Structure and magnetic properties of epitaxial $\text{CaFe}_2\text{O}_4$ thin films

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$\text{CaFe}_2\text{O}_4$ is a highly anisotropic antiferromagnet reported to display two spin arrangements with up-up-down-down (phase A) and up-down-up-down (phase B) configurations. The relative stability of these phases is ruled by the competing ferromagnetic and antiferromagnetic interactions between $\text{Fe}^{3+}$ spins arranged in two different environments, but a complete understanding of the magnetic structure of this material does not exist yet. In this study we investigate epitaxial $\text{CaFe}_2\text{O}_4$ thin films grown on TiO$_2$ (110) substrates by means of Pulsed Laser Deposition (PLD). Structural characterization reveals the coexistence of two out-of-plane crystal orientations and the formation of three in-plane oriented domains. The magnetic properties of the films, investigated macroscopically as well as locally, including highly sensitive Mössbauer spectroscopy, reveal long-range ordering below $T = 185$ K and a non-zero in-plane magnetization, consistent with the presence of uncompensated spins at the A/B phase boundaries, as proposed by Stock et al. for bulk samples.

INTRODUCTION

$\text{CaFe}_2\text{O}_4$ is an oxide semiconductor that, unlike most of the other ferrites with the same unit formula, does not have the Spinel structure[1] and, instead, crystallizes in a orthorhombic prototype structure with space group $Pnma$ and lattice parameters $a=9.230\text{Å}$, $b=3.924\text{Å}$ and $c=10.705\text{Å}$[2, 3].

An extensive literature focuses on the catalytic activity of $\text{CaFe}_2\text{O}_4$ nanoparticles [4, 5] and heterostructures [6–9], with particular attention to its application as photo-cathode in $H_2$ generation and water splitting reactions. On the other hand, single crystals of this material are only moderately investigated [10–16] and reports of epitaxial growth of $\text{CaFe}_2\text{O}_4$ thin films are almost absent [17].

Since the first studies [10, 11], the unusual magnetic structure of $\text{CaFe}_2\text{O}_4$ has been subject to debate and to date it has not yet been completely understood [18]. Recently, renewed interest in the topic has arisen following the neutron diffraction studies of Stock et al.[15, 16] on $\text{CaFe}_2\text{O}_4$ single crystals.

In the $\text{CaFe}_2\text{O}_4$ structure, the $\text{Fe}^{3+}$ ions occupy two crystallographically distinct positions, $\text{Fe}(1)$ and $\text{Fe}(2)$, each surrounded by 6 oxygen atoms in octahedral coordination, that form zig-zag chains that run parallel to the b-axis. $\text{FeO}_6$ octahedra within the same chain share edges, whereas neighbouring chains are connected through corners, as shown in fig.1a [18]. As in many oxides, the magnetic coupling between spins occurs via oxygen mediated superexchange, whose strength and sign depend on the $\text{Fe} – \text{O} – \text{Fe}$ bond angles. Thus, strong inter-chain AF interactions, $J_3$ and $J_4$, are found between corner sharing $\text{Fe}(1)\text{O}_6$ and $\text{Fe}(2)\text{O}_6$ octahedra, where the bond angles are about $120^\circ$. On the other hand, weaker couplings, $J_1$ and $J_2$, occur between edge-sharing $\text{FeO}_6$ octahedra within the same zig-zag chain, connected through angles of approximately $100^\circ$. Recently, Das et al.[18] have suggested that the magnetic structure of $\text{CaFe}_2\text{O}_4$ can be viewed as an armchair-type structure extending along the a-axis.

FIG. 1. Structure of $\text{CaFe}_2\text{O}_4$ reproduced from the CIF file published by Galuskina et al.[3] (a) Schematic representation of the distorted honeycomb lattice projected from the b-axis. The magnetic exchange is predominantly two dimensional with strong coupling ($J_3$ and $J_4$) along a and weak coupling ($J_1$ and $J_2$) along c. Green and brown colours indicate $\text{Fe}(1)$ and $\text{Fe}(2)$ sites. (b)-(c) Representation of the A and B spin structures with FM and AFM intra-chain ($J_1$ and $J_2$) interactions, respectively. Blue and red colours indicate $\text{Fe}^{3+}$ spins parallel and antiparallel to the b-axis.

Below the Nel temperature two competing spin arrangements, named A and B, exist, that differ for the sign of the weak intra-chain couplings and, thus, on the c-axis stacking of $\text{Fe}^{3+}$ spins [10, 15]. Specifically, the B structure is characterized by alternating spin up and spin down stripes in the c-direction, while in the A structure the periodicity is doubled with an up-up-down-down configuration (see fig.1b-c). In both structures $\text{Fe}^{3+}$ spins align parallel to the b-axis, giving rise to an Ising-like system with large magnetocrystalline anisotropy [14]. At the Nel temperature ($T_N=200$ K)

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the material orders in a pure B phase. Upon decreasing temperature below 150 K, the A phase also appears and the coexistence of these two structures has been reported to occur down to low-temperatures, where the A arrangement is favoured [16, 19]. Interestingly, each phase can also be visualized as the local structure of the antiphase boundary between two domains of the other phase, where the “orphan spins” generate an uncompensated magnetic moment along the b-axis[16].

The magnetic properties of this material have been investigated by means of neutron diffraction, DC and AC magnetometry, on single-crystalline and polycrystalline samples. [14, 15, 18, 20, 21] However, there is no complete agreement in the literature on interpreting the magnetic susceptibility measurements. In particular, the magnetic properties of CaFe$_2$O$_4$ seem to be very sensitive to the oxygen content. For example, only one magnetic transition at lower $T_N$ has been observed in oxygen-deficient CaFe$_2$O$_4$ [18]. In addition, oxygen vacancies-driven partial conversion of Fe$^{3+}$ (HS $S=5/2$) into Fe$^{2+}$ (LS $S=2$) ions has been reported to cause incomplete cancellation of the magnetization below $T_N$ inducing ferrimagnetic behaviour. On the other hand, a ferrimagnetic state is also observed in oxygen superstoichiometric CaFe$_2$O$_4$ due to the presence of Fe$^{4+}$ ions and the charge disproportionation between Fe$^{3+}$ and Fe$^{4+}$ ions occupying two inequivalent sublattices[21].

Because of the central role of the Fe − O − Fe bond angle in determining the strength of the magnetic interactions, any modification of the crystal structure will strongly influence the stability of the spin arrangements in CaFe$_2$O$_4$. Therefore, in this work we investigate the possibility to exploit epitaxial strain imposed on CaFe$_2$O$_4$ thin films by a crystalline substrate as a means for tuning the magnetic properties of the material[22].

**RESULTS**

**Synthesis and crystal structure**

Finding a suitable substrate is the first step for the epitaxial growth of thin films. Unlike for Perovskite and Spinel-type materials, most of the commonly used crystalline substrates do not match the lattice parameters of the CaFe$_2$O$_4$ prototype structure, making predictions of the epitaxial relation between the CaFe$_2$O$_4$ film and substrate not straightforward. A previous work on thin films of this material has used TiO$_2$ (100) substrates [17], due to the similarity between the oxygen octahedra in the rutile-type and CaFe$_2$O$_4$ structure. Thus, in our work, we also selected TiO$_2$ crystals as substrates, but cut along the (110) direction, in order to obtain a different out-of-plane orientation of the film.

The optimization of the growth of CaFe$_2$O$_4$ thin films on TiO$_2$ (110) substrates by Pulsed Laser Deposition (PLD) requires the control of several physical parameters (see Methods section). Because of the large nominal strain between film and substrate (9%), polycrystalline or amorphous films are easily obtained for a large window of growth parameters. However, we observed that relatively thick films of around 100 nm, prepared with a number of laser pulses in between 6 and 20 thousand, as well as a high laser repetition rate (10-15 Hz), are crystalline and textured.

Following the films growth *in-situ* by reflection high energy electron diffraction (RHEED) indicates island-growth mode: during the first minutes of deposition, the initial sharp reciprocal rods of the atomically flat substrate evolve into a transmission diffraction pattern typical of 3D islands [23]. Finally, at the end of the deposition, no more rods are visible, indicating high surface roughness (see inset fig.2a). Despite this, a well-defined epitaxial relation between the films and the substrate is observed, as discussed below.

![FIG. 2. Orientation determination via X-Ray Diffraction.](image)

(a) Plot of the two-theta-omega scan from 10° to 80° for films of increasing thickness from 66 to 150 nm. In addition to the substrate peaks (2θ=27° (110) and 2θ=56° (220)) two film peaks are visible at 2θ=33.6° and 2θ=70.5°. The insets show the RHEED patterns before and during the film deposition. (b) X-Ray pole figure taken at 2θ=25.5° (202). The peaks at Chi=50° indicate the presence of 3 domains with (004) out-of-plane orientation, while those at χ=10° and 70° originate from three (302) domains. (c)-(d) RSMs collected at $\chi=\phi=0°$ showing the presence of the both the (-206) and (600) peaks, which is only possible if the (004) and (302) orientations coexist within the same film.

Increased crystallinity of the films, estimated by the intensity of the out-of-plane peak in the X-Ray diffraction (XRD) pattern (fig.2a), was achieved with a substrate temperature of 850 °C and partial oxygen pressure $P_{O_2}=0.2$ mbar. A relatively high energy density of 2.8 J/cm$^2$ was required in order to ablate Fe and Ca atoms in equal proportion from the ceramic target.
and achieve near stoichiometric transfer (see fig.S1 of the Supplementary Information). As a result, Ca atoms travelling in the plasma plume reach the TiO$_2$ surface with high energy and are able to interact chemically with it. This leads to the formation of a Calcium Titanate layer at the interface between film and substrate.

Fig.2 shows the characterization of the films by means of X-Ray Diffraction (XRD). Two strong peaks in the two-theta-omega scans (fig.2a) are seen at angles of 33.6° and 70.5°. The former can belong to both the (004) and (302) planes of CaFe$_2$O$_4$ and the latter to their second order diffraction. These two families of planes not only share the same lattice spacing, $d = 2.67\ \AA$, but also display a very similar arrangement of atoms, making it non-trivial to tell them apart in X-Ray experiments (for more details see fig.S2 of the Supplementary Information). Therefore, in order to precisely determine the films orientation, the data from specular reflections need to be complemented by Reciprocal Space Maps (RSMs) around off-specular peaks. In the first map (fig.2c), we observe a peak at $2\theta=55.23^\circ$ and $\omega=6.48^\circ$, which is the (-206) peak if [004] is the out-of-plane orientation. No peak should be observed in that position in case of the [302] orientation. In the second map (fig.2d), we observe a peak at $2\theta=60.25^\circ$ and $\omega=-1^\circ$, which is the (600), if [302] is the out-of-plane orientation. Again, no peak should be found at these position in case of the [004] orientation. Therefore, the presence of both the (-206) and (600) peaks is only consistent with the coexistence of both [004] and [302] out-of-plane orientations within the same film. Moreover, from the RSMs we can deduce the epitaxial relation between films and substrate. In both crystal orientations, the [010] direction of the film is in-plane and aligned with the [1-10] direction of the substrate. On the other hand, the substrate [001] direction is parallel to the [100] and [10-2] directions of CaFe$_2$O$_4$ for [004] and [302] oriented crystals, respectively. This is particularly relevant for the magnetic properties of the films, being the [010] (b-axis) the magnetization direction, which indicates that the Fe$^{3+}$ spins are oriented in the plane of the films.

Further proof of the coexistence of the (004) and (302) orientations is provided by X-Ray pole Figures. Fig.2b shows the measurement collected at $2\theta=25.5^\circ$ that corresponds to the lattice spacing of the (202) planes of CaFe$_2$O$_4$. The normal to such planes forms an angle of 50° with the [004] direction and 10° with the [302] direction. Therefore, 2 peaks (at $\theta=90^\circ$ and 270° from the [010] direction) are expected to appear when rotating the sample with respect to the film normal, for $\chi=50^\circ$ and 10°. In fig.2d, six peaks for each value of $\chi$ appear, indicating that both orientations exist and each of them contains three domains (see the next section). Moreover, we also observe six peaks at $\chi=70^\circ$, corresponding to the (-103) planes, with a d-spacing close to that of the (202) planes, forming a 70° angle with the (302) planes.

The local structure of the films was further analysed by Transmission Electron Microscopy (TEM) (fig.3). High angle annular dark field scanning TEM (HAADF-STEM) and corresponding energy dispersive spectroscopy (EDS) analysis revealed the presence of a 10 nm CaTiO$_3$ layer with the perovskite structure between the substrate and the CaFe$_2$O$_4$ film, arising out of a chemical reaction between the high energy Ca$^{2+}$ ions in the plasma and the TiO$_2$ substrate surface (see Fig.S1 of the Supplementary Information). The CaTiO$_3$ layer is (010) oriented, and fully relaxed by means of dislocations, with 6 planes of the films corresponding to 5 planes of TiO$_2$ (inset of fig.3c).

**FIG. 3.** Transmission electron microscopy (TEM). Cross-section images of a 90 nm thick CaFe$_2$O$_4$ film with an intermediate CaTiO$_3$ layer of about 7 nm imaged along the [120] and [001] zone axes, respectively. (a) HAADF-STEM overview image showing the TiO$_2$ substrate surface. CaTiO$_3$ layer and CaFe$_2$O$_4$ film on top. (b) HAADF-STEM magnification of the CaFe$_2$O$_4$ lattice. In the inset the FFT, from which the out-of-plane lattice parameter is measured, is shown. (b) iDPC-STEM magnification of the Perovskite CaTiO$_3$ lattice. In the inset the FFT is shown, from which the in-plane and out-of-plane lattice parameters are measured. The second inset shows the TiO$_6$ octahedra tilt imaged along the CaTiO$_3$ [001] direction, revealing the a-a-c+ oxygen octahedral tilt pattern characteristic of the Pnma space group.

HAADF-STEM image of the CaFe$_2$O$_4$ layer is shown in fig.3b. The square-like pattern corresponds to the projection from the [120] zone axis of a crystallite with [004] out-of-plane orientation. The in-plane lattice parameter of $d=2.53\ \AA^{-1}$ corresponds to the (210) d-spacing. This indicates that, in the domain imaged here, the CaFe$_2$O$_4$ [010] is tilted with respect to the to substrate [1-10] by an angle of approximately 55°. This is consistent with the domain structure observed by means of Atomic Force Microscopy (AFM) and discussed in the next section.

The oxygen column imaging was further performed through differential phase contrast (DPC) STEM. The integrated DPC-STEM image on the CaTiO$_3$ layer (fig.3c and corresponding inset) clearly reveals a-a-c+ oxygen octahedral tilt pattern, corresponding to orthorhombic Pnma symmetry. Furthermore, the CaTiO$_3$
layer also exhibits 178° ferroelastic domain boundaries, reminiscent of bulk CaTiO₃[24] (for more details see fig.S3 of the Supplementary Information).

Domain Structure

The CaFe₂O₄ thin films prepared in this study display a distinctive domain structure, as clearly seen in the images collected by means of Atomic Force Microscopy (AFM). Each domain is composed by needle-like crystallites with the long axis parallel to the [010] direction. Three specific crystallographic orientations of the domains are found as shown in fig.4a: 1- with the [010] parallel to the substrate [1-10], 2 - forming a 55° angle with 1 and 3 -forming a -55° angle with 1. Consistent results are obtained from X-Ray pole figure measurements. Fig.4b shows the data collected at 2θ=33.65°, that corresponds to the spacing of CaFe₂O₄ (302) and (004) planes (first film peak in the 2theta-omega scan of fig.2a). Here, for a single domain sample, two peaks are expected to appear at χ=60° and φ=90°, 270° from the [010] direction. However, together with these, we observe 4 more peaks at ϕ=55°, 125°, 235° and 305°, which indicate the presence of 3 CaFe₂O₄ domains. Finally, the same domain structure emerges when studying the films by means of Electron Backscattered Diffraction (EBSD) in a scanning electron microscope (SEM), which allows to determine the crystallites orientation (see Fig.S4 of the Supplementary Information).

To explain the formation of 55° domains in the above mentioned directions, we put forward a model based on optimum structural matching between the crystal lattice of CaFe₂O₄ and that of the underlying CaTiO₃ layer. We notice that 55° is the angle between the CaTiO₃ [001] and [101] in-plane directions. The arrangement of the atoms in the (302) and (004) planes of CaFe₂O₄ consists of similarly spaced rows of cations that run parallel to the [010] direction. In both cases, two Fe rows alternate with one Ca row. As fig.4c shows, the atoms belonging to the two layers overlap best when the cations rows of CaFe₂O₄ are either parallel to the CaTiO₃ [001] direction or at ±55° from it. Because the growth of the films of this study follows an island-growth mode, islands with one of the 3 orientations start growing independently and later merge together yielding a rough film. The boundary between 2 adjacent domains is sharp with an herringbone pattern, whereas at the conjunction between 3 or more crystallites, vortex-like structures that can have triangular or diamond shape, are visible.

Magnetic properties

After optimization of the growth process, we investigated the magnetic properties of CaFe₂O₄ thin films at both local and macro scales. The magnetization of the films is measured as a function of temperature using a SQUID magnetometer for different values of applied magnetic field (H). The magnetic susceptibility (χ=M/H) from 4 to 400 K in a 100 Oe field parallel to the magnetization direction (b-axis of CaFe₂O₄) is plotted in fig.5a. Here, a clear transition is observed at TN=188 K (determined by the onset of DC magnetization), where χ steeply increases in the field-cooled (FC) curve and decreases in the zero-field-cooled (ZFC) curve.

![FIG. 5. Magnetic properties of CaFe₂O₄ thin films measured with field parallel to the magnetization direction (b-axis). (a) Plot of the magnetic susceptibility (χ) of a 84 nm thick sample as a function of temperature (T) from 5 to 400 K in a 100 Oe magnetic field. (b) Magnetization (M) of a 90 nm thick sample measured as a function of T from 5 to 300 K in zero applied DC field after field cooling under 100 Oe (red) and -100 Oe (purple). (c) Magnetization (M) of a 96 nm thick sample as a function of applied field (H) measured at 130 K between 7 and -7 T. (d) Magnetization (M) of a 90 nm thick sample as a function of applied field (H) measured at 100 K between 550 and -550 Oe after ZFC (black), 500 Oe FC (red) and -500 Oe FC (purple).](image-url)
at \( T = 140 \) K after FC, while at the same temperature, \( \chi \) reaches a minimum after ZFC. The noticeable splitting of the FC and ZFC data, also observed in our ceramic PLD target (see fig.S5 of the Supplementary Information), evidences the presence of a ferrimagnetic contribution added to the expected AF response. Moreover, in the films case, a small ZFC/FC splitting persists up to temperatures above \( T_N \), where the magnetization value is non-zero. This could be due to the remanent fields that are unavoidably present in the SQUID magnetometer, with different sign depending on the history of the previously applied field[25, 26].

In addition, differently from bulk, in the \( \chi \) vs. \( T \) plots (fig.5a) a paramagnetic (PM) tail can be found at below 30 K, that can probably be attributed to the \( \text{CaTiO}_3 \) layer at the interface between films and substrates (the latter being diamagnetic). Moreover, the magnetic susceptibility of \( \text{CaFe}_2\text{O}_4 \) thin films shows strong orientation dependence, being noticeably lower when the applied magnetic field is perpendicular to the b-axis (see fig.6a of the Supplementary Information). This indicates strong magnetocrystalline anisotropy, which is expected for an Ising-like system as \( \text{CaFe}_2\text{O}_4 \)[14].

To further investigate the ferrimagnetic behaviour of \( \text{CaFe}_2\text{O}_4 \), we measured the magnetization (\( M \)) as a function of temperature (\( T \)) in zero applied field. Fig.5b shows the data collected after cooling in a field of \( \pm 100 \) Oe parallel to the b-axis. The measured magnetic response indicates the presence of a spontaneous magnetization in \( \text{CaFe}_2\text{O}_4 \) films. On the other hand, here the low temperature tail observed in 5a is absent, confirming its paramagnetic nature. Next to the ordering temperature at \( T_N = 188 \) K, an anomaaly at around 35 K and a broader feature above 200 K are also visible. Such features were also observed in previous studies and have been assigned to a slow spin dynamical process [18] and room-temperature spin interactions [14, 18], respectively.

The presence of an uncompensated magnetic moment is also supported by the hysteresis of the \( M - H \) loops measured at various temperatures. In fig.5c the measurement at 130 K is shown, where the maximum hysteresis is observed (see fig.S6c of the Supplementary Information for the data at 30 and 175 K). Furthermore, when the sample is cooled down through \( T_N \) in the presence of a magnetic field parallel to the b-axis, the loop is subjected to a vertical shift in the direction of the applied field. Such shift is absent if the field is applied perpendicular to the magnetization direction.

Measuring \( M - H \) loops at low fields (up to 500 Oe) also reveals a small hysteresis that persists above \( T_N \) (see fig.S6c of the Supplementary Information), but no induced shift is observed under FC conditions.

In order to further characterize the magnetic structure of \( \text{CaFe}_2\text{O}_4 \) films, investigate the oxidation state of \( Fe \) and rule out the possibility of contamination with different \( Fe \)-containing phases or oxides, we also performed Mssbauer Spectrometry in electron conversion mode (CEMS) (fig.6). The room-temperature CEMS spectrum (fig.6a) exhibits a sharp paramagnetic doublet without any trace of magnetic parasitic phases containing \( Fe \). Therefore, we can exclude contamination by iron oxides or other calcium ferrite phases with higher \( T_N \), such as brownmillerite \( \text{Ca}_2\text{Fe}_3\text{O}_5 \)[27] or \( \text{CaFe}_3\text{O}_5 \)[28, 29]. A high resolution CEMS spectrum recorded at RT in a narrow velocity scale is reported in fig.6b. This spectrum shows well-defined lines and was fitted with two paramagnetic quadrupolar doublets corresponding to the two inequivalent \( Fe^{3+} \) sites \( Fe(1) \) and \( Fe(2) \), as expected for a pure \( \text{CaFe}_2\text{O}_4 \) phase[11, 30–34]. Both components have almost equal spectral area and linewidths (full width at half maximum \( \Gamma \approx 0.24 \) mm s\(^{-1}\)). The isomer shift values are also similar (\( \delta = 0.368 \pm 0.001 \) mm s\(^{-1}\)), but the quadrupole splitting (\( \Delta E_Q \)) is different, with values of 0.313\( \pm 0.001 \) mm s\(^{-1}\) and 0.743\( \pm 0.001 \) mm s\(^{-1}\) for \( Fe(1) \) and \( Fe(2) \), respectively.

The isomer shift values are typical of \( Fe^{3+} \) ions, and the absence of signal belonging to \( Fe^{2+} \) ions suggests low oxygen vacancy content in the film. An asymmetry of the line intensity of the doublet, different for each site, is clearly evidenced. Such asymmetry, in case of single crystal and isotropic Lamb-Mssbauer factor, is due to a preferred orientation of the symmetry axis of the electric field gradient (EFG) at the nucleus. If the principal axis of the EFG makes an angle \( \theta \) with the incident \( \gamma \)-beam direction, the line intensity ratio of the quadrupolar dou-
The function for $I_2/I_1 = 3(1 + \cos^2 \theta)/(5 - 3 \cos^2 \theta)$, with
values ranging from 3 for $\theta=0$ to 0.6 for $\theta=90^\circ$. Here the
fit of the spectrum yields $\theta= 41^\circ$ and $53^\circ$ for $Fe(1)$ and
$Fe(2)$, respectively.

In fig.6a also some selected CEMS spectra at temperatures
below room-temperature are reported. The CEMS
spectra below 185 K clearly show the onset of long range
magnetic order by the appearance of a magnetic sextet
due to nuclear Zeeman splitting. For each temperature,
the line intensity ratios are close to 3:4:1:4:3:1 for the
magnetic sextet, evidencing in plane orientation of the
$Fe$ spins. The temperature dependence of the mean mag-
neti hyperfine field $B_{hf}$ deduced from the fit can be
approximated using a power law $B_{hf}(T) = B_{hf}(0)(1-
T/T_N)^\beta$, where $\beta$ is the critical exponent or the AF order
parameter (the staggered sub-unit cell magnetization). A
reasonably good fit (fig.6c) leads to $B_{hf}(0)= (54.8\pm 4.0)$
T, $\beta= 0.28 \pm 0.05$, and $T_N= (181.2 \pm 1.6)$ K. The value
of the critical exponent is consistent with the $\beta= 1/3$ value
expected for a 3D Ising antiferromagnet. The Nel tem-
perature obtained from the fit is also consistent with the
transition temperature deduced from the SQUID mea-
surements.

The local magnetic response of the $CaFe_2O_4$ films was
also studied by means of scanning SQUID microscopy.
Scans collected at 4 K (fig.7) indicate clear magnetic ac-
tivity. The observed patterns resemble those of a weak
ferromagnet [35], but no clear structure in the signal is
visible. This is due to the spatial resolution of the scan-
ing SQUID setup (approximately 5 µm) that causes av-
eraging over multiple domains. Different sample thick-
nesses give rise to similar magnetic patterns but with dif-
ferent intensities: for a 120 nm film (fig.7a) the magnetic
field measured is 7-8 µT, while when the thickness is re-
duced to 66 nm the field is approximately halved (fig.7b).
These values are well above the scanning SQUID sen-
sitivity of approximately 50 nT. This confirms that the
signal originates from the full $CaFe_2O_4$ film, and is not
just limited to the surface.

In addition, in order to directly compare the magnetic
and topographic features of the samples, we also per-
formed magnetic force microscopy (MFM) experiments,
that yields a spatial resolution of about 100 nm. Topog-
raphy and MFM phase were recorded at various temper-
atures between 300 and 12 K, with a lift of either 30 nm
and 50 nm from the sample surface.

The first images, collected from room-temperature down
to 200 K (see fig.8a-b-c) do not show any magnetic re-
ponse. Here, the low contrast observed in fig.8b can be
attributed to simple cross-talk with the film topography,
as an analogous signal is observed when the experiment
is repeated with a non-magnetic tip, as shown in fig.57a-
b of the Supplementary Information.

Only when the temperature is lowered below the mate-
rial’s $T_N$ of 185 K a sharp contrast in the phase signal
appears. Fig.8d-e-f show scans collected at 100 K. In
these images we observe signatures of magnetic dipoles
(alternating red and blue contrast), several of which seem
to correspond to some of the edges of the needle-like crys-
tals. Such signal increases in intensity and sharpness at
lower scan lifts.

Fig.8g-h-i also shows MFM images collected at 12 K
in an applied magnetic field. Here, the color contrast
in the second-pass phase is inverted upon reversing the
magnetic field sign, from 0.05 T in 8h to -0.1 T in 8i (the
difference between the two images can be seen in fig.8c
of the Supplementary Information). This indicates that
the interaction between the tip and the sample goes from
FM to AF, and vice versa, upon reversing the tip mag-
netization.

These results are in good agreement with the expected
scenario, in which the $Fe^{3+}$ spins align along the [010]
direction that lies in the plane of the films. Such di-
rection corresponds to the long axis of the needle-like
domains, thus the magnetic field lines are only picked-up
in MFM experiments (with sensitivity limited to out-of-
plane magnetization) at the end of the crystallites, where

![FIG. 7. Scanning SQUID microscopy. 250µmx250µm scan of a (a) 120 nm film and (b) 66 nm film measured at 4 K.](image-url)
the magnetic field lines bend in the out-of-plane direction. These results are also consistent with the SQUID measurements, showing that CaFe$_2$O$_4$ thin films do not display the pure AF behaviour.

**DISCUSSION**

Despite the single out-of-plane peak observed by XRD in the two-theta-omega scans, in-depth characterization reveals the coexistence of two crystal orientations with identical lattice spacing, namely (004) and (302). Distinguishing between such orientations is complicated by the similar arrangement of Ca and Fe atoms in these two families of crystal planes. The similarity between these two orientations combined with the high frequency deposition, causes islands of both to nucleate at the surface and merge in an homogeneous film as thickness increases. TEM characterization also reveals that the epitaxial growth of CaFe$_2$O$_4$ films is achieved through the formation of a perovskite CaTiO$_3$ layer at the interface with the TiO$_2$ substrate. The presence of this layer explains the domain structure of the films: oriented needle-like crystallites connected together by herringbone walls. We explain this in terms of optimum matching between the cation positions in the CaFe$_2$O$_4$ and CaTiO$_3$ lattices, which is achieved when the film [010] direction is parallel to the CaTiO$_3$ [001] (which is in turn epitaxial with the substrate [1-10]) or at $\pm 55^\circ$ from it. The presence of these domain variants gives rise to vortex-like structures. Interestingly, the magnetic easy axes of the two crystal orientations coincide, as well as the direction of the net magnetic moment at the antiphase boundaries [16].

As expected for an Ising-like system, the magnetic response of CaFe$_2$O$_4$ films studied by means of SQUID magnetometry, displays a strong orientation dependence, being higher when the magnetic field is parallel to the $b$-axis of the crystals (comparison between fig.5a and fig.S6a of the Supplementary Information). The behaviour of the magnetic susceptibility as a function of temperature (fig.5a-b) is characterized by a single magnetic transition, defined as the onset of DC magnetization, which occurs at $T_N= 188$ K, and a maximum around $T=140$ K. Such value of $T_N$ lies in between those observed for the ordering of the A and B-phases in single crystalline samples by Stock and coworkers [16].

Another distinctive feature of the $\chi$ vs $T$ plots is the splitting of the FC and ZFC curves below $T_N$, with the latter having opposite sign for low applied magnetic fields. This indicates the presence of an irreversible contribution to the magnetization of CaFe$_2$O$_4$, which can not be switched below a critical field. Moreover, the presence of a spontaneous magnetization is supported by the vertical shift appearing in the $M-H$ loops below $T_N$ when the sample is cooled in a magnetic field (fig.5c). Vertical shifts in the M-H loops under field-Cooling have been observed before in uncompensated antiferromagnets[36] or inhomogeneous systems characterized by ferrimagnetic moments embedded in a AF matrix.

The local magnetic response of CaFe$_2$O$_4$ films, studied by means of low temperature MFM (fig.8), is also consistent with the presence of a magnetic moment: the MFM magnetic signal, which is only sensitive to out-of-plane magnetization, appears below 185 K, and is often localized at the borders of the domains or needle bunches. The observed contrast is opposite (field in- and field out- of the plane) at both sides of the needles, in good agreement with the expected behaviour of magnetic moment aligned along the needle long axis direction, which produces magnetic field lines that bend in the out-of-plane direction when the needles end.

Thus, the overall magnetic response of CaFe$_2$O$_4$ thin films is more consistent with an uncompensated AF behaviour than pure AF behaviour. In oxygen-deficient polycrystalline samples, Das and coworkers [13] detect the formation of ferrimagnetic clusters induced by oxygen vacancies. These accumulate at the domain boundaries and, by requirement of charge neutrality, introduce a proportional amount of Fe$^{2+}$ which in turn causes incomplete cancellation of the magnetic moments. Oxygen vacancies are also common in oxide thin films grown by means of PLD. Thus, it is possible that oxygen vacancies are also present in our films, despite having annealed them in 200 mbar oxygen atmosphere after the growth. However, the absence of Fe$^{2+}$ signature in Mssbauer Spectrometry experiments (fig.6) suggests that the spontaneous magnetization of our samples does not originate from oxygen-vacancies induced ferrimagnetic clusters. More consistently with our data, the net magnetization in CaFe$_2$O$_4$ can be caused by the formation of “orphan spins” at the boundaries between different magnetic domains, as proposed by Stock et al. [16]. This scenario is supported by the fact that the largest $M - H$ hysteresis is observed at 130 K (fig.5c), where the coexistence of A and B phases is expected to be maximum.

Previous studies, reported a broad feature in the $\chi$ vs $T$ plot above $T_N$ [14, 18], that can be fitted using the Bonner-Fisher model for linear magnetic chains with anisotropic coupling [37]. This might indicate the existence of short-range and low-dimensional AF exchange, before reaching three-dimensional long-range ordering. However, the absence of hyperfine magnetic splitting at room-temperature in Mssbauer Spectrometry experiments contradicts the hypothesis of room-temperature interaction between Fe$^{3+}$ spins in the samples of this study.

To conclude, CaFe$_2$O$_4$ thin films have been grown
for the first time on TiO$_2$ substrates by means of PLD with thickness in the order of 100 nm. The films form domains that consist of needle-like crystals with the long axis along the magnetic easy axis, displaying a clear epitaxial relation with the substrate. The magnetic properties of the CaFe$_2$O$_4$ thin films studied by means of SQUID magnetometry, Mössbauer spectrometry and low-temperature MFM are consistent and reveal an ordering temperature of about 185 K, concomitant with the presence of a net magnetic moment along the b-axis. The vertical shifts of the M – H loops depending on the field-cooling conditions, evidence that this is not standard ferrimagnetic behaviour. The results are consistent with an antiferromagnet with orphan spins arising from the coexistence of differently modulated A and B phases (see fig.1), as proposed in bulk samples,\cite{16}

Outlook: Further characterization of the magnetic structure of CaFe$_2$O$_4$ films is needed to completely explain our results. Important questions are still open regarding the stability and coexistence of the A and B magnetic phases observed in bulk samples and the influence of epitaxial strain on the magnetic phase diagram. Eventually, our goal is to control the relative stability of the A and B phases, in order to obtain a highly responsive system at the boundary between multiple spatial modulations. We believe that CaFe$_2$O$_4$ thin films represent an interesting perspective system for the study of “spatial chaos”\cite{38} arising from competing interactions. In such systems, the presence of multiple accessible states close in energy, leads to enhanced susceptibility and adaptability, that are crucial for applications in adaptable electronics, such as neuromorphic computing. Finally, the polar nature of the domain boundaries of the CaTiO$_3$ layer provides an opportunity to explore the multiferroic properties of these CaTiO$_3$/CaFe$_2$O$_4$ self-organized heterostructures.

METHODS

Sample growth. The CaFe$_2$O$_4$ films of this study have been deposited by PLD using a KrF ($\lambda=248$ nm) excimer laser. The target was a home-made ceramic pellet of CaFe$_2$O$_4$, prepared by solid state synthesis \cite{39–41} from CaCO$_3$ (3N Sigma Aldrich) and Fe$_2$O$_3$ (99.998% Alfa Aesar) precursors. The powders were mixed and milled in an agate ball mill at 200 rpm for 2 hours and pressed into a 20 mm diameter pellet with 9.5 tons. Calcination and sintering were executed at 600 °C and 1200 °C respectively. The crystal structure was determined to be single phase CaFe$_2$O$_4$ via XRD using a Panalytical X’Pert Pro diffractometer in Bragg Brentano geometry. Prior to growth, single crystal TiO$_2$ (110) substrates (CrysTec Gmbh) were treated to reveal the step edges \cite{42, 43} by etching for 1 min with buffered oxide etch (BHF) followed by 1 hour annealing at 900 °C under a constant oxygen flux of 17 l/h. The optimal growth parameters were determined to be as follows. The laser was focused on the target positioned at 50 mm from the substrate with a spot size of 1.8 mm$^2$. The laser fluence and frequency were 2.8 J/cm$^2$ and 10 Hz respectively. The substrate temperature during growth was 850 °C and the partial oxygen pressure ($P_{O2}$) in the chamber 0.2 mbar. After deposition the samples were cooled with a rate of -1 °C/min in $P_{O2}$=200 mbar. The number of pulses was varied in a range from 6000 to 15000 to obtain different film thicknesses. The film surface was monitored during growth via in-situ RHEED.

Structural characterization. Characterization of the films surface was performed using AFM (Bruker Dimension XR microscope) and SEM (FEI Nova NanoSEM 650). XRD measurements were done with a laboratory diffractometer (Panalytical X’Pert MRD Cradle), using Cu K$_\alpha$ radiation (1.540598 nm). TEM experiments were conducted on a Cs corrected Themis Z (Thermofischer inc.) microscope. Electron beam was operated at a high tension of 300 kV, and STEM imaging was performed at a beam convergence angle of 23.5 m rad. HAADF-STEM images were acquired with an annular detector in the collection range of 65-200 mrad. DPC images were obtained and analysed using segmented detectors. EDS spectra were collected in the ChemiSTEM mode with 4 symmetric detectors along the optical axis.

Mössbauer Spectrometry. The samples used for Mössbauer Spectrometry were grown from a $^{57}$Fe enriched target with the same parameters as above. The target was synthesized as described before, but adding to the standard Fe$_2$O$_3$ precursors 80% of the enriched oxide, prepared by annealing of $^{57}$Fe powders at 800 °C for 2 hours in a constant oxygen flow of 18 l/h \cite{44}. CEMS measurements were performed in normal incidence using a home-made gas flow ($He – CH_4$) proportional counter \cite{45}. For the measurements at low temperatures, the counter was mounted inside a closed-cycle He cryostat \cite{46}. The source was $^{57}$Co in Rh matrix of about 1.85 GBq activity, mounted in a velocity transducer operating in constant acceleration mode. The spectra were least squares fitted using the histogram method and assuming Lorentzian lines. Isomer shifts are given with respect to $\alpha – Fe$ at 300 K.

Magnetometry and data analysis. The magnetic properties were studied by means of SQUID magnetometry (Quantum Design MPMS-XL 7) with RSO option in a range of temperature varying from 5 K to 400 K and at fields ranging from 100 Oe up to 7 T. The field was applied either parallel or perpendicular to the magnetization direction of the structural domain with [010] parallel to the substrate [1-10] direction. The long moment values obtained from the SQUID-MPMS has been analyzed using Origin software as follows. First the experimental data has been subtracted of the signal of a clean sub-
strate, measured in the same conditions as the sample. This introduces a small error due to the fact that in the data used as background reference does not contain the signal of the intermediate CaTiO$_3$ layer formed during growth. Then, the experimental data (in emu) has been divided by the magnetic field (in Oe) and the number of moles to yield the magnetic susceptibility of CaFe$_2$O$_4$ in emu/mol Oe (for the $M-H$ loops, the magnetization has been further converted into units of Bohr Magnetrons per formula unit). This step also introduces an error in our estimation, due to the imprecise estimation of the film thickness via TEM, which is necessary to normalized for the amount of material. Therefore, in this study we do not attempt to provide a precise quantitative analysis of the magnetic response.

**Scanning SQUID microscopy** The experiments were performed with a scanning SQUID microscope [47] with a spatial resolution of approximately 5 µm [35] and field resolution of approximately 50 nT. The samples were cooled and measured in zero background field at 4 K. Various sets of 12 scans of 250x250 µm size, with 250 µm spacing in between (total covered area about 1.75x1.75 mm), were collected in different areas to test for homogeneity of the samples.

**Magnetic force microscopy** The MFM experiments presented in this study are performed with a customized Attocube scanning probe microscope inserted in a Quantum Design Physical Property Measurement System (PPMS). Multiple scans were collected at different temperatures upon cooling the sample from 300 K to 12 K. In some cases, a magnetic field ranging from -0.1 to 0.1 T was also applied perpendicular to the film surface. The sample surface was scanned using commercial (Nanoworld) Co–Cr coated tips that were magnetized prior to use. The images were collected in dual-pass tapping mode, with a second scan lift of 30 or 50 nm. The data were then processed with the open source software Gwyddion.

**DATA AVAILABILITY**

Supplementary Information for this paper is available at:

All relevant data are available from the corresponding author.

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**AUTHOR CONTRIBUTIONS STATEMENT**

B.N. conceived the project. S.D. designed the experiments, synthesized the samples, performed the basic structural and magnetic characterization and data analysis. P.N. performed the TEM experiments and analyzed the data. J.J. performed the Mössbauer Spectrometry experiments and analyzed the data. P.R performed the scanning SQUID microscopy experiments under the supervision of H.H. S.D., B.N. and P.N. discussed the results. S.D. wrote the manuscript which was reviewed by all the authors.

**Competing interests:** the authors declare no competing interests.

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Supporting Information for “Structure and magnetic properties of epitaxial $CaFe_2O_4$ thin films”

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I. TARGET ABLATION

For the deposition of $CaFe_2O_4$ films a home-made ceramic pellet of single phase $CaFe_2O_4$ was used as a target. After ablation no change in the XRD peaks position was observed, but only a broadening due to melting of the material. Fig.S1a shows a SEM image of the as-synthesized target and relative EDS elemental analysis. During the growth optimization process we observed that in order to ablate in equal amount $Ca$ and $Fe$ atoms from the target an high laser fluence (about 2.8 $J/cm^2$) was required. At lower energies, the ablated region of the target under an SEM microscope displays a rough morphology characterized by high pillars of non-ablated material. On top of each pillar an island of $Fe$-rich material is found (lighter contrast in fig.S1b). This is due to the higher melting point that prevents $Fe$ to be transferred to the plasma plume thus blocking the laser to reach the material underneath. Therefore, films grown in this condition are $Fe$-deficient. On the other hand, when the laser fluence is above 2.5 $J/cm^2$, the ablated area appears more homogeneous and no difference in composition before and after the deposition is measured via Energy dispersive X-ray spectroscopy (EDS) (see fig. S1c).

![Target ablation SEM images](image)

**FIG. S1.** Target ablation. SEM images collected with a back-scattered electron detector of the ceramic $CaFe_2O_4$ target. (a) Pristine state, (b) after ablation at 1 $J/cm^2$ and (c) after ablation at 2.5 $J/cm^2$. The red line indicates the area from which the under-laying EDS spectrum was collected.

II. SIMILARITY BETWEEN (004) AND (302) ORIENTATIONS

In this study we encountered difficulties in the films characterization due to the similarities between $CaFe_2O_4$ (004) and (302) planes. The arrangement of the atoms in such planes is indeed very similar and based on alternating ($Fe$−$Fe$−$Ca$−$Fe$−$Fe$−$Ca$) chains of cations ordered along the b-axis, as shown in fig.S2a-b. This results in almost indistinguishable, besides the modulation of the spots intensity, electron diffraction patterns (see fig.S2c).

![Electron diffraction patterns](image)

**FIG. S2.** Similarity between (004) and (302) orientations. Schematic representation of cations arrangement in $CaFe_2O_4$ planes. $Ca$, $Fe$(1), and $Fe$(2) atoms are depicted in white, blue and red respectively. (a) $CaFe_2O_4$ 004 plane (b) $CaFe_2O_4$ (302) plane (c) simulation of electron diffraction pattern from the (001) and (201) zones.

III. EDS

Fig.S3a shows the distribution of $Ca$, $Fe$ and $Ti$ atoms through a cross section of our films measured by means of energy dispersive X-ray spectroscopy (EDS). $Fe$ and $Ti$ contrast is only observed in the upper and lower layers respectively while $Ca$ is found everywhere. Combination of EDS with imaging of the lattice by means of TEM allowed us to determine that a perovskite $CaTiO_3$ (10 nm) layer is present at the interface between $CaFe_2O_4$ film and $TiO_2$ substrate. Based on the oxygen tilts, and the lattice parameters, we can deduce that the $CaTiO_3$ layer crystallizes in an orthorhombic structure with $Pnma$ space group. It is oriented along the b-axis out of plane, and contains ferroelastic domains separated by polar (110) domain walls (fig.S3b), reminiscent of bulk $CaTiO_3$. Possible magnetoelectric coupling between these domain walls and the $CaFe_2O_4$ layer is a subject of future investigation.

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FIG. S3. Chemical analysis of the thin-film stack and domain boundaries in CaTiO$_3$ layer. (a) Elemental distribution of Ca blue, Fe orange and Ti green across the three layers obtained through STEM-EDS, clearly revealing a 10 nm Calcium Titanate layer at the interface. (b) HAADF-STEM image of the CaTiO$_3$ layer imaged along the [001] zone axis where a (110) ferroelastic domain wall (white-dashed line) can be seen. The purple and blue arrows on either side of the domain wall show an orientation mismatch of about 1° between the domains, corresponding to the well-reported 179° domains in bulk CaTiO$_3$.

IV. EBSD

Fig. S4 shows the results of orientation imaging microscopy performed of CaFe$_2$O$_4$ thin films. The experiments are performed by means of Electron backscatter diffraction (EBSD) in a SEM. The color map and corresponding pole figure of S4b show the orientation of the domains imaged in S4a. Three crystal orientations are found, all with [302] out-of-plane but different in-plane directions. In the map the red color indicates areas of the film where the CaFe$_2$O$_4$ [010] is parallel to the substrate [1-10], while red and blue indicate domains with a ±55° tilt from it. These results are in good agreement with what found in x-ray pole figures and RSMs shown in the main text.

FIG. S4. EBSD measurement. (a) SEM image (collected with a secondary electron detector) and grain boundaries (1.5°). (b) Orientation map and pole figure of a 96 nm thick film. Red, green and blue indicate crystals with the same out-of-plane orientation, namely [302], but different in-plane orientation. A pole figure of the orientations is shown in the inset.

V. BULK MAGNETIC PROPERTIES

The magnetic response of the CaFe$_2$O$_4$ ceramic target used for the films deposition has been studied by means of SQUID magnetometry. Plots of the susceptibility as a function of temperature are reported in fig.S5a and b measured in a 100 Oe and 2 T fields respectively. The response is consistent with the literature data regarding bulk CaFe$_2$O$_4$, with a Nel temperature of 175 K and a strong ZFC/FC splitting in the low field measurement.

FIG. S5. Bulk magnetic properties. Plot of the magnetic susceptibility (χ) as a function of temperature (T) from 5 to 300K in a (a) 100 Oe and (b) 2 T applied field.

VI. MACRO SCALE MAGNETIC PROPERTIES

To complement the SQUID measurement data shown in the main text, fig.S6a and b display the response of CaFe$_2$O$_4$ thin films to fields applied perpendicular to the magnetization direction. In fig.S6a the FC and ZFC susceptibility (χ) is plotted as a function of temperature at 100 Oe. The same features as for the parallel measurement are found (paramagnetic tail at low-T, $T_N$=188 K, ZFC/FC splitting), albeit lower values are measured. In particular, the maximum reached by χ below $T_N$ is almost absent for $B \perp$ b. Moreover, the ZFC curve does not show sign reversal. Fig.S6b shows the magnetization measured at zero applied DC field after positive field cooling. Here again an analogous trend is observed, except for the absence of the paramagnetic contribution below 20 K.

$M-H$ loops were also collected at different temperatures (5-30-100-130-175-200-300 K) to study the evolution of the spontaneous magnetization with the ordering of A and B magnetic phases. The same results are obtained upon directly measuring the loops during cooling or by heating the sample above $T_N$ between each loop. Fig.5c of the main text shows the loop at 130 K, where the maximum hysteresis appears. Here (fig.S6c) we report the $M-H$ loops collected at 175 and 30 K for comparison. At these temperatures lower and no magnetic hysteresis is observed, respectively, consistently with the disapparence of antiphase boundaries.

Fig.S6d displays the absence of field-cooling induced vertical shift in the $M-H$ loops, when the measurement is performed above $T_N$, despite a small hysteresis persists up to 300 K.

VII. LOW TEMPERATURE MFM

To further prove that the signal observed in the phase of the low-temperature MFM experiments (fig.8 of the
FIG. S6. (a) Plot of the magnetic susceptibility (χ) of a 84 nm thick sample as a function of temperature (T) in a 100 Oe magnetic field perpendicular to the b-axis. (b) Magnetization (M) of a 90 nm thick sample measured as a function of temperature in zero applied DC field after cooling in 100 Oe field applied perpendicular to the b-axis. (c) Plot of the M−H loops measured at 175 (red) and 30 (black) K from 7 to -7 T, with H parallel to the b-axis. (d) Plot of the M−H loops measured at 200 (full dots) and 100 (open dots) K from 550 to -550 Oe, with H parallel to the b-axis.

FIG. S7. MFM at 12K in Attocube AFM (PPMS insert) of a 120 nm thick CaFe$_2$O$_4$ film. (a) Topography and (b) dual-pass phase recorded using a non magnetic tip. (c) Difference between fig.8h and fig.8i of the main text (dual-pass phase at 0.05 and -0.1 T applied field respectively), calculated with the software gwyddion.