

Cite this: *Nanoscale*, 2019, **11**, 19870

Evidence of anomalous switching of the in-plane magnetic easy axis with temperature in Fe₃O₄ film on SrTiO₃:Nb by v-MOKE and ferromagnetic resonance†

José Luis Fdez. Cuñado,^{a,b} Julio Camarero,^{a,b} Francisco J. Pedrosa,^a Norbert M. Nemes,^c Mikel Sanz,^d Mohamed Oujja,^d Esther Rebollar,^d José F. Marco,^d Juan de la Figuera,^d Matteo Monti,^d Marta Castillejo,^d Titusz Feher,^e Balint Nafradi,^f Laszlo Forró^f and Alberto Bollero^{*,a}

The evolution of the magnetic anisotropy directions has been studied in a magnetite (Fe₃O₄) thin film grown by infrared pulsed-laser deposition on SrTiO₃(100):Nb substrate. The magnetic easy axes at room temperature are found along the in-plane $\langle 100 \rangle$ film directions, which means a rotation of the easy axis by 45° with respect to the directions typically reported for bulk magnetite and films grown on single-crystal substrates. Moreover, when undergoing the Verwey transition temperature, T_V , the easy axis orientation evolves to the $\langle 110 \rangle$ film directions. This anomalous behavior has been demonstrated by measuring first the angular dependence of coercivity and remanence well above and below T_V by high-resolution vectorial magneto-optical Kerr effect (v-MOKE). Ferromagnetic resonance (FMR) measurements have additionally proven a well-defined fourfold magnetic anisotropy induced during growth with confirmed easy axis directions along $\langle 100 \rangle$ for $T > T_V$ and $\langle 110 \rangle$ for $T < T_V$. These results provide a clear proof of the possibility of tuning magnetic anisotropy in Fe₃O₄ thin films by proper control on the growth parameters and substrate choice.

Received 16th May 2019,
Accepted 28th September 2019

DOI: 10.1039/c9nr04198b

rsc.li/nanoscale

Introduction

Magnetite (Fe₃O₄) has attracted strong interest over the years due to its robust ferrimagnetism down to nanometer thickness, good electrical conductivity and presumed half-metal character.¹ Fe₃O₄ undergoes a metal-insulator transition (Verwey transition)² at low temperature accompanied by a change from cubic to monoclinic crystal symmetry.³ The temperature at which these changes take place is known as the Verwey transition temperature (T_V) and occurs at around 122 K in bulk magnetite,⁴ although this value may vary (typically 110–123 K) in thin film systems depending on growth parameters, substrate choice and thickness.⁵ An open question is to what extent the preparation of Fe₃O₄ films on different sub-

strates can affect their magnetic properties and, in particular, the magnetic anisotropy axis. This might allow for proper tuning according to the final application. This information is of relevance for an efficient use of Fe₃O₄ in technological multiphase magnets and spintronic applications (magnetic tunnel junctions and spin injectors among others).^{6–9}

Diverse substrates have been reported for the growth of Fe₃O₄ thin films.^{5,10–17} MgO is commonly used as a substrate because the O atoms form a face-centered cubic structure with a small lattice mismatch between the two materials of only 0.3%; this allows pseudomorphic growth causing tensile stress during an early stage of growth.¹² By comparison, MgAl₂O₄ has a lattice mismatch of about –4% leading to compressive stress during growth.⁵ SrTiO₃ is a very interesting material used in microelectronics industry with applications going from varistors to tuneable high temperature microwave filters. Doping SrTiO₃ with niobium (Nb) makes it electrically conductive, which is of interest as an electrode in capacitor-like structures.¹⁸ On this basis, there are many reports on the magnetic and transport properties of Fe₃O₄ thin films grown on undoped^{19–21} and doped^{14,16,17,22–24} SrTiO₃ substrates.

The most often reported evolution of the magnetocrystalline anisotropy of magnetite films follows the behavior found

^aIMDEA Nanoscience, Madrid, Spain. E-mail: alberto.bollero@imdea.org

^bDep. de Física de la Materia Condensada, Univ. Autónoma de Madrid, Spain

^cDep. Física de Materiales, UCM, Madrid, Spain

^dInstituto Química Física Rocasolano, CSIC, Madrid, Spain

^eDep. of Physics, BME and MTA-BME PROSPIN, Budapest, Hungary

^fInstitute of Condensed Matter Physics, EPFL-SB-ICMP-LPMC, Lausanne, Switzerland

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c9nr04198b

in bulk magnetite.^{4,25} At room temperature a first order negative cubic anisotropy induces the magnetic easy axes to be oriented along $\langle 111 \rangle$ directions. Upon cooling the material, the anisotropy decreases until, at around 140 K, the isotropic point is reached, at which the first order magnetocrystalline anisotropy vanishes. Continuing to cool down, and still in the cubic phase, the magnetocrystalline anisotropy changes sign and induces easy axes along $\langle 100 \rangle$, until the Verwey transition is reached, at which the anisotropy becomes uniaxial along the monoclinic c axis, and increases substantially. At the surfaces of bulk crystals, a similar behaviour has been reported.^{25–28} This is modified by the shape anisotropy in $[100]$ films, which drives the magnetization in plane, into the in-plane $\langle 110 \rangle$ directions from room temperature to the isotropic point, and to in-plane $\langle 100 \rangle$ directions below.

However, there are reports of different behavior for magnetite films. Prieto *et al.*¹⁵ have carried out recently a systematic work comparing Fe_3O_4 films grown by ion-assisted deposition on silicon, amorphous glass, and different (001) single crystal substrates (MgO , SrTiO_3 and LaAlO_3). High-resolution v-MOKE measurements done at room temperature showed isotropic behavior for a polycrystalline film grown on silicon, in-plane uniaxial magnetic anisotropy for a film grown on glass, and a fourfold symmetry when growing Fe_3O_4 on the $\langle 001 \rangle$ single crystal substrates.¹⁵ The authors explained this different behavior as a direct consequence of average grain size (silicon and glass substrates) and magnetocrystalline anisotropy, with the mismatch at the interface defining the quality of the observed fourfold symmetry. All those Fe_3O_4 thin films had an in-plane magnetic anisotropy, but there exist reports of anomalous out-of-plane component of the magnetization in Fe_3O_4 thin films deposited on $\langle 001 \rangle$ and $\langle 110 \rangle$ MgO substrates,¹² Fe_3O_4 thin films grown on different (001)-oriented substrates (MgO , MgAl_2O_4 , SrTiO_3 and $\text{SrTiO}_3\text{:Nb}$),¹⁷ and a prominent perpendicular magnetic anisotropy in Fe_3O_4 films grown on $\text{MgO}(111)$ substrate.²⁹ These results are a clear indication that the orientation (in-plane or out-of-plane) of the magnetic anisotropy can be controlled by a proper choice of the substrate. The magnetic anisotropy is defined by the morphology and the microstructure at the film/substrate interface and those induced during the subsequent growth of the film. Recent studies^{14,15,17,30} have shown that also the in-plane magnetic easy axis directions in Fe_3O_4 thin films can be modified, from the expected evolution already detected for the surface of bulk crystals, and reported in cases for magnetite films.³¹ Schemme *et al.*³⁰ reported an in-plane 45° rotation of the magnetic anisotropy (room temperature magnetic easy axes along the in-plane $\langle 100 \rangle$ directions) in ultrathin magnetite films reactively grown on Fe precovered $\text{MgO}(001)$ substrate, by comparison with magnetite films directly grown on $\text{MgO}(001)$. They ascribed this anomalous behavior to the low crystalline quality of the magnetite films due to complete oxidation of the iron buffer layer, which might lead to the formation of APBs. Authors of that study pointed that – as previously suggested by Monti *et al.*¹⁴ – the rotation of the magnetic easy axes might find its origin in the presence of APBs.

We have previously reported in-plane easy axis along $\langle 100 \rangle$ directions at room temperature.^{14,17} By comparison with the low crystalline quality of the magnetite samples grown on oxidized iron prepared by Schemme *et al.*,³⁰ the high quality of the Fe_3O_4 thin film grown by infrared pulsed laser deposition (PLD) on $\text{SrTiO}_3(100)\text{:Nb}$ substrate was proven through a systematic study comprising X-ray Diffraction (XRD), Mössbauer and Low Energy Electron Diffraction and Microscopy (LEED, LEEM).¹⁴ The room temperature easy axis directions were measured by vectorial magneto-optical Kerr effect (v-MOKE). An important open question still remains related to the behavior of the magnetic anisotropy in the complete temperature range, *i.e.* including conclusive results when decreasing the temperature below T_V . This is precisely the scope of this work, by studying the evolution of the magnetic easy axis direction in $\text{Fe}_3\text{O}_4/\text{SrTiO}_3(100)\text{:Nb}$ starting from room temperature and undergoing T_V . In addition, and based on the scarcity of studies showing this rotation by 45° in comparison with the in-plane easy axis directions massively reported in literature over the years, we have complemented the v-MOKE analysis with ferromagnetic resonance (FMR) measurements at room and low temperature ($T < T_V$). The aim is to provide in this manner unequivocal information on the evolution of the magnetic easy axis directions of the system with temperature. FMR is one of the most sensitive techniques to investigate the surface anisotropy in magnetic thin films.^{32–35} This technique has been applied (room temperature measurements) with accuracy in the past to Fe_3O_4 thin films^{31,36} and also to Fe_3O_4 nanoparticles.³⁷ Those studies concluded that the room temperature magnetic easy axis lie along $\langle 110 \rangle$ directions, and thus different to those measured in the present study by using the same technique.

Experimental methods

The experimental setup for PLD consists of a stainless-steel vacuum deposition chamber pumped down to 6×10^{-5} Pa by a turbo-molecular pump. Hematite targets were prepared from a >99% iron(III) oxide powder (Sigma Aldrich, particle size $< 5 \mu\text{m}$) that was pelletized into disks of 10 mm diameter and about 2 mm of thickness using a hydrostatic press at 8 Ton cm^{-2} followed by sintering at 900 °C in air for 8 h. Targets were placed on a rotating sample holder and ablated with a Q-switched Nd:YAG laser (FWHM 15 ns, 10 Hz) at the excitation wavelengths of 1064 nm. The laser beam was focused onto the target at 45° to a spot of 0.14 mm^2 with a typical fluence of 8 times the ablation threshold fluence. Ablation threshold fluence (laser energy per unit area) of target at 1064 nm was determined by measuring the minimum single pulse energy necessary to yield a luminous plume as detected by eye. The diameter of the irradiated region was determined by measuring the print left on an unplasticized polyvinyl chloride sheet. Based on the obtained ablation threshold the irradiation fluence was 4 J cm^{-2} . $\text{SrTiO}_3(100)$ substrates doped with 0.1% Nb from Crystek were ultrasonically degreased in

acetone and methanol for 10 min and heated to 750 K. The substrates were placed in front of the target at a distance of 40 mm. Deposits were grown by delivering 144 000 pulses to the target (resulting in a deposition time of around 4 hours). Fe_3O_4 films with a thickness of 160 nm were obtained.

High morphological and structural quality of the film was proven by XRD, atomic force microscopy (AFM), and Raman and Mössbauer spectroscopies in a previous study.¹⁴

In this work a home-made high-resolution vectorial magneto-optical Kerr effect (v-MOKE) setup able of operating in the temperature range 4–500 K was used to measure the temperature and angular dependencies of averaged magnetization reversal processes in the Fe_3O_4 thin film.³⁸ The cryostat installed in the v-MOKE had a motorized rotatable sample holder with azimuthal correction, which allowed recording magnetization curves of the Fe_3O_4 film in the complete 0–360° angular range with an angular step of 5°. An external 31 mm gap electromagnet from Evico Magnetics GmbH was used to generate the external in-plane magnetic field. The criterion followed in this study to identify the in-plane orientation of the applied field has been $\alpha_H = 0^\circ$ as the angle when the field is set along the [100] direction of the substrate.

A standard Bruker 300E electron spin resonance (ESR) spectrometer operating at 9.4 GHz has been used for FMR measurements. The spectrometer uses magnetic field modulation with phase-sensitive detection and thus the measured signal is proportional to the field-derivative of the absorbed power. The static and microwave magnetic fields were oriented horizontally and vertically, respectively. The magnetic field was maintained at 0.7 T during temperature and direction (rotations of the sample) changes. The sample was rotated along the vertical axis, such that the static field always remained within the plane of the film. The sample was thermalized for 30 min before recording measurements at each selected temperature.

Results and discussion

As shown in our previous study,¹⁴ measurement of the magnetite low-energy electron diffraction (LEED) pattern confirmed a cube-on-cube epitaxial relationship between the $\text{SrTiO}_3(001)$:Nb substrate and the Fe_3O_4 film, in addition to verifying its monocrystalline nature. The stoichiometric composition of the film was proven by integral conversion electron Mössbauer spectroscopy (ICEMS).¹⁴ The ICEMS spectrum recorded at room temperature for the magnetite film was fitted with two components with the expected values for stoichiometric magnetite, in isomer shift (0.23 and 0.69 mm s^{-1}), quadrupole shift (−0.04 and 0.01 mm s^{-1}), and hyperfine magnetic fields (49.0 and 46.4 T).¹⁴ The ratio of the two components was 1.9 indicating that the film is stoichiometric. It is worth remarking that no contamination was detected by XPS,¹⁴ which showed only Fe and O, the former corresponding to a typical magnetite spectra³⁹ with a mixture of Fe^{2+} and Fe^{3+} . Fig. 1 shows the dependence of the magnetization on temperature. A large step

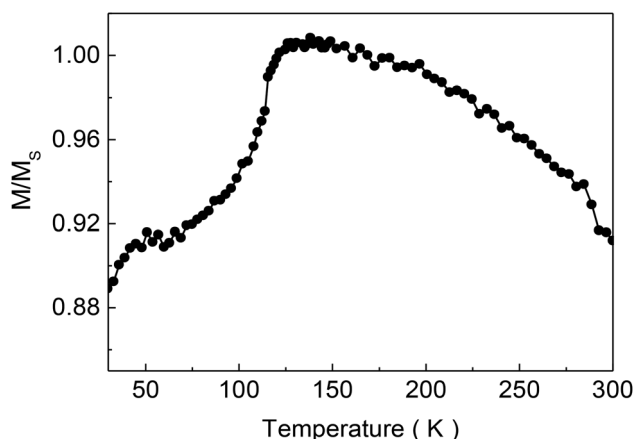


Fig. 1 Dependence of the magnetization on temperature (warming curve) with an in-plane applied field of 2 kOe for the Fe_3O_4 film grown on SrTiO_3 :Nb substrate. The Verwey transition occurs at a temperature $T_V = 115$ K.

in magnetization can be observed when increasing the temperature as a result of the change in the crystal structure from monoclinic to cubic, which is accompanied by a switching of the easy axis directions. The temperature at which this transition occurs is the Verwey transition temperature, with a value $T_V = 115$ K determined by taking the maximum slope of the magnetization plotted in Fig. 1. The transition appears significantly smeared out. This might be explained considering the lattice mismatch (7.5%) between magnetite and SrTiO_3 . This large mismatch, which is also expected to occur between our Fe_3O_4 film and the SrTiO_3 :Nb substrate, introduces an interfacial strain which is relieved by the formation of a large concentration of misfit dislocations at the film/substrate interface.^{14,15,19–21}

Hysteresis loops have been measured by v-MOKE at temperatures above and below the Verwey transition temperature ($T_V = 115$ K). For comparison, two hysteresis loops were recorded at each temperature: the first one with the external magnetic field applied along the [100] direction (*i.e.* parallel to the substrate edge, $\alpha_H = 0^\circ$), and a second one with the field along [110] ($\alpha_H = 45^\circ$) [see Fig. 2]. Fig. 2(a) shows hysteresis loops measured at 140 K ($T > T_V$). The higher remanence and coercivity measured along the [100] direction suggests that this is a preferred easy axis direction by comparison with the [110] direction. Advancing on that study, the magnetic response of the system also below T_V can be seen in Fig. 2(b). In contrast with the evolution observed at $T > T_V$, when measuring the hysteresis loops along the same directions but at a lower temperature of 110 K ($T < T_V$), the [110] direction clearly becomes an easier direction than [100] as proven by the larger coercivity and remanence values. As a first conclusion, these results point to a different evolution of the magnetic anisotropy with temperature by comparison with the most reported results on Fe_3O_4 thin films and bulk magnetite. In order to check this anomalous behavior, we have run a complete battery of measurements: temperature evolution of coercivity when

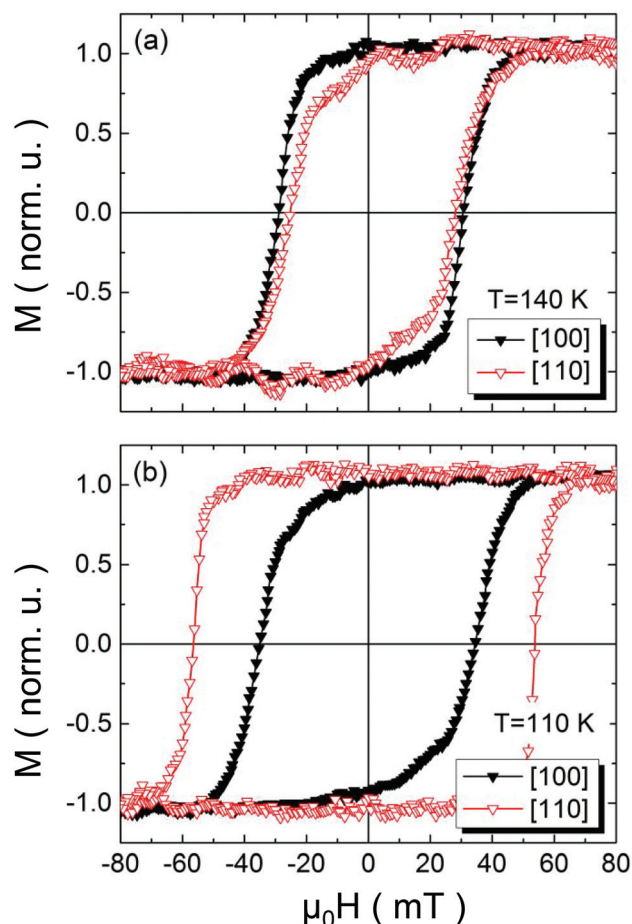


Fig. 2 In-plane hysteresis loops measured by v-MOKE with the external magnetic field applied along [100] (full symbol) and [110] (open) directions at two different temperatures: (a) $T = 140$ K ($T > T_V$) and (b) $T = 110$ K ($T < T_V$).

measuring along in-plane [100] and [110] directions; angular evolutions of coercivity and remanence above and below T_V ; and ferromagnetic resonance spectra recorded also in both temperature regimes. Fig. 3 shows the evolution of the coerciv-

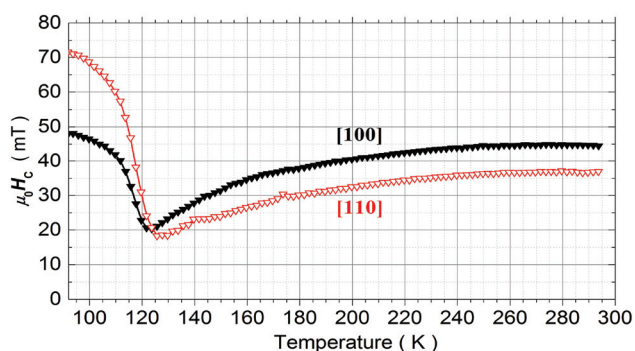


Fig. 3 Evolution of coercivity, $\mu_0 H_c$, with the measuring temperature (warming curves) when applying the external magnetic field along the in-plane directions [100] ($\alpha_H = 0^\circ$) (full symbol) and [110] ($\alpha_H = 45^\circ$) (open symbol).

ity with temperature (warming curve from 95 to 295 K) when applying the external magnetic field along [100] and [110] directions. In both cases a minimum in coercivity is measured when going through T_V , which varies only by 3.5 K, most likely due to thermal effects occurring during the warming ramp. However, and more important for the aim of this study, is the observation of higher coercivity along the [110] than along [100] below 115.7 K (± 4.5 K considering the thermally induced shift between the two curves shown in Fig. 3), in good agreement with the Verwey temperature value ($T_V = 115$ K) determined from the dependence of the magnetization on temperature (Fig. 1). The angular dependence of both coercivity and remanence above and below T_V will provide a more solid proof of the orientation of the easy axis directions in the system in the different temperature regimes. The evolution of both properties measured at 295 K ($T > T_V$) shows a well-defined four-fold symmetry with the highest values found at 0, 90, 180 and 270° , i.e. easy axis along the $\langle 100 \rangle$ directions (Fig. 4a and b). As previously shown at room temperature,^{14,15,17} this means that the easy axis directions are switched by 45° in comparison with those reported in literature for bulk magnetite and with the vast majority of studies done on Fe_3O_4 films. It was suggested that a particular distribution of antiphase domain boundaries (stacking defects which lead to partial antiferromagnetic coupling) in the Fe_3O_4 film might be responsible for this difference in the magnetic axis directions.^{14,17} This symmetry finds its origin in the magnetocrystalline anisotropy of the Fe_3O_4 film grown on the single crystal substrate.¹⁵ The open question is now how the magnetic anisotropy changes when decreasing the temperature below T_V . Fig. 4(c and d)

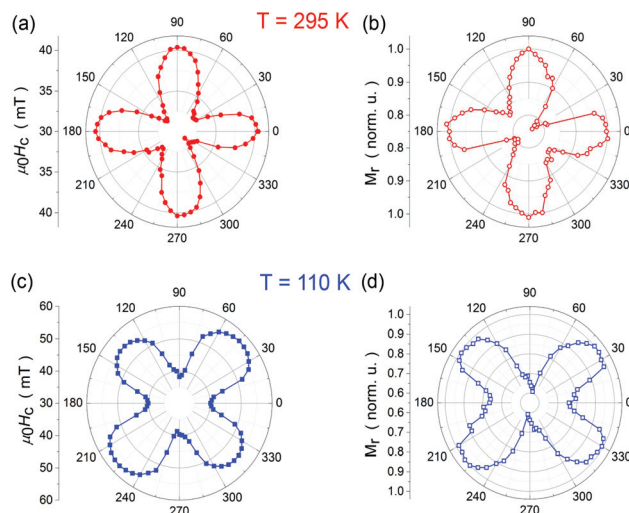


Fig. 4 Angular evolutions (polar plots) of (a) coercivity, $\mu_0 H_c$, and (b) remanence, M_r , for Fe_3O_4 film grown on $\text{SrTiO}_3\text{:Nb}$ substrate measured at 295 K ($T > T_V$). Angular evolutions of (c) coercivity and (d) remanence for the same sample measured at 110 K ($T < T_V$). Angular evolution of magnetic properties is determined from in-plane hysteresis loops measured by v-MOKE when rotating the film in the 0 – 360° angular range. Criteria: $\alpha_H = 0^\circ$ ($\alpha_H = 45^\circ$) corresponds to measurement done with the external magnetic field applied parallel to the in-plane [100] ([110]) direction of the substrate.

shows the angular evolution of coercivity and remanence at a measuring temperature of 110 K ($T < T_V$). It can be seen that now the easy axis directions are found along $\langle 110 \rangle$ directions, as it is proven by the maxima attained by both coercivity and remanence at 45, 135, 225 and 315°. This is the definitive demonstration that easy axis switch from $\langle 100 \rangle$ film directions for $T > T_V$ to $\langle 110 \rangle$ directions for $T < T_V$. To our knowledge, the present study constitutes the first experimental evidence showing this anomalous orientation of the magnetic easy axis directions in both temperature regimes $T_V < T < T_V$. On this basis, and for validation of the achieved conclusions, ferromagnetic resonance (FMR) measurements have been carried out.

The FMR spectra shown in Fig. 5 have been recorded along the in-plane $[100]$ ($\alpha_H = 0^\circ$) and $[110]$ ($\alpha_H = 45^\circ$) film directions at three selected temperatures: 295 K (*i.e.* well above T_V); 130 K (approaching T_V); and 110 K (below T_V). Minima of the spectra take place at magnetic field values of 158.5 mT ($\alpha_H = 0^\circ$) and 186.0 mT ($\alpha_H = 45^\circ$) at 295 K; 160.0 mT ($\alpha_H = 0^\circ$) and 167.0 mT ($\alpha_H = 45^\circ$) at 130 K; 190.5 mT ($\alpha_H = 0^\circ$) and 128.3 mT ($\alpha_H = 45^\circ$) at 110 K. This means that minima along the $[100]$ ($\alpha_H = 0^\circ$) film direction occur at a lower applied field than those at $[110]$ ($\alpha_H = 45^\circ$) for temperatures above T_V . When the measuring temperature approaches T_V the minima along $[100]$ and $[110]$ are found at closer fields (27.5 and 7.0 mT difference at 295 and 130 K, respectively). Decreasing temperature below T_V reverts the situation and the minimum along the $[110]$ direction is obtained at a lower field than that measured along the $[100]$ direction. These results indicate that the magnetic easy axis changes from $\langle 100 \rangle$ to $\langle 110 \rangle$ directions for $T > T_V$ and $T < T_V$, respectively. The FMR peak-positions calculated from the spectra presented in Fig. 5 are shown in Fig. 6, confirming the conclusions advanced from the interpretation of the FMR absorption derivative spectra. Considering that the minima in the angular evolution of the resonance field are indicative of the easy axis directions,^{40,41} there is a clear switching of 45° when going through T_V from $\langle 100 \rangle$ ($T > T_V$) to $\langle 110 \rangle$ ($T < T_V$). Moreover, it is interesting to observe that as the temperature descends to the vicinity of T_V , the anisotropy becomes weaker, but a preferred orientation of the magnetic anisotropy along $\langle 100 \rangle$ is still distinguishable (see angular evolution of the resonance field at 130 K in Fig. 6). This contrasts with previous FMR results on Fe_3O_4 thin films grown on MgO substrates.^{31,36} A direct comparison between our results and those previously reported in literature for the minima (easy axis) and maxima (hard axis) – obtained from the angular dependence plot of the in-plane resonance field – shows the mentioned switching of easy axis directions. Minima (maxima) measured in those studies at room temperature in the 0 – 180° angular range are found for $\alpha_H = 45^\circ$ and 135° ($\alpha_H = 0^\circ$, 90° and 180°), which indicates easy axis (hard axis) directions along the in-plane $\langle 110 \rangle$ ($\langle 100 \rangle$) directions.^{31,36} In contrast, Fig. 6 shows minima (maxima) of the resonance field measured at room temperature for $\alpha_H = 0^\circ$, 90° and 180° ($\alpha_H = 45^\circ$ and 135°), *i.e.* easy axis (hard axis) along the in-plane $\langle 100 \rangle$ ($\langle 110 \rangle$) directions. The same behavior shown in Fig. 6 for the in-plane resonance field at different temperatures was observed when measuring the

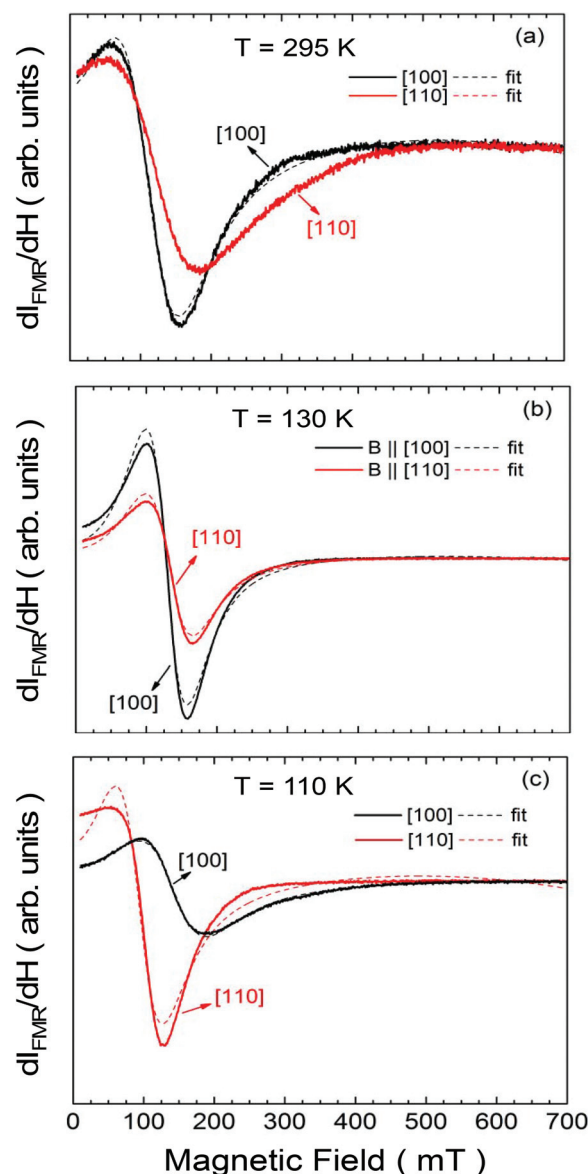


Fig. 5 FMR absorption derivative spectra for Fe_3O_4 film on $\text{SrTiO}_3\text{:Nb}$ substrate measured at three different temperatures: (a) 295 K ($T > T_V$); (b) 130 K ($T > T_V$); and (c) 110 K ($T < T_V$). The magnetic field was applied in two different configurations: parallel to $[100]$ and $[110]$ directions, respectively. Dashed lines show the best-fit derivative Lorentzian absorption curves.

angular evolution of the resonance linewidth (see ESI†). Looking in more detail to Fig. 6, it must be noted that the resonance field obtained at 295 K shows some deviation from the expected sinusoidal angular dependence along the $\langle 110 \rangle$ directions by presenting double maxima. This is most likely an artefact of the Lorentzian fit resulting from significant broadening of the FMR lineshape near the hard axis (Fig. 5). In contrast, the minima (indicative of the easy axis directions) obtained at 295 K are well defined with no doubling effect, as a result of the absence of any distortions in the measurement. Maxima and minima obtained at 295 and 130 K are distributed uni-

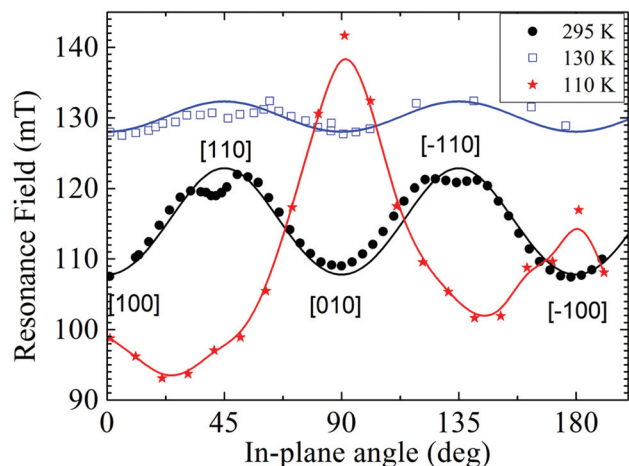


Fig. 6 Angular dependence (0–180°) of the in-plane resonance field obtained from FMR experiments (determined from Lorentzian fits to spectra as shown in Fig. 5) at three temperatures: 295 K ($T > T_V$); 130 K ($T > T_V$); and 110 K ($T < T_V$). Lines are simulations described in the text.

formly in four-fold symmetry, which is an indication that both easy axes are equivalent in strength and orthogonal. In contrast, the angular dependence measured at 110 K shows that, in spite of minima tend to be oriented along $\langle 110 \rangle$ directions, the effective easy axes are slightly tilted towards $\langle 100 \rangle$ directions as indicated by the unequal angular separation of the minima. This is indeed in very good agreement with a comparable tilt observed in the lobes obtained in the angular evolution of the remanence when measuring at 110 K [see Fig. 4(d)]. This tilt might be explained as due to a possible deformation of the unit cell of the monoclinic and/or to the presence of an additional uniaxial magnetic anisotropy lined-up with the $\langle 100 \rangle$ direction. This uniaxial contribution would be responsible of attempting to pull the magnetocrystalline anisotropy symmetrically towards $\langle 100 \rangle$ directions. This contribution might be due to an unequal distribution of twins,⁴² which find its origin in the strain induced on the film during the first stages of the growth and the formation of antiphase boundaries (APBs). On this basis, the conclusion related to the effective room temperature magnetic axis in $\text{Fe}_3\text{O}_4/\text{SrTiO}_3$ found along the in-plane $\langle 100 \rangle$ correlating with the directionality and the magnetic coupling of the APBs formed during growth,¹⁷ might be extended to the low temperature regime to address the in-plane $\langle 110 \rangle$ orientation here reported for $\text{Fe}_3\text{O}_4/\text{SrTiO}_3:\text{Nb}$ found when going down through T_V . Accordingly, the APBs directionality would play a main role on determining the magnetic easy axis direction in Fe_3O_4 thin films,¹⁷ thus resulting in different behavior to bulk Fe_3O_4 . Further work is currently in progress to confirm this argument, which agrees with one of the main conclusions extracted by Celotto *et al.*⁴³ in a detailed study done at room temperature on the occurrence of APBs in high-quality epitaxial Fe_3O_4 films grown by molecular beam epitaxy (MBE) with a thickness varying between 6 and 50 nm. Authors analyzed the APBs directional-

ity and density from transmission electron microscopy (TEM) dark field images and found that the directionality of the APBs was predominantly close to $\pm[100]$ and $\pm[010]$. It has been shown in previous studies that the growth temperature and its duration, and the application of any post-growth annealing, influence the partial migration of APBs,⁵ and, moreover as concluded by Celotto *et al.*,⁴³ determine the directionality of the APBs. These points, combined with the conclusion extracted from our previous study¹³ indicating that the use of nanosecond IR laser at 1064 nm enhances the quality of magnetite thin films prepared by PLD, compared to the extensively used UV wavelengths, might lead to a situation similar to that described by Celotto *et al.*,⁴³ resulting in a well defined preferential orientation of APBs leading to a magnetic easy axis orientation along the in-plane $\langle 100 \rangle$ film directions at room temperature.

Conclusions

This study has shown the possibility of varying the in-plane easy magnetization axis in a magnetite thin film grown onto a $\text{SrTiO}_3:\text{Nb}$ substrate from $\langle 100 \rangle$ to $\langle 110 \rangle$ directions when undergoing the Verwey transition temperature T_V . This evolution contrasts with that typically observed in bulk and Fe_3O_4 thin film systems. The change of the magnetic anisotropy direction has been demonstrated by measuring the angular dependence of coercivity and remanence from room to low temperature ($T < T_V$) by vectorial magneto-optical Kerr effect (v-MOKE). A well-defined in-plane fourfold magnetic anisotropy is induced during film growth with in-plane easy axis directions switching during warming from $\langle 100 \rangle$ to $\langle 110 \rangle$ when going through T_V . Ferromagnetic resonance (FMR) measurements show a weak anisotropy for temperatures in the vicinity of T_V where the structural transformation begins to take place and both structures might be coexisting. However, and for temperatures well-above T_V (below T_V) –with a well-defined crystal structure – the in-plane easy axis directions are unequivocally $\langle 100 \rangle$ ($\langle 110 \rangle$). This study constitutes the first demonstration of such anomalous magnetic anisotropy in the complete temperature range, above and below the Verwey transition temperature. This finding is of fundamental importance in view of practical applications of this system in spintronic devices.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was supported by the Regional Government of Madrid through NANOMAGCOST project (P2018/NMT-4321) and by the Spanish Ministry of Economy and Competitiveness (MINECO) through Project CTQ2016-75880-P. M. O. thanks CSIC for contract and E. R. thanks MINECO for the tenure of a Ramón y Cajal contract (No. RYC-2011-08069). The work in

Lausanne was supported by the Sinergia grant “Mott physics beyond the Heisenberg model” of the Swiss NSF. The work in BUTE (Hungary) was supported by NKFIH Grant No. K119442 and 2017-1.2.1-NKP-2017-00001, and by the BME-Nanotechnology FIKP grant of EMMI (BME FIKP-NAT). IMDEA Nanoscience is supported by the ‘Severo Ochoa’ Programme for Centres of Excellence in R&D, MINECO [grant number SEV-2016-0686].

References

- 1 C. N. R. Rao, Transition metal oxides, *Annu. Rev. Phys. Chem.*, 1989, **40**, 291.
- 2 E. J. W. Verwey, *Nature*, 1939, **144**, 327.
- 3 J. Yoshida and S. Iida, *J. Phys. Soc. Jpn.*, 1977, **42**, 230.
- 4 A. R. Muxworthy and E. McClelland, *Geophys. J. Int.*, 2000, **140**, 101.
- 5 A. Bollero, M. Ziese, R. Höhne, H. C. Semmelhack, U. Köhler, A. Setzer and P. Esquinazi, *J. Magn. Magn. Mater.*, 1995, **285**, 279.
- 6 P. Seneor, A. Fert, J. L. Maurice, F. Montaigne, F. Petroff and A. Vaurés, *Appl. Phys. Lett.*, 1999, **74**, 4017.
- 7 T. Kado, *Appl. Phys. Lett.*, 2008, **92**, 092502.
- 8 L. Marnitz, K. Rott, S. Niehörster, C. Klewe, D. Meier, S. Fabretti, M. Witzkiok, A. Krampf, O. Kuschel and T. Schemme, *AIP Adv.*, 2015, **5**, 047103.
- 9 E. Wada, K. Watanabe, Y. Shirahata, M. Itoh, M. Yamaguchi and T. Taniyama, *Appl. Phys. Lett.*, 2010, **96**, 102510.
- 10 C. A. Kleint, H. C. Semmelhack, M. Lorentz and M. K. Krause, *J. Magn. Magn. Mater.*, 1995, **140**, 725.
- 11 D. T. Margulies, F. T. Parker, F. E. Spada, R. S. Goldman, J. Li, R. Sinclair and A. E. Berkowitz, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **53**, 9175.
- 12 D. T. Margulies, F. T. Parker, M. L. Rudee, F. E. Spada, J. N. Chapman, P. R. Aitchison and A. E. Berkowitz, *Phys. Rev. Lett.*, 1997, **79**, 5162.
- 13 M. Sanz, M. Oujja, M. Rebollar, J. F. Marco, J. de la Figuera, M. Monti, A. Bollero, J. Camarero, F. J. Pedrosa, M. Garcia-Hernandez and M. Castillejo, *Appl. Surf. Sci.*, 2013, **282**, 642.
- 14 M. Monti, M. Sanz, M. Oujja, E. Rebollar, M. Castillejo, F. J. Pedrosa, A. Bollero, J. Camarero, J. L. F. Cuñado, N. M. Nemes, F. J. Mompean, M. Garcia-Hernandez, S. Nie, K. F. McCarty, A. T. N'diaye, G. Chen, A. K. Schmid, J. F. Marco and J. de la Figuera, *J. Appl. Phys.*, 2013, **114**, 223902.
- 15 P. Prieto, J. E. Prieto, R. Gargallo-Caballero, J. F. Marco and J. de la Figuera, *Appl. Surf. Sci.*, 2015, **359**, 742.
- 16 O. Kuschel, N. Pathé, T. Schemme, K. Ruwisch, J. Rodewald, R. Buss, F. Bertram, T. Kuschel, K. Kuepper and J. Wollschläger, *Materials*, 2018, **11**, 1122.
- 17 F. J. Pedrosa, J. L. F. Cuñado, P. Perna, M. Sanz, M. Oujja, E. Rebollar, J. F. Marco, J. de la Figuera, M. Monti, M. Castillejo, M. García-Hernández, F. Mompeán, J. Camarero and A. Bollero, 2019, arXiv:1905.04961.
- 18 M. Alexe, M. Ziese, D. Hesse, P. Esquinazi, K. Yamauchi, T. Fukushima, S. Picozzi and U. Gosele, *Adv. Mater.*, 2009, **21**, 4452.
- 19 S. Kale, S. M. Bhagat, S. E. Lofland, T. Scabarozzi, S. B. Ogale, A. Orozco, S. R. Shinde, T. Venkatesan, B. Hannoyer, B. Mercey and W. Prellier, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2001, **64**, 205413.
- 20 Y. Z. Chen, J. R. Sun, Y. N. Han, X. Y. Xie, J. Shen, C. B. Rong, S. L. He and B. G. Shen, *J. Appl. Phys.*, 2008, **103**, 07D703.
- 21 X. H. Liu, W. Liu and Z. D. Zhang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2017, **96**, 094405.
- 22 B. Carvello and L. Ranno, *J. Magn. Magn. Mater.*, 2004, **272–276**, 1926.
- 23 M. Ziese, U. Köhler, A. Bollero, R. Höhne and P. Esquinazi, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **71**, 180406.
- 24 D. C. Kundaliya, S. B. Ogale, L. F. Fu, S. J. Welz, J. S. Higgins, G. Langham, S. Dhar, N. D. Browning and T. Venkatesan, *J. Appl. Phys.*, 2006, **99**, 08K304.
- 25 R. Řezníček, V. Chlan, H. Štěpánková, P. Novák and M. Maryško, *J. Phys.: Condens. Matter*, 2012, **24**, 055501.
- 26 L. Martin-Garcia, G. Chen, Y. Montana, A. Mascaraque, B. M. Pabon, A. K. Schmid and J. de la Figuera, *Sci. Rep.*, 2018, **8**, 5991.
- 27 L. Martín-García, A. Mascaraque, B. M. Pabón, R. Bliem, G. S. Parkinson, G. Chen, A. K. Schmid and J. de la Figuera, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2016, **93**, 134419.
- 28 J. de la Figuera, L. Vergara, A. T. N'Diaye, A. Quesada and A. K. Schmid, *Ultramicroscopy*, 2013, **130**, 77.
- 29 O. Chichvarina, T. S. Herng, W. Xiao, X. Hong and J. Ding, *J. Appl. Phys.*, 2015, **117**, 17D722.
- 30 T. Schemme, A. Krampf, F. Bertram, T. Kuschel, K. Kuepper and J. Wollschläger, *J. Appl. Phys.*, 2015, **118**, 113904.
- 31 P. A. A. van der Heijden, M. G. van Opstal, C. H. W. Swüste, P. H. J. Bloemen, J. M. Gaines and W. J. M. de Jonge, *J. Magn. Magn. Mater.*, 1998, **182**, 71.
- 32 G. A. Prinz and J. J. Krebs, *Appl. Phys. Lett.*, 1981, **39**, 397.
- 33 B. Heinrich, K. B. Urquhart, A. S. Arrott, J. F. Cochran, K. Myrtle and S. T. Purcell, *Phys. Rev. Lett.*, 1987, **59**, 1756.
- 34 Z. Zhang, P. E. Wigen and S. S. P. Parkin, *J. Appl. Phys.*, 1991, **69**, 5649.
- 35 S. S. Kalarickal, P. Krivosik, M. Wu, C. E. Patton, M. L. Schneider, P. Kabos, T. J. Silva and J. P. Nibarger, *J. Appl. Phys.*, 2006, **99**, 093909.
- 36 B. Aktas, *Thin Solid Films*, 1997, **307**, 250.
- 37 M. M. Can, M. Coskun and T. Firat, *J. Alloys Compd.*, 2012, **542**, 241.
- 38 J. L. F. Cuñado, J. Pedrosa, F. Ajejas, A. Bollero, P. Perna, F. J. Teran, R. Miranda and J. Camarero, *Rev. Sci. Instrum.*, 2015, **86**, 046109.
- 39 T. Fujii, F. M. F. de Groot, G. A. Sawatzky, F. C. Voogt, T. Hibma and K. Okada, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 3195.
- 40 L. R. Bickford, *Phys. Rev.*, 1950, **78**, 449.
- 41 C. Kittel, *J. Phys. Rad.*, 1951, **12**, 291–302.
- 42 R. Höhne, C. A. Kleint, A. V. Pan, M. K. Krause, M. Ziese and P. Esquinazi, *J. Magn. Magn. Mater.*, 2000, **211**, 271.
- 43 S. Celotto, W. Eerenstein and T. Hibma, *Eur. Phys. J. B*, 2003, **36**, 271.