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DOI:00.0000/xxxxxxxxx

# Exploring Interfacial Magnetism in All-Spinel $Fe_3O_4/MgCr_2O_4/Fe_3O_4$ Epitaxial Heterostructures<sup>†</sup>

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Epitaxial heterostructures integrating thin Fe<sub>3</sub>O<sub>4</sub> films hold great potential for spintronics, magnetoionics, and multifunctional device development. In this work, the morpho-structural and magnetic properties of all-spinel Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub>/Fe<sub>3</sub>O<sub>4</sub> trilayers grown on a MgCr<sub>2</sub>O<sub>4</sub> buffer layer, exhibiting very close lattice matching, were investigated by using both surface and bulk sensitive techniques. The close lattice match between Fe<sub>3</sub>O<sub>4</sub> and MgCr<sub>2</sub>O<sub>4</sub> enables the growth of epitaxial heterostructures with magnetically decoupled Fe<sub>3</sub>O<sub>4</sub> layers for spacer thicknesses  $\geq 1.6$  nm, while reducing the formation of antiphase boundaries. Despite localized interphase diffusion, which leads to the formation of a mixed Cr/Fe spinel oxide with magnetically polarized Cr ions at the Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub> layers. This study sheds light on the magnetic interactions within Fe<sub>3</sub>O<sub>4</sub> layers mediated by a MgCr<sub>2</sub>O<sub>4</sub> spacer, and demonstrates the feasibility of the approach in preserving the properties of thin Fe<sub>3</sub>O<sub>4</sub> films, in complex heterostructures, thus offering a promising pathway for designing advanced all-spinel oxide devices.

## 1 Introduction

Ferroic transition metal oxides (TMOs) have attracted a great deal of attention for both fundamental studies and technological appli-

cations.<sup>1</sup> The variable oxidation states of transition metals allow the formation of several compounds, exhibiting a wide range of physical properties resulting from the strong coupling between charge, spin, orbital and lattice symmetry.<sup>2,3</sup> Novel functional materials, in form of thin films, with tailored chemical and physical properties can be designed by changing the nature of each component, their relative thickness, or by tuning the interface interactions. Magnetic spinel oxides (MFe<sub>2</sub>O<sub>4</sub>) containing 3*d* metals (M = Fe, Co, Ni, Mn, ...) represent one of the most interesting classes of TMOs due to their excellent chemical stability and rich crystal chemistry, allowing for an excellent fine-tuning of the magnetic properties.<sup>4,5</sup>

Among family members, magnetite (Fe<sub>3</sub>O<sub>4</sub>) is of particular interest due to its unique magnetic and electrical properties. <sup>6</sup> Fe<sub>3</sub>O<sub>4</sub> is a conductive and biocompatible material, showing ferrimagnetic characteristics, with a high Curie temperature (858 K), a theoretically predicted half-metal behavior and an experimentally observed spin polarization of almost 100% at the Fermi level.<sup>7</sup> These remarkable properties make Fe<sub>3</sub>O<sub>4</sub> highly promising for various fields, including biomedicine, <sup>8</sup> spintronics, <sup>9</sup> magnetoionics, <sup>10</sup> soft robotics, <sup>11</sup> and multi-physics devices. <sup>12</sup> Owing to its

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peculiar properties, Fe<sub>3</sub>O<sub>4</sub> films have been widely investigated as key component of different thin film heterostructures including hard/soft all-oxide composites, hybrid and all-oxide spintronic structures, and multilayers/superlattices consisting of magnetite thin films separated by a thin spacer layer. <sup>13–24</sup> Previous studies on Fe<sub>3</sub>O<sub>4</sub>-based multilayers/superlattices have demonstrated the richness of interface-induced phenomena occurring in such structures as a function of the spacer, including thickness-dependent antiferromagnetic/ferrimagnetic interface coupling, stabilization of thin magnetite layers, modulation of saturation magnetization and magnetic anisotropy.<sup>17-23</sup> The intricate interplay at the interface drives the magnetic characteristics of those structures, underscoring the significance of interface conditions in shaping the overall magnetic behaviour. 19,22,25 To date, only a few spacers, such as MgO, MgFe<sub>2</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>, PtSe<sub>2</sub>, and TiN, have been explored, implying that there is potential to observe additional phenomena using alternative materials with selected characteristics.

In this work, we have investigated the interface structure of Fe<sub>3</sub>O<sub>4</sub>-based trilayers consisting of thin ferrimagnetic Fe<sub>3</sub>O<sub>4</sub> layers (7 nm) separated by a ultra-thin MgCr<sub>2</sub>O<sub>4</sub> spacer with thicknesses of 0.6 nm, 1.6 nm and 2.4 nm grown on an MgAl<sub>2</sub>O<sub>4</sub> (100) substrate covered with a thick MgCr<sub>2</sub>O<sub>4</sub> buffer layer. MgCr<sub>2</sub>O<sub>4</sub> is a spinel oxide exhibiting a favorable lattice parameter match with Fe<sub>3</sub>O<sub>4</sub> ( $a_{Fe_3O_4}$  = 8.394 Å,  $a_{MgCr_2O_4}$  = 8.333 Å, where  $a_X$  is the lattice constant of the X compound).<sup>26</sup> Bulk  $MgCr_2O_4$  is a semiconductive antiferromagnet that is paramagnetic above 12.5 K,<sup>27,28</sup> which is expected to exhibit insulating behavior at low thicknesses, similar to other TMOs.<sup>29</sup> The same crystal symmetry and the comparable lattice constant are expected to result in epitaxial Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub> heterostructures with coherently grown interfaces. Our results demonstrate that epitaxial structures indeed form, with the two Fe<sub>3</sub>O<sub>4</sub> layers behaving independently for spacer thickness  $\geq$  1.6 nm. The heterostructure shows reduced coercivity compared to thick Fe<sub>3</sub>O<sub>4</sub> films directly deposited on MgO (100) substrates, an effect attributed to a reduction of the antiphase boundary due to the excellent lattice match between Fe<sub>3</sub>O<sub>4</sub> and the MgCr<sub>2</sub>O<sub>4</sub> buffer layer. Although localized intermixing at the Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub> interfaces induces magnetic polarization in Cr ions, this has minimal influence on the overall magnetic behaviour, which remains primarily governed by the individual Fe<sub>3</sub>O<sub>4</sub> layers. These insights deepen our understanding of the magnetic interaction among spinel oxide layers, facilitating the development of functional full-oxide devices.

#### 2 Experimental

Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub>/Fe<sub>3</sub>O<sub>4</sub> thin film heterostructures were deposited on an MgCr<sub>2</sub>O<sub>4</sub> buffer layer grown on single-crystal (100)oriented MgAl<sub>2</sub>O<sub>4</sub> spinel substrates by Pulsed Laser Deposition (PLD) at the NFFA laboratories, located within the Elettra synchrotron radiation facility in Trieste, Italy.<sup>30</sup> While ultraviolet excimer lasers ( $\lambda = 248$  nm) are conventionally employed for the deposition of complex oxide heterostructures<sup>31</sup>, this study used a first harmonic Nd:YAG solid-state laser (1064 nm), which has recently demonstrated efficacy in producing high quality oxide films while offering a simpler experimental setup.<sup>32–35</sup> The deposition parameters were optimized for the individual Fe<sub>3</sub>O<sub>4</sub> and MgCr<sub>2</sub>O<sub>4</sub> layers, with the substrate temperature set to 500°C. The growth was performed at laser repetition rates of 0.5 Hz and 1 Hz for Fe<sub>3</sub>O<sub>4</sub> and MgCr<sub>2</sub>O<sub>4</sub>, respectively. Calibration of the growth rates via X-ray reflectivity yielded values of 0.02 nm and 0.008 nm per laser pulse, ensuring precise control over the layer thickness during deposition (see Supplementary Information for growth details). While a commercial target was used for Fe<sub>3</sub>O<sub>4</sub>, an home-made one was employed for MgCr<sub>2</sub>O<sub>4</sub> (see Supplementary Information for fabrication details). To minimize the lattice mismatch between  $Fe_3O_4$  and the substrate  $[(a_{Fe_3O_4} - a_{Fe_3O_4})]$  $a_{MgAl_2O_4})/a_{MgAl_2O_4} \sim 3.8\%$ ) and promote the formation of epitaxial thin films, the MgAl<sub>2</sub>O<sub>4</sub> substrate was coated with a MgCr<sub>2</sub>O<sub>4</sub> buffer layer with a nominal thickness of 30 nm, high enough to relax the strain induced by the substrate and reach the lattice parameter of bulk MgCr<sub>2</sub>O<sub>4</sub>, which closely matches that of the Fe<sub>3</sub>O<sub>4</sub> layer, [ $(a_{Fe3O4}-a_{MgCr2O4})/a_{MgCr2O4} \sim 0.7\%$ ). The critical thickness  $t_c$  of the MgCr<sub>2</sub>O<sub>4</sub> on the MgAl<sub>2</sub>O<sub>4</sub> substrate, above which the system exhibits strain relaxation, was estimated employing the Fischer, Kuhne, and Richards (FKR) model,<sup>36</sup> obtaining a value of about  $t_c = 17$  nm (details in the Supplementary Information). On top of this buffer layer, trilayers consisting of two thin Fe<sub>3</sub>O<sub>4</sub> films, each with a thickness of 7 nm, separated by an MgCr<sub>2</sub>O<sub>4</sub> spacer with varying thicknesses (0.6 nm, 1.6 nm and 2.4 nm) were grown. For comparison, a thick Fe<sub>3</sub>O<sub>4</sub> film with a thickness of 60 nm on MgO (100) single crystal substrate, as well as a single 7 nm thick Fe<sub>3</sub>O<sub>4</sub> film deposited on MgAl<sub>2</sub>O<sub>4</sub>(100), with and without an MgCr<sub>2</sub>O<sub>4</sub> buffer layer, were grown under identical experimental conditions.

A comprehensive set of advanced measurements was conducted at room temperature to correlate the morpho-structural and magnetic properties of the samples. Magneto optical Kerr effect (MOKE) measurements, 37 with laser wavelength of 405 nm, and X-ray absorption spectroscopy (XAS) with in remanence  $(\pm 0.05 \text{ T})$  X-ray magnetic circular dichroism (XMCD) investigation at the Cr and Fe  $L_{2,3}$  absorption thresholds were executed under ultra-high vacuum conditions at the APE-HE beamline.<sup>38</sup> These latter measurements were performed in total electron yield (TEY) mode with the X-ray beam incident at 45° and an energy resolution of about 0.1 eV. In addition, HArd X-ray PhotoEmission Spectroscopy (HAXPES) measurements were conducted at beamline I09 of the Diamond Light Source (UK),<sup>39</sup> on samples transported in protective atmosphere and introduced in the experimental chamber without air exposition. Photon energies of hv = 1.78, 4.05, 8.08 keV (in all cases incidence angle was  $20^{\circ}$ from the sample surface) were set to obtain information at different depths with a total energy resolution at the different photon energies of 0.39, 0.25, and 0.27 meV, respectively. Structural characterization involved the use of ex-situ X-ray reflectivity and high resolution scanning transmission electron microscope (HR-STEM). STEM observations on thin-film cross-sections (see Supplementary Information for details about sample preparation) were performed using a probe Cs-corrected FEI Titan<sup>3</sup> G2 60-300 STEM equipped with ChemiSTEM technology (X-FEG field emission gun and Super-X EDX detector system) developed at FEI.<sup>40</sup> The latter allows for the chemical composition analysis of the layers down to the nanoscale with the energy-dispersive X-

ray (EDX) microanalysis. Integral magnetic measurements were performed at room temperature using a commercial MicroSense Model 10 vibrating sample magnetometer (VSM) with the magnetic field applied in the film plane along the (100) direction of the MgAl<sub>2</sub>O<sub>4</sub> substrate. Semi-empirical calculations of the XAS and XMCD spectra were performed within the framework of the atomic multiplet and ligand field theory using the QUANTY program.<sup>41</sup> Details of the theoretical model can be found in the book of de Groot and Kotani.<sup>42</sup>

3 Results and discussion

#### 3.1 Structural characterization

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Figures 1(a) and 1(b) present the crystallographic structures of  $Fe_3O_4$  and MgCr<sub>2</sub>O<sub>4</sub>, highlighting the ion site occupancy, and the schematic structure of the multilayer, respectively. Figure 1(c,d) show the high-resolution (HR) high-angle annular dark field (HAADF) STEM images of samples with a MgCr<sub>2</sub>O<sub>4</sub> spacer thickness of 0.6 and 2.4 nm, respectively. The high degree of epitaxial matching is evident in all the investigated samples, hence highlighting the structural quality of the whole heterostructure (see also the noise-filtered images reported in Figures SI1 and SI5 of the Supplementary Information). The samples reveal the expected cubic structure (Figures SI2 and SI6) with the (001) planes parallel to the substrate surface, and pictures (c) and (d) are taken in [100] and [110] zone-axis orientation.

Close inspection of the STEM image in panel (d) points out the presence of anti-phase boundaries (APBs) in the MgCr<sub>2</sub>O<sub>4</sub> buffer layer, associated with displacement vectors of a/4 <110>.43,44 In the white squared inset, the contrast variation in the periodic distribution of atoms in the MgCr<sub>2</sub>O<sub>4</sub> buffer layer along the direction indicated by the dashed line is evident, and it is assigned to the presence of an  $a/4[1\overline{1}0]$  APB producing the corresponding shift of the  $(\overline{1}11)$  lattice planes. Although generally expected in all samples, APBs are not visible in panel (c) because the sample is in [100] zone axis orientation and, as can be deduced from the inset of Figure SI5(b): a shift of a/4[011] of the lattice does not give rise to a new atomic distribution that can be distinguished by the Z (atomic number)-contrast of the HAADF-STEM technique. The presence of APBs in the MgCr<sub>2</sub>O<sub>4</sub> buffer layer is due to the formation of partial dislocations that relax the strain induced by the mismatch with the MgAl<sub>2</sub>O<sub>4</sub> substrate.<sup>36</sup> The mismatch evolution across the whole heterostructures was investigated by performing fast Fourier transforms (FFTs) in different regions of the images [insets in Figure 1(c) and 1(d)] and calculating the d(040) and d(220) interplanar distances, which are parallel to the substrate, reported in Table 1 [the values tabulated at the International Centre for Diffraction Data (ICDD) for MgAl<sub>2</sub>O<sub>4</sub> (ICDD card n° 21-1152) are used to calibrate the FFT images]. The values listed in Table 1 show that the MgCr<sub>2</sub>O<sub>4</sub> buffer layer is relaxed in proximity to the bottom Fe<sub>3</sub>O<sub>4</sub> layer because its measured interplanar distances agree with the tabulated values for the bulk material (ICDD card no. 10-0351) within experimental errors. Similarly, the interplanar distances of the Fe<sub>3</sub>O<sub>4</sub> layers are consistent with the bulk values (ICDD card n° 19-0629), indicating a complete relaxation of the magnetic films. Despite the perfect lattice matching at the interface between the MgCr<sub>2</sub>O<sub>4</sub> buffer layer and the Fe<sub>3</sub>O<sub>4</sub> film, HR-STEM analysis reveals the presence of APBs in the Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub>/Fe<sub>3</sub>O<sub>4</sub> trilayers (see Figure SI3). In this case, the origin of the APBs cannot be attributed to the mismatch between the cell parameters of the MgCr<sub>2</sub>O<sub>4</sub> buffer layer and the Fe<sub>3</sub>O<sub>4</sub>, since they show relaxed values, and therefore a comparable lattice parameter, but more likely due to the propagation of the APBs defects from the MgCr<sub>2</sub>O<sub>4</sub> to the Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub>/Fe<sub>3</sub>O<sub>4</sub> trilayers. Noticeably, STEM-EDX measurements demonstrate that the elemental distribution inside the epitaxial heterostructures, shown in Figure 1(c,d) and Figures SI4 - SI7, is largely consistent with the actual thickness of each layer. These measurements are consistent with the results from the X-ray reflectivity analysis (see Supplementary Information, Figure S8), which indicate the presence of relatively flat interfaces with a root mean square roughness of 0.2-0.3 nm. The elemental intensity profiles along the vertical direction are shown in panels (e,f) of Figure 1, starting from the sample surface (left side) towards the MgAl<sub>2</sub>O<sub>4</sub> substrate (right side). It is interesting to observe that Fe and Cr appear to diffuse into each other's layer at the top of the sample, and that the Fe signal is visible in the whole MgCr<sub>2</sub>O<sub>4</sub> interlayer. Moreover, the spectral comparison clearly indicates that the Fe intensity significantly decreases as the distance from the interfaces increases for the 2.4 nm thick interlayer, thus suggesting a greater ability of the spacer to separate the magnetic phases as its thickness increases. Considering the presence of interdiffusion, the formation of regions with intermediate stoichiometries cannot be excluded.

#### 3.2 Chemical states

The chemical states of Fe and Cr ions were investigated by corelevel HAXPES. This information is particularly relevant to recognize the presence of secondary phases formed during the growth, and/or at the boundaries among the layers that might also involve significant changes of the chemical states for the Fe and Cr ions. Figure 2 shows the Fe 2p and Cr 2p core level spectra of the thin film heterostructure with a MgCr<sub>2</sub>O<sub>4</sub> spacer thickness of 0.6 nm. The spectra acquired for samples with a thicker  $MgCr_2O_4$  spacer provide similar results. With the incident photon energy varying from 1.78 keV to 8 keV, the information depth ranges from about 6 nm (hv = 1.78 keV) to 25 nm (hv = 8 keV), as sketched in the inset of panel (a), hence the spectra refer to different regions of the heterostructure. Thus, the Fe 2p spectrum collected at 1.78 keV is only related to the upper Fe<sub>3</sub>O<sub>4</sub> layer, consistently with the absence of Cr 2s and any spectral contribution of Cr in the survey spectrum (not shown here), suggesting that Cr diffusion in the top magnetite layer is mainly localized at the interface only. At higher photon energy, the Fe 2p spectra encompass the entire trilayer structure and also the Cr 2s and Cr 2p peaks [Figure 2(b)] are observed. Additionally, the Cr spectra for hv = 4 keV are indicative only of the MgCr<sub>2</sub>O<sub>4</sub> interlayer, while those for hv = 8keV contain a large bulk contribution of the underlying MgCr<sub>2</sub>O<sub>4</sub> buffer layer. The latter thus provides a useful reference to distinguish changes in the electronic states of Cr ions in the thin MgCr<sub>2</sub>O<sub>4</sub> interlayer.

The Fe 2p spectra shown in Figure 2 exhibit typical characteris-

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Fig. 1 (a) inverse and normal spinel structure of  $Fe_3O_4$  and  $MgCr_2O_4$ : in  $Fe_3O_4$  quarter of the tetrahedral positions of the lattice are occupied by  $Fe^{2+}$  ions while in half of the octahedral ones sit  $Fe^{2+}$  and  $Fe^{3+}$  cations; in MgCr<sub>2</sub>O<sub>4</sub>, Mg<sup>2+</sup> occupy the tetrahedral positions and Cr<sup>3+</sup> cations the octahedral ones. (b) Sketch of the  $Fe_3O_4/MgCr_2O_4/Fe_3O_4$  heterostructure deposited on top of a thick  $MgCr_2O_4$  buffer layer grown on the  $MgAl_2O_4(001)$  substrate. (c,d) High-resolution HAADF-STEM image for heterostructures with a  $MgCr_2O_4$  spacer of 0.6 nm (c) and 2.4 nm (d). Black dashed lines indicates the different compound regions. The samples in panels (c) and (d) were [100] and [110] zone-axis oriented, respectively. Insets display FFTs performed in the corresponding regions of the heterostructures. The resulting interplanar distances are reported in Table 1. (e,f) Elemental distribution among the layers as achieved by STEM-EDX measurements. The intensity is not scaled to the formula unit composition. To better elucidate the details of STEM images, further information such as EDX elemental maps for AI, Mg, Fe and Cr and noise-filtered HR-STEM images are reported in Figures SI1-SI7 of the Supplementary Information.

tics of the Fe<sub>3</sub>O<sub>4</sub> phase, as reported in previous studies.<sup>45,46</sup> The consistency of the spectra across a wide range of probing depth highlights the high quality of both magnetite layers and suggest the absence of significant deviations from the nominal stoichiometry. This conclusion is further supported by the fitting analysis of the Fe  $2p_{3/2}$  peaks performed following the model described by Grosvenor *et al.*, where the contribution of Fe  $^{2+}$  (Fe  $^{3+}$ ) ion is identified at lower (higher) binding energy and each of the two is made up of several components deriving from multiplet splitting, surface components and satellites.<sup>47</sup> This analysis successfully disentangles the spectral terms contributions from  $Fe^{2+}$  and  ${\rm Fe}^{3+},$  yielding a  ${\rm Fe}^{3+}/{\rm Fe}^{2+}$  intensity ratio of  $\sim$  1.7, in good agreement with the expected ideal concentration ratio of 2:1. Note also that, in the spectral region between the two spin-orbit-splitted edges, the satellite structure that is prominent in the photoemission spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) is not visible in the present case.<sup>48</sup> Such satellite structure is due to charge transfer screening and it is visible, at somehow different binding energies, for iron oxides purely Fe<sup>2+</sup> (such as FeO) or  $Fe^{3+}$  (such as  $Fe_2O_3$ ), its intensity smearing out when both ionic components are present (such as in Fe<sub>3</sub>O<sub>4</sub>).<sup>49</sup> This implies that only magnetite is present in the investigated heterostructures and no other iron oxide phases are formed. This is particularly relevant for the Fe 2p spectrum for hv = 1.78 keV, being the most sensitive to the surface.

The Cr 2s and Cr 2p spectra shown in panel (a) and (b), respectively, provide further confirmation of these results. The similarity of the spectra, despite the substantial differences of the probing depth, indicates that the chemical state of the Cr ions of the spacer closely resembles that of the thick MgCr<sub>2</sub>O<sub>4</sub> buffer layer, suggesting the absence of secondary phases related to different chemical states, e.g. as  $Cr^{2+}$  in  $CrO_2$ . The multiplet splitting features resulting from the fitting analysis of the Cr  $2p_{3/2}$  spectrum, with the energy splitting  $\Delta_{AB} = 1.04 - 1.09$  eV, resemble closely those of the  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> or CrFe<sub>2</sub>O<sub>4</sub> phase, where the Cr<sup>3+</sup> ions exclusively occupy octahedral lattice sites. <sup>50,51</sup> This strongly suggests that Cr ions in our sample predominantly reside in the octahedral sites, as expected for the normal spinel structure of MgCr<sub>2</sub>O<sub>4</sub>. On the other hand, the observed spectral features are also compatible with the formation of a Cr/Fe mixed spinel oxide as long as this phase maintains the chemical state and site symmetry of the Fe and Cr ions. The formation of such phase at both the Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub> interfaces cannot be ruled out, and indeed it is the most plausible hypothesis to explain the observed magnetic Nanoscale

Table 1 Interplanar distances obtained from FFTs of images taken from various regions of the heterostructure and for different  $MgCr_2O_4$  interlayer thicknesses, as shown in Figure 1(c) and 1(d). The top and bottom  $Fe_3O_4$  layers were analyzed, yielding identical interplanar distances in both cases.

|                                | Bulk material $d(040)$ (nm) | Bulk material $d(220)$ (nm) | MgCr <sub>2</sub> O <sub>4</sub> 0.6 nm $d(040)$ (nm) | MgCr <sub>2</sub> O <sub>4</sub> 2.4 nm<br>d(220) (nm) |
|--------------------------------|-----------------------------|-----------------------------|---|--|
| Fe <sub>3</sub> O <sub>4</sub> | 0.2099                      | 0.2967                      | $0.210{\pm}0.002$                                     | $0.296{\pm}0.002$                                      |
| Fe <sub>3</sub> O <sub>4</sub> | 0.2099                      | 0.2967                      | $0.210{\pm}0.002$                                     | $0.296{\pm}0.002$                                      |
| $MgCr_2O_4$                    | 0.2083                      | 0.2945                      | $0.206{\pm}0.002$                                     | $0.293{\pm}0.002$                                      |
| $MgAl_2O_4$                    | 0.2020                      | 0.2858                      |   |  |



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Fig. 2 Fe 2p (a) and Cr 2p (b) core level spectra for the Fe<sub>3</sub>O<sub>4</sub>(7 nm)/MgCr<sub>2</sub>O<sub>4</sub>(0.6 nm)/Fe<sub>3</sub>O<sub>4</sub>(7 nm) trilayer. Spectra are normalized to the maximum intensity. The Fe 2p spectra also shows Cr 2s peak closely located to the Fe 2p<sub>3/2</sub> one. The information depth of the spectra, sketched in the inset of panel (a), ranges from about 6 nm (hv = 1.78 keV) to 25 nm (hv = 8 keV).

measurements, as described in the next sections.

#### 3.3 Magnetic investigation

The overall magnetic behaviour of the spinel oxide heterostructures is elucidated by a comparative study of VSM and MOKE measurements, shown in Figure 3 and Fig. SI9. Field-dependent magnetization loops of thin film heterostructures for different



Fig. 3 (a,b) In-plane VSM (left scale) and longitudinal MOKE (right scale) field-dependent magnetization loops, M(H), at 300 K of trilayer heterostructures with an MgCr<sub>2</sub>O<sub>4</sub> spacer thickness of (a) 0.6 nm and (b) 2.4 nm; (c) M(H) loop of a 7 nm thick Fe<sub>3</sub>O<sub>4</sub> film reference film grown on an MgCr<sub>2</sub>O<sub>4</sub> buffer layer.

MgCr<sub>2</sub>O<sub>4</sub> spacer thicknesses are compared to that of a 7 nm thick Fe<sub>3</sub>O<sub>4</sub> film deposited on the MgCr<sub>2</sub>O<sub>4</sub> buffer layer to gain insights into the factors influencing the magnetic properties of the spinel oxide heterostructure. If we consider the penetration depth of the laser ( $\lambda = 400$  nm) of about 20 nm,<sup>52</sup> the magnetic information obtained by MOKE primarily relates to the thin film heterostructure and the MgCr<sub>2</sub>O<sub>4</sub> buffer layer, while VSM provides the magnetization evolution of the entire sample, potentially including any magnetic contributions from the substrate. Due to the presence of ferro(i)magnetic impurities within the substrate, VSM measurements were corrected to account for both the dia-

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magnetism of the substrate and the ferromagnetic contribution of the contaminants (Figure SI10 in the Supplementary Information). However, precise quantification of contamination levels in each sample proved challenging, impacting the correction's precision. This issue may lead to underestimations or overestimations of the magnetization value based on the correction method (as detailed in the Supplementary Information and shown in Figure SI10), especially in the high-field region, where the approach of magnetization to saturation can potentially be influenced by the presence of APBs.<sup>53</sup> Therefore, a reliable determination of the saturation magnetization is unfeasible. On the other hand, the correction had a minimal effect in the low-field region, as detailed in the Supplementary Information. The agreement of the corrected VSM loops with the MOKE loops, collected in the  $\pm 0.1$ T field region, supports the reliability of the magnetic measurements within this specific range, offering a dependable benchmark for studying and comparing the samples' magnetic properties. Both the single  $Fe_3O_4$  layer and the trilayers exhibit almost square loops, indicating a magnetically homogeneous film with a strong level of magnetic ordering.<sup>54</sup> Furthermore, the measured hysteresis loops reveal relatively low coercive field, with  $\mu_0 H_c =$ 7.0(5) mT for the single Fe<sub>3</sub>O<sub>4</sub> layer, and  $\mu_0 H_c = 12.5(5)$  mT, 6.5(3) mT and 5.0(3) mT for the trilayers containing  $MgCr_2O_4$ spacers of 0.6 nm, 1.6 nm and a 2.4 nm thickness, respectively. These values are significantly lower than those observed for Fe<sub>3</sub>O<sub>4</sub> thin films deposited directly on MgAl<sub>2</sub>O<sub>4</sub>(100) substrates without an MgCr<sub>2</sub>O<sub>4</sub> buffer layer (see Figure SI11 in the Supplementary Information), thus suggesting that adding an  $MgCr_2O_4$  buffer layer can reduce the density of APBs, typically resulting in increased coercivity through pinning effects. 55,56 Additionally, the similarity in coercivity between the trilayer with a 1.6 nm and 2.4 nm thick  $MgCr_2O_4$  spacer and the single  $Fe_3O_4$  film suggests that the two magnetite films are effectively separated, behaving almost as individual entities. The rise in coercivity in the trilayer with a 0.6 nm thick MgCr<sub>2</sub>O<sub>4</sub> spacer may be linked to the films' quasi-continuous nature, as greater thicknesses may correspond to higher coercivity, as observed in some studies focusing on similar low thickness regions. 53,57,58 This scenario could be somehow more complex if we consider the formation of a mixed Cr/Fe spinel oxide at Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub> interfaces, contributing to the overall magnetic configuration, as reported by Vasconcelos et al. for the corresponding thin films.<sup>59</sup> Thus, besides the occurrence of APBs, the presence of mixed interface phases could play a role for driving the magnetic properties of the entire heterostructure.

#### 3.4 XAS and surface magnetic properties

Figure 4 summarizes the XAS/XMCD results obtained for samples with MgCr<sub>2</sub>O<sub>4</sub> spacer thickness ranging from 0.6 nm to 2.4 nm. The quantitative estimation of the XAS/XMCD depth sensitivity in total yield mode still remains not completely defined. While it has been clarified that the sample depth probed by these measurements must be less than 20 nm<sup>60</sup>, XAS measurements of Fe L<sub>2,3</sub> absorption thresholds from Fe<sub>3</sub>O<sub>4</sub> are reported with *mean probing depth* values from about 1 to 5 nm<sup>61,62</sup>, which demonstrates the

high uncertainty in this value and the relatively high surface sensitivity of the technique. Therefore, we can safely assume that the spectra of Figure 4 probe the upper part of the trilayer structure, i.e. the top Fe<sub>3</sub>O<sub>4</sub> layer and the MgCr<sub>2</sub>O<sub>4</sub> spacer, in particular excluding any contribution from the interface at the MgCr<sub>2</sub>O<sub>4</sub> buffer layer. The x-ray absorption spectra of the Fe and Cr  $L_{2,3}$  absorption thresholds for the sample with MgCr<sub>2</sub>O<sub>4</sub> spacer thickness 0.6 nm, obtained by averaging over the dichroic curves, are shown in panels (a,b). Similar spectra (not shown) are obtained for the other MgCr<sub>2</sub>O<sub>4</sub> spacer thicknesses. The Fe  $L_{2,3}$  spectrum is consistent with most of those reported in literature for magnetite, hence confirming the good quality of these layers.<sup>63,64</sup> On the other hand, the Cr  $L_{2,3}$  spectrum is very similar to that of compounds hosting  $Cr^{3+}$  (3d<sup>3</sup>) ions located in lattice sites with local octahedral symmetry  $O_h$ , such as in Cr<sub>2</sub>O<sub>3</sub>, <sup>59,65–67</sup> thus reinforcing the hypothesis to having obtained the correct MgCr<sub>2</sub>O<sub>4</sub> crystallographic structure, where indeed the chromium ions solely occupy the octahedral sites. Thus, the analysis of the Fe  $L_{2,3}$  and Cr  $L_{2,3}$ absorption spectra suggest the heterostructure does not host spurious phases containing different oxidation states, in agreement with the HAXPES results. In particular, the absence of significant contribution by  $Cr^{2+}$  ions rule out the presence of roomtemperature ferromagnetic CrO<sub>2</sub>. In order to put these considerations on a firmer ground, we performed theoretical calculations, shown as red lines superimposed to the experimental spectra of Figure 4(a) and Figure 4(b), confirming the above interpretation: The Cr  $L_{2,3}$  absorption spectrum was calculated for Cr<sup>3+</sup> valence state in octahedral local symmetry, consistently with the position of Cr ions in the MgCr<sub>2</sub>O<sub>4</sub> lattice, while the calculation for the Fe  $L_{2,3}$  absorption spectrum accurately incorporates the contribution of all Fe cations, i.e.  $Fe^{2+}$  in octahedral symmetry ( $O_h$ ),  $Fe^{3+}$ in tetrahedral symmetry  $(T_d)$  and Fe<sup>3+</sup> in octahedral symmetry  $(O_h)$ . The calculations were performed for an infinite material and then adjusted to match the experimental intensity. In particular, for the iron case, the theoretical curve is obtained from the sum of the three different Fe contributions, weighted in order to obtain the best representation of the experimental data. The corresponding theoretical XMCD curves for each ion species are reported in panels (e,f). 63,64,68,69

Although the shape and strength of the Fe XMCD is largely consistent with previous results about thin films of magnetite, <sup>70</sup> the occurrence of a sizeable XMCD for Cr in MgCr<sub>2</sub>O<sub>4</sub> is unexpected, as MgCr<sub>2</sub>O<sub>4</sub> is an antiferromagnetic semiconductor with a Néel temperature of about 13 K, and paramagnetic at room temperature. Accordingly, we indeed find out that the XMCD signal at the Cr  $L_{2,3}$  absorption edges was vanishing in a single MgCr<sub>2</sub>O<sub>4</sub> film (not shown). The XMCD curves of Cr and Fe ions in panel (c) and (d), respectively, show consistent lineshape but varying intensity for increasing spacer thickness. In particular, the trilayers with MgCr<sub>2</sub>O<sub>4</sub> spacers of 1.6 nm and 2.4 nm show nearly identical XMCD spectral features and comparable amplitude, indicating that both configurations result in effective magnetic decoupling of the  $Fe_3O_4$  layers. Note that the calculation shown in Figure 4(e), indicating a sizable XMCD for Cr<sup>3+</sup> ion, do not take into account the whole MgCr<sub>2</sub>O<sub>4</sub> structure. The sign of the XMCD curves for Fe and Cr indicates that the Cr magnetic moments are oriented

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Fig. 4 XAS/XMCD measurements at the Fe and Cr  $L_{2,3}$  absorption thresholds. (a,b) experimental (black dotted lines) and calculated (red lines) x-ray absorption curves. All spectra were collected at room temperature with the samples in the remanent state. (c,d) XMCD curves for different thickness of the MgCr<sub>2</sub>O<sub>4</sub> spacer. The XMCD curves are normalized to the maximum average intensity of the  $L_3$  absorption threshold in the respective Fe and Cr spectra. The XMCD curves are well reproduced by calculations (red lines) reported in panels (e,f). Calculated XMCD curves used to reproduce the experimental results. Details of calculations are reported in the text.

as those of the  $Fe^{2+/3+}$  ions in the octahedral sites of the magnetite, thus ruling out the presence of Cr ions in the tetrahedral sites. This condition resembles the ferromagnetic state of Cr for the iron chromite CrFe<sub>2</sub>O<sub>4</sub>,<sup>65</sup> where the Cr<sup>3+</sup> ions only occupy lattice sites with Oh symmetry. Furthermore, the XMCD curves of Cr are fully consistent with the XMCD calculation shown in panel (e) based on the same configurational parameters of the absorption threshold, except for a scale factor adopted to fit the change of the experimental XMCD amplitude. This indicates the formation of mixed phases at the Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub> boundaries in which the replacement of Fe by Cr in the lattice promotes the magnetic ordering of the Cr magnetic moments.

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To investigate this replacement process in the Fe<sub>3</sub>O<sub>4</sub> lattice, we have analysed in detail the lineshape of the Fe XMCD curves in the  $L_3$  energy region. In Figure 5, the XMCD curves for the samples with the thinner (0.6 nm) and larger (2.4 nm) MgCr<sub>2</sub>O<sub>4</sub> spacer thickness, and for a 60 nm thick film of Fe<sub>3</sub>O<sub>4</sub> used as reference for the bulk, are normalized to the maximum XMCD. This procedure highlights the reduction of XMCD in the energy region associated to the Fe<sup>2+</sup> contribution upon increasing MgCr<sub>2</sub>O<sub>4</sub> spacer thickness. We have evaluated the relative concentration of the  $\text{Fe}^{2+}(O_h)$ ,  $\text{Fe}^{3+}(T_d)$ , and  $\text{Fe}^{3+}(O_h)$  components in the Fe XMCD curves by fitting the  $L_3$  energy region with the three dichroic contributions shown in Figure 4(f). This apThis article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

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Fig. 5 Experimental and theoretical XMCD curves at the Fe  $L_3$  absorption threshold for different MgCr<sub>2</sub>O<sub>4</sub> thickness and the reference Fe<sub>3</sub>O<sub>4</sub> thick layer. The XMCD curves are normalized to the maximum to emphasize the change in the low energy region. The theoretical XMCD curves were obtained by fitting the contribution of the different Fe ions in the Fe<sub>3</sub>O<sub>4</sub> lattice.

proach proved fruitful information in other cases involving Fe<sub>3</sub>O<sub>4</sub> or Fe<sub>2</sub>O<sub>3</sub>.<sup>64</sup> As shown in Figure 5, the fitting results obtained by proper weighting of the three dichroic contributions confirm the evolution of the experimental curves, with the relative amount of Fe<sup>2+</sup>( $O_h$ ):Fe<sup>3+</sup>( $T_d$ ):Fe<sup>3+</sup>( $O_h$ ) passing from 0.92:1:1 for the thinner MgCr<sub>2</sub>O<sub>4</sub> spacer to 0.85:1:1 for the thicker one.

Such behavior is consistent with a scenario in which Fe<sub>3</sub>O<sub>4</sub> with MgCr<sub>2</sub>O<sub>4</sub> diffuse at their interface, forming a mixed region, as also evidenced by the EDX-STEM results, where Cr<sup>3+</sup> partially replaces  $Fe^{2+}$  (in octahedral coordination), which could then be oxidized to Fe<sup>3+</sup>.<sup>71</sup> This leads to the formation of a mixed spinel oxide at the Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub> interfaces, containing both iron and chromium ions. Compared to pure Fe<sub>3</sub>O<sub>4</sub>, this phase exhibits lower saturation magnetization and softer magnetic properties, in agreement with literature data on mixed Cr/Fe spinel oxides.<sup>59</sup> In this phase,  $Cr^{3+}$  ions acquire a magnetic polarization, and the relative proportions of iron species in Fe<sub>3</sub>O<sub>4</sub> are modified, consistent with the characteristics of mixed Cr/Fe spinel oxides. As a result, the enhanced XMCD signal observed in the thinner MgCr<sub>2</sub>O<sub>4</sub> layer [ $\sim$  20%, as shown in Figure 4(c)] may be linked to the low chromium content at the interface. As the thickness of the MgCr<sub>2</sub>O<sub>4</sub> layer increases, more Cr ions is available to diffuse thorough the interface, leading to the formation of a mixed Cr/Fe spinel phase with a higher chromium concentration compatible with a decrease in the Cr XMCD signal and in a decrease in the coercive field, as observed by Vasconcelos Borges Pinho et al.<sup>59</sup>

characterized by the interaction of different Fe valences, the exact balance between the various Fe ions is fundamental for establishing certain magnetic behaviours. For example, it is quite common that in Fe<sub>3</sub>O<sub>4</sub> films an Fe(ochtahedral)-O termination is the most favourable,<sup>72</sup> and in general it has been reported that the Fe<sub>3</sub>O<sub>4</sub> surface is richer of Fe<sup>3+</sup> ( $O_h$ ) than the bulk, <sup>73,74</sup> leading to a decrease of the saturation magnetization. In particular, in the present case, the exact nature of the Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub> interface could play a role in the magnetic behaviour of the investigated heterostructures. In this respect it might be helpful to quantify the magnetic moment of iron in Fe<sub>3</sub>O<sub>4</sub> via the XMCD sum rules, <sup>75</sup> keeping in mind that the obtained values may have some uncertainties as due, for example, to the exact value of the number of 3d holes used (here 13.5 for all the samples) and the integration range for the magnetic moment estimation.<sup>62,76</sup> As a consequence, the absolute values of the obtained magnetic moments might be questionable, while a relative comparison among the values obtained for the different samples remains reliable. The values of the spin ( $\mu_{spin}$ ), orbital ( $\mu_{orb}$ ) and total ( $\mu$ ) Fe magnetic moments in the three investigated trilayers, the 60 nm thick Fe<sub>3</sub>O<sub>4</sub> grown on MgO(100) and the 7 nm thin Fe<sub>3</sub>O<sub>4</sub> grown on  $MgCr_2O_4/MgAl_2O_4(100)$ , are collected in Table 2.

It has to be noted that in a complex system such as magnetite,

Table 2 Fe magnetic moments obtained by XMCD sum rules.

| Sample                                  | $\mu_{spin}$ ( $\mu_B$ ) | $\mu_{orb}$ ( $\mu_B$ ) | $\mu (\mu_B)$ |
|---|--------------------------|-------------------------|---------------|
| 60 nm Fe <sub>3</sub> O <sub>4</sub>    | 1.88                     | 1.10                    | 1.98          |
| 7 nm Fe <sub>3</sub> O <sub>4</sub>     | 1.11                     | 0.30                    | 1.41          |
| 0.6 nm MgCr <sub>2</sub> O <sub>4</sub> | 1.84                     | 0.17                    | 2.01          |
| 1.6 nm MgCr <sub>2</sub> O <sub>4</sub> | 1.51                     | 0.07                    | 1.58          |
| $2.4 \text{ nm MgCr}_2O_4$              | 1.36                     | 0.15                    | 1.51          |

The iron magnetic moment of the trilayer with the thinnest MgCr<sub>2</sub>O<sub>4</sub> spacer is basically equal to that of the 60 nm thick reference Fe<sub>3</sub>O<sub>4</sub> sample (both values being however lower than the bulk value) and larger than that of a single 7 nm Fe<sub>3</sub>O<sub>4</sub> film (corresponding XMCD spectra not shown in Figure 4 and reported in Supplementary Information Figure SI12). This observation suggests that the thinnest MgCr<sub>2</sub>O<sub>4</sub> spacer does not fully decouple the two magnetite layers, causing the heterostructure to behave as a single Fe<sub>3</sub>O<sub>4</sub> ferromagnetic film with an equivalent thickness of approximately 15 nm, as if the layers were in direct contact. In contrast, for MgCr<sub>2</sub>O<sub>4</sub> spacers  $\geq$  1.6 nm, the magnetic moment in Fe<sub>3</sub>O<sub>4</sub> decreases significantly to values similar to those of a single 7 nm Fe<sub>3</sub>O<sub>4</sub> film. This indicates that the two layers behave almost independently, as they are effectively decoupled by the MgCr<sub>2</sub>O<sub>4</sub> spacer with the Cr<sub>x</sub>Fe<sub>3-x</sub>O<sub>4</sub> phase being confined to the boundaries with Fe<sub>3</sub>O<sub>4</sub>, consistent with conclusions drawn from the magnetization curves. Indeed, the incorporation of Cr in Fe<sub>3</sub>O<sub>4</sub>, with the formation of the  $Cr_xFe_{3-x}O_4$ , results in a reduction of the Fe magnetic moment with respect to pure magnetite, <sup>59</sup> thus if this alloy phase had not been limited to the interface alone, an even greater reduction in magnetic moments would have been observed.

## Conclusions

Epitaxial all-spinel Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub>/Fe<sub>3</sub>O<sub>4</sub> heterostructures with variable spacer thicknesses were thoroughly investigated with a combination of chemical, morphological, structural, magnetic, and surface characterizations. For spacer thicknesses > 1.6 nm, the two magnetite layers are effectively decoupled and behave as independent ferrimagnetic layers, thus demonstrating the feasibility of designing intricate all-oxide heterostructures that retain the intrinsic properties of individual thin Fe<sub>3</sub>O<sub>4</sub> films. These samples exhibit relatively low coercivity, which is attributed to a reduced presence of antiphase boundaries due to the excellent lattice match between Fe<sub>3</sub>O<sub>4</sub> and MgCr<sub>2</sub>O<sub>4</sub> buffer layer. Limited cation interdiffusion occurs at the Fe<sub>3</sub>O<sub>4</sub>/MgCr<sub>2</sub>O<sub>4</sub> interface, resulting in the formation of a mixed Cr/Fe spinel oxide phase localized at the interphase boundaries, which does not significantly affect the overall magnetic properties, remaining largely consistent with those of the individual Fe<sub>3</sub>O<sub>4</sub> layers. This study provide insides into the magnetic interactions between Fe<sub>3</sub>O<sub>4</sub> layers mediated by an MgCr<sub>2</sub>O<sub>4</sub> spacer, demonstrating that thin Fe<sub>3</sub>O<sub>4</sub> films can retain their intrinsic properties within complex heterostructures, paving the way for advanced all-spinel oxide devices with tailored functionalities.

## Author contributions

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# Conflicts of interest

There are no conflicts to declare.

# Data availability

The data supporting this article have been included as part of the Supplementary Information.

# Acknowledgements

This work has been performed in the framework of the Nanoscience Foundry and Fine Analysis (NFFA- MUR Italy Progetti Internazionali) project (www.trieste.NFFA.eu) and has received funding from the European Union's Horizon 2020 Research and Innovation Programme under Project SINFONIA, Grant 964396. The support of Diamond Light Source, instrument I09 (proposal SI32921-1), is gratefully acknowledged. G. V. and D. P. acknowledge the support from the Italian Ministry Research (MUR) under the PRIN program, project No. 2020PY8KTC. G. P. thanks Next Generation EU funds under the Italian Ministry of University and Research (MUR) National Innovation Ecosystem grant ECS00000041 - VITALITY- CUP B43C22000470005. Financial support from the Research Subsidy No. 16.16.110.663 of the AGH University of Krakow is acknowledged (B. R.). We thank Andrea Fondacaro for technical support and fruitful discussions. D.P. and G.V. thank Mr. Enrico Patrizi for his assistance with the magnetic measurements.

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The data supporting this article have been included as part of the Supplementary Information.

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