2+} cations results in a larger percentage of octahedral cations at the antiphase boundary being antiferromagnetically aligned as well. The combination of antiphase boundaries and a partially inverse crystal structure results in it being more common for the Fe³⁺ octahedral cations to be antiferromagnetically aligned for $Co_{1-x}Fe_{2+x}O_4$ samples with small x values, even though, due to strong coupling between the Fe³⁺ octahedral and tetrahedral cations, the spin axes do not change. Since octahedral Co²⁺ and Fe²⁺ cations are coupled ferromagnetically to the Fe³⁺ octahedral cations via double exchange, the increased antiferromagnetic alignment of Fe³⁺

octahedral cations will result in an increased antiferromagnetic alignment of the Co²⁺ and Fe²⁺ cations as well. This is in agreement with both the XMLD spectra and the exchange field energies used in modeling the XMCD spectra. All of these factors result in a reduced magnetic moment for CoFe₂O₄, which tends closer to bulk values as *x* increases from 0 to 1 and becomes more nonlinear closer to x = 1.

V. CONCLUSIONS

In summary, we have determined the magnetic structure of $\text{Co}_{1-x}\text{Fe}_{2+x}O_4$ by examining the bulk magnetic properties with SQUID magnetometry and the cation specific magnetic properties with XMLD and XMCD. For all samples, antiferromagnetic alignment of Fe^{3+} tetrahedral cations is likely caused by antiphase boundaries, while canting among the octahedral Co^{2+} and Fe^{2+} cations is caused by strain. $\text{Co}_{1-x}\text{Fe}_{2+x}O_4$ samples with small values of *x* also have a large number of antiferromagnetically aligned Fe^{3+} octahedral cations due to a partially inverse crystal structure, the likelihood of antiphase boundaries, and a weaker double exchange interaction between Co^{2+} and Fe^{3+} cations as compared with the $\text{Fe}^{2+}/\text{Fe}^{3+}$ double exchange interaction. $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ samples with large *x* grown on higher symmetry substrates present a material in which small changes in stoichiometry can result in large changes in the magnetic moment, a result that can be utilized to tune the magnetic properties of $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$ in a spintronic device.

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