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Modulated phases of ferroic oxides

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Modulated phases of ferroic oxides

CaFe_2O_4 and BaTiO_3 thin films

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 groningen**

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CaFe_2O_4 and BaTiO_3 thin films

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Chapter 1

Introduction

Periodic phases and patterns can be found in a large variety of physical and chemical systems at equilibrium [1]. Some examples in 2 and 3 dimensions are domain patterns in ferroelectric [2–6], magnetic [7–9], organic [10], superconducting [11] and ferrofluidic films [12], gas atoms adsorbed on crystalline substrates [13], liquid crystals [14], diblock-copolymers assemblies [15] and bulk magnetic spin structures [16, 17]. Because a small set of simple morphological features, i.e. stripes and bubbles, predominate over more complex structures, patterns form that are common to very different systems, regardless of their microscopic structure and interactions [18]. However, the characteristic scale, or period, of the patterns can vary from hundreds of angstroms to as much as centimetres. Periodic equilibrium patterns often also exhibit common modes of evolution, suggesting a possible general mechanism to account for the formation of these textures. Therefore, there exists extensive discussion on models to describe the behaviour of such different but intimately related systems [19].

Materials in which competing interactions lead to the appearance of modulated phases are not only fascinating from a fundamental point of view, but are also promising candidates for applications. In particular, at the transition point between different periodicities, chaotic behaviour and large fluctuations are expected, that can be exploited as deliberate means to enhance electronic adaptability. Even though the concept of “edge of chaos” [20, 21] is well developed in dynamical systems, described by periodicity doubling cascades and bifurcation theory, and it is often linked to self-adaptation and learning in complex systems [22], its use in relation to enhanced electronic functionalities is under-explored [23]. Because an analogy has been made between chaos and the existence of modulated phases in systems with competing interactions, these could be employed with the goal of creating highly adaptable systems at “the edge of (spatial) chaos” [24]. This thesis focuses on the materials science aspects around developing this type of adaptability and can be considered as a first step in this direction.

To do so, understanding and possibly control on the relative stability of the competing structures is needed. Therefore, for this research, we have selected two examples of solid state systems, CaFe_2O_4 and BaTiO_3 , displaying multiple periodic structures that can be accessed in the laboratory. The modulation in CaFe_2O_4 arises from the alternation of chains of parallel spins in two overall antiferromagnetic structures. In BaTiO_3 the modulation is given by periodic ferroelastic domains with alternating polarization direction. In both cases, growing the material in thin film form on a crystalline substrate allows to exploit epitaxial strain as a handle to tune the relative stability of the different phases. In the case of CaFe_2O_4 , which is the main

focus of this project, the strong dependence of the magnetic exchange constants on lattice parameters and the role of magnetoelastic coupling make the system extremely sensitive to modifications of the crystal structure that can be induced by strain. In the case of $BaTiO_3$ thin films under low epitaxial strain, novel domain arrangements develop, that are not present in the bulk non-strained material, whose evolution can be closely studied across the phase transition.

In this chapter the topic of modulated phases and patterns in condensed matter is introduced together with a general description of how systems evolve towards such stable configurations. Finally, the two selected example systems, $CaFe_2O_4$ and $BaTiO_3$, will be described more in depth.

1.1 Modulated phases

It is generally accepted that modulated phases arise in systems displaying competing interactions between their constituting elements [1]. The period of the modulation is determined by the relative strength of the interactions and can be tuned by varying external parameters such as temperature, strain or applied magnetic and electric fields. Modulated phases may also develop in the presence of two or more coupled order parameters [24], each individually favouring a different equilibrium state. Typically, one of the periods is that of the crystal lattice, while the other can be a modulated structure of diverse nature, giving rise to phases that can either be commensurate (if the modulation is a simple rational fraction of the lattice period) or incommensurate. In general, the transformation of an initially ordered state into one with different periodicity under changes of external parameters occurs in exceptional circumstances and the proliferation of disorder is a far more prevalent scenario. Examples of this are the labyrinthine patterns observed in thin films of magnetic metals [25] or Garnets [26] that bear striking similarities to those found in Langmuir films [27], polymers [28] and colloids [29].

A simple model system with a phase diagram displaying all commensurate, incommensurate and disordered phases is the anisotropic-next-nearest-neighbour Ising (ANNNI) model [30, 31]. In the three dimensional version of the model, depicted in the inset of figure 1.1, Ising spins ($S = \pm 1$) occupy a simple tetragonal lattice and interact with each other as follows:

1. Ferromagnetic ($J_0 > 0$) nearest-neighbour interaction in the xy plane
2. Ferromagnetic ($J_1 > 0$) nearest-neighbour interaction along the z axis
3. Antiferromagnetic ($J_2 < 0$) next-nearest-neighbour interaction along the z axis

Thus, the ANNNI Hamiltonian can be written as [30]:

$$H = -\sum_i (\sum_a J_0 S_i S_{i+a} + \sum_b J_1 S_i S_{i+b} + \sum_b J_2 S_i S_{i+2b}) \quad (1.1)$$

Where S_i indicates the spin occupying the i -th lattice site and a and b are the tetragonal lattice vectors. The competition between J_1 and J_2 in the z direction causes

spatially modulated spin patterns to arise along z , while all the spins in a xy plane are identically oriented.

A phase diagram of the ANNNI model in the K, T plane, with $K = -J_2/J_1$, is shown in figure 1.1 obtained by an effective-field method. At zero temperature the model can be solved exactly. For $K < 0.5$ the ground state is a homogeneous ferromagnetic phase (F). For $K > 0.5$ the energy is minimized by the so-called $< 2 >$ structure, a spin configuration consisting of a sequence of couples of planes with alternating magnetization (see inset of fig. 1.1). In addition, the $< 3 >$ phase, consisting of a sequence of triplets of planes with alternating magnetization, is stable in a range of K, T values forming a wedge at the centre of the phase diagram. At the conjunction between these three phases, the so-called Multiphase point $M = (0.5, 0)$, the ground state is infinitely degenerate and an infinite number of distinct commensurate phases spring from M forming a fan of stable phases at non-zero T [24]. On the right side of the phase diagram, combinations of the $< 3 >$ and $< 2 >$ structures of the type $< 2^j 3 >$ and $< 2 3^j >$, with $j = 0, 1, 2, \dots$ can be found. Similarly, on the left side of the diagram, other mixed phases can also be stable in the K, T plane in between two basic structures that are adjacent at low temperature (e.g. $< 3 >$ and $< 4 >$). Where the region of stability of a mixed phase starts, a branching point is observed. Numerical calculations have shown that the branching process continues indefinitely creating a cascade of commensurate mixed phases. Upon increasing temperature further, the high-order mixed phases occupy smaller and smaller regions of the parameter space, until they are replaced by incommensurate structures. Thus the whole region near the order to disorder (D) transition line is incommensurate, with tongues of commensurate structures of low periodicity which do not reach the phase transition line.

Despite the ANNNI model being purely theoretical, the understanding of complex properties emerging from simple competing interactions has helped to identify and study similar features in experiments. Therefore, the ANNNI model can be considered as a prototype of spatially modulated patterns or superstructures, that can be observed in a large variety of real physical systems.

Long-range modulated magnetic phases are common: spiral, sinusoidal and conical spin structures have been long since observed in a large number of pure substances and compounds [16, 17]. Experimentally, modulated spins structures were first observed in $MnAu_2$ and MnO_2 , which are classical examples of spiral magnets [16]. Later, spiral and sine-wave modulations were found in the rare-earth elements Tb, Dy, Ho, Er and Tm in a temperature interval going from the ordering temperature down to the onset of a commensurate structure, that can be either a ferromagnetic phase, an antiphase-type or a helical structure [32]. Today several extensive classes of materials with diverse modulated magnetic phases are known, displaying a large variety of exotic spin structures.

In general, a periodic magnetic structure can be described as a perturbation of a FM commensurate phase (q_0) and has a wavevector $q = q_0 + \delta$ [16]. The magnetic modulation can be related to the amplitude and/or the orientation of the magnetization. Sine-wave structures are an example of the former, while spin spirals exemplify the latter [33]. For insulators and semiconductors, the competition typically

Figure 1.1: Phase diagram of the 3D ANNNI model. Only the basic structures with short periodicity are depicted. The dotted lines connect points in the parameter space where the incommensurate phase has the same periodicity as the corresponding commensurate structure. The inset shows the magnetic interactions between spins ordered in the $\langle 2 \rangle$ phase. Adapted with permission from Ref.[31].

occurs between exchange interactions with different signs, as described in the case of the ANNNI model, whereas for metals, the conduction electrons play a role in the appearance of the modulation via the Ruderman-Kittel-Kasuya-Yosida (RKKY) long-distance interaction [34]. For some crystals with low symmetry, the competition can also be due to forces of relativistic origin, such as the Dzyaloshinskii-Moriya interaction (DMI) [17].

A classical example of spiral modulation is that of an Heisenberg chain of spins with nearest-neighbour FM ($J_1 > 0$) and next-nearest-neighbour AF interactions ($J_2 < 0$). In contrast to the ANNNI chain, where the $\langle 2 \rangle$ antiphase is stable, here, in the absence of spin anisotropy, the competing interactions induce a rotation of the spins along the chain direction. If further complexity is added to the system (e.g. magnetic anisotropy), multiple periodicities can coexist giving rise to diverse phases that consist of combinations of the basics modulations described so far. For example, if we consider the same Heisenberg spins but in a triangular lattice in the xy plane, new states appear, like multi- q states, flop state and skyrmion crystal. [35]. Often these systems are referred to as “frustrated” magnets, to emphasize the preclusion of simple magnetic orders [36].

Recently, skyrmion lattices have drawn special attention after having been experimentally observed within a certain interval of temperature and field in so-called B20 compounds with helimagnetic order, including metallic, semiconducting, and insulating systems such as $MnSi$, $Fe_{1-x}Co_xSi$ and Cu_2OSeO_3 [37–39]. The skyrmion phase can also be stabilized in multilayered thin films at the interface between a magnetic

metal and one with large spin-orbit coupling, by means of the interfacial DMI [40].

Another largely investigated example of periodic structures are the domains that form spontaneously or under the effect of external fields in (multi)ferroic materials [41] in both bulk [42] and thin film forms [43]. In the case of thin films, bubble, stripe and labyrinthine domains are the most common, but the additional effect of strain and anisotropy can also lead to the formation of morphologies that are not found in bulk materials, such as anisotropic fractal domains [44] and vortices [45, 46].

The driving force for the spontaneous domain formation in magnetic materials is considered to be the presence of non-local magnetic interactions that compete with the energy cost of local variations of the order parameter (here the magnetization) associated with domain walls formation. On the other hand, it is the interplay between polarization and elastic strain that accounts for domain structures in most ferroelectrics. Thus, particular domain patterns, that lead to the release of the elastic (volume) energy at the expense of increasing the interfacial energy associated with the domain walls (DWs), form. In addition, DWs must have well-defined orientations that maintain compatibility of strains and polarizations across the domains [47]. As a result the stable, minimum-energy width of the domains (w) scales with the square-root of the sample thickness (d) according to the universal Kittel's law $w \propto \sqrt{d}$ [48].

Normally, ferroelectric DWs can be classified into 180° and non- 180° walls by using the relative angle between the orientations of the polarization axes of the adjacent domains. The latter, including 90° DWs in tetragonal ferroelectrics and 71° or 109° DWs in rhombohedral ferroelectrics, respond to both electric fields and mechanical stress and are thus also ferroelastic. Ferroelectric domains are usually designated as either a or c when the polarization direction is either in-plane (parallel to the film surface) or out-of-plane, respectively, in ferroelectric thin films.

1.1.1 CaFe_2O_4

Unlike many the other compounds with the unit formula AM_2O_4 , CaFe_2O_4 does not have the Spinel structure [49] and, instead, crystallizes in a orthorhombic structure with space group $Pnma$ and lattice parameters $a = 9.230 \text{ \AA}$, $b = 3.024 \text{ \AA}$ and $c = 10.705 \text{ \AA}$, that was first characterized in the late 1950s [50–52]. The Fe^{3+} ions of the CaFe_2O_4 structure occupy two crystallographically distinct positions, $\text{Fe}(1)$ and $\text{Fe}(2)$, each surrounded by 6 oxygen atoms in octahedral coordination. Both Fe types forms zig-zag chains that run parallel to the b -axis. FeO_6 octahedra within the same chain share edges, whereas neighbouring chains are connected through corners. This connectivity results into a tunnel structure with the Ca^{2+} cations occupying bicapped triangular prismatic cavities with oxygen coordination number of 8. The same characteristic MO_6 octahedra network is also found in several other compounds, including CaCr_2O_4 , CaV_2O_4 , CaMn_2O_4 , CaTi_2O_4 ¹ and Eu_3O_4 , [53] as well as many rare-earth oxides with large alkali cations, that are sometimes referred to as calcium ferrate(III)-type compounds. In the $a - c$ plane (fig. 1.2) for corner sharing $\text{Fe}(1)\text{O}_6$ and $\text{Fe}(2)\text{O}_6$ octahedra the $\text{Fe}-\text{O}-\text{Fe}$ bond angles are about 120° , whereas the bond angle between different Fe types through the edge sharing octahedra is approximately

¹although CaMn_2O_4 and CaTi_2O_4 do not share the $Pnma$ space group

99° (fig. 1.2d). Because most of the magnetic interactions in oxides occur through oxygen-mediated superexchange, Decker and Kasper, in their seminal paper from 1957 [52], already recognized the implications that these bond angles could have on the magnetic structure of CaFe_2O_4 . They predicted strong antiferromagnetic coupling (J_3 and J_4) along the a axis and weak antiferromagnetic coupling along c (J_1 and J_2). A complete list of the exchange interactions in CaFe_2O_4 obtained from more recent theoretical calculations is given in table 1.1, with reference to the exchange paths shown in figure 1.2c.

Figure 1.2: Structure of CaFe_2O_4 produced from the CIF file in Ref.[54]: $\text{Fe}(1)$ is depicted in red and $\text{Fe}(2)$ in blue, Ca and O are not shown. **a** Distorted honeycomb lattice formed by the Fe atoms projected from the $[010]$ direction. 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 . **b** Armchair-type structure extending along a that is obtained by neglecting J_1 and J_2 (dashed lines). **c** Enlargement of the exchange paths between neighbouring Fe atoms. **d** Bond angles in antiferromagnetically coupled corner-sharing FeO_6 octahedra and edge-sharing FeO_6 octahedra with coupling close to the threshold between positive and negative exchange. Here O is depicted in black.

This proved to be partially correct when the first neutron diffraction experiments were performed [57]. The material showed overall antiferromagnetic ordering and uniaxial anisotropy, with chains of parallel Fe^{3+} spins running along the b -axis (magnetic easy axis). In the $a - c$ plane, J_1 , J_2 , J_3 and J_4 were all found to be negative

Table 1.1: List of the nearest-neighbour antiferromagnetic exchange interactions in CaFe_2O_4 .

exchange path	J_i (meV)	
	Ref.[55]	Ref.[56]
b1	0.093	0.03(1)
b2	0.093	0.38(1)
1	0.36	0.047(2)
2	0.47	0.047(2)
3	1.27	3.2(3)
4	2.06	3.4(3)

below the Néel temperature $T_N = 200 \text{ K}$ ². However, when the temperature is lowered below approximately 150 K, a second magnetic phase was also detected, displaying positive values of J_1 and J_2 . Therefore CaFe_2O_4 is characterized by the coexistence of two modulated spin structures, termed B and A, that differ for the c -axis stacking of Fe^{3+} spins chains. Specifically, the B structure (fig. 1.3b) consists of 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 (fig. 1.3a) [58]. The magnetic structure of CaFe_2O_4 was also studied by means of Mössbauer spectroscopy [59, 60], that yielded similar results as neutron diffraction.

Figure 1.3: Magnetic structure of the **a** A ($\uparrow\uparrow\downarrow\downarrow$) and **b** B ($\uparrow\downarrow\uparrow\downarrow$) phases of CaFe_2O_4 produced from the CIF file published in Ref.[54]: red indicates Fe atoms with spin up and blue Fe atoms with spin down. Ca and O are depicted in white and black respectively. A and B differ in the sign of the weak J_1 and J_2 magnetic exchange interactions between edge-sharing FeO_6 along c . **c** Schematic representation of the antiphase boundaries between different magnetic domains in the A and B phases, where the local structure is that of the other phase, reprinted with permission from Ref.[61].

After the first interest in this material during the 1950s, fewer reports followed, some focusing on the effect of doping with Cr [62, 63]. Here, Cr is found to destabilize the A phase, with only B prevailing down to low temperatures. Past the year 2000, renewed interest in CaFe_2O_4 has been shown, due to the possibilities offered by

²In Ref.[57] T_N was actually found to be higher but all reports afterwards placed the Néel temperature around 200 K.

improved characterization techniques and theoretical methods [64]. However, there seemed not to be complete agreement in the literature regarding the magnetic behaviour of CaFe_2O_4 . First of all, despite the antiferromagnetic character of both A and B, the presence of a spontaneous magnetization has been reported, that is evident from hysteresis in the $M - H$ loops. The observed magnetization is temperature dependent, being largest around 120 K, where the maximum coexistence of the A and B phases is expected. Moreover, a non-standard temperature dependence of the magnetic susceptibility (χ) is observed, with large spitting between field-cooled and zero-field-cooled data and non Curie-Weiss behaviour in the paramagnetic state up to 400 K. In most reports the $\chi - T$ plots display a single magnetic transition at about $T_N = 175$ K and a peak around 120-140 K. However, in one report [61], two transitions were actually observed attributed to the ordering of the B and A at 200 K and 150 K, respectively.

Different explanations for this peculiar behaviour have been offered, some of which focus on the presence of ferrimagnetism due to oxygen off-stoichiometry. In particular, oxygen vacancies-driven partial conversion of Fe^{3+} (HS $S = 5/2$) into Fe^{2+} (LS $S = 2$) ions has been proposed [55, 65], resulting in the formation of ferrimagnetic clusters. On the other hand, a ferrimagnetic state is also observed in oxygen superstoichiometric CaFe_2O_4 due to the presence of Fe^{4+} ions and the charge disproportionation between Fe^{3+} and Fe^{4+} ions occupying two inequivalent sublattices [66]. However, a clear quantification of the oxygen stoichiometry in CaFe_2O_4 crystals and powders seems to be difficult to achieve. Recently, the oxygen content dependence of the electrical properties of CaFe_2O_4 has also been investigated [67]. Here, the authors report a significant increase in resistivity upon annealing in inert atmosphere, but do not observe lattice oxygen deficiency or Fe valence change. In contrast, they associate the modification of in-band-gap energy structure with a removal of interstitial oxygen, suggesting a key role of oxygen atoms in the transport properties.

Recently, another explanation for the spontaneous magnetization in CaFe_2O_4 has been put forward by Stock *et al.* [61, 68]. Via neutron scattering experiments the authors show localized excitations originating from defect states, termed “orphan spins”, at the antiphase boundaries between magnetic domains of each phase. Interestingly, as shown in figure 1.3c, the local structure of the antiphase boundaries of phase A coincides with phase B and vice versa. The spins near these boundaries are weakly correlated and decoupled from the A and B magnetic order parameters, allowing them to coexist in CaFe_2O_4 down to low temperatures. These “orphan spins” also carry an uncompensated ferromagnetic moment along b and, as a result, the net magnetization of the system is larger in the temperature range where A and B coexist, around 120 K.

However, such excitations are not observed in the work by Songvilay *et al.* [69], who instead attribute the complex excitation spectrum of the B phase to magnetic exchange disorder. In powder samples, they observe coexistence of the A and B phases only limited to the range of temperatures between 130 K and 175 K, with A prevailing at the lowest temperatures. In addition, from a comparison between pure and Cr doped CaFe_2O_4 , where only the B phase is present, they suggest that the stabilization of the A phase in undoped samples occurs through the magnetoelastic

effect, which leads to changes in bond lengths and angles, enhancing the ferromagnetic J_1 and J_2 .

Very recently Lane *et al.* [56] have also suggested that the low-temperature A ordering is metastable and originates from the freezing of antiphase boundaries created by thermal fluctuations in the parent B structure.

Thus CaFe_2O_4 represents a very interesting example of system where competing magnetic interactions are at the origin of the formation of two modulated magnetic orderings. In addition, at the time when this study was started, the literature on this material contained contradictory results with significant variations between sample types (eg. powders [69] or single crystals [61]) and no complete agreement on the magnetic phase diagram of the material. To summarize, the following questions were still open regarding the magnetic properties and structure of CaFe_2O_4 :

- relative stability of A and B over the temperature range between 5 and 200 K
- mechanism for the formation and coexistence of the A and B magnetic structures
- origin of the spontaneous magnetization and role of uncompensated spins at the magnetic antiphase boundaries.

Interestingly, CaFe_2O_4 is also the parent member of a family of calcium-iron oxides with chemical formula $\text{CaFe}_{2+n}\text{O}_{4+n}$. The compounds in this family are constituted by n blocks of Wurtzite FeO and one unit with composition CaFe_2O_4 . Here n is not necessarily an integer, but compounds with fractional n have also been reported [70]. The result is a large family of complex oxides where Fe is present in two oxidation states: 2+ in the FeO block and 3+ in the CaFe_2O_4 unit [71, 72]. Thus, CaFe_2O_4 is the only member in which Fe does not display mixed valence. As a result, unlike the other members of this family that are semiconductors with a Verwey-type transition [73], CaFe_2O_4 is an insulator. The reported value of band gap is 1.9 eV [67, 74].

1.1.2 BaTiO_3 thin films

BaTiO_3 is one of the most studied ferroelectric materials and is widely applied in capacitors and baristors, thanks to its high dielectric constant and high remanent ferroelectric polarization ($25 \mu\text{C cm}^{-2}$) [75]. The room temperature structure of BaTiO_3 is tetragonal Perovskite with lattice parameters $a = b = 3.9939 \text{ \AA}$ and $c = 4.0343 \text{ \AA}$ [76].

When ferroelectrics are grown in thin film form, local minimization of the depolarizing field energy induces the formation of domains in a periodic manner, very much like in ferromagnets [48, 77–79]. In addition, in epitaxial films, the lattice mismatch with a crystalline substrate can be accommodated by creating ferroelastic domains. This results in complex periodic domain patterns that have been largely investigated in the case of BaTiO_3 , both theoretically [80–83] and experimentally [84, 85]. The rich strain-temperature phase diagram of this system is shown in figure 1.4. Here a large number of phases and domain configurations are possible, as BaTiO_3 can assume orthorhombic, rhombohedral and monoclinic symmetries. Some of the main

low-temperature domain configurations of $BaTiO_3$ are depicted in figure 1.4b, where the domain wall in between two semi-periods is highlighted.

Figure 1.4: **a** Enlargement of the low misfit strain region of the theoretical phase diagram of $BaTiO_3$ epitaxial films. Thick and thin lines represent first and second order phase transitions respectively. **b** Unit cell of the predicted domain states (represented by a half unit cell separated by a domain wall): a/c , a_1/a_2 , ca_1/ca_2 and aa^*/ca^* . Reprinted with permission from Ref.[85].

Particularly interesting is the low strain region of the phase diagram that can be accessed by growing the material on orthorhombic $NdScO_3$ Perovskite substrates cut along the [110] direction. In this orientation, $NdScO_3$ has in-plane lattice parameters of $a_{PC} = 4.014 \text{ \AA}$ and $c_{PC} = 4.002 \text{ \AA}$, in pseudo-cubic notation, which leads to a small tensile strain when the in-plane orientation of $BaTiO_3$ is [100] and small compressive strain when it is [001] [86]. In this condition, a room temperature monoclinic phase has been stabilized [85] with alternating polarization direction along the [100] and [010]. In both domains, a small additional polarization component along the [001] is also found and thus the configuration is termed ca_1/ca_2 . This phase transforms into a aa^*/ca^* phase, with polarization direction alternating along the [100] and [001] with a small [010] component, above 50 °C. Both these domain configurations do not exist in $BaTiO_3$ single crystals. In the room temperature phase, the polarization lies mostly in-plane and thus, in this thesis, it will be referred to as an alternating in-plane ferroelectric a/b phase. On the other hand, in the higher temperature phase, the polarization mostly displays alternating in-plane and out-of-plane direction and will thus be considered as an a/c phase. The first order transition between these two phases represents an ideal condition for the study of the evolution of domains patterns, as it occurs in an accessible temperature range and displays a phase coexistence region.

1.2 Phase transitions and critical phenomena

In general terms, a phase transition³ is a phenomenon in which a drastic change between thermodynamic phases occurs as the system evolves towards a different region in the parameter space of thermodynamic variables [90]. While a phase is characterized by a thermodynamic function, typically the free energy, which is analytical, at the boundary between different phases a discontinuity in the derivatives of the free energy occurs [89]. According to the conventional classification, phase transitions are thus divided into two types depending on degree of singularity in the physical quantities.

When the first-order derivative of the free energy shows a discontinuity, the transition is of first order. Conversely, the transition is called continuous, or second-order, if the higher-order derivatives of the free energy show a discontinuity or a divergence (while the first order derivatives do not). First-order phase transitions take place by nucleation and growth of one phase into the other and are characterized by phase coexistence over a large region of the parameters space and hysteretic character. Contrarily, in second-order phase transitions, two or more phases become indistinguishable at the critical point leading to anomalous macroscopic behaviour. At the critical point, long-range spatial and temporal correlations emerge spanning through the whole system, even though the physical interactions are limited to (next)nearest-neighbour constituting elements. Moreover, as the largest number of metastable states exists at the transition point, large fluctuations of physical parameters occur. This makes critical systems extremely sensitive to external stimuli: small perturbations can start avalanche-like mechanisms that alter significantly the entire system.

Especially important in the description of phase transition is the evolution of so-called order parameters, which are macroscopic quantities that are zero in the high temperature phase and non-zero in the low temperature phase. In solids, they reflect the symmetry element that the system has gained at the phase transition. Therefore, the order parameter measures the degree of ordering of microscopic elements within a given phase. For example, in ferromagnets the magnetization is associated with the breaking of symmetry of the magnetically ordered phase and thus is non-zero below the Curie temperature and vanishes in the paramagnetic state; while to describe ferroelectric to paraelectric transitions, a good order parameter is the remanent polarization of the system. The degree of divergence of the order parameters near the critical point is described by critical exponents, that can thus be used as basic quantities to characterize critical phenomena. The observation of critical exponents that do not depend on the nature of the basic interactions between the constituent elements of the system has led to the concept of universality class. Critical exponents are also related among themselves through scaling laws [92]. Deeply linked to phase transition and critical phenomena is therefore this idea of scaling, that expresses the self-similarity and organization of the system at different length scales [93].

³Phase transitions and critical phenomena have been discussed in many scientific articles and books. The aim of this chapter is not to give a comprehensive review of this topic, but just to introduce the concepts that are relevant to the next Chapters. For a more in-depth description the interested reader is referred to Ref. [87–91]

1.3 Outline

The rest of this thesis is organised as follows:

Chapter 2 contains a description of the main experimental techniques utilized for this work. They include thin film grow methods, structural characterization (from x-ray diffraction to scanning probe and microscopy techniques) and magnetic and electrical properties measurements.

Chapter 3 deals with the optimization of the growth of CaFe_2O_4 thin films on TiO_2 (110) substrates by means of pulsed laser deposition (PLD), which had not been reported before. The films are crystalline and display a unique domain structure that is characterized in-depth by means of complementary techniques. Although the initial goal of manipulating the magnetic structures via strain was not achieved, we obtained high-quality samples, that are key to decouple the intrinsic properties from the effects of defects and disorder and obtain a better picture of the magnetic structure of this material.

Chapter 4 contains a comprehensive report of the magnetic properties of CaFe_2O_4 thin films at a global and local scale. Due to the relaxed crystal structure, the films display bulk-like behaviour, characterized by antiferromagnetism with the addition of a net in-plane magnetization peaking in the region of coexistence of the A and B magnetic orderings. Here, we show that long-range ordering occurs below 185 K and the magnetic transition has critical nature.

Chapter 5 shows the study of the angular dependent magnetoresistance of Pt Hall bar devices deposited on CaFe_2O_4 thin films. Here, measurements of both single- and multi-domains have been achieved by means of challenging experiments using Hall bar devices as small as $10\text{ }\mu\text{m} \times 3\text{ }\mu\text{m}$. The results are inconsistent with the spin Hall magnetoresistance effect expected for pure antiferromagnetic ordering but indicate the presence of uncompensated, uncoupled spins.

Chapter 6 is about the substitution of Fe by Cr in CaFe_2O_4 thin films and its effect on the epitaxial relation with the substrate and the magnetic properties. Increasing amounts of Cr lead to the formation of polycrystalline films that maintain a single-axis relation with the substrate. In addition, a shift of the Néel temperature towards lower values is observed, as expected, until a complete change of magnetic behaviour is reached at high Cr concentrations. Here however, the presence of magnetic impurities prevents use of these samples in devices.

Chapter 7 illustrates the study of the phase transition between a_1/a_2 and a/c domain structures in BaTiO_3 thin films by means of piezoresponse force microscopy. Here, it is shown how the equilibrium periodicity in the two phases is achieved via sequential period-doubling events, which are reminiscent of the bifurcation phenomena typical of chaotic systems [24].

1.4 Comments on valorization and sustainability

The submission of this PhD thesis occurred almost at the same time as the announcement of the Nobel Prize in Physics 2021 for “groundbreaking contributions to

our understanding of complex systems”. One half of the prize was awarded jointly to Syukuro Manabe and Klaus Hasselmann “for the physical modelling of Earth’s climate, quantifying variability and reliably predicting global warming” and the other half to Giorgio Parisi “for the discovery of the interplay of disorder and fluctuations in physical systems from atomic to planetary scales”.

In particular, the work of Giorgio Parisi on this topic has focused on the interaction of microscopic components of complex systems to predict behaviour at larger scales and has covered multiple areas of physics such as fundamental particles, condensed matter, statistical physics and disordered materials [94]. The contribution of Giorgio Parisi to the modelling of complex systems is rooted in the theory of disordered systems in which different elements are subject to multiple, potentially conflicting forces that can lead to frustration. His study of the spontaneous evolution of patterns in disordered systems has led to reliable predictions on the statistical properties of glassy systems, such as supercooled liquids, to amorphous solids and systems of spins among other things [95]. This cannot but underline the importance of the study of complex systems for modern day physics and how the related theories can be applied at all scales: glass, brains, finance, the flight of birds, climate and much more.

The other half of the Nobel Prize also reminds us of how scientific research is not disconnected to every day’s life and how a powerful and beneficial tool it can be when applied to societal issues, such as climate change. To do so, research not only has to focus on the relevant themes, but also has to be sustainable in itself. In the case of materials science, this means that researchers must be conscious of their choices of reagents and processes. The environmental impact of materials used in fundamental research, for example, is often disregarded in view of the small quantities utilized at a laboratory scale. However, nowadays more and more attention is paid to this issue from the early stages.

In the specific case of this work, there are indeed improvements that can be made to increase sustainability. The main one has to do with the environmental impact and availability of the substrates and especially rare-earth containing $NdScO_3$ (Chapter 7). Despite their favourable crustal abundance, rare-earth elements deposits are quite uncommon and usually modest in size, with the main ones being found at Mountain Pass (California), Mount Weld (Western Australia) and Bayan Obo (China). The extraction of rare-earth elements from natural deposit is an expensive and difficult process involving concentration, chemical extraction and separation, necessary due to the similar physical and chemical properties of all the rare-earth elements [96]. In addition, a body of evidence has shown that the chemicals used in the refining process of rare-earth elements are responsible for diseases and occupational poisoning of local residents, water pollution, and farmland destruction [97]. Therefore, mining and concentration of rare-earth ores present multiple environmental challenges that require the best practices of waste disposal, which notably increase the price for the commercialization of these materials and are thus not always observed [98]. Scandium is also a critical resource, mainly recovered as by-product from the production of rare-earths and other metals [99]. In view of its high economical importance, researchers are still looking for new and more sustainable scandium sources. Therefore, alternatives to rare-earth scandates substrates should be considered for the growth

of thin films destined to electronic applications. One possibility is to utilize buffer layers to achieve the desired epitaxial strain. This route is currently being explored in our research group in the context of the PhD project of Ruben Hamming-Green, who is exploring the growth of $SrSnO_3$ buffered $BaTiO_3$ films on multiple Perovskite substrates.

On the other hand, the majority of this work focuses on thin films of the antiferromagnet $CaFe_2O_4$ that is synthesized from the widely available and harmless $CaCO_3$ and Fe_2O_3 . The former is continuously replenished by means of natural cycles in rivers, lakes, and oceans and is even formed as mineral in animals, in the form of shells and skeletons, and in caves as stalactites and stalagmites [100]. Today, the increasing atmospheric concentration of CO_2 is causing the Carbonate compensation depth (i.e. the depth in the oceans below which the rate of supply of calcium carbonate is lower than its rate of solvation), to rise with detrimental consequences on the environment [101]. The latter, occurs naturally in the form of the mineral Hematite, the main source of iron for the steel industry [102]. $CaFe_2O_4$ films are grown on TiO_2 crystals that are also obtained without major drawbacks for health and the environment. This material occurs in nature as the minerals Rutile and Anatase and is mainly sourced from ilmenite ore. TiO_2 is largely utilized for its optical properties as white pigment, even in the cosmetic industry, and it can be safely recycled [103].

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Chapter 2

Experimental techniques

2.1 Introduction

In this chapter the concepts at the basis of the main experimental techniques exploited in this PhD project are presented. The majority of the experiments were conducted within the facilities and expertise of the Nanostructures of Functional Oxides research group of the University of Groningen. A few of them, that were realized in the context of collaborations within the University of Groningen or external, are listed in separate section.

2.2 Pulsed laser deposition

Pulsed laser deposition (PLD) is a physical vapour deposition process used for the growth of thin films and multi-layers. Together with other techniques, such as sputtering and molecular beam epitaxy (MBE), it is commonly used for the preparation of a large number of materials ranging from metals and simple oxides to multi-component materials with atomic control [1].

PLD uses a pulsed laser to ablate the desired compound from a target, transfer it into a plasma plume and then condense it onto an substrate. One of the main advantages of PLD growth is the (near)stoichiometric transfer of material from target to substrate. However, to achieve this, fine tuning of multiple parameters is necessary, including laser energy density, laser spot size, repetition rate, target-substrate distance, background gas pressure and temperature. Optimization of the growth conditions allows for preparation of samples with precise control over thickness, composition, crystallinity, quality of the interface and therefore, reproducible properties [2].

The choice of target and substrate plays a significant role in the growth of thin films via PLD. The former, does not necessarily need to have the same phase as desired in the film, but only the proper cation stoichiometry. Desirable target properties are the high optical absorption coefficient at the laser wavelength and high density. Therefore, single crystal targets are usually preferable, but polycrystalline ceramic targets, much easier to synthesize with large sizes, are more often used. The substrates used in PLD are usually single crystals cut along a specific crystallographic facet. Before growth, they can be treated to display optimized surface properties, such as atomic-height steps (due to the intrinsic deviation or miscut from the theoretical crystallographic orientation) and single chemical termination. The substrate can be heated during growth to favour crystallization of the desired film phase.

During a thin film deposition, a background gas is also often introduced that can serve two purposes: as a reactant for chemical interaction with the plume (for example when reactive PLD targets, that consist of the constituent cations, are used while the anion is supplied by the background gas) and/or to reduce the kinetic energy of the deposition flux (in the range of 1-100 eV). The presence of a background gas plays in fact a very important role in the propagation dynamics of the species from target to substrate.

In PLD, for sufficiently high laser energy, the ablated material is ejected from the target in a highly forward direction. The atomic species travel then from the target to the substrate, where they crystallize [3]. Numerous studies [2, 4, 5] have investigated the composition of the plume as a function of growth conditions in (mostly Perovskite) materials. In general, it has been shown that the main deviations from stoichiometric transfer of the cations occur at the ablation and propagation levels. At first, appropriate light wavelength, pulse length and laser fluence must be selected to avoid incongruent ablation of the target material and consequent off-stoichiometric composition of the plasma plume. The latter is especially critical in depositions from multicomponent targets, containing volatile metals (such as Bismuth and Ruthenium). Even in the case of congruent material ablation, the ratio and chemical state in which the atomic species arrive to the substrate can vary during the subsequent stages of the plume expansion and, principally, depend on the propagation mechanisms of the plume as a function of pressure.

A very pragmatic approach [4] identifies three propagation regimes characterized by increasing interaction with the background gas: “vacuum-like”, “transition” and “diffusion-like” regimes. For each of these the mean free path (λ) of the species can be estimated as:

$$\lambda = \frac{k_B T}{\sqrt{2} P \pi d^2} \quad (2.1)$$

where T is the temperature of the gas, P is the pressure, d is the diameter of the species and k_B the Boltzmann constant. λ is then compared with the target-substrate distance assuming that the target-substrate angle is kept to 0° .

In the “vacuum-like” regime, the mean free path is much larger than the substrate-target distance: here free ballistic expansion of the plume is expected, resulting in high but dissimilar velocities between different species and thus different arrival times at the substrate. When the mean free path and the target-substrate distance are comparable, in the “transition” regime, preferential scattering of the lighter elements with the background gas leads to the largest film compositional deviations. Nevertheless, most depositions are still carried out in this regime, because it permits the start of chemical interactions between the plasma plume and the background gas, enabling for example the incorporation of oxygen in the film, while still allowing relatively high kinetic energies of the arriving species. Finally, in the “diffusion-like” regime all species are confined in a slow expanding plume and travel following a shock-wave type propagation at a similar velocity. This results in films with homogeneous thickness and composition, but non necessarily the original one due to loss of material that also causes the films to be less dense. Further complexity of the plume dynamics arises by the possibility of formation of multiple other species next to electrons and atoms, such

as ions, diatomics (metal-oxygen species) and clusters, all of which can be in either excited or ground states. Moreover, the heater temperature can have an influence on the propagation dynamics, by affecting, for example, the gas density profile in the chamber.

The last stage of PLD is the growth and crystallization of the film at the substrate surface. Here, the lifetime of the adatoms before being incorporated into a step, their diffusivity on the terrace surface and the deposition flux provide the basic ingredients to create the simplest possible model of film growth. Three main growth mechanisms have been identified, that are governed by the interplay between kinetic and elastic effects [1, 6]. These are: step flow, consisting of parallel advance of the step edges; step bunching, characterized by accumulation of material at the step edges and the creation of large terraces; and island formation, where nucleation and coalescence of islands predominate. Usually, the first is preferable, leading to two-dimensional growth with low roughness. Finally, further complexity can be introduced by strain relaxation, by defect formation and interfacial diffusion, which are absent in the case of homoepitaxial growth.

Figure 2.1: PLD setup. **a** Schematic representation of a PLD setup courtesy of Ivar Dijk. **b** Photo of the growth of a CaFe_2O_4 thin film of this work, showing the target on the center and the bright plasma plume.

2.2.1 Reflection high-energy electron diffraction

Many PLD systems are equipped with in-situ reflection high-energy electron diffraction (RHEED) ¹. A schematics of the setup is shown in figure 2.1a: an electron beam is focused on the substrate at low incidence angle (usually below 5°), while the reflected electrons are collected and measured by a fluorescent screen in combination with a CCD camera. The grazing incidence geometry ensures that the penetration depth of the electrons is in the nm range, making RHEED an ideal analytical technique for surface analysis. In particular, it is mostly used as a tool to monitor growth

¹Our PLD systems is in fact from TSST, a spin-off of the University of Twente, where the first PLD chambers with in-situ RHEED were developed [7].

rate, lattice spacing/strain, and surface morphology of films [8].

According to the Laue condition for diffraction (see next section), constructive interference between waves diffracted by parallel planes of atoms in a crystal only occurs when the scattering vector $\Delta\vec{K}$, defined as the difference between the wavevectors of the incoming (k_0) and diffracted (k_1) beams, is equal to a reciprocal lattice vector. This is equivalent to say that the diffraction conditions are satisfied when the reciprocal lattice points intersect the so-called Ewald sphere of radius $r = 2\pi/\lambda$, where λ is the wavelength of the incoming beam [9]. Here, the structure of the reciprocal lattice originating from the two dimensional crystal surface consists of truncation rods instead of lattice points, due to the reduction of dimension. The intersections between the Ewald sphere and the truncation rods are points, which lie on concentric Laue circles and appear as diffraction spots on the phosphorous screen, as shown in figure 2.2 [10].

Kikuchi lines, originating from the diffraction of inelastic scattered electrons, can also sometimes be observed. Rotating the azimuthal angle of the sample allows to access diffraction from different crystal directions making RHEED images a rich source of information about the crystal symmetry.

Figure 2.2: The basic geometrical setup of RHEED with the Ewald sphere construction highlighted. Reprinted with permission from Ref.[8].

Actual samples are not always ideal and surface roughness, domains and defects, such as step edges or islands, limit the distance over which long range order, and hence coherent interference, are maintained, resulting in broadening of the crystal truncation rods and thus streaky RHEED patterns. Thus, analysis of the the RHEED images also provides insight into the surface structure. A complete description of RHEED patterns originating from different surfaces is provided in Ref.[10]. Therefore, the temporal changes in the RHEED images can be used to follow the evolution of the sample surface during the growth process and to determine the film growth mode. Conventionally, the integrated intensities of one or more specular Bragg diffraction spots are plotted as a function of time. For step-flow growth mode, the diffracted intensity fluctuates in a periodic manner as a consequence of the periodic roughing and smoothing of the surface upon deposition of material atomic layer by atomic layer.

Here, counting the number of RHEED oscillations provides information about the thickness of the film and the width of each oscillation allows to quantify the number of pulses needed to deposit a single layer of material. On the other hand, island-growth mode is characterized by a rapid damping of the diffracted intensity, because of the increased roughness, and usually terminates with a transmission diffraction pattern of a 3D crystal, which, unlike that of the flat surface, is independent of the azimuth angle.

The PLD setup used to grow the samples of this work consists of a *KrF* excimer laser (Lambda Physik COMpLex Pro 205 KrF) with wavelength $\lambda = 248$ nm and a vacuum chamber by Twente Solid State Technology (TSST) equipped with a heater stage for the substrate and a target carousel that can host up to 5 targets simultaneously. The laser beam reaches the main chamber through an optical path composed by multiple reflective UV mirrors, a slit and a focusing lens. In this way, a sharp image of the aperture can be focused on the target yielding the desired spot size. Experimentally, the appropriate path lengths are calculated by the lens formula:

$$\frac{1}{f} = \frac{1}{o} + \frac{1}{i} \quad (2.2)$$

where f is the focal length of the lens, o the object distance between the slit and the lens and i the image distance between the lens and the target. Optimal focus conditions are necessary to achieve a uniform fluence and a well-defined spot size. During deposition, the film growth was investigated in-situ by monitoring the surface structure using a RHEED setup operated at 30 keV.

2.3 X-Ray diffraction

X-ray diffraction (XRD) is a widely used technique for the characterization of the structure of materials. Based on the determination of the spatial distribution of the electron density in materials, it is extremely versatile in both the information and accuracy it can provide. XRD finds in fact application in the study of almost all types of materials, from inorganic crystals to proteins and DNA, as well as a broad range of structural parameters, from atoms position and bond lengths to domains and superstructures. Here, following the example of several classic textbooks [9, 11–13], the discussion will be limited to the scattering of x-rays by crystals and we consider the case of elastic scattering only.

When a monochromatic plane wave of x-rays, propagating with wavevector $\vec{k}_0$, falls on a crystal lattice, it is scattered by the electrons of its periodically arranged atoms. In this process, the individual wavelets scattered by different atoms are subject to a phase shift, due to the difference in optical path. Such phase shift is calculated as the dot product between the lattice vector describing the atom position and the scattering vector $\Delta\vec{K}$ defined as the wavevector difference:

$$\Delta\vec{K} = \vec{k}_0 - \vec{k}_1 \quad (2.3)$$

where $\vec{k}_0$ and $\vec{k}_1$ are the wavevector of the incident and scattered waves. Therefore, the scattered amplitude at the detector will be non-vanishing only in the case of constructive interference between wavelets, which occurs when the difference in their optical path is an integer multiple of the wavelength λ . This condition is expressed by the Laue condition for diffraction, which states that the scattering vector $\Delta\vec{K}$ must be equal to a reciprocal lattice vector ($\vec{G}$):

$$\Delta\vec{K} = \vec{G} \quad (2.4)$$

A useful way to visualize diffraction events is provided by the Ewald sphere, which defines the portion of the reciprocal space probed for a fixed λ in a diffraction experiment. The Ewald sphere is constructed with the origin at the crystal surface (end of the $\vec{k}_0$ vector) and with radius $r = |k| = 2\pi/\lambda$. If any reciprocal lattice points fall on the border of the sphere, then the Laue condition is fulfilled and a diffraction peak is observed.

During the course of this work, various XRD experiments have been carried out using different instruments and setups depicted in figure 2.3:

Figure 2.3: Schematic representation of various XRD experiment setups: **a** single crystal XRD, with the geometry of the scattering vector construction shown in the inset, **b** Bragg-Brentano geometry used for powder XRD and $2\theta - \omega$ scans, **c** reciprocal space mapping and **d** pole figure measurement.

- Single crystal XRD experiments have been done using a Bruker D8 Venture Single crystal diffractometer equipped with a *Mo* x-ray tube source ($\lambda = 0.70926$ nm) and a Photon III 14 2D detector. In this set up the single crystal sample is spun along three perpendicular reference axis meanwhile the position of

x-ray source and detector is kept constant, as shown in figure 2.3a. All the orientations for which the Laue condition is met by a family of crystallographic planes in the crystal will give rise to a bright spot in the detector. This allows to map the desired portion of reciprocal space. Analysis of the symmetry, intensity and systematic absences of the collected spots allows to determine the lattice parameters and space group of the sample.

- Powder XRD experiments made use of a Bruker D8 Advance diffractometer with *Cu* x-ray tube source ($\lambda = 0.15406$ nm) and a Lynxeye 1D detector. The system operates in Bragg-Brentano geometry with motorized slits. In such configuration, the angles formed by the sample holder with source and detector are kept equal (θ) and scanned over the desired range, meanwhile the sample is rotating along its surface normal axis (fig. 2.3b). For a powder sample, formed by randomly oriented crystallites, the measured intensity results in a diffraction pattern where Bragg peaks appears at the values of 2θ for which the Laue diffraction condition is met by the different families of crystallographic planes.
- The analysis of thin films is performed on a lab PANalytical four axes X'Pert MRD Cradle diffractometer, with a *Cu* x-ray tube source ($\lambda = 0.15406$ nm) and a PIXcel 3D detector, which can measure up to 256×256 individual pixels. The most basic type of measurement with this setup is the radial scan, also called $2\theta - \omega$ scans, where 2θ and ω are the angles that the incoming beam forms with scattered beam and sample surface respectively. In this mode, 2θ is scanned over the desired range while ω is fixed according to the relation:

$$\omega = \frac{1}{2}2\theta + \delta \quad (2.5)$$

where δ is called omega offset. For $\delta = 0$ source and detector are symmetric with respect to the sample and only the specular (out-of-plane) reflections are collected. In this way, the amplitude of $\Delta\vec{K}$ is changed but not its direction. Conversely, in an ω scan, the direction of $\Delta\vec{K}$ is changed but not its amplitude. A combination of these two motions and recording the scattered intensity as a function of both 2θ and ω creates a two dimensional reciprocal space map (RSM). The relationship between the measured angles in real space and the reciprocal lattice is described by the following equations and shown in figure 2.3c:

$$\Delta K = 2k_0 \sin \theta \quad (2.6)$$

$$\Delta K_{\text{perp}} = |\Delta K| \cos \delta \quad (2.7)$$

$$\Delta K_{\text{par}} = |\Delta K| \sin \delta \quad (2.8)$$

- Finally, pole figure measurements are also possible, where for a fixed diffraction angle 2θ , the diffracted intensity is measured as a function of χ , which is the rotation angle away from the sample surface normal, and ϕ , the rotation angle around sample surface normal, as shown in figure 2.3d. The collected intensity

is then plotted in the form of stereographic projections, which represent the orientation distribution of the crystallographic lattice planes contributing at the particular angle. Analysis of pole figures provides information regarding symmetry, texture and domain structure of the sample [13–15].

2.4 Microscopy

Microscopy techniques are an incredibly powerful tool for research in the field of nanoscience. Specific literature can be found, that describes in detail the working principles of each of the many techniques that belong to this ample class, thus in the following sections the discussion will only focus on the ones used in this work. To a first approximation, these can be divided in two main categories: scanning probe and scanning electron microscopies.

Scanning probe microscopy (SPM) is an umbrella term referring to those techniques by which an image of the surfaces of a sample is created by means of its interaction with a physical probe, usually a tip, that is mechanically scanned at a close distance from the surface [16]. The first SPM technique to be developed, in 1981 [17], was scanning tunneling microscopy (STM), where the tunneling current between tip and sample is used to probe the surface properties. A few years later, atomic force microscopy (AFM) also appeared [18], which allowed for the imaging of insulators as well. With its many variations (conducting AFM, magnetic force microscopy, piezoresponse force microscopy, kelvin probe force microscopy), the scanning tip can be made sensitive to many physical phenomena, such as electrostatic and magnetostatic interactions between tip and sample, current conduction and piezoelectric displacement, which makes this technique ideal for a comprehensive characterization of the surface of a specimen. Because of the near-field character of such interactions, the lateral range of SPM techniques can go from several 100 μm down to the pm range, allowing resolution and manipulation at the atomic scale [19, 20]. Thus today AFM is routinely used in research labs for the characterization of thin films and crystals, but further optimization of atomic force microscopes continues, pushing the boundaries of their performances. For example, recent advances in low-temperature magnetic force microscopy (MFM) have allowed to successfully image the magnetic structure of skyrmion lattices with a resolution below 100 nm [21, 22].

On the other hand, scanning electron microscopy relies on a focused beam of electrons to create an image of the sample. The diffraction limit for electrons, considering a de Broglie wavelength of $\lambda = 0.005$ nm corresponding to a reasonable 50 kV acceleration voltage, gives a sub-atomic theoretical resolution. However, in practice, the spatial resolution of an electron microscope is limited by aberration effects of the lenses [23]. Therefore, in the past years, great effort has been put into finding new methods for overcoming such problem. Today typical aberration corrected (C_s) scanning electron microscopes provide a spatial resolution in the nm range, while the resolution of (scanning) transmission electron microscopes is in the range of 10 pm. Thus this technique has been exploited in the study of all sort of materials, from graphene and *BN* to ferroelectrics [24, 25], to name but a few.

2.4.1 Atomic force microscopy

Atomic force microscopy (AFM) is a technique developed for the topographical imaging of flat surfaces. In a standard AFM setup, an atomically sharp tip connected to a force sensing cantilever is brought in close proximity with the sample surface, where it is subject to short-range chemical, van der Waals and adhesive forces.

AFM has many operation modes, among which contact and non-contact mode are the most commonly used, the latter being the preferred mode in this work, unless otherwise stated. In contact mode, the tip is brought into actual contact with the surface and the force between tip and sample directly translates into a vertical deflection of the cantilever. Usually, a deflection setpoint can be chosen, which is maintained constant during the scan by a feedback system, and that determines the force between the tip and the surface. This allows to reconstruct an height image of the topography of the sample [26].

In non-contact (tapping) mode, the cantilever is lifted from the sample surface and deliberately vibrated by means of a piezoelectric actuator, with fixed driving amplitude (A_d) and frequency (f_d). The interaction between tip and sample causes a deviation of both amplitude and frequency from their driving values. In the amplitude modulation mode, the amplitude is monitored and used as feedback signal by a feedback loop, that adjusts the tip-sample distance accordingly. In addition, the phase shift can also be recorded, which provides information regarding the adhesion properties of the surface. In the frequency modulation mode, the cantilever oscillation is driven at the tip resonance frequency f_0 . Forces between tip and sample cause a change in the frequency of oscillation $f = f_0 + \Delta f$, and from the frequency shift, Δf , the tip-sample force gradient can be determined.

Clearly, f_0 is a key parameter in AFM experiments, which is given by:

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m_0}} \quad (2.9)$$

where k is the spring constant and m_0 the effective mass. Maximization of k (soft spring) allows to achieve the maximum deflection for a given force but, at the same time, higher f_0 increases the sensitivity to vibrational noise [18]. Thus, a trade off between these two regimes needs to be found, which varies depending on the sample material. Other relevant parameters used by most AFMs are the gain values (integral and proportional) of the feedback loop. These determine how fast the amplitude is brought back to its setpoint.

An AFM image is composed by multiple linescans, obtained from trace and retrace of the tip in the scanning direction. Thus, instabilities in the passage between different lines can easily lead to artefacts. Among the most commons, is the difference in slope caused by non-flat samples. This can be compensated during the measurement itself (see next section) or via post-production of the image. The presence of large particles or contamination of the tip is also a very common cause of errors in the measurement.

In this work the AFM images were collected using a Bruker Dimension XR microscope, that utilizes a photosensitive detector to measure the deflection of a laser beam reflected by the back of the cantilever, which is in turn proportional to the

cantilever bending. This, being a 2D detector, allows to measure both vertical and lateral deflections. The tips used for AFM measurements are *Si* probes with an *Al* reflective coating and a resonance frequency of 300 kHz.

2.4.2 Magnetic force microscopy

Magnetic force microscopy (MFM) is a variation of AFM where the magnetostatic interaction between sample and tip is probed. To do so, a tip with a magnetic coating, that gets previously magnetized, is used.

Usually, MFM experiments are conducted in tapping mode, with the tip oscillating at a fixed distance from the sample. First, the tip moves along a line on the sample surface and the height profile is recorded. Then, instead of moving to the following line, the tip is lifted by a chosen amount, and traces the linescan again (both trace and retrace) following the contours of the topography measured in the first pass. The tip-sample force is thus recorded again in frequency modulation mode. This type of operation, usually referred as dual-pass, allows to separate within the signal the short-range interactions, originating from the topography, from the long-range purely magnetic information. However, this comes with the disadvantage that, keeping the tip at a larger distance from the sample, sensitivity and resolution decreases. This is because the physical quantity actually measured by the tip is the magnetic stray field H_s above the sample, which decays with the distance following an inverse-square law [27]. The energy (U) of the interaction is thus:

$$U = - \int_{probe} H_s(r) M_p dV \quad (2.10)$$

where M_p is the magnetization of the tip, assumed uniform. Thus the magnetic force acting on the cantilever in the vertical direction ($F_z(r)$) and consequent frequency shift Δf are given by:

$$F_z(r) = - \frac{\partial U}{\partial z} \quad (2.11)$$

$$\Delta f = - \frac{f_0}{2k} \frac{\partial F_z(r)}{\partial z} \quad (2.12)$$

From these relationships it is evident that standard MFM experiments are only sensitive to out-of-plane magnetization and that ferromagnetic and antiferromagnetic coupling between tip and sample will result in forces with opposite sign and thus light and dark contrast in the MFM image. However, in order to obtain quantitative information from these images, a complex three dimensional spatial integration is necessary [28], which is beyond the scopes of this discussion. Moreover, the assumption that the sample magnetization is not affected by the tip magnetic field and vice versa is only valid if the magnetic anisotropy is larger than the external field. Clearly, the chosen lift height for the second pass is a critical parameter which can also cause artefacts in the image. The most commons types are cross-talk with the topographical signal, which occurs at low heights, and incorrect compensation of the sample slope in both scanning and lateral directions. In fact, if the second pass lift

height is maintained constant across the image, but the sample is not flat, this can eventually result in crashing of the tip.

The MFM experiments of this work have been done using a customized Attocube scanning probe microscope, designed with extremely reduced sizes. This is achieved, by replacing the standard photosensitive detector with an infrared laser interferometer connected to the microscope head through a optic fibre. The light coming out of the ferruler is reflected by the back of the cantilever, creating an interference pattern. Prior to measuring, a proper cavity (distance between cantilever and ferruler) must be found, to achieve high intensity of the signal ². Then, a so called dither-spectroscopy is performed, where a sinusoidal interference pattern is collected as a function of the voltage applied to a piezoelectric actuator connected to the cantilever. With this operation, the proper working point (WP) for the experiment can be found, that is related to the amplitude peak-to-peak (ΔI) of the sine wave. In tapping mode, used for MFM, the WP is the inflexion point between two peaks, where the slope and thus the sensitivity is maximum. Finally, the cantilever is driven by an AC bias at the resonance frequency and a scan can be started in amplitude modulation mode, as described for standard AFM, but with dual-pass. Here, it is the phase shift in the second pass that is used to create an image of the magnetic interaction between tip and sample (MFM image). In such measurements the sensitivity is limited by the oscillation amplitude. The lateral resolution, on the other hand, depends mostly on the cantilever lift in the second pass, due to the spatial spreading of the magnetic field lines.

In our setup, the microscope is used in combination with a Quantum Design Physical Properties Measurement System (PPMS), which allows for low-temperature measurements (down to 2 K) and the application of a magnetic field (up to 9 T) perpendicular to the sample surface. The tips used in these experiments, provided by Nanoworld, have a *Co - Cr* coating and f_0 of 75 kHz.

2.4.3 Piezoresponse force microscopy

In piezoresponse force microscopy (PFM) electromechanical coupling between tip and sample is used to probe the piezoelectric response of a ferroelectric sample. For the converse piezoelectric effect, the piezoelectric strain (S_j) is linearly proportional to the applied field (E_i) according to:

$$S_j = d_{ij} E_i \quad (2.13)$$

where d_{ij} are the components of the piezoelectric tensor expressed in Voigt notation [29]. In a standard vertical-PFM experiment, both the bias and strain are directed along the out-of-plane direction, thus the d_{33} coefficient is tested. However, lateral-PFM experiments are also possible, where the torsional vibration of the tip is also recorded, yielding a complete three-dimensional reconstruction of the polarization orientation in the sample surface [30].

²It is to be noted how with this design the Attocube SPM can not measure the lateral deflection of the cantilever, regardless the operation mode. Thus, measurements such as lateral piezoresponse force microscopy are impossible with this system.

In practice, to decouple the cantilever deflection due to the piezoelectric deformation from the superimposed signal due to the surface roughness, an AC modulation voltage is used and a dynamic piezoresponse imaging is employed instead of the static one. Here, the first harmonic component of the bias induced tip deflection is measured, whose amplitude depends on the strength of the electromechanical coupling between tip and sample and phase contains information on the polarization direction with respect to the bias. In this way, it is possible to distinguish between areas of the sample where the polarization is pointing in different directions [31]: oppositely polarize domains will give a 180° difference in the PFM phase. In addition, domain walls (DWs) will also appear as minima in the amplitude signal as the piezoelectric response cancels out in these points.

Different PFM modes can be distinguished depending on the frequency used for the AC bias with respect to the contact resonance frequency (f_C) of the clamped system composed by the tip in contact with the surface. Off-resonance PFM that employs an AC frequency several times lower than the contact resonance is possible, for samples with large piezoelectric response and that can endure large voltages. In most cases however (eg. when measuring thin films) resonance enhanced PFM is used, where the PFM amplitude signal is increased due to proximity to f_C . The main disadvantage of this application is being susceptible to artefacts due to cross-talk with topography. This is because, upon scanning the surface, the contact resonance can shift leading to a change of amplitude and a non 180° phase shift. To correct for resonance shifts Dual Frequency Resonance Tracking (DFRT or DART) PFM has been introduced. Here, in addition to the resonance, two lateral sidebands are also excited and their relative amplitude is kept constant through the scan by a feedback loop. The closer these two frequencies (i.e. small bandwidth), the higher signal amplification obtained, but, at the same time, the higher the risk to loose the peak if f_C changes too fast. This allows to decouple the PFM signal from the topography while still taking advantage of the resonance enhancement, and is particularly suitable for rougher samples [32, 33].

In the last chapter of this thesis, DART-PFM experiments on ferroelastic $BaTiO_3$ thin films have been performed using an Asylum Research Cypher AFM, equipped with an heating stage that allows measurements up to 600° C. The tips used are made conducting by the application of a metallic $Co - Cr$ coating and have a resonance frequency around 75 kHz.

The SPM tip can also be used to observe local ferroelectric switching of the polarization, by applying a ramping DC voltage (V) through the tip and measuring the current (I) flowing through the sample. This allows to plot the I-V curve and, from it, reconstruct the polarization hysteresis loop. If the deformation is simultaneously measured, then the characteristic strain loop can also be observed. Moreover, if the DC voltage exceeds the coercive field of the sample, then scanning the surface in contact mode, allows to reorient the polarization, in a process called “writing”. To date, interpretation of PFM phase and amplitude is quite well understood, but quantification of the PFM data is still non trivial, mostly due to the non-uniformity of the field below the SPM tip and the presence of additional electrostatic interactions between tip and sample.

2.4.4 Scanning electron microscopy

A scanning electron microscope (SEM) is a type of microscope that produces images of a sample by scanning its surface with an electron beam. From the interaction between electrons and atoms in the sample, various signals, that contain information about the the surface topography, composition and structure are produced.

In the most common operational mode, the secondary electrons (SE) emitted by the excited atoms are collected using a scintillator (ETD) detector. From the signal intensity a topographical image is constructed. In addition, high-energy electrons are produced by the elastic scattering of the primary beam with the atom nuclei. These Back Scattered Electrons (BSC) are emitted in higher number by heavy atoms and can thus be used to probe the composition of the surface [23]. After the emission of a SE from a valence shell, an unstable vacancy is created that can be filled by an electron from an outer shell. The difference of energy of this transition is emitted by the atom in the form of x-rays with a characteristic wavelength. Thus the study of the emission spectrum of the sample can be used in-situ for elemental analysis and chemical characterization. This technique takes the name of energy-dispersive x-ray spectroscopy (EDS) and is commonly performed in combination with SEM imaging. The main challenges in EDS arise during the simultaneous quantification of different elements. Here the accuracy is limited by x-ray absorption effects and the presence of a background spectrum, the so-called Bremsstrahlung, produced by the electrons deceleration. Moreover, the choice the acceleration voltage and spot size of the primary beam, cannot always be optimized for all the elements contained in the specimen, thus producing large quantification errors.

In this work a FEI Nova NanoSEM 650 equipped with an Ametek EDAX-TSL EBSD system has been routinely used for the imaging and analysis of various samples in the form of thin films, ceramic pellets and crystals. This SEM setup offers, in addition to the most standard measurements, the possibility to perform Electron Backscatter Diffraction (EBSD) characterization of (poly)crystalline materials. This technique makes use of the scattering of the BSC electrons, to determine the microstructure, phase, crystal orientation or strain in the material. When travelling inside the sample, these electrons get, in fact, scattered by the periodic crystal lattice planes. Whenever their angle is such that the condition for diffraction is satisfied, this results into the creation of an image on the phosphorous screen of a CCD camera. Such image is characterized by a series of Kikuchi bands, each of which corresponds to an individual family of diffracting crystal planes. Thus, from a careful indexing and fitting of the Kikuchi patterns the crystal structure and its orientation can be determined. Because this experiment occurs within the SEM chamber, the primary beam can be focused on a specific area of the sample surface, thus obtaining very local information. Moreover, upon scanning the beam over a larger area, EBSD maps can be created showing the texture of the sample.

Among the most interesting aspects of EBSD is perhaps the statistical analysis of the orientation data and the possibility to generate numerous maps, charts and plots. Standard examples of these are grain orientation and image quality maps, grain boundaries, grain size and misorientation angles plots and texture pole figure. The EBSD maps shown in this thesis were obtained by or with the help of Ir. Dr.

Václav Ocelík.

2.5 SQUID Magnetometry

In order to study the magnetization, M , of a sample, many magnetometry techniques are available, ranging from laboratory-based vibrating sample magnetometry (VSM) and superconducting quantum interference device (SQUID) magnetometry, through optical techniques like the magneto-optical Kerr effect, to sophisticated techniques like polarized neutron scattering or x-ray magnetic dichroism that requires large-scale facilities. Many of these can also be turned into susceptometries, where the frequency-dependent magnetic susceptibility, χ , is measured upon modulating the applied field H [34] as:

$$\chi = \frac{\partial M}{\partial H} \quad (2.14)$$

Among these techniques, SQUID magnetometry is perhaps the most common, for its ease of use and very high sensitivity, which in modern instrument is in the order of $\mu\Phi_0$, limited by thermal and $1/f$ noise. SQUID magnetometers exploit a combination of the physical phenomena of flux quantization and Josephson tunneling to accurately measure the variation of the magnetic flux (Φ) across the SQUID loop. The supercurrent, I_s , flowing through a Josephson junction is given by:

$$I_s = I_c \sin(\varphi) \quad (2.15)$$

where I_c is the critical current and φ the phase difference across the junction. Phase coherence across the loop imposes that:

$$\varphi = -\frac{2\pi\Phi}{\Phi_0} \quad (2.16)$$

where $\Phi_0 = h/2e = 2.0678 \cdot 10^{-15} \text{ T m}^2$ is the magnetic flux quantum. Thus, in the presence of an external magnetic flux, Φ_{ex} , the total flux, Φ_T , can be written as:

$$\Phi_T = \Phi_{ex} - LI_c \sin\left(\frac{-2\pi\Phi}{\Phi_0}\right) \quad (2.17)$$

Two kinds of SQUID sensors exist, dc-SQUIDs and rf-SQUIDs, that differ in both architecture and flux measurement mechanisms, but behave essentially as flux-to-voltage transducers [35]. The former are composed by a superconducting loop containing two Josephson junctions, while in the latter the superconducting loop contains a single junction and is coupled to the inductor of a resonant tank circuit. In order to act as sensors, these devices are biased with a static or periodic current, respectively. In dc-SQUIDs, the change in Φ_T created by mechanically moving the sample through a superconducting pick-up coil inductively coupled to the SQUID loop, is directly converted into a voltage which is linear in Φ_{ex} . In rf-SQUIDs the change in Φ_T creates an oscillating voltage across the tank circuit that is periodic in Φ_{ex} with a period Φ_0 . Thus, in both cases, the output of the system is the SQUID

voltage V that can be correlated to the position of the sample in the pick-up coil [36].

The magnetometer used in this study is a rf-SQUID Quantum Design MPMS XL-7, which allows to measure temperature dependent magnetization from 2 to 400 K and field dependent magnetization from -7 to 7 T. In order to increase the sensitivity, this device is equipped with an axial gradiometer, which is a special kind input circuit, composed by 2 clockwise and 2 counterclockwise superconducting loops connected to the input coil. This allows to increase the effective area and, at the same time, prevents external static fields from generating a net flux in the loops. In this setup the SQUID magnetometer acts as a vector device and measures only changes in the magnetic field component perpendicular to the plane of the flux pickup loop. In addition, the use of the Reciprocating Sample Option (RSO) allows to oscillate the sample through the gradiometer (instead of moving it in discrete steps as in the standard DC mode), shortening the measurement time so that an average between multiple measurements can be obtained, which makes the measurement less sensitive to magnetic drift.

The sample preparation involves attaching the sample to a holder with no magnetic signal. For this purpose it is customary to use a transparent drinking straw and kapton tape. For measurements in parallel geometry, the thin film sample is fixed to the outside of the straw, while in perpendicular geometry the sample is placed between two halves of a straw. In both cases, it is important that the sample environment is as homogeneous as possible. Prior to measuring, the sample is centred with respect to the pick-up coils. To apply the required magnetic field, the MPMS XL-7 utilizes a superconducting magnet and a shield to protect the SQUID loop.

A known issue with these magnets is the remanent field which originates from trapped magnetic flux pinned at defects in the material of the superconducting coil (as mentioned before, the use of a gradiometer prevents to directly measure the magnetic field at the location of the sample, thus the remanent field can not be easily quantified). Such field is directed antiparallel to the last experienced strong field by the magnet and is the cause of common measurement artefacts such as residual hysteresis and inverted susceptibility curves [37]. Similar artefacts have been observed in the course of this study and they will be pointed out in the relative chapters.

Another important source of error can be introduced during the data analysis, upon conversion of the magnetic moment (in emu) into magnetization (in emu per mole or μ_B per formula unit). Here, an uncertainty in the sample's volume or mass may introduce an error well above the standard deviation of the raw data. This is especially true for thin films, where the thickness determination and the subtraction of the signal from the substrate are not straightforward. In this work, the long moment values obtained from the SQUID-MPMS have been analysed using the Origin software as follows: first the experimental data has been subtracted of the signal of a clean substrate, measured in the same conditions as the sample. Then, the experimental data (in emu) has been divided by the magnetic field (in Oe) and the mass of material to yield the magnetic susceptibility (in units of emu/Oe g). For the magnetization hysteresis loops, the magnetization has been further converted into units of Bohr magnetons per formula unit.

2.6 Electrical measurements

In Chapter 5 the measurements of the Spin Hall magnetoresistance (SMR) of *Pt* Hall-bar devices deposited on *CaFe₂O₄* thin films are described. Experimentally, the SMR effect can be measured using the lock-in detection technique [38, 39].

Here a reference Stanford Research 830 lock-in amplifier provides an AC voltage, with frequency ω (in our case 17 Hz) and phase ϕ , to a Stanford Research System Model CS580 Voltage Controlled Current Source that in turn generates a corresponding input AC current ($I(t)$):

$$I(t) = \sqrt{2}I_0 \sin(\omega t) \quad (2.18)$$

where the current rms value, I_0 , was chosen between 100 and 400 μA for the measurements in this thesis. The current is led to the sample via a custom built switchbox, that is also used to collect the output signal in the form of output voltage:

$$V(t) = R_1 I(t) + R_2 I(t)^2 + R_3 I(t)^3 \dots \quad (2.19)$$

where $V^n = R_n I(t)^n$ is the n -th order response. After amplification of the output voltage by means of a Stanford research SR560 low-noise preamplifier, used to increase the signal-to-noise ratio, the signal is measured by a number of Stanford Research 830 lock-in amplifiers that record simultaneously the different harmonic voltage responses. To do so, the output signal from the device and the reference input signal are multiplied and integrated over time in the interval $[0, T]$ as:

$$V^{nf} = \frac{\sqrt{2}}{T} \int_0^T \sin(n\omega t + \phi) V(t) dt \quad (2.20)$$

This allows to separate the different harmonic responses with reduced noise, being the measurement only sensitive to a reduced range of frequencies.

The voltage component with linear response $V^1 = I_0 R_1$ ($\phi = 0^\circ$) is attributed to the SMR response of the sample, while the second order voltage, $V^2 = I_0^2 R_2 / \sqrt{2}$ ($\phi = -90^\circ$), is correlated to the presence of spin Seebeck effect [40, 41]. Thus in our work V^1 and V^2 are measured simultaneously. In addition, some of the higher order harmonics were also checked and, being considerably smaller than the first two, their contribution was neglected.

To measure the angular dependence of the magnetoresistance of the *Pt* strip, the sample was mounted in a Quantum Design Physical Properties Measurement System (PPMS) with Torque option that allows for rotation of the sample in a static magnetic field. The measurements were performed with a field magnitude between -9 to +9 T and in a temperature range from 5 to 400 K. The control of the experimental setup was performed using a home-made LabVIEW code (National Instruments' software).

2.7 Other techniques

This section contains a brief description of the experimental techniques performed by collaborators that have been of great importance in this thesis.

2.7.1 Scanning transmission electron microscopy

If instead of measuring the signals emitted from a sample exposed to a scanning electron beam, the transmission of the primary electrons is detected, a scanning transmission electron microscopy (STEM) image is created [24].

For the electrons to be able to penetrate the sample, very low thickness is necessary. Thus conventional sample preparation for STEM, involves the creation of a lamella by cutting and thinning by means of a focused-ion-beam (FIB). Nowadays a typical Transmission Electron Microscope (TEM) can operate in dual-mode TEM/STEM despite the principle of image formation in the two cases is very different: the scanning method generates the image serially point by point, rather than simultaneously as in TEM.

To obtain high spatial resolution, STEMs need field-emission sources that operate in ultra high vacuum conditions. Conventional (S)TEM imaging techniques measure the phase of the transmission function, which can be interpreted as the projected potential of the sample, through different contrast transfer mechanisms. Most STEM images are acquired using a high-angle annular dark-field (HAADF) detector, that collects electrons scattered through relatively large angles. Like in SEM, because the scattering is proportional to the atomic number squared, heavy atoms appear as bright dots on a dark background. Imaging of lighter atoms (such as oxygen and hydrogen) is therefore much more critical and only recently advances in this technique made it possible [42, 43].

Another way to image both light and heavy atoms in a thin sample is via integrated differential phase contrast STEM (iDPC-STEM). Here the electromagnetic fields in the sample induces phase shift of the electron wave passing through, that can be measured and is directly proportional to the (projected) electrostatic potential. This yields a contrast that is linearly proportional to the atomic number [44].

The STEM images reported in this thesis were collected on a C_s corrected Themis Z Thermofischer microscope, equipped with an annular detector for HAADF imaging and a four quadrants segmented detector for DPC imaging. In-situ EDS analysis is also possible and maps of the elemental composition of the scanned area can be created. The experiments were performed by Dr. Pavan Nukala, during his stay as research fellow in our research group, and by Dr. Majid Ahmadi, our collaborator from the the Nanostructured Materials and Interfaces group led by Prof. Dr. Bart Kooi.

2.7.2 Scanning SQUID microscopy

Scanning SQUID microscopy (SSM) is another technique of the SPM family developed for imaging the magnetic fields generated by a sample. Its relative simple design,

consists of a dc-SQUID sensor attached to a pick up coil that is scanned over the surface. The main advantages of SSM over other techniques, such as MFM, are the high sensitivity of the dc-SQUID probe and the easier quantitative analysis of the data, based on the dipole approximation. On the other hand, the spatial resolution of SSM is relatively low, just below the μm regime, limited by a combination of the size of the pick-up loop and the sample-sensor distance. [45].

SSM is sensitive to the component of the magnetic field perpendicular to the coil plane (fig. 2.4a and c), but can also image the in-plane magnetic moments through their stray fields. This will result in a field signal that is strongest at a small distance away from the point-dipole, as shown in figure 2.4b. If the sample is composed by several dipoles with a separation below the lateral resolution, an image similar to that shown in figure 2.4d will appear.

Figure 2.4: Simulation of the magnetic field images of magnetic dipoles oriented at **a** 0° , **b** 90° and **c** 180° from the normal to the coil plane. **d** Image corresponding to the distribution of in-plane dipoles of panel **e**. Reprinted with permission from Ref.[45].

The SSM measurements in this work have been performed by our collaborator at the University of Twente Dr. Pim Reith, under the supervision of Prof. Dr. Hans Hilgenkamp. The microscope used is operated at 4 K in 0 background field, with field and spatial resolution of about 50 nT and 5 μm , respectively.

2.7.3 Mössbauer Spectroscopy

Mössbauer spectroscopy is a versatile characterization technique that utilizes the nuclear energy level transitions associated with the emission or absorption of γ -rays to probe the chemical, structural, magnetic and time-dependent properties of a material [46]. At the basis of this technique there is the discovery of recoil-less nuclear resonance fluorescence in solids, so-called Mössbauer effect, which allows to overcome the problem of the near absence of resonant overlap in free atoms emitting and absorbing γ -rays due to recoil and Doppler broadening. However, the necessity to have isotopes with low lying and short lived excited states (being the resolution limited by the natural line-width of the spectral lines) greatly restricts the number of isotopes that can be used successfully for Mössbauer spectroscopy. Among these, ^{57}Fe is the most commonly used.

In a Mössbauer spectroscopy experiment, a linear motor is used to mechanically oscillate the γ -ray source, so that the energy of the outgoing radiation is modulated in very small increments by means of the Doppler effect. When such radiation reaches the sample, absorption occurs only for those energies that precisely match a nuclear

transition in the absorber nuclei, resulting in a valley in the transmission spectrum. In this way, the change of position of the spectral lines with respect to the unperturbed state, can be used to probe the small (in the order of 10^{-9} eV) hyperfine interactions between the atoms and their environment. The environment can affect the nuclear energy levels in three main ways:

- Isomer shift. A positive or negative shift of the whole spectrum due to the s-electrons charge density at the nucleus. It depends on the valence of the atom, ligand bonding and the presence of electron withdrawing/donating groups.
- Electric quadrupole splitting. Splitting of the Mössbauer peaks due to the presence of an asymmetrical electric field gradient. This is only visible if the nucleus is in a state with an angular momentum quantum number $I > 1/2$ with quadrupole moment. It provides information regarding the coordination symmetry of the atom.
- Magnetic splitting. Zeeman splitting of the Mössbauer peaks due to the interaction of the nuclear spin moment with magnetic fields. The positions of the lines are related to the splitting of the energy levels, and their intensities to the angle between the Mössbauer gamma-ray and the nuclear spin moment. Thus, it provides information about the magnetic ordering in the sample and the direction of the magnetization.

Figure 2.5 shows an example of hyperfine splitting using the transition between the nuclear states with $I = 1/2$ and $I = 3/2$ in ^{57}Fe . In figure 2.5a the shift toward higher energies, δ , of the Mössbauer peaks is depicted, that could be observed for ions like Fe^{2+} and Fe^{3+} , that have a $3d^6$ and $3d^5$ electronic configuration respectively, and thus lower s-electrons at the nucleus due to the greater screening of the d-electrons, with respect to pure $\alpha\text{-Fe}$. Moreover, in the presence of an asymmetric environment, such as an asymmetric octahedral ligand field (fig. 2.5b), the $I = 3/2$ state splits into two sub-states with $m_I = \pm 1/2$ and $m_I = \pm 3/2$. The difference in energy between these two states ΔE is reflected in the peaks splitting and is proportional to the nuclear quadrupole moment. Finally, in the presence of a magnetic field B_{eff} , that originates from magnetic ordering within the sample, the nuclear levels split into $2I + 1$ sub-states (fig. 2.5c). Because the selection rules impose that only transitions with m_I change of 0 or 1 are allowed, the result for this transition is a characteristic sextet, with the line spacing being proportional to B_{eff} .

In this work, highly sensitive Mössbauer spectroscopy has been used to assess the oxidation state, magnetic ordering temperature and purity of ^{57}Fe enriched CaFe_2O_4 thin films. The experiments were performed by our collaborator Dr. Jean Juraszek at the Normandie Université. They were carried out in normal incidence using a home-made gas flow ($\text{He} - \text{CH}_4$) proportional counter, mounted inside a closed-cycle He cryostat for the low temperature measurements [47]. The source used was ^{57}Co in Rh matrix of about 1.85 GBq activity, mounted in a velocity transducer operating in constant acceleration mode.

Figure 2.5: Example of hyperfine splitting in ^{57}Fe : **a** isomer shift, **b** electric quadrupole splitting and **c** magnetic splitting.

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Chapter 3

Growth and structural characterization of CaFe_2O_4 thin films

Abstract

CaFe_2O_4 is a highly anisotropic antiferromagnet reported to display two magnetic phases, termed A and B, whose relative stability is ruled by the competing ferromagnetic and antiferromagnetic interactions between Fe^{3+} spins. However, contrasting results have been reported from single crystal and powder samples, suggesting that strain effects also play an important role. This calls for the need of preparing pure samples in which the strain state can be controlled. In this chapter we investigate the growth of epitaxial CaFe_2O_4 thin films 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 structural domains, that are induced by an underlying native CaTiO_3 layer.

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3.1 Introduction

As mentioned in the Introduction, CaFe_2O_4 is an antiferromagnet displaying two coexisting periodic magnetic structures below the Néel temperature of about 200 K. Theoretical calculations have shown that the expected exchange interactions between Fe^{3+} spins in this material are antiferromagnetic, leading to the magnetic structure named B ($\uparrow\downarrow\uparrow\downarrow$). However, at temperatures below 150 K a second spin arrangement appears, A ($\uparrow\uparrow\downarrow\downarrow$), that displays ferromagnetic coupling between Fe spins of the same type along the c axis. Sign reversal of the magnetic exchange is often related to structural phase transitions, however no such changes occur in CaFe_2O_4 below its ordering temperature of 200 K. Therefore a different explanation for the formation and coexistence of the two magnetic phases needs to be found. In addition, discrepancies between single crystal and power samples suggest that strain could have a large effect on the magnetic ordering of the material [1]. Thus, driven by the interest in growing high-quality samples of CaFe_2O_4 and possibly have a handle to alter its crystal structure by means of epitaxial strain, we decided to grow thin films of this material by means of PLD.

Turning to the literature, next to the structural and magnetic studies on single crystals and polycrystalline samples described in the Introduction, there are almost no reports of this material in epitaxial thin film form. To the best of our knowledge, the only prior attempt was made by Nishiyama *et al.* [2]. However, in this study only a structural characterization of the samples is reported, without mention to the effects on the physical properties. A much more extensive literature focuses instead on the catalytic activity of CaFe_2O_4 nanoparticles [3, 4] and heterostructures [5–8], with particular attention to their application as photo-cathode in H_2 generation and water splitting reactions. Although this provides a further example of the versatility and wide interest on CaFe_2O_4 , in this study we do not focus on this kind of applications. On the other hand, we are interested in gaining further insight in the fundamental properties of this material, with the prospect of exploiting the coexistence of modulated phases to develop a material with enhanced susceptibility. CaFe_2O_4 is the ideal candidate for such a study, given its relatively high ordering temperature and large reported interval of phase coexistence. Last but not least, all the constituting elements of CaFe_2O_4 are largely available and non-toxic.

3.2 Effect of growth conditions

3.2.1 Substrates

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_2O_4 prototype structure, making predictions of the epitaxial relation between the CaFe_2O_4 film and substrate not straightforward. The only previous work reporting thin films of this material has used TiO_2 (100) substrates [2], due to the similarity between the oxygen octahedra in the Rutile-type and CaFe_2O_4 structures. However, guided by the interest in the possibility of growing CaFe_2O_4 films with perpendicular magnetic anisotropy, which would make characterization by means of MFM easier, we discarded this option. TiO_2 (101) was the first possible candidate having in-plane parameters $\sqrt{a^2 + c^2} = 5.463$ Å and $d_{010} = 4.593$ Å, that would match one half of the CaFe_2O_4 $d_{001} = 10.705$ Å and one half of $d_{100} = 9.23$ Å with a mismatch of 2.1% and -0.5%, respectively. Even though these values are not negligible, previous examples of larger (6%) strain has been reported, where the films (TbMnO_3 on SrTiO_3) were able to grow epitaxially thanks to domain formation and strain relief at the domain walls [9].

Other possible substrate materials taken into consideration were LaAlO_3 (111), with in-plane mismatch of -0.3% and 0.9%, and MgO (111), with in-plane mismatch of -1.6% and -5.9%. In these substrates, the hexagonal configuration of the (111) surface may resemble the distorted hexagonal pattern formed by Fe atoms in the (010) plane. However, attempts to grown on all these materials were not successful, leading to amorphous or polycrystalline films. Epitaxial growth and high quality crystalline films were instead obtained on TiO_2 (110). Nevertheless, on this substrate, the initially desired [010] out-of-plane orientation could not be achieved. Instead another interesting structural relationship with the substrate develops, which is the

subject of discussion of this chapter.

Commercial TiO_2 mechanically polished crystals are provided by CrysTec GmbH, with a size of 5 mm x 5 mm and 0.5 mm thickness. Prior to use as PLD substrates, the following wet chemical preparation was performed to achieve an atomically flat surface and reveal the step edges [10]. First, the substrates were sonicated for 15 min acetone, subsequently in ethanol and deionised water and dried in a stream of nitrogen between each solvent. The purpose of this first stage is to clean the surface from any debris or contamination from organic material. Then, the surface was etched for 1 min with buffered oxide etch (BHF). The acid treatment is known for eliminating surface contamination that results in a reduction of the process temperature of the following stage of the process. Finally, the substrates were annealed in a tube furnace at 900 °C under a constant oxygen flux of 17 l/h, during which a flat, well-ordered surface forms through diffusion. The oxygen atmosphere was used to avoid the formation of oxygen vacancies and surface reconstruction with Ti interstitial defects typical of TiO_2 (110) with reduced oxygen content [11]. Figure 3.1a and b show AFM images of the surface of a TiO_2 (110) substrate before and after chemical treatment.

Figure 3.1: AFM images of TiO_2 (110) substrates. Topography **a** before and **b** after wet chemical treatment. The inset shows the height profile. AFM phase of **c** trace and **d** retrace.

It is evident that step edges appear on the annealed surface (fig. 3.1b) and from the measurement of multiple steps (see an example in the inset of 3.1b) the average height was found to be close to 3.2 Å, as expected for a single-unit cell of bulk TiO_2 [12]. From the AFM phase images (fig. 3.1c-d) opposite colour contrast can be seen at the step edges upon scanning in opposite directions, which confirms that the surface termination is uniform in composition. Note that the orientation of the step edges does is only due to the direction of the miscut of individual crystals and thus does

not follow any specific crystal direction.

3.2.2 Targets

The first target used for the growth of CaFe_2O_4 thin films was a home-made ceramic pellet of CaFe_2O_4 , prepared by solid state synthesis [13–15]. The oxide precursors, CaCO_3 (3N Sigma Aldrich) and Fe_2O_3 (99.998% Alfa Aesar) were mixed in an agate mortar with 5 agate balls and milled at 200 rpm for 2 hours in a Pulverisette ball mill. Subsequently, the powders were pressed into a 20 mm diameter pellet with 9.5 tons using an hydraulic press. Calcination and sintering were executed in air at 600 °C for 30 min and at 1200 °C for 90 min, respectively.

The structure and composition of the target was studied by means of powder XRD, shown in figure 3.2, and determined to be single phase CaFe_2O_4 . The same experiment was repeated after a few months (not shown) of use as a PLD target to check for ageing effects: no change in the XRD peaks position was observed, but only a broadening of the peaks that could be due to inhomogeneous recrystallization after the melting of the material.

Figure 3.2: Powder XRD of the PLD targets. Plot of the measured intensity as a function of 2θ from 18° to 65° of a ceramic CaFe_2O_4 target (black), ^{57}Fe enriched ceramic target (red) and powders obtained by crushing a floating zone grown crystal (blue). The black stars indicate the peaks of the CaFe_2O_3 impurity phase found in the enriched target.

Figure 3.3a shows a SEM image of the as-synthesized target and corresponding EDS elemental analysis. During the growth optimization process we observed that, in order to ablate Ca and Fe atoms from the target in equal amount, a high laser fluence (about 2.8 J/cm²) was required. At lower energies, the ablated region of the target under a 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 figure 3.3b). 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 EDS (fig. 3.3c).

Figure 3.3: SEM images collected with a back-scattered electron detector of the ceramic CaFe_2O_4 target and respective EDS spectra. **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 underlying EDS spectrum was collected.

In order to characterize the thin films magnetic properties by means of Mössbauer spectroscopy, a 80% ^{57}Fe enriched target was also prepared. The synthesis was carried out as described before, but adding to the standard Fe_2O_3 precursor 80% of the enriched oxide, that was, in turn, prepared by annealing of pure ^{57}Fe powders at 800°C for 2 hours in a constant oxygen flow of 18 l/h [16]. The enriched target was also characterized by powder XRD, yielding mostly CaFe_2O_4 phase with a small amount of CaFeO_3 impurity (see fig. 3.2).

Because single crystal targets are known to yield higher quality films, we also proceeded to synthesize a large CaFe_2O_4 crystal using a travelling solvent floating zone method. The experiment was realized in the context of the Master Research project of Rick Scholtens following the report of Das *et al.* [17]. As the first step of the crystal synthesis, a polycrystalline sample was prepared by a solid-state reaction to be used as feed and seed rod. A total of 21 g of CaCO_3 (3N Sigma Aldrich) and Fe_2O_3 (99.998% Alfa Aesar) were mixed in stoichiometric amounts and ball milled in an agate mortar with 5 agate balls at 200 rpm for 2 hours. The collected powder was then calcined in air and reground three times: first at 900°C for 12 hours, then at 950°C for 10 hours and finally at 1000°C for 24 hours. Subsequently, the powder was packed in a rubber sleeve, shaped into a cylindrical rod of about 8 mm in diameter and 10 cm long, and hydrostatically pressed with 40 tons. The rod was broken in half and sintered at 1000°C for 24 hours in air and loaded in the four-mirror optical furnace. At last, a final densification was carried out inside the furnace by applying

35.5 % of power to the lamps of the floating zone oven while moving the rods at 5 mm/h with respect to the lamps and rotating at 30 rpm with respect to each other. The power of the furnace lamps was then adjusted to 38.0 % to keep a thin melt profile layer during growth (the expected temperature is in the range of 1205 °C - 1216 °C, which are eutectic and incogruent melt formation temperatures [18]). The other growth parameters were as follows: 0.1 MPa oxygen pressure, 3 mm/h growth rate and relative rotation speed of 22 rpm between the seed and feed rods. The growth was stopped after a crystal of about 20 mm in length was obtained.

The crystal structure of this target was studied by means of single crystal and powder XRD (after crashing a small portion of the sample) and determined to be single phase CaFe_2O_4 (see fig. 3.2). The structure was refined in the $Pnma$ space group with refinement and crystallographic parameters given in table 3.1. Figure 3.4 also shows the precession images obtained from the raw data.

Figure 3.4: Reciprocal lattice planes from raw single-crystal XRD data at 100 K: **a** $0kl$, **b** $h0l$ and **c** $hk0$ plane. The peaks in the $0kl$ and $hk0$ planes follow the condition for diffraction of the $Pnma$ space group with $0kl$: $k + l = 2n$ and $hk0$: $h + k = 2n$.

Prior to use for PLD growth, ablation tests were performed on the single crystal target, to check if the behaviour was analogous to that of the ceramic ones. To do so, different areas of the crystal were exposed to the laser beam with different energies and the effect of morphology and composition was studied by means of SEM and EDS. Indeed, similar results were obtained as those shown in figure 3.3. Moreover, no difference in the films topography, structure or properties were observed upon growing with the ceramic or single crystal target. This suggests that the growth of the CaFe_2O_4 films is reproducible and the optimization of the growth parameters is quite robust upon small variations in the target material, as long as the cation stoichiometry is maintained.

Table 3.1: Crystallographic data of a fragment cut from the floating zone grown CaFe_2O_4 crystal target.

parameter	value
temperature (K)	100(2)
radiation wavelength (nm)	0.71073 (Mo $K\alpha$)
formula	CaFe_2O_4
formula weight (g/mol)	215.78
crystal size (mm^3)	0.10 x 0.08 x 0.05
crystal system	orthorhombic
space group	$Pnma$ (no 62)
symmetry	centrosymmetric
Z	4
D (calculated) (g/cm^3)	4.823
F(000)	416
a ($\text{\AA}$)	9.2206(5)
b ($\text{\AA}$)	3.0137(2))
c ($\text{\AA}$)	10.6942(6)
α ($^\circ$)	90
β ($^\circ$)	90
γ ($^\circ$)	90
volume ($\text{\AA}^3$)	297.17(3)
μ (mm^{-1})	11.307
min/max transmission	0.398 / 0.602
θ range ($^\circ$)	2.917 - 40.308
index ranges	-16 < h < 16 -5 < k < 5 -19 < l < 19
data/restraints/parameters	1071/0/44
GooF of F^2	1.10550
no. total reflections	23022
no. unique reflections	1071
no. obs $F_o > 4\sigma(F_o)$	960
R1 [$F_o > 4\sigma(F_o)$]	0.0178
R1 [all data]	0.0231
wR2 [$F_o > 4\sigma(F_o)$]	0.0363
wR2 [all data]	0.0374
largest peak/hole ($\text{e}/\text{\AA}^3$)	0.804 / -0.613

3.2.3 Deposition parameters

The optimization of the growth of CaFe_2O_4 thin films on TiO_2 (110) substrates by PLD requires the control of several physical parameters. In this work, we have been varying laser fluence between 1.2 and 2.8 J/cm^2 , growth temperature between 750 $^\circ\text{C}$ and 900 $^\circ\text{C}$ and oxygen pressure between 0.01 and 0.2 mbar. After growth, all the films were cooled down at $-3^\circ/\text{min}$ in a oxygen atmosphere of 200 mbar, unless differently specified.

Polycrystalline films are easily obtained for a large window of growth parameters, as expected for a large mismatch between film and substrate orientation. However, we have observed that that oriented needle-like crystals tend to form for laser fluence higher than 2 J/cm^2 (enough to maintain the desired cation stoichiometry) and temperature below 850 $^\circ\text{C}$. Such needles resemble very much the shape of naturally occurring CaFe_2O_4 crystals, known as Harmunite [19], and have a size and separation

that depends on the amount of material deposited (see for example the comparison between figure 3.5a and b). Above 850 °C square-shaped crystallites start to appear (fig. 3.5c), that predominate over the needles at higher temperatures and lower laser fluence (fig. 3.5d). Thus we restricted the growth temperature between 800 °C and 850 °C.

Figure 3.5: AFM images of CaFe_2O_4 films for optimization of the PLD parameters. Effect of thickness: films grown at 2.2 J/cm^2 and 800 °C with **a** 850 and **b** 3600 pulses. Effect of temperature: films grown at 2.2 J/cm^2 with 2000 pulses at **c** 850 °C and **d** 900 °C.

Changes in oxygen pressure do not seem to influence the films morphology as well as their crystallinity, evaluated from the intensity of the peaks in the XRD spectrum. Thus, we selected a relative high oxygen pressure of 0.2 mbar to decrease the risk of oxygen vacancies formation. Finally, we observed that relatively thick films (around 100 nm), prepared with a number of laser pulses in between 6 and 20 thousand, as well as a high laser fluence (between 2.6 and 2.8 J/cm^2) and high repetition rate (10-15 Hz) were crystalline and textured.

Following the films growth in-situ by 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 [20]. Finally, at the end of the deposition, no more rods are visible, indicating high surface roughness (see inset of figure 2.2a). Despite this, a well-defined epitaxial relation between the films and the substrate is observed, as discussed in the next section.

3.3 Structure and orientation

Figure 3.6 shows the characterization of films of different thickness by means of specular 2θ - ω x-ray diffraction (XRD) scans. The thickness of the samples was obtained by measuring the cross-section of several films grown with a different amount of laser pulses in the SEM. The thickness of the remaining samples was extrapolated assuming a linear increase of thickness with growth time in a range of laser pulses going from 6000 to 20000. A more accurate determination of the samples thickness by means of x-ray reflectivity was not possible as no oscillation were observed above the critical angle. This is possibly due to a combined effect of the similar electron density between the CaFe_2O_4 films and TiO_2 substrate and high roughness of the films and interface.

Figure 3.6: XRD 2θ - ω scans of CaFe_2O_4 films with increasing thickness from about 66 to 150 nm. Plot of the measured intensity as a function of 2θ from 10° to 80° .

Next to the substrate peaks, two strong peaks in the 2θ - ω scans are seen at angles of 33.6° and 70.5° . The former can belong to both the (004) and (302) planes of CaFe_2O_4 and the latter to their second order diffraction. These two families of planes not only share the same lattice spacing, $d = 2.67 \text{ \AA}$, but also display a very similar arrangement of atoms, making it non-trivial to tell them apart in x-ray experiments. Therefore, in order to precisely determine the films orientation, the data from specular reflections need to be complemented by RSMs around off-specular peaks (fig. 3.7). In addition, a small and sharp peak is also found at $2\theta = 16.6^\circ$. This can correspond to the films (002) family of planes, but the smaller width of the peak might also indicate that it originates from the substrate instead.

In figure 3.7a the epitaxial relation between out-of-plane peaks of film and substrate is shown. In the second map (fig. 3.7b), we observe a peak at $2\theta = 55.23^\circ$ and $\omega =$

6.48° , which is the $(\bar{2}06)$ 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 third map (fig. 3.7c), 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 $(\bar{2}06)$ and (600) peaks is only consistent with the coexistence of both (004) and (302) out-of-plane orientations within the same film.

Figure 3.7: XRD RSMs of CaFe_2O_4 thin films. **a** Specular reflections of film and substrate, here the r.l.u refer to bulk TiO_2 lattice constants. **b-c** RSMs showing the presence of the both the $(\bar{2}06)$ and (600) peaks, which is only possible if the (004) and (302) orientations coexist within the same film. Here, the r.l.u refer to bulk CaFe_2O_4 lattice constants. All the maps are collected at $\chi = \phi = 0^\circ$.

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 $[\bar{1}\bar{1}0]$ direction of the substrate. On the other hand, the substrate [001] direction is parallel to the [100] and [102] directions of CaFe_2O_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 magnetic easy axis, 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. Figure 3.8 shows the measurement collected at $2\theta = 25.5^\circ$ that corresponds to the lattice spacing of the (202) planes of CaFe_2O_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 $\phi = 90^\circ$ 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 figure 3.8, six peaks for each value of χ appear, indicating that both orientations exist and each of them contains three in-plane domains (see the next section). Moreover, we also observe six peaks at $\chi = 70^\circ$, corresponding to the $(\bar{1}03)$ planes, with a *d*-spacing close to that of the (202) planes, forming a 70° angle with the (302) planes. The intensity in the center of the pole figure (out-of-plane) is a tail of the substrate (110) peak at $2\theta = 27.45^\circ$.

Figure 3.8: X-ray pole figure of a 84 nm thick CaFe_2O_4 film taken at $2\theta = 25.5^\circ$ (202). The peaks at $\chi = 50^\circ$ indicate the presence of 3 domains with (004) out-of-plane orientation, while those at $\chi = 10^\circ$ and 70° originate from three (302) oriented domains.

The local structure of the films was further analysed by scanning transmission electron Microscopy (STEM) (fig. 3.9). The most evident feature is the unexpected appearance of an intermediate layer between film and substrate, that will be discussed in the following section. We also utilized this technique to estimate the thickness of the films as a function of number of pulses used during growth. However, due to the high roughness of the films and the very local nature of STEM, these values are only indicative and constitute a large source of error when used for quantitative analysis.

The CaFe_2O_4 lattice and its fast Fourier transform (FFT), shown in figure 3.9b and c, respectively, are characterized by square-like arrangement of atoms. This was not expected for most of the planes (that have often hexagonal symmetry) and indicates a non-trivial orientation of the lattice. The out-of-plane d -spacing of the film is measured to be 2.66 Å, in good agreement with (004) or (302) orientation. The in-plane d -spacing is 2.58 Å, corresponding to the bulk value of the (2 $\bar{1}$ 0) planes. A simulation of the HAADF-STEM FFT (fig. 3.12d) reveals that the zone axis is [120], with (004) out-of-plane orientation. This direction is at 55° from the [001], consistent with the domain structure and epitaxial relationship found from XRD experiments. To probe the second in-plane lattice parameter of the CaFe_2O_4 orthorhombic structure we also cut a second lamella, shown in figure 3.10, perpendicular to the first one. However, here the inter-atomic distance could not be measured due to the proximity of the atoms below the resolution of the image. This is also in agreement with the arrangements of atoms expected for the CaFe_2O_4 structure with [010] in-plane direction parallel to the substrate [1 $\bar{1}$ 0] and (302) out-of-plane ($d_{302} = 2.66$ Å). Thus, even though an epitaxial relation with the substrate exists, the CaFe_2O_4 films display bulk-like structure.

Figure 3.9: Cross section HAADF-STEM images of a 90 nm thick CaFe_2O_4 film with in-plane direction parallel to the substrate $[001]$. **a** Full stack of film, intermediate layer and substrate. **b** CaFe_2O_4 lattice and **c** its FFT, from which the lattice spacing are obtained. **d** Simulation of the electron diffraction pattern from the $[120]$ zone axis. Image taken by Dr. Pavan Nukala.

Figure 3.10: Cross section HAADF-STEM images of a 90 nm thick CaFe_2O_4 film with in-plane direction parallel to the substrate $[1\bar{1}0]$. **a** CaFe_2O_4 lattice and **b** its FFT, from which the out-of-plane lattice spacing is obtained. **c** Simulation of the electron diffraction pattern from the $[\bar{2}03]$ zone axis. Image taken by Dr. Pavan Nukala.

3.3.1 Interfacial CaTiO_3 Layer

HAADF-STEM and corresponding energy dispersive spectroscopy (EDS) analysis (fig. 3.11) also revealed the presence of a CaTiO_3 layer (5 to 10 nm thick) with the Perovskite structure between the substrate and the CaFe_2O_4 film.

This intermediate layer most likely arises from the chemical reaction between the high energy Ca^{2+} ions in the plasma and the TiO_2 substrate surface. The exact mechanism of the formation of this layer is not fully understood. The intermixing of atoms observed at the CaTiO_3 - CaFe_2O_4 interface points to the diffusion of the Ti

Figure 3.11: Chemical analysis of the thin film stack: elemental distribution of *Ca* (blue), *Fe* (orange) and *Ti* (green) across the three layers obtained through STEM-EDS. Image taken by Dr. Pavan Nukala.

atoms from the substrate into the growing film as a possible cause. In this scenario, an excess of *Fe* in the film or at the interface would be expected, which was however not observed in the samples. Another possibility, would be a non-stoichiometric transfer from the PLD target to the plume, similar to what is found for lower laser fluence values, but only limited to the first stages of the deposition. Further systematic investigation of the relation between the films thickness and the thickness of the CaTiO_3 layer could provide useful insight to clarify this open question.

Figure 3.12 shows the structure of the CaTiO_3 layer. The out-of-plane d -spacing is measured to be $2.76 \text{ \AA}$ corresponding to the bulk value of the (020) planes and thus (010) orientation. The in-plane d -spacing is $3.83 \text{ \AA}$, corresponding to the bulk value of the (002) planes, thus the epitaxial relation with the substrate is: $\text{TiO}_2 [1\bar{1}0] - \text{CaTiO}_3 [001]$. The lattice of the CaTiO_3 layer is fully relaxed by means of dislocations, with 6 planes of the films corresponding to 5 planes of TiO_2 (see yellow box in figure 3.12a).

Furthermore, oxygen column imaging was performed through differential phase contrast (DPC) STEM. The integrated DPC-STEM image on the CaTiO_3 layer (3.12d) clearly reveals $a^-a^-c^+$ oxygen octahedral tilt pattern, corresponding to orthorhombic $Pnma$ symmetry. Finally, the CaTiO_3 layer displays ferroelastic domains separated by (110) domain walls, reminiscent of bulk CaTiO_3 [21, 22]. Possible magnetoelectric coupling between these domain walls and the CaFe_2O_4 layer is an interesting subject of future investigation.

None of the macroscopic XRD experiments discussed so far was able to reveal the formation of this layer, because of the overlap between the reflections of this material

with the CaFe_2O_4 ones. In particular, the CaTiO_3 (020) and (040) peaks appear at $2\theta = 32.9099^\circ$ and $2\theta = 68.9984^\circ$, respectively. However, these values are very close to the CaFe_2O_4 out-of-plane reflections: (302)-(004) $2\theta = 33.6123^\circ - 33.4931^\circ$ and (604)-(008) $2\theta = 70.6579^\circ - 70.3784^\circ$. Thus, considering the broadening of the peaks expected for a thin layer, distinguishing between these values is below the resolution of our XRD experiments. However, it is possible that the shoulder present on the right side of the film peaks of figure 3.6 could be caused by the CaTiO_3 reflections.

Figure 3.12: Cross section HAAFD-STEM images of the CaTiO_3 layer. **a** Overview of the CaTiO_3 - TiO_2 interface. The yellow box indicates a dislocation containing 5 planes of the film and 6 of substrate. **b** CaTiO_3 lattice and **c** its FFT, from which the lattice spacing are obtained. **d** iDPC-STEM magnification of an area displaying the TiO_6 octahedra tilting along the $[110]$ direction. Image taken by Dr. Pavan Nukala.

3.4 Domain structure

The CaFe_2O_4 thin films prepared in this study display a distinctive domain structure, as clearly seen in the AFM images of figure 3.13.

Each domain is composed of needle-like crystallites with the long axis being the $[010]$ direction of the crystal. The presence of multiple crystals results in a high roughness of about 20 nm for a 100 nm thick film. Three specific crystallographic orientations of the domains are found as shown in figure 3.13b: 1- with the $[010]$ parallel to the substrate $[1\bar{1}0]$, 2- forming a 55° angle with 1 and 3- forming a -55° angle with 1. The boundary between two adjacent domains is sharp with an herringbone pattern, whereas at the conjunction between three or more crystallites, vortex-like structures that can have triangular (3.13c) or diamond shape (3.13d), are visible.

Consistent results are obtained from XRD pole figure and RSM measurements. Figure 3.14a-b show the pole figures collected at $2\theta = 33.65^\circ$ and $2\theta = 70.5^\circ$, that correspond to the spacing of CaFe_2O_4 (302)-(004) planes and (008)-(604), respectively (first and second film peaks in the $2\theta - \omega$ scan of figure 2.2a).

Figure 3.13: AFM images of CaFe_2O_4 thin films. **a-b** Overview over areas of $15\ \mu\text{m} \times 15\ \mu\text{m}$. The numbers indicate the three different kinds of domains. **c** diamond-like structure at the conjunction between 4 domains and **d** triangular structure at the conjunction between 3 domains.

Figure 3.14: X-ray pole figures of a $84\ \text{nm}$ thick CaFe_2O_4 film collected at **a** $2\theta = 33.6^\circ$ and **b** $2\theta = 70.5^\circ$, with the substrate $[1\bar{1}0]$ parallel to the scattering plane.

In these pole figures, intensity in the centre is expected, which belongs to the specular reflection of the out-of-plane family of planes. Moreover, because (302) and (004) planes share the same lattice spacing, for a single domain sample, two peaks

are expected to appear at $\chi = 60^\circ$ and $\phi = 90^\circ, 270^\circ$ from the $[010]$ direction. However, together with these, we observe 4 more peaks at $\phi = 55^\circ, 125^\circ, 235^\circ$ and 305° , which indicate the presence of 3 CaFe_2O_4 in-plane domains. The same domain structure emerges from the pole figure collected at $2\theta = 33.6^\circ(004)\text{--}(302)$ and $2\theta = 70.5^\circ(008)\text{--}(604)$ (fig. 3.14). In figure 3.14b additional substrate (301) ($\chi = 51^\circ$ and $\phi = 55\text{--}125\text{--}235\text{--}305^\circ$) and (112) ($\chi = 65^\circ$ and $\phi = 0\text{--}180^\circ$) peaks are also visible. Correct attribution of these peaks to the substrate is confirmed when repeating the experiment on a bare substrate.

Furthermore, figure 3.15 shows 2 sets of reciprocal space maps around the CaFe_2O_4 (600) peak ($2\theta = 60.25^\circ, \omega = -1^\circ$ and $\chi = 0^\circ$) and around the $(\bar{2}06)$ peak ($2\theta = 55.23^\circ, \omega = 6.48^\circ$ and $\chi = 0^\circ$). For each set, the value of the in-plane rotation angle ϕ is changed to match the orientation of a different domain: the first map is collected at $\phi = 0^\circ$ (a-d), while the second (b-e) and third (c-f) at $\phi = 55^\circ$ and $\phi = -55^\circ$ respectively. As it can be seen, a peak appears in all six maps confirming the presence of three in-plane domains for both out-of-plane orientations. The intensity of the peaks however, is not identical, with the first being higher than the others (see scale bar in figure 3.15a), in this particular film.

Figure 3.15: Reciprocal space maps of the (600) and $(\bar{2}06)$ peaks of a 90 nm thick CaFe_2O_4 film collected at **a-d** $\phi = 0^\circ$, **b-e** $\phi = 55^\circ$ and **c-f** $\phi = -55^\circ$. The scale bar is kept constant in all the six plots.

3.4.1 EBSD study

In-depth characterization of the domain structure of CaFe_2O_4 has been achieved by means of electron backscatter diffraction (EBSD) in a scanning electron microscope. As depicted in figure 3.16a, 6 overall different domain types are found by EBSD, consistently with the previous measurements. The first 3 types display the same (001) out-of-plane direction but differ for the in-plane. Specifically, in type $T1$ (lilac) the CaFe_2O_4 $\langle 010 \rangle$ direction is parallel to the $[100]$ sample axis (vertical in the presented EBSD map), which in turn is parallel to the substrate $[1\bar{1}0]$. In types $T2$ (gray) and $T3$ (brown) the $\langle 010 \rangle$ direction is parallel to the reference $[5\bar{7}0]$ and $[570]$ respectively. This corresponds to a $\pm 55^\circ$ rotation with respect to $T1$. The remaining 6 domain types display $[302]$ out-of-plane direction. For these domains, the same 3 in-plane orientations are also found, resulting in domain types $T4a$ (azure), $T5a$ (cyan) and $T6a$ (blue). In addition, a rotation of 180° along the out-of-plane direction of the unit cell generates a twin variant of each domain type, namely $T4b$ (violet), $T5b$ (orange) and $T6b$ (light blue). The same rotation applied to domains $T1$, $T2$ and $T3$ does not lead to a different crystallographic orientation as it coincides with a rotation around the crystallographic axis $\langle 001 \rangle$.

A schematic representation of the unit cell spatial orientation of the various domains is visible in figure 3.16b as axonometric projections (top view), superimposed on the correspondent SEM image. The data from the same EBSD scan is also reproduced in the maps of figure 3.16c-d where only the out-of-plane and in-plane directions of the domains are shown. In figure 3.16c all the domains with (001) out-of-plane ($T1, T2, T3$) are depicted in red, while those with (302) out-of-plane ($T4, T5, T6$) are blue. Similarly, domains with the $\langle 010 \rangle$ direction parallel to the reference $[100]$ ($T1, T4$) are orange, $[570]$ ($T2, T5$) are green and at $[5\bar{7}0]$ ($T3, T6$) are purple in figure 3.16d.

A list of the domain types and their orientation is reported in table 3.2, as well as a quantitative estimation of the relative abundance of each domain obtained from a large EBSD scans of $250 \mu\text{m} \times 500 \mu\text{m}$ (not shown). Considering the two out-of-plane orientations, in this sample, the (302) is the most abundant, occupying approximately 73% of the surface. Comparing the three the in-plane orientations shows that the domains with $[010]$ parallel to the substrate $[1\bar{1}0]$ are about 7% of the total, while those tilted of $\pm 55^\circ$ amount for approximately 45% each. (The values do not sum up to 100% due to a fraction of the surface not being indexed due to the presence of defects or impurities on the surface).

Analyzing the surface of different samples, we found that the relative amounts of the different domain types can vary significantly, possibly due to fluctuations of the laser energy and sample alignment during the PLD growth. However, very interestingly, the domain types always appear in pairs of similar relative abundance. Such pairs are: $T2$ and $T3$, $T4a$ and $T4b$, $T5a$ and $T6a$, $T5b$ and $T6b$, (see table 3.2), which makes our results generally applicable to all our samples.

Figure 3.16: EBSD scan of a $62\ \mu\text{m} \times 60\ \mu\text{m}$ area of the surface of a $84\ \text{nm}$ thick CaFe_2O_4 thin film. **a** EBSD map showing the 9 crystal orientations (solid colour). **b** Map of the SEM secondary electrons contrast with superimposed axonometric projections of unit cell orientation in red. **c** EBSD map highlighting the 2 out-of-plane directions: (001) ($T1$ - $T3$) depicted in red and (302) ($T4$ - $T6$) in blue. **d** EBSD map highlighting the 3 in-plane directions: domains with the $\langle 010 \rangle$ crystal direction parallel to the reference $[100]$ ($T1, T4$) are orange, to the $[570]$ ($T2, T5$) are blue and to the $[5-70]$ ($T3, T6$) are purple. The grain boundaries are indicated with black solid lines in all the maps. Image taken with the help of Ir. Dr. Václav Ocelík.

Table 3.2: Crystal orientation of the domain types in the CaFe_2O_4 thin film shown in figure 3.16, expressed via $\{hkl\}[\text{uvw}]$ pair, where the first gives the pole of crystal planes parallel to the sample surface and the second gives the crystal direction parallel to the vertical direction of the EBSD maps and also parallel to $[1\bar{1}0]$ crystal direction of the substrate.

Domain	Orientation	Volume fraction
T1	$\{00\bar{1}\}//[010]$	0.222
T2	$\{001\}//[370]$	0.024
T3	$\{00\bar{1}\}//[370]$	0.022
T4a	$\{302\}//[010]$	0.137
T4b	$\{302\}//[0\bar{1}0]$	0.146
T5a	$\{302\}//[293]$	0.143
T5b	$\{302\}//[293]$	0.053
T6a	$\{302\}//[293]$	0.153
T6b	$\{302\}//[293]$	0.052

3.4.2 Epitaxial relationship

To explain the formation of the particular domain structure of CaFe_2O_4 thin films, we put forward a model based on optimum structural matching between the crystal lattice of CaFe_2O_4 and that of the underlying CaTiO_3 layer (fig. 3.17a). First of all, the similarity between the (004) and (302) planes of CaFe_2O_4 is remarkable, which made the characterization of the films particularly difficult. The arrangement of the cations in such planes is very similar and based on alternating ($\text{Fe} - \text{Fe} - \text{Ca} - \text{Fe} - \text{Fe} - \text{Ca}$) chains of cations ordered along the b -axis. This results in almost indistinguishable, besides the modulation of the spots intensity, electron diffraction patterns (fig. 3.17b,c). Therefore, even plan view observation in STEM was not enough to give a conclusive answer on the out-of-plane orientation. Due to this similarity, it is not surprising that islands of material with both orientations can coexist on the substrate.

Figure 3.17: a Schematic representation of the epitaxial relation between domains 2 and 3 of a CaFe_2O_4 film and under-laying CaTiO_3 layer. $\text{Fe}(1)$ is shown in red, $\text{Fe}(2)$ in blue and Ca in yellow. The black circles indicate the cations in the underlying CaTiO_3 layer, with empty circles for Ca positions and filled circles for Ti . b,c Simulations of electron diffraction pattern from the [001] and [201] zones axis, respectively.

As far as the three in-plane orientations are concerned, we noticed that 55° is the angle between the CaTiO_3 [001] and [101] in-plane directions. As figure 3.17a shows, the cations in the film overlap best with the underlying CaTiO_3 , when the cations rows of CaFe_2O_4 (in both (004) and (302) out-of-plane domains) are either parallel to the CaTiO_3 [001] direction or at $\pm 55^\circ$ from it. Therefore, because the growth of the films of this study follows an island-growth mode, we hypothesize that islands with one of the 6 orientations start growing independently and later merge together yielding a rough and textured film. This is surprising, as the MO_6 octahedra network of CaFe_2O_4 is different from that of Perovskite CaTiO_3 , making predictions of the epitaxial relationship between the two layers based on cations positions only

non straightforward. However, no specific relation between the oxygen positions in the two lattices has been noticed in this scenario.

In order to verify our hypothesis regarding the nucleation and growth of separate oriented islands of CaFe_2O_4 on CaTiO_3 , we stopped the deposition of the films at different stages of the growth process and analysed the structure by means of AFM, XRD and EBSD. Initially a very thin layer was grown with 700 laser pulses. Such film displays a rough morphology, but no peaks corresponding to CaFe_2O_4 or CaTiO_3 were observed and the EBSD response was consistent with pure TiO_2 (110) oriented. Subsequently, we grew films with 3000 and 4500 laser pulses, as shown in figure 3.18.

Figure 3.18: AFM topography of films grown with **a** 4500 and **b** 3000 laser pulses. EBSD scan of a $9\ \mu\text{m} \times 22\ \mu\text{m}$ area of the surface of the 4500p sample: maps showing **c** image quality, **d** phase and **e** crystal orientation. **f** Kikuchi pattern originating from the 3000p sample and **g** its fit with CaTiO_3 (010). **h** Schematic representation of the corresponding CaTiO_3 unit cell spatial orientation. EBSD images taken by Ir. Dr. Václav Ocelík.

As it can be seen, while the film grown with 3000 pulses (fig. 3.18b) has a uniform AFM topography, in the thicker film (fig. 3.18a) some islands of needle-like crystals are already visible. The Kikuchi pattern measured for the 3000 pulses thick layer was also uniform throughout the sample (fig. 3.18f-g) and could be fitted by a single-oriented CaTiO_3 crystal, with the unit cell oriented as shown in figures 3.18h. No more signal originating from the TiO_2 substrate was observed at this point of the growth process. The absence of signal from CaFe_2O_4 at this stage is another indication that the CaTiO_3 is a product of a reaction between the Ca ions in the plume and the TiO_2

substrate, instead of due to the diffusion of Fe away from the interface.

EBSD analysis of the needle-like crystals of the 4000 pulses sample (fig. 3.18c-e) revealed that the phase and crystal orientations of such islands are the same of the domains of the thicker films. However, the crystal quality in parts of the film surrounding the islands was not enough to produce a distinguishable EBSD signal, as shown by the white areas in the image quality map of figure 3.18c. This is probably due to the superposition between the signal from the $CaTiO_3$ layer, found in a few spots of the map, and the new $CaFe_2O_4$ forming on top, both of low thickness. These results are in good agreement with the scenario of island-growth mode of the epitaxial $CaFe_2O_4$ film, with nucleation of oriented domains matching the underlying lattice of the $CaTiO_3$ layer formed at the interface with the substrate.

3.5 Conclusions

To conclude, in this chapter we have shown that PLD growth of relaxed epitaxial $CaFe_2O_4$ thin films on TiO_2 (110) substrates is possible, using high laser fluence, relative high oxygen pressure and a temperature around 820 °C. Despite the single out-of-plane peak observed by XRD in the 2θ - ω scans, in-depth characterization reveals the coexistence of two out-of-plane crystal orientations with identical lattice spacing, namely (004) and (302). Distinguishing between such orientations is complicated by the very 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. Interestingly, the direction of the magnetic easy axis ([010]) in the two crystal orientations coincides, making the crystallites of the two kinds equivalent from a magnetic point of view. This allows to study the orientation dependence of the magnetic properties, despite the rather complex microstructure of the samples.

TEM characterization reveals that the epitaxial growth of $CaFe_2O_4$ films is achieved through the formation of a Perovskite $CaTiO_3$ (010) layer at the interface with the TiO_2 substrate. The presence of this layer induces a specific domain structure in 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 $CaFe_2O_4$ and $CaTiO_3$ lattices, which is achieved when the film [010] direction is parallel to the $CaTiO_3$ [001] or at $\pm 55^\circ$ from it. The presence of these domain variants gives rise to vortex-like structures. Despite the complexity of such domain structure, the very clean morphology of our films allows to address different domains as individual crystals and be independently utilized in devices, as it will be discussed in Chapter 5.

Finally, the question regarding the possibility of growing $CaFe_2O_4$ thin films with (010) out-of-plane orientation is still open. Our observations regarding the growth of TiO_2 (110) provide an interesting insight in this direction: the possibility of exploiting the epitaxy with $CaTiO_3$. Single crystals of this material are very difficult to grow, but yet can be made available as direct substrate material or it can be grown as a buffer layer on several standard Perovskite substrates [23], such as $LaAlO_3$ and

SrTiO_3 . Within this project we have indeed made some attempts to the latter option. However, due to scarcity of time, optimization of the growth conditions was never achieved.

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Chapter 4

Magnetic properties of CaFe_2O_4 thin films

Abstract

CaFe_2O_4 is a highly anisotropic antiferromagnet reported to display two spin arrangements with $\uparrow\uparrow\downarrow\downarrow$ (phase A) and $\uparrow\downarrow\uparrow\downarrow$ (phase B) configurations. The relative stability of these phases is ruled by the competing ferromagnetic and antiferromagnetic interactions between Fe^{3+} spins, but a complete understanding of the magnetic properties and phase diagram of this material does not exist yet. In this chapter we investigate the magnetic properties of epitaxial CaFe_2O_4 thin films grown on TiO_2 (110). Macroscopic as well as local measurements, including highly sensitive Mössbauer spectroscopy, reveal a single critical transition below $T = 185$ K and a non-zero in-plane magnetization peaking at around 130 K, consistent with the presence of uncompensated spins at the A/B phase boundaries, as proposed by Stock et al. for bulk samples.

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4.1 Introduction

After optimizing the growth process, we proceeded to investigate the magnetic properties of epitaxial thin films of CaFe_2O_4 on TiO_2 (110). Our goal was to compare the properties of the films with the previous reports on powder and single crystal samples. Because the films display bulk-like crystal structure, as described in Chapter 3, we expected to observe the formation of both A and B spin arrangements. However, the temperature range of coexistence of the two magnetic phases is expected to depend on the strain state of the sample [24], therefore differences in this regard could be found. To our knowledge this is the most comprehensive report of the properties of this material, where data from a large number of complementary techniques is collected from the same kind of samples, and the only study in thin film form. In addition, next to the macroscopic measurements, the well defined microstructure of the films also allowed us to perform local magnetic characterization, yet unreported for this material.

4.1.1 Comparison with bulk magnetic properties

Prior to diving into a deep characterization of the magnetic properties of CaFe_2O_4 thin films, we performed SQUID magnetometry measurements on the ceramic targets. These can be used as a means of comparison between thin film and bulk behaviour, as well as with previous literature reports.

In figure 4.1a the magnetization is plotted as a function of temperature from 4 to 400 K in a 100 Oe field (black) and 1 T field (red). Here, a single transition is observed at $T_N = 175$ 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) one. 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 *et al.* [1], but is in agreement with the ordering of the A phase according to Songvilay *et al.* [2].

In the measurement with a 100 Oe field, at this temperature the onset of the FC/ZFC splitting is also observed: in the FC curve χ rapidly increases and reaches a maximum at $T = 155$ K, while it symmetrically decreases in the ZFC one. The negative values of the susceptibility after ZFC, are probably due to the trapped fields that are unavoidably present in the SQUID magnetometer, whose sign depends on the history of the previous measurements (see Chapter 2 Section 2.5 and Ref. [3, 4]).

Figure 4.1: Magnetic properties of a CaFe_2O_4 ceramic pellet. **a** Plot of the magnetic susceptibility (χ) as a function of temperature (T) from 5 to 400 K in 100 Oe (black) and 1 T (red) magnetic field. The field-cooled (FC) data is plotted with closed dots while zero-field-cooled (ZFC) with open dots. **b** Plot of the magnetization (M) as a function of field (H) between -7 and +7 T measured at 100 K (black) and 130 K after ZFC (red) and FC in a 1 T field (violet).

On the other hand, in the measurement with a 1 T field, both FC and ZFC curves see an increase of χ after T_N , that reaches a maximum at $T = 165$ K. Here splitting of ZFC and FC curves is also observed, with χ decreasing rapidly in the first case and more slowly in the second, following a similar trend as in the 100 Oe measurement. This seems to indicate the presence of an irreversible component of the magnetization of CaFe_2O_4 that can only be switched in larger applied fields.

Another difference between the 100 Oe and 1 T measurements is found in the high-temperature behaviour. In both cases a non Curie-Weiss evolution of the magnetization is seen well above T_N , with the inverse susceptibility (not shown) becoming linear only above 335 K and 375 K, for the lower and higher field measurements, respectively. In addition, a broad bump in the susceptibility, as well as a higher saturation value, is seen at 1 T. Other previous studies reported a broad feature in the $\chi - T$ plot above T_N [5, 6], that can be fitted using the Bonner-Fisher model for linear magnetic chains with anisotropic coupling [7]. This might indicate the existence of short-range and low-dimensional antiferromagnetic exchange, at temperatures above the onset of three-dimensional long-range ordering.

Figure 4.1b shows the plot of the magnetization, M , as a function of applied field, H , at 100 K and 130 K after cooling in zero field and at 130 K after cooling in a 1 T field. Accordingly to previous reports [1], an opening of the $M - H$ loops is expected around 130 K. In this temperature range coexistence of the A and B phases is expected to occur. Therefore, larger magnetic hysteresis in this window supports the idea of the presence of “orphan spins” at the A/B antiphase boundaries, that carry an uncompensated magnetic moment (see Chapter 1 figure 1.3c). In addition M is found to increase linearly with H up to 7 T, at which it reaches approximately $0.1 \mu_B/\text{f.u.}$, that is much lower than the expected saturation value of $47.36 \mu_B/\text{f.u.}$ (8 Fe^{3+} per unit cell with moment $5.92 \mu_B$). The linear increase and the low magnetization are thus consistent with a signal originating from an antiferromagnetic matrix containing a second contribution that is ferromagnetic in the temperature range around 130 K.

Furthermore, when the sample is cooled down through T_N in the presence of a magnetic field, the loop is subjected to a vertical shift according to the sign of the magnetic field. Vertical shifts in the $M - H$ loops under field-cooling have been observed before in uncompensated antiferromagnets or in inhomogeneous systems characterized by ferrimagnetic moments embedded in an antiferromagnetic matrix [8].

Finally, we utilized a large set $M - H$ isotherms of our CaFe_2O_4 ceramic to perform Arrot-plot analysis. It is well known [9], that the spontaneous magnetization is an order parameter (OP) for ferromagnetic materials. Thus, if the transition is second-order, its evolution around the critical temperature (T_C) can be described with universal scaling laws. For systems that follow a mean-field behaviour, plotting the M^2 as a function of H/M , known as Arrott plots, will show a linear behaviour and the isotherm at T_C will pass through the origin. For non mean-field systems, the correct model and critical exponents can also be extracted from the (modified) Arrott plots following an iterative method [10]. For an antiferromagnetic transition however, the staggered (sub-unit cell) magnetization is expected to be the good order parameter, and thus linear M^2 vs H/M curves are not expected [11]. Keeping in mind that this model is valid only in the mean-field limit, thus in absence of hysteresis, we can, nevertheless, utilize such analysis to the $M - H$ loops of CaFe_2O_4 to pin-point the critical temperature of the transition, which can be difficult to extract from simple $\chi - T$ measurements.

The Arrott plots of our samples at different temperatures are shown in figure 4.2a. The most evident feature of this data is the high non linearity of the plots and their variable curvature near the origin: positive below 170 K (fig. 4.2c-d) and negative

above 180 K (fig. 4.2e). In addition, for increasing temperatures from 5 to 150 K the plots are displaced towards lower fields, while between 160 K and 210 K, increasing temperatures displace the curves to higher fields. All these features indicate that T_N is poised at about 175 K. Moreover, only above 190 K the plots pass through the origin, confirming the presence of a remanent magnetization below the ordering temperature that persists, although with lower value, down to 5 K. This is shown in figure 4.2b where the remanent magnetization for $H = 0$ extracted from the $M - H$ loops is plotted as a function of T . Therefore, we can conclude that our CaFe_2O_4 ceramics behave accordingly to what previously is reported in the literature: AF ordering is found below approximately 175 K with an additional net magnetization, which has been attributed to magnetic antiphase boundaries [1].

Figure 4.2: **a** Arrott plots for CaFe_2O_4 ceramics at different temperatures ranging from 5 to 300 K. **b** Plot of the remanent magnetization (for $H = 0$) as a function of T . In the inset the area around T_N is highlighted. Zoom of the Arrott plots near the origin for the selected temperatures: **c** below 50 K, **d** below T_N and **e** above T_N .

4.2 Macroscopic magnetic properties

The exact determination of cations and oxygen stoichiometry in PLD grown films is a delicate issue that is often under debate. Because of the small volume of the films, techniques with high sensitivity are needed to quantify the different chemical species with enough accuracy. In this work, we mostly relied on the Mössbauer

spectroscopy data to rule out the presence of oxygen vacancies and *Fe* containing impurities, as shown in the next sections. Because our samples are grown from an 80% ^{57}Fe enriched target, the detection limit of the technique is very low and estimated to be about 2-3% at room temperature. In addition, we complemented these results with other investigation methods such as EDS and x-ray photoelectron spectroscopy (XPS), shown in Appendix A, which, despite their limitations, allowed us to establish that the films do not contain a detectable amount of defects. Therefore, in discussing the magnetic properties of the films in the following sections we consider the observed behaviour to be intrinsic of the film and not arising from impurities and defects.

4.2.1 SQUID magnetometry

Standard characterization of magnetic materials by means of SQUID magnetometry includes collection of temperature and field dependent magnetization response. The magnetic susceptibility of a CaFe_2O_4 thin film from 4 to 400 K in a 100 Oe field parallel to the magnetic easy axis (*b*-axis of CaFe_2O_4)¹ is plotted in figure 4.3. Here, a single transition is observed at $T_N = 188$ 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) one. Such value of T_N is slightly higher than what found for bulk CaFe_2O_4 of the ceramic targets. Upon further decreasing temperature, χ reaches a maximum at $T = 140$ K after FC, while at the same temperature, χ reaches a minimum after ZFC. The noticeable splitting of the FC and ZFC data, is also observed in our ceramics and other literature reports as mentioned above. However, in the films case, a small ZFC/FC splitting persists up to temperatures above T_N , where the behaviour is non Curie Weiss.

In addition, differently from bulk, in the $\chi - T$ plots (fig. 4.3) a sharp increase of χ is observed below 30 K. At this temperature, a peak in the AC susceptibility was reported in oxygen-deficient CaFe_2O_4 crystals [6], suggesting spin-glass type frustration in the system. Fitting the low temperature data in figure 4.3 with a Curie-law decay yields a number of Fe^{3+} atoms per gram of $1.37 \cdot 10^{21}$ which is in the order of magnitude of what is expected per g of CaFe_2O_4 ($1.39 \cdot 10^{21}$). A more accurate quantitative analysis of the SQUID data is problematic due to the poor estimation of the films thickness, that is only measured from cross-sectional microscopy images, and the non-Curie Weiss susceptibility that prevents a linear fit of $1/\chi$ as function of T over a broad temperature range. Alternatively, this paramagnetic signal could be caused by the CaTiO_3 layer at the interface between films and substrates (the latter being diamagnetic). Moreover, the magnetic susceptibility of CaFe_2O_4 thin films shows strong orientation dependence, being noticeably lower when the applied magnetic field is perpendicular to the *b*-axis (comparison between figures 4.3a and b). This indicates large anisotropy, which is expected for a uniaxial antiferromagnet as CaFe_2O_4 , but also with the shape anisotropy of the needle-like crystals [5].

¹For the magnetic measurements we aligned the magnetic field with the magnetic easy axis of the main crystallographic domains in the films, which are $T1$ and $T4$. Due to the symmetry of the domain structure discussed in Chapter 3, the contributions of the other domains perpendicular to this direction cancel each other out.

Figure 4.3: 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 applied **a** parallel and **b** perpendicular to the substrate $[1\bar{1}0]$ direction. The field-cooled (FC) data is plotted with closed black dots while zero-field-cooled (ZFC) data is plotted with open dots. **c-d** Plots of the temperature (T) dependent remanent magnetization (M) of a 90 nm thick sample. The response is measured from 5 to 300 K in zero field after cooling in a positive (red) or negative (violet) 500 Oe field applied parallel and perpendicular to the substrate $[1\bar{1}0]$ direction, respectively.

To investigate the deviation from regular antiferromagnetic behaviour, we also measured the response as a function of temperature in zero applied field, as shown in figure 4.3c-d. First the sample was cooled down to 5 K in a positive or negative 100 Oe magnetic field. Then the field was removed and the magnetization was measured upon heating (fig. 4.3c). The same process was repeated for fields applied parallel and perpendicular to the easy axis. The measured magnetic response indicates the presence of a remanent magnetization in CaFe_2O_4 films. Next to the ordering temperature at $T_N = 188$ K, an anomaly at around 35 K is also visible, which in previous studies has been assigned to a slow spin dynamical process [6]. On the other hand, here the low temperature tail observed in figure 4.3 is absent, confirming its paramagnetic nature.

The presence of an uncompensated magnetic moment is also supported by the hysteresis of the $M - H$ loops measured at various temperatures, as shown in figure 4.4.

Figure 4.4: Plot of the magnetization (M) of a 96 nm thick sample as a function of magnetic field (H), applied parallel to the substrate $[1\bar{1}0]$ direction, between 7 and -7 T measured at **a** 130 K and **b** 30 K (black) and 175 K (red). **c** Plot of M of a 90 nm thick sample as a function of H measured at 100 K between 550 and -550 Oe after ZFC (black), 500 Oe FC (red), and -500 Oe FC (violet). **d** Plot of the derivative of the loops of panels a and b. The inset shows the derivative of the loops in panel c.

Here, the maximum hysteresis is observed at 130 K (fig. 4.4a), whereas the opening is almost absent at 175 K and totally absent at 30 K (fig. 4.4b). Figure 4.4d shows the derivative of the loops of panels a and b. Here, the only anomalies that can be seen are due to the opening of the hysteresis loops, but no evident sign of a spin-flop transition is seen between 1 and 9 T. This might indicate that the spin-flop transition already occurs at lower fields. This is also consistent with the linear increase of M with H up to 7 T, at which it reaches the value of about $0.4 \mu_B/\text{f.u.}$, that is, as in the ceramic case, much lower than the saturation value of $47.36 \mu_B/\text{f.u.}$, although this estimation is affected by the inaccuracy of the determination of the film thickness. In the inset the derivative of the loops of panel c collected at lower fields is also shown. Here two peaks are seen that could correspond to the opening of the loop or to a spin-flop transition.

Field-induced vertical shift of the $M - H$ is also observed in CaFe_2O_4 thin films (fig. 4.4c). When the sample is cooled through T_N in a positive applied field the $M - H$ loops are shifted toward positive values of M and, vice versa, they move

towards negative values in a negative applied field. In addition, the effect of the field-cooling is orientation dependent: the shift is only found when H is applied parallel to the magnetic easy axis and it is absent if the field is applied perpendicular to it or under ZFC conditions. Differently from bulk, here a small lateral shift of the loop is also observed, which is typical of systems with exchange bias [12].

4.2.2 Mössbauer spectroscopy

In order to further characterize the magnetic structure of CaFe_2O_4 films, investigate the oxidation state of Fe and rule out the possibility of contamination with different Fe -containing phases, we also performed Mössbauer spectrometry in electron conversion mode (CEMS) (fig. 4.5).

Figure 4.5: Mössbauer spectra of a 96 nm thick 80% ^{57}Fe -enriched CaFe_2O_4 thin film. **a** Conversion electron Mössbauer spectra at temperatures ranging between 300 K and 100 K. **b** CEMS spectrum at 300 K recorded in a narrow velocity range. **c** Temperature dependence of the hyperfine field (B_{hf}) and its fit with a power law behaviour. The inset shows the data plotted in log-log scale. Data taken by Dr. Jean Juraszek.

The room-temperature CEMS spectrum 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 $Ca_2Fe_2O_5$ [13] or $CaFe_3O_5$ [14, 15].

A high resolution CEMS spectrum recorded at RT in a narrow velocity scale is reported in figure 4.5b. 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 $CaFe_2O_4$ phase [16–21]. Both components have almost equal spectral area and linewidths (full width at half maximum $\Gamma \sim 0.24$ mm s⁻¹). The isomer shift values are also similar ($\delta = 0.368 \pm 0.001$ mm s⁻¹), but the quadrupole splitting (ΔE_Q) is different, with values of 0.313 ± 0.001 mm s⁻¹ and 0.743 ± 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+} suggests that the oxygen vacancy content in the film is below the experimental detection limit.

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-Mössbauer 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 θ with the incident γ -beam direction, the line intensity ratio of the quadrupolar doublet is given by:

$$\frac{I_2}{I_1} = \frac{3(1 + \cos^2 \theta)}{5 - 3 \cos^2 \theta} \quad (4.1)$$

with values ranging from 3 for $\theta = 0^\circ$ to 0.6 for $\theta = 90^\circ$. Here the fit of the spectrum yields $\theta = 41^\circ$ and 53° for $Fe(1)$ and $Fe(2)$, respectively.

In figure 4.5a, some selected CEMS spectra at temperatures below room-temperature are also reported. The CEMS spectra below 185 K clearly show the onset of long range magnetic order² by the appearance of a magnetic sextet due to nuclear Zeeman splitting. For each temperature, the line intensity ratios are close to 3:4:1:1:4:3 for the magnetic sextet, evidencing in-plane orientation of the Fe^{3+} spins.

The temperature dependence of the mean magnetic hyperfine field B_{hf} deduced from the fit can be approximated using a power law:

$$B_{hf}(T) = B_{hf}(0) \left(1 - \frac{T}{T_N}\right)^\beta \quad (4.2)$$

where β is the critical exponent or the antiferromagnetic order parameter: the staggered sub-unit cell magnetization. A reasonably good fit (fig. 4.5c) 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 Néel temperature obtained from the fit is also consistent with the transition temperature deduced from the SQUID measurements. However, some error in these values can be expected due to the imperfect fit of the experimental data close to T_N , where the critical model is valid. The cause of such deviation is probably the difficulty to reach the adiabatic condition close to the critical transition. In conclusion, this behaviour of the hyperfine field thermal variation from the Mössbauer data indicates a critical transition at the Néel temperature, which is not consistent with the sce-

²This can either belong to FM or AF transition, as Mössbauer spectroscopy can not distinguish between the two if no magnetic field is applied during the measurement.

nario of nucleation and growth at the antiphase boundaries of magnetic domains. In contrast, there seems to be a single stable ground state for the pure CaFe_2O_4 films.

4.3 Local magnetic properties

4.3.1 Scanning SQUID microscopy

The interesting surface topography and relatively low (if compared to bulk samples) surface roughness of the CaFe_2O_4 films make these samples ideal candidates for the study of local magnetic response, never reported in this material before. Therefore, we performed scanning SQUID microscopy (SSM) measurements in collaboration with Dr. Pim Reith and Prof. Dr. Hans Hilgenkamp at the University of Twente.

Here, the samples were cooled and measured in zero background field at 4 K by scanning the SQUID sensor at a distance of 1 μm from the surface. Various sets of 12 scans of 250 μm x 250 μm size, with 250 μm spacing in between (total covered area about 1.75 mm x 1.75 mm), were collected in different areas to test for homogeneity of the samples.

Figure 4.6: SSM images: 250 μm x 250 μm scan of **a** a 120 nm and **b** a 66 nm thick films measured at 4 K in zero background field. Image taken with the help of Dr. Pim Reith.

The results (fig. 4.6) indicate clear magnetic activity: the observed patterns resemble those of a weak ferromagnet [22], but no evident structure in the signal is visible. This is due to the spatial resolution of the scanning SQUID setup (approximately 5 μm) that causes averaging over multiple domains. Different sample thickness give rise to similar magnetic patterns but with different intensities: for a 120 nm film (fig. 4.6a) the magnetic field measured is 7-8 μT , while when the thickness is reduced to 66 nm the field is approximately halved (fig. 4.6b). These values are well above the scanning SQUID sensitivity 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.

4.3.2 Low-temperature MFM

In addition to SSM, in order to directly compare the magnetic and topographic features of the samples, we performed magnetic force microscopy (MFM) experiments,

that yield a spatial resolution of about 100 nm. Topography and MFM phase were recorded in dual-pass mode at various temperatures between 300 and 12 K, with a tip lift height of either 30 nm and 50 nm from the sample surface. Images were collected at various temperatures from room-temperature down to 12 K, upon both cooling and heating, in zero background field. The red and blue contrast in the MFM phase images indicates ferromagnetic and antiferromagnetic coupling between the magnetization of the tip and the stray fields originating from the sample surface.

Figure 4.7 shows some selected images.

Figure 4.7: Low temperature MFM images of a 120 nm thick CaFe_2O_4 film. **a** Topography and dual-pass phase at **b** 30 nm and **c** 50 nm lift measured at 200 K, above T_N . **d** Topography and dual-pass phase at **e** 30 nm lift and **f** at 50 nm lift measured at 100 K, below T_N . **g** Topography, **h** dual-pass phase at 30 nm lift with 0.05 T applied field and **i** dual-pass phase at 30 nm lift with -0.1 T applied field. **j** difference between panels **h** and **i**. **k** Topography, and **l** dual-pass phase at 30 nm measured at 12 K using a non magnetic tip.

The first, panels (fig. 4.7a-c) collected at 200 K, above T_N , do not show any magnetic response, as can be seen from the absence of signal in the MFM phase. The very low contrast perceivable at the lower lift height (fig. 4.7b) can be simply attributed to cross-talk with the film topography, as an analogous signal is observed when the experiment is repeated with a non-magnetic tip (fig. 4.7l). Only when the temperature is lowered below the material's T_N of about 185 K, a sharp contrast in the phase signal appears. Figure 3.3d-f show a scan collected at 100 K. In these images we observe signatures of magnetic dipoles (alternating red and blue contrast), corresponding to some of the edges of the needle-like crystals. Such signal increases in intensity and sharpness at lower scan lifts, as expected for a real magnetic signal, due to the divergence of the magnetic field lines.

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 direction 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 the magnetic field lines bend in the out-of-plane direction, as schematically represented in figure 4.8.

Figure 4.8: Schematic depiction of the stray fields emerging from the edges of a needle-like crystal, that couple ferromagnetically (red) and antiferromagnetically (blue) with the magnetization of the microscope tip.

Figure 4.7g-i also show MFM images collected at 12 K in an applied magnetic field perpendicular to the film surface. Here, the colour contrast in the second-pass phase is inverted upon reversing the magnetic field sign, from 0.05 T in figure 4.7h to -0.1 T in figure 4.7i. The difference between these two panels is shown in figure 4.7j and consists of pure crosstalk with topography, that gets accentuated upon subtracting the signal from the two images. This is also consistent with the scenario where the Fe^{3+} spins are ordered in-plane: in fact, reversing the sign of the perpendicular applied field does not affect the magnetization of the film, but switches the tip magnetization (the larger negative value of -0.1 T is in good agreement with the coercive field of *Cr*, material used for the magnetic coating of the tip). As a result, the interaction between the tip and the sample goes from being ferromagnetic to antiferromagnetic, and vice versa, upon reversing the magnetic field.

To further prove that the signal observed in the phase of the low-temperature MFM experiments is indeed of magnetic nature, we repeated the measurement using a non magnetic tip (fig. 4.7k and l). Here, the strong contrast in the phase signal is absent, even at the lower lift height of 30 nm. This allows us to conclude that the

signal observed in low-temperature MFM experiment has magnetic origin and can be separated by the topographical information despite the films non-negligible surface roughness.

4.4 Conclusions

The thorough investigation of the magnetic properties of CaFe_2O_4 at both the global and local scale indicate non standard antiferromagnetic behaviour and reveals the following: a single magnetic transition is found at T_N approximately 185 K with various complementary techniques. Fitting the hyperfine field thermal variation from the Mössbauer data yields a critical transition with critical exponent consistent with a uniaxial antiferromagnet. This provides the first direct evidence of a single thermodynamical ground state in CaFe_2O_4 thin films. After the publication of our work, Lane *et al.* [24] reached a similar conclusion for single crystal samples, suggesting that the B ordering is the parent phase, while A finds its origin in the freezing of the antiphase boundaries. Large fluctuations and short-range ordering could also explain the non-Curie Weiss signal measured above T_N .

The magnetic behaviour of CaFe_2O_4 films is not purely antiferromagnetic, but an uncompensated moment is also observed below the Néel temperature in SSM, MFM, $M - T$ and $M - H$ measurements, that lies in the plane of the films as the magnetic easy axis. In addition, the magnetic hysteresis is found to be larger around 130 K, where the phase coexistence between the A and B phases is reported to be maximum, in agreement with the “orphan spins” picture proposed by Stock *et al.* [1]. Moreover, the persistence of paramagnetic signatures down to low temperatures brings forward the possibility of a second phase transition towards a spin-glass-type state. Mössbauer spectroscopy and XPS measurements (see Appendix A and Ref. [25, 26]) excluding the presence of Fe in the 2+ oxidation state, disprove the alternative scenario proposed by Das *et al.* [6], in which the net magnetic moment is due to ferrimagnetic clusters formation induced by oxygen vacancies.

Further characterization of the magnetic structure of CaFe_2O_4 films is needed to completely explain this rare phenomenon of coexistence of two magnetic phases in a broad temperature range. Of particular interest is the role of magnetoelastic effect in the stabilization of the A phase [2] and the influence of epitaxial strain on the magnetic phase diagram. Further insight on the properties of this material will be given in the next chapter, where the spin Hall magnetoresistance effect at the interface between CaFe_2O_4 and Pt is discussed.

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Chapter 5

Antiferromagnetic ordering and uncoupled spins in CaFe_2O_4 thin films probed by spin Hall magnetoresistance

Abstract

In this chapter we probe the spin Hall magnetoresistance (SMR) at the interface between Pt and CaFe_2O_4 and exploit the crystallographic domain structure of thin film samples to perform single- and multi-domain scale measurements. The SMR response, upon rotating the magnetic field along three orthogonal planes, shows little effect of the strong magnetocrystalline and shape anisotropies. Together with the response to a varying magnetic field strength, the modulations in the SMR signal allow us to extract two contributions: one corresponds to the long-range antiferromagnetic ordering, supporting a single ground state scenario; while the second contribution originates from uncompensated, non-interacting spins. These are expected to exist at the antiphase boundaries between antiferromagnetic domains. Here we show that these are also uncoupled from the antiferromagnetic ordering. Nonetheless, the long range correlations that emerge in the proximity of the critical antiferromagnetic transition could give rise to ordering of the uncompensated spins and be responsible for the net magnetization observed in this antiferromagnet.

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5.1 Introduction

Spin-dependent transport phenomena in magnetic materials are of great interest, not only from the fundamental point of view, but also for their potential application in devices where spin represents an added degree of freedom with respect to traditional electronics. The field of spintronics (spin-transport electronics) has been a rapidly growing research area in the past 40 years, showing a huge potential to overcome the barriers related to the continuous miniaturization and energy losses (through Joule heating) faced by conventional silicon-based electronics.

Within the field of spintronics, antiferromagnets have lately gained more attention [1–4] because of several advantages that these materials offer compared to ferromagnets. First of all, in the absence of a net magnetization, stray fields that cause

the interaction between device components, impairing further miniaturization, can be avoided. Furthermore, the spin dynamics in antiferromagnets occur with eigenfrequencies in the THz, about 3 orders of magnitude higher than in ferromagnets. Moreover in antiferromagnetic materials, larger magnetoelastic couplings are found that can provide a handle to tune their magnetic properties through structure manipulation. Finally, antiferromagnets are more abundant and display interesting magnetic structures that arise from complex magnetic exchange interactions between spins in three dimensions, that can allow for more complex functionalities. From an application perspective, however, the absence of a net magnetization makes antiferromagnets less responsive to external fields and requires new strategies for magnetization control and readout. To this end, electrical probing of spin textures has recently proven successful for the implementation of antiferromagnets in spintronic devices, giving rise to the field of antiferromagnetic spintronics [5]. This is mainly achieved via the interconversion of a charge current into a spin current at the interface between a heavy metal (HM) and a magnetic insulator (MI) by means of the Spin Hall Magnetoresistance (SMR) effect.

The first experimental reports of spin current injection were in bilayers using collinear ferrimagnets, with YIG/Pt interfaces being the prototypical system [6, 7]. Subsequently, other systems have been investigated including GIG/Pt [8], $\text{Fe}_3\text{O}_4/\text{Pt}$ [9], $\text{NiFe}_2\text{O}_4/\text{Pt}$ [10] and $\text{CoFe}_2\text{O}_4/\text{Pt}$ [11]. Very recently it has also been established that bilayers of Pt with antiferromagnetic materials like NiO [12–14], Cr_2O_3 [15] and $\alpha\text{-Fe}_2\text{O}_3$ [16] display the SMR too. In addition, SMR experiments have also proven to be a very powerful tool for the study of more complex spin textures such as canted spins [17, 18] and spin spirals [19]. The SMR has also been observed in paramagnetic YIG [20] and other materials above the critical temperature [15, 21], manifesting a more complex microscopic description of this effect. Finally, experiments have been performed on HM/AF/FM trilayers that have allowed for the characterization of the interfacial coupling between them [22].

5.2 Theory of the SMR

In the field of spintronics, the spin-dependent electrical transport is often described by the two spin channel model. Here an electric charge current $\vec{J}_c$ can be written as sum of spin-up ($\vec{J}_\uparrow$) and spin-down ($\vec{J}_\downarrow$) currents, whereas a spin current $\vec{J}_s$ is given by their (normalized) difference:

$$\vec{J}_c = \vec{J}_\uparrow + \vec{J}_\downarrow \quad (5.1)$$

$$\vec{J}_s = \frac{\hbar}{2e}(\vec{J}_\uparrow - \vec{J}_\downarrow) \quad (5.2)$$

In a pure charge current, $\vec{J}_\uparrow$ and $\vec{J}_\downarrow$ have the same magnitude and propagate in the same direction, leading to a net charge flow, but no flow of angular momentum. When, on the other hand, equal $\vec{J}_\uparrow$ and $\vec{J}_\downarrow$ propagate in opposite directions, a pure spin current is obtained, consisting on a flow of angular momentum alone (hence

the use of the pre-factor $\frac{\hbar}{2e}$). In the intermediate case, with $\vec{J}_\uparrow \neq \vec{J}_\downarrow$, both charge and spin information are transported through the material and the current is called spin-polarized [19].

The conversion of charge degree of freedom into spin degrees of freedom, and vice versa, has been made possible in nanostructured devices by means of the so-called spin Hall effect (SHE). The SHE, predicted in analogy to the classical Hall effect¹, is a transport phenomenon consisting on the appearance of spin accumulation on the lateral surfaces of a non-magnetic conductor carrying an electric current [23]. The SHE originates from the spin-orbit interaction that causes a spin-asymmetric scattering of the conduction electrons and thus is mostly observed experimentally in metals with large spin-orbit coupling. The inverse effect (ISHE) also occurs: when a pure spin current is created in a non magnetic conductor, the carriers with opposite spin are deflected in the same direction generating a transverse charge current and thus a charge accumulation near the edges.

In the SHE the efficiency of the charge to spin current interconversion is a material dependent property that can be quantified by means of a dimensionless parameter, known as spin Hall angle θ_{SH} :

$$\vec{J}_s = \theta_{SH} \vec{\sigma} \times \vec{J}_c \quad (5.3)$$

where $\vec{\sigma}$ is the spin polarization direction.

When an in-plane $\vec{J}_c$ is sent through a non magnetic metal with finite θ_{SH} and put into contact with a magnetic insulator (FMI/AFI), a modulation in its resistance is observed, depending on the direction of the order parameter (magnetization $\vec{M}$ for ferromagnets and Néel vector $\vec{l}$ for antiferromagnets). Such spin-current driven magnetoresistance effect is known as spin Hall magnetoresistance (SMR) [13] and is schematically represented in figure 5.1.

The in-plane charge current $\vec{J}_c$ creates a local spin accumulation at the sides of the metal due to the SHE. The polarized spins at the metal/magnetic insulator interface can be absorbed by the magnetic insulator or reflected back depending on the underlying magnetic ordering. Specifically, if the magnetization $\vec{M}$ (or $\vec{l}$) is non-collinear with $\vec{\sigma}$ a spin transfer torque can be exerted on the magnetic moments resulting in a $\vec{J}_s$ in the magnetic insulator (fig. 5.1a-d). The spin current that flow across the interface represents a dissipation channel for $\vec{J}_c$, and thus increases the longitudinal resistivity (ρ_L) in the HM (fig. 5.1a-d). On the other hand, if $\vec{M}$ (or $\vec{l}$) is collinear with $\vec{\sigma}$ the gradient of the spin accumulation leads to a diffusive spin current back-flow into the metal and an extra charge current via ISHE (fig. 5.1b-c). This corresponds to a low resistance state of the HM.

¹The classical Hall effect, observed for the first time by Edwin Hall in 1879, is a transport phenomenon consisting of the the production of a steady electrical potential across a conductor, transverse to both a charge current in the conductor and an applied magnetic field. This phenomenon arises from the deviation of the charge carriers from their straight trajectory due to the Lorentz force under a magnetic field applied perpendicular to the electric current

Figure 5.1: Schematic drawing of the spin Hall magnetoresistance (SMR) of a single-domain **a,c,e** collinear ferromagnetic insulator/heavy metal (FMI/HM) and **b,d,f** antiferromagnetic insulator/heavy metal (AFI/HM) bilayer. When the applied field ($\vec{H}$) is parallel to the charge current $\vec{J}_c$ the longitudinal resistivity ρ_L of the HM is **a** large in the case of underlying FMI and **b** small for a AFI layer. Conversely, for an applied field perpendicular to the charge current $\vec{J}_c$ the longitudinal resistivity ρ_L of the HM is **c** small in the case of underlying FMI and **d** large for a AFI layer. The expected angular-dependence of ρ_L is sketched in **e** and **f** as a function of the angle α between $\vec{H}$ and $\vec{J}_c$. Adapted with permission from Ref.[13].

Considering $\vec{M} = m_x\hat{x} + m_y\hat{y} + m_z\hat{z}$ and $\vec{l} = l_x\hat{x} + l_y\hat{y} + l_z\hat{z}$, the resistance measured in longitudinal geometry depends on the magnetization projection in the $x - y$ plane [19]:

$$\begin{aligned}\rho_L^{FM} &= \rho_0 - \Delta\rho_1 m_y^2 \\ \rho_L^{AF} &= \rho_0 - \Delta\rho_1 l_y^2\end{aligned}\tag{5.4}$$

Here ρ_0 is a constant positive offset, close to the resistivity of the pure heavy metal, while $\Delta\rho_1$ represent the magnitude of the resistivity change. This is influenced by several factors, among which θ_{SH} , the spin relaxation and diffusion length, the bulk

conductivity and the spin-mixing conductance [19]. From an experimental point of view, this results in a strong dependence of the SMR on the metal thickness and the quality of metal/insulator interface [7, 10]. For a complete theoretical description of the SMR, which is beyond the scope of this thesis, the interested reader is referred to Ref.[24].

When an external magnetic field $\vec{H}$ is applied large enough to overcome the anisotropy field, the angular-dependence of ρ_L follows a $\cos^2$ modulation with the angle α between $\vec{H}$ and $\vec{J}_c$, as depicted in figure 5.1e-f. It is worth noticing that the period of the modulation is 180° , half of that of the ordinary Hall effect. In case of FM ordering, $\vec{M}$ aligns parallel to $\vec{H}$ and the amplitude of the modulation positive by convention [14]. By contrast, in case of AF ordering, there is a range of applied fields at which the configuration with lowest Zeeman energy is the one with $\vec{l}$ perpendicular to $\vec{H}$ (spin-flop state). Therefore the modulation of the resistance is shifted of 90° with respect to the ferromagnetic case, yielding a negative SMR.

Moreover, when $\vec{M}$ (or $\vec{l}$) makes an angle with $\vec{\sigma}$, a $\vec{J}_c$ that has a component in the transverse direction is also generated that depends on both the x and y components of the order parameter [19]:

$$\begin{aligned}\rho_T^{FM} &= \Delta\rho_1 m_x m_y \\ \rho_T^{AF} &= \Delta\rho_1 l_x l_y\end{aligned}\tag{5.5}$$

This leads to the observation of an angular dependent magnetoresistance (ADMR) in transverse geometry as well, whose modulation displays a 45° phase shift with respect to the longitudinal one. Thus, in a simple case where influence of the magnetic anisotropy or magnetic domains are neglected (valid for magnetic field energies larger than the magnetic anisotropy and smaller than the exchange interactions) the full angular dependence of the SMR for ferromagnets and antiferromagnets can be summarized as follows [3]:

$$\begin{aligned}\rho_L^{FM}(\alpha) &= \rho_0 + \rho_1 \cos^2(\alpha) \\ \rho_T^{FM}(\alpha) &= \rho_3 \sin(\alpha) \cos(\alpha) \\ \rho_L^{FM}(\beta) &= \rho_0 + \rho_1 \cos^2(\beta) \\ \rho_L^{FM}(\gamma) &= \rho_0 + \rho_1\end{aligned}\tag{5.6}$$

$$\begin{aligned}\rho_L^{AF}(\alpha) &= \rho_0 + \rho_1 \sin^2(\alpha) \\ \rho_T^{AF}(\alpha) &= -\rho_3 \sin(\alpha) \cos(\alpha) \\ \rho_L^{AF}(\beta) &= \rho_0 + \rho_1 \\ \rho_L^{AF}(\gamma) &= \rho_1\end{aligned}\tag{5.7}$$

where β and γ are the out-of-plane angles that $\vec{H}$ forms with $\vec{J}_c$ when rotating in the planes perpendicular and parallel to $\vec{J}_c$ respectively. ρ_1 and ρ_3 are SMR coefficients.

In practice, in most antiferromagnetic materials the full SMR response is more

complex than described above, as the equilibrium position of the antiferromagnetic sublattices depends on a fine balance between Zeeman energy, anisotropy and exchange interactions and in many cases the presence of a domain structure must also be taken into account. In the case of a uniaxial antiferromagnet, different mechanisms can influence its magnetic order, depending on the field direction and amplitude compared to the magnetic anisotropy and exchange interactions. If a large enough magnetic field is applied along the easy axis, a spin-flop transition occurs, [4] which results in an orientation of the Néel vector of the AF ordering perpendicular to the field direction. Rotating the magnetic field can then have two effects: either it induces a rotation of $\vec{l}$ in the individual AF domains along with $\vec{H}$ and, in the presence of multiple energetically equivalent magnetic domains, it breaks their degeneracy and creates a force that pushes the domain walls toward the less stable domains. In both cases, the angular dependent magnetoresistance (ADMR) would show a 90° phase shift with respect to prototypical YIG/Pt (ferrimagnetic) bilayers, giving rise to a negative amplitude. This negative SMR has been observed in easy-plane antiferromagnets such as NiO [12, 13] and $\alpha\text{-Fe}_2\text{O}_3$ [16] and also in ferrimagnets close to the compensation temperature, where the spin-flop transition is possible at lower magnetic fields [8, 25–27].

In addition, a tilt of the spins constituting the two magnetic sublattices in the direction of the field can also occur, inducing a net magnetization that affects the SMR response [4]. If the magnitude of such tilt is larger than 45° from the spin-flop direction, then this contribution will dominate and will give rise to an overall positive amplitude of the SMR. Therefore, the in-plane ADMR is a combination of these two out-of-phase responses. On the other hand, the expected behaviour for pure FM and AF ordering is different when the magnetic field is rotated in the planes normal to the sample surface. In particular, when the field rotates within the plane containing the current direction ($n-i$), a $\vec{M}$ rotating coherently with $\vec{H}$ is always perpendicular to the spin accumulation and thus no longitudinal resistance modulation is observed for pure FM ordering. On the other hand, a modulation can be expected in an antiferromagnet with the easy axis parallel to the current direction. In this case, R_L is highest when $\vec{H}$ is perpendicular to the surface and lowest when it is parallel to i , pushing $\vec{l}$ from i to t . Interestingly, the amplitude of the modulation here decreases with increasing applied field as the component of $\vec{l}$ parallel to the spin accumulation direction decreases in the low resistance state. With a similar argument, when $\vec{H}$ rotates within the plane perpendicular to the current direction ($n-t$), $\vec{l}$ aligns always perpendicular to the spin accumulation because of the easy axis direction. Therefore, a modulation of R_L in this plane cannot arise from the spin-flop state and indicates the presence of a magnetization. Therefore, for a complete picture of the contributions playing a role in the ADMR for a complex material like CaFe_2O_4 , the response needs to be studied in all three orientations.

5.3 Device fabrication and measurement technique

To study the transport properties and, in particular the SMR, in $\text{Pt}/\text{CaFe}_2\text{O}_4$ bilayers we have utilized the PLD grown films described in the previous chapters. Because

such films are composed of multiple crystallographic domains, we studied the SMR response both localized at individual crystal domains and also averaged over a large number of domains.

To do so, two kinds of devices have been fabricated: large Hall-bars (100 μm long and 20 μm wide) randomly positioned on the sample surface covering multiple domains (fig. 5.2b) and smaller Hall-bars localized at single CaFe_2O_4 domains (fig. 5.2c). In the large devices, the propagation direction of the charge current is oriented parallel to the substrate's $[1\bar{1}0]$ edge. Because of the specific requirements dictated by the domains shape, each of the small Hall-bars has a slightly unique design but comparable size of approximately 10 μm in length and 3 μm width. In these devices, the long channel of the Hall-bar and propagation direction of the charge current was parallel to the b -axis of the underlying CaFe_2O_4 domain. The fabrication process was carried out in the NanoLab Groningen cleanroom facilities by our collaborator Dr. Alexey Kaverzin of the Physics of Nanodevices group by means of the e-beam lithography.

Figure 5.2: Hall-bar devices for the measurement of the transport properties at the $\text{Pt}/\text{CaFe}_2\text{O}_4$ interface. **a** SEM image of the Au markers. Optical images of **b** a large device randomly positioned and **c** a small device deposited on the selected single domain indicated with the green arrow in panel a.

In the first stage, Au markers were deposited on the sample by means of DC sputtering through polymethylmethacrylate (PMMA) shadow mask. The PMMA masks were prepared on a separate substrate and later placed on top of the sample with alignment done under the optical microscope. After deposition the masks are removed mechanically without dissolving PMMA. This methodology assures that sample surface at all stages of the fabrication process is never in contact with PMMA dissolved in solution. This considerably reduces the amount of polymer residues typically present after conventional fabrication methods. Squares of 20 μm x 20 μm with

a separation of 50-75 μm were deposited yielding a total covered area 2 mm x 2 mm. Each square is identified by a unique pattern of squares which encodes the information to localize it on the sample surface (inset of figure 5.2a). Then, the samples were put in the SEM where we individuated suitable crystal domains for hosting the hall bars. Exemplars of all six domains variants were chosen.

In the second stage, 8 nm of platinum were sputtered in a shape of the Hall-bar (either large or small) again using PMMA shadow masks in order to ensure minimal level of contamination of the interface between Pt and CaFe_2O_4 . In the last step, via conventional PMMA-based e-beam lithography, we have connected the arms of the Hall-bars with Ti/Au (5 nm/55 nm) contacts which were later on bonded with Al wires to the chip carrier of the used measurement setup.

Experimentally, the SMR can be measured using the lock-in detection technique as described in the Introduction and in Ref.[19]. The input AC current ($I(t)$) used was a sine wave with frequency of 17 Hz and amplitude of 100-200 μA for the small devices and 100-400 μA for the large ones. The ADMR of the Pt strip was measured in magnetic fields between -9 to +9 T and in a temperature range from 5 to 400 K. During the measurements, the sample was rotated in a static field, with α , β and γ being the in-plane and out-of-plane angles between $\vec{H}$ and the main channel of the Hall bar device. Because the SMR is a 1st order effect, the SMR voltage scales linearly with the current amplitude. Thus, we were mostly interested in the 1st harmonic voltage signal V^1 . However, the second order responses were also monitored to verify the absence of extra contributions to the signal and because it is linked to the presence of Spin-Seebeck effect [19].

The first order resistance was obtained as $R^1 = V^1/I$, where I is the rms value of the source current. The transverse first order resistivity ρ_T^1 normalized over the sheet resistance ρ_0 was then calculated as [13]:

$$\rho_T^1/\rho_0 = (R_T - R_{0T})/(R_{0L}/g) \quad (5.8)$$

where $R_T = V_T/I$ and $R_L = V_L/I$ are the first harmonic transverse and longitudinal resistances and R_{0T} and R_{0L} their value at 0 field. $g = l/w$ is a geometric conversion factor given by the ratio between the distance of two longitudinal probes (l) and the width of the Hall-bar (w). Similarly the normalized longitudinal first order resistivity ρ_L^1 is given by:

$$\rho_L^1/\rho_0 = (R_L - R_{0L})/(R_{0L}) \quad (5.9)$$

5.4 Results

5.4.1 In-plane rotation

The dependence of the transverse resistance on the in-plane angle, α , was measured in the large Hall-bars at various temperatures upon heating from 5 K to 300 K. The plot of the angular dependent magnetoresistance (ADMR) at 7 T for three selected temperatures is shown in figure 5.3a. In the whole temperature range the measured

ADMR can be described with a function of the type:

$$y = y_0 + A_a \sin(\alpha + \phi_a) \cos(\alpha + \phi_a) + B \sin(\alpha + \phi_{OH}) \quad (5.10)$$

The first modulation, having a period of 180° , corresponds to the SMR contribution to the transverse resistance. In addition to this, a second component, with period 360° is also present. This is an ordinary Hall effect contribution, caused by an unwanted component of the magnetic field normal to the film surface. An ordinary Hall contribution of $0.127 \text{ m}\Omega$ at 7 T and 400 μA corresponds to a misalignment of less than 2° , that is plausible given the difficulties to place the sample exactly flat on the holder (this value has been estimated by comparison with the amplitude of the ordinary Hall effect when rotating the magnetic field out-of-plane). The phase of this component and its amplitude, normalized by the carrier concentration, are constant through the whole temperature range, as expected.

Figure 5.3c shows the temperature dependence of the amplitude (A_a) of the SMR contribution extracted from the fit (see Appendix A for a complete account of the fit parameters). The phase ϕ_a is close to 0° in all measurements. At 5 K, the $\sin(\alpha)\cos(\alpha)$ modulation displays a negative amplitude A_a , corresponding to the typical (negative) SMR response of antiferromagnets [12, 16]. Upon increasing temperature, the magnitude of the negative modulation decreases and at about 120 K the SMR changes sign, indicating a cross-over from AF to FM/PM behaviour. At the zero-crossing point, the value of A_a becomes comparable in magnitude to the amplitude of the ordinary Hall effect contribution, B . Therefore, at this temperature, the shape of the ADMR curve deviates from a periodic modulation, but it is still well-fitted by eq.(5.10), as shown in figure 5.3a. Above 120 K, A_a continues to increase with increasing temperature until 300 K. Surprisingly, no abrupt transition is observed at the Néel temperature of $T_N = 185 \text{ K}$, as observed by means of SQUID magnetometry and Mössbauer spectroscopy in similarly grown samples [28].

Because the multi-domain nature of the films used in this study adds a further degree of complexity in the interpretation of the ADMR, we turned to measure the six individual CaFe_2O_4 structural domains independently. Figure 5.3b-d shows the dependence of the transverse resistance on the in-plane angle, α , in one of the small Hall-bar devices. The ADMR at 5, 130 and 300 K measured at 200 μA in a field of 7 T is plotted in figure 5.3b. As in the case of the larger Hall-bars, the data can be fitted with the model described by eq.(5.10). However, here A_a is positive across the whole temperature range, indicating the presence of a field-induced magnetic moment dominating over the AF contribution.

The amplitude of the SMR contribution, shown in figure 5.3d follows a non-linear trend with temperature, similar to that observed for the multi-domain bars of figure 5.3c: it first decreases between 5 and 50 K, to then increase between 100 K and 200 K and saturate above T_N . Again, a larger amplitude of the SMR is found above T_N , compared with the value in the ordered state. At 300 K the magnitude of the SMR is comparable to that measured in the easy-plane antiferromagnet NiO [12] and the spin-spiral phase of CoCr_2O_4 [21], but lower than the values reported for $\alpha - \text{Fe}_2\text{O}_3$ [16]. However, for an accurate quantitative comparison between these systems the quality of the metal/magnetic insulator interface [5] and Pt thickness [7] should also

Figure 5.3: In-plane ADMR at $H = 7$ T. Plot of the normalized first harmonic transverse resistivity, ρ_T^1/ρ_0 , as a function of α , together with its fit to eq.(5.10), at 3 selected temperatures and measured in a **a** multi-domain device and **b** single-domain device fabricated on 90 nm and 93 nm thick CaFe_2O_4 films, respectively. **c,d** Plot of the T dependence of the amplitude (A_a) of the SMR contributions extracted from the fits. In the insets, the geometry of the experiments is indicated, with i , n and t being the directions of the charge current, surface normal and transverse, respectively. $\vec{H}$ is the applied magnetic field.

be taken into account.

To exclude that the negative and positive components of the in-plane SMR found in the large devices arise from different structural domains, we have measured individually all the domain types present in the film. Similar sinusoidal modulations of ρ_T and ρ_L , as well as the same field and temperature behaviours, are observed in all cases, regardless of the crystal orientation. This isotropic character of the modulation indicates that the mechanism for the SMR in CaFe_2O_4 originates on the free rotation of the spin with the applied magnetic field.

In both single- and multi-domain devices, a large positive SMR is observed above the Néel temperature. A non-zero SMR in the paramagnetic state has been measured before in FM (YIG) samples [20] as well as in AF oxides [15, 21]. However, its amplitude is expected to decrease following a Curie-Weiss behaviour. Here, on the other hand, the amplitude of the modulation above T_N tends to saturate to a fixed value. This is consistent with the non Curie-Weiss susceptibility observed up to 400 K in CaFe_2O_4 [28, 29] and could be explained by the presence of 1D short-

range correlations between Fe spins found in bulk samples [29]. Below 200 K, the amplitude of the SMR decreases, as the material orders antiferromagnetically. At this temperature however, the amplitude of the modulation is still positive, indicating that the contribution of a net magnetization predominates for applied fields above 1 T. Interestingly, in the multi-domain devices, a cross-over to negative SMR occurs at 120 K, while in the single-domain ones the sign of the modulation is positive at all temperatures. This difference is puzzling as a more intrinsic (AF-like character) is expected in the single domain devices. The net magnetic moment detected by ADMR is, therefore, not caused by defects uncompensated moments at the boundaries between the different structural domains.

5.4.2 Out-of-plane rotation

The ADMR of the large Hall-bar devices was also measured upon rotating the magnetic field outside of the plane of the film. Plots of the longitudinal resistivity, measured at 100 μ A in a field of 7 T, as a function of the angles β ($\vec{H}$ rotating within the $n-t$ plane perpendicular to the current direction) and γ ($\vec{H}$ rotating with the $n-i$ plane containing the current direction) are shown in figure 5.4a-b. In both cases a sinusoidal modulation of the ADMR with period 180° has been observed and the data could be fitted with functions of the type:

$$y = y_0 + A_b \cos^2(\beta + \phi_b) \quad (5.11)$$

$$y = y_0 + A_g \cos^2(\gamma + \phi_g) \quad (5.12)$$

Where ϕ_b and ϕ_g are close to 90° , indicating that the high resistance state corresponds to the field being perpendicular to the film surface. In addition to the SMR, a linear term with time is also added to the fit describing the thermal drifts during the measurement.

Figure 5.4c-d shows the temperature evolution of the amplitude of the out-of-plane SMR contributions extracted from the fits. As it can be seen, in both plots the sign of the modulation is constant throughout the whole temperature range, while the magnitude of the effect evolves differently with temperature. When the field rotates in the $n-t$ plane (fig. 5.4a,c), a relatively large SMR is observed at all temperatures between 5 and 350 K. Here no appreciable variation of A_b and ϕ_b with T is found, as the values are within the error of the fit. On the other hand, when $\vec{H}$ rotates in the $n-i$ plane (fig. 5.4a,d) the modulation is largest at low temperatures and decreases significantly upon increasing T . A steeper slope is observed between 50 and 150 K, that corresponds to the reported ordering of the A magnetic phase, followed by a slower increase until $T_N = 200$ K. Above the T_N and up to 300 K a small modulation is still visible in the data, but the signal size becomes comparable to the noise.

Figure 5.4: Out-of-plane ADMR of a multi-domain device fabricated on a 90 nm thick CaFe_2O_4 film at $H = 7$ T. Plot of the normalized first harmonic longitudinal resistivity, ρ_L^1/ρ_0 as a function of **a** β and **b** γ , together with their fits to eq.(5.11) and eq.(5.12), at 2 selected temperatures. Plot of the T dependence of the amplitudes, **c** A_b and **d** A_g , of the SMR contributions extracted from the fits. In the insets, the geometry of the experiments is indicated, with i , n and t being the directions of the charge current, surface normal and transverse, respectively. $\vec{H}$ is the applied magnetic field.

Therefore, the presence of a modulation with both β and γ indicates that both a FM (or PM) component and an AF component contribute to the SMR in the large devices, originating from the rotation of $\vec{M}$ and $\vec{l}$ with the applied field. Combining the temperature evolution of the ADMR of the two out-of-plane geometries yields a similar trend as that observed for the in-plane measurement. This offers further support to the interpretation of the in-plane signal as arising from two components, which now can be isolated in the out-of-plane measurements.

5.4.3 Field dependence

The magnetic field dependence of the ADMR has also been investigated and is shown in figure 5.5. Figure 5.5a displays a plot of ρ_T^1/ρ_0 of a single-domain device as a function of H , applied in-plane at $\alpha = 45^\circ$ from the current direction (maximum of the ADMR) at three different temperatures: 5, 100 and 200 K. In all cases an increase of the resistance is found with increasing field with a tendency to saturate above 7 T.

Figure 5.5: Field dependence of the resistance of a single-domain device fabricated on a domain $T5$ of a 93 nm thick $CaFe_2O_4$ film. **a** Plot of the normalized first harmonic transverse resistivity ρ_T^1/ρ_0 as a function of H , applied at $\alpha = 45^\circ$, measured at 5 K (blue), 100 K (black) and 200 K (red). The fit of the curve at 200 K with $\rho_T^1/\rho_0 = A|H| - BH^2$ ($A, B > 0$) is also shown in dark red. **b** Plot of the normalized first harmonic transverse resistivity ρ_T^1/ρ_0 as a function of α measured at 100 K for increasing values of H from 0 to 9 T.

For a pure antiferromagnet, R_T and R_L scale with H^2 . Here, instead, the data is better fitted by a combination of contributions; one with a negative, quadratic increase and one with a positive, linear increase with increasing magnetic field strength, which predominates at lower fields. The latter is observed in paramagnets and indicates the presence of uncoupled spins. Figure 5.5b shows the ADMR measured at 100 K at different values of applied field from 0 to 9 T. As it can be seen, the amplitude of the modulation is positive and increases with increasing H . This too is inconsistent with the behaviour expected for an uniaxial antiferromagnet, as discussed in the next paragraph.

5.5 Simulations

In order to improve our understanding of the mechanisms that give rise to the SMR in $Pt/CaFe_2O_4$ bilayers, we built a simple theoretical model that simulates the spin configuration of the system and its SMR response in the case in which the Ising condition is lifted. The magnetic properties of an orthorhombic antiferromagnet with uniaxial anisotropy can be described by a Hamiltonian consisting of contributions from Zeeman, exchange, and magnetic anisotropy energies in the form [4, 30]:

$$H = -\gamma\hbar \sum_i \vec{H}_0 \cdot \vec{S}_i + \sum_{i,j} 2J_{ij} \vec{S}_i \cdot \vec{S}_j - D_y \sum_i (S_i^y)^2 + D_z \sum_i (S_i^z)^2 \quad (5.13)$$

where $\gamma = g\mu_B/\hbar$ is the gyromagnetic ratio, g the spectroscopic splitting factor, μ_B the Bohr magneton and $\hbar$ the reduced Plank constant. $\vec{S}_i$ indicates the spin at a generic

lattice site i , $\vec{H}_0$ the applied magnetic field and J_{ij} the exchange constant of the interaction between spins. The system is characterized by two distinct anisotropies, a positive one (hard) with constant D_z along the $\langle 001 \rangle$ direction that forces the spins into the $a - b$ plane and a negative (easy) with constant D_y along the magnetic easy axis $\langle 010 \rangle$. In this simple model the shape anisotropy along the b -axis is not considered, but we expect that it would induce a similar effect as that of D_y . CaFe_2O_4 has been previously described as a 3D Ising antiferromagnet [31], where the two antiferromagnetic sublattices are antiparallel to each other and the spins can only display two states, described by two scalar values. In this case, no tilt or rotation of the spins is possible under the effect of the magnetic field and, thus, the SMR response should be purely antiferromagnetic (negative amplitude). Therefore, in order to take into account the scenario in which tilting of the spins sublattices is at the origin of the measured positive contribution to the SMR, we utilize in our model a more general Heisenberg Hamiltonian and allow the spins to assume any orientation in space.

In order to find the spin equilibrium configuration, we follow the approach described in Ref.[4] and express the energy per unit volume of the system as a function of the angles that the two AF sublattices make with i (easy axis and current direction), θ_1 and θ_2 , and with n , φ_1 and φ_2 . The coordinates of the energy minima correspond to the equilibrium orientation of the sublattices for different applied magnetic field strengths and directions. The material dependent parameters in the model are the effective exchange, H_E , and anisotropy, H_A , fields defined by [4, 30]:

$$H_E = 2SnJ/\gamma\hbar, \quad H_{Ay} = 2D_yS/\gamma\hbar, \quad H_{Az} = 2D_nS/\gamma\hbar \quad (5.14)$$

being n the number of nearest neighbours.

In practice, these simulations were performed using a simple code written in python. The code utilizes the `scipy.minimize` package for a numerical minimization of the energy as a function of θ_1 , θ_2 , φ_1 and φ_2 for a given set of parameters H_E , H_{Ay} , H_{Az} and H_0 . The process is repeated for different values of the applied field direction. Considering a single domain with $\vec{H}_0$ rotating in the film plane, the energy is given by:

$$\begin{aligned} E/M = & -H_0 \cos(\alpha) [\cos(\theta_1) \sin(\varphi_1) + \cos(\theta_2) \sin(\varphi_2)] \\ & -H_0 \sin(\alpha) [\sin(\theta_1) \sin(\varphi_1) + \sin(\theta_2) \sin(\varphi_2)] \\ & + H_E [\sin(\varphi_1) \sin(\varphi_2) \cos(\theta_1 - \theta_2) + \cos(\varphi_1) \cos(\varphi_2)] \\ & - H_{Ay} [\cos^2(\theta_1) \sin^2(\varphi_1) + \cos^2(\theta_2) \sin^2(\varphi_2)] + H_{Az} [\cos^2(\varphi_1) + \cos^2(\varphi_2)] \end{aligned} \quad (5.15)$$

where α is the angle between $\vec{H}_0$ and the easy axis b . Similar expressions have been used to model the response when the field is rotated outside of the film plane. To simulate the response of the different domains, the relative in-plane and out-of-plane tilts from the b and c -axis have also been taken into account.

The magnetization and Néel vectors are then calculated as sum and difference of the vectors describing the position of the two AF sublattices at the energy minimum. Finally the FM and AF contributions to the SMR are calculated as the negative

squared dot product between the relative order parameter vector and the spin accumulation direction at the interface. Because the modulus of each sublattice vector is arbitrarily set equal to 1 and the amplitude of the spin accumulation is not known, the model does not provide a quantitative measure of the magnitude of the SMR.

For CaFe_2O_4 we base our simulations on the values reported in literature for the bulk material: $S = 5/2$ and $g = 2$ [32]. The anisotropy constants for CaFe_2O_4 have not, to our knowledge, been reported. However indirect measurements have shown an in-plane anisotropy field of 443 Oe at 300 K [29] and a resonance field along the c -axis of 3380 Oe. The theoretically predicted AF exchange constants are $J_1 = -4.19$ K, $J_2 = -5.44$ K, $J_3 = -14.69$ K and $J_4 = -23.93$ K [33]. Thus, the negative inter-chain J_3 and J_4 are the dominant inter-sublattice interactions. Therefore, for simplification, we can consider one unique exchange interaction with magnitude mean between J_3 and J_4 and number of nearest neighbours $n = 4$, corresponding to the adjacent Fe^{3+} spins connected through corner-sharing O_6 octahedra (see fig. 1.2). This leads to a calculated H_E of 287 T, that is lower than what is reported for the easy-plane antiferromagnet NiO , but higher than the easy-axis MnF_2 and FeF_2 [4]. The corresponding spin-flop field would be $H_{SF} = \sqrt{2H_A H_E} = 5$ T. Using this set of parameters, where H_E is two orders of magnitude larger than the applied H_0 and H_{Ay} much smaller, the expected SMR response, shown in figure 5.6, is governed by the AF exchange and differs largely from what is observed experimentally in all 3 planes of rotation.

In fact, when a 7 T field is applied along the magnetic easy axis the simulation of the equilibrium position of the AF sublattices, the two sublattices align antiferromagnetically in the direction perpendicular to the applied field (spin-flop state) with $\theta_1 = \varphi_1 = \varphi_2 = 90^\circ$ and $\theta_2 = -90^\circ$, as observed in figure 5.6a-b. Rotating the magnetic field in the $i-t$ plane produces a coherent rotation of θ_1 and θ_2 with α which leads to a sinusoidal modulation of the SMR with negative amplitude. Increasing the strength of the magnetic field increases the amplitude of the modulation, as shown in figure 5.6c up to 9 T. On the contrary, when the H is below the spin-flop value of about 5 T, the modulation deviates from sinusoidal, as the sublattices only slightly rotate around the equilibrium configuration with $\theta_1 = 0^\circ$ and $\theta_2 = 180^\circ$. This is inconsistent with the experimental results where a positive modulation is observed between 1 and 9 T (fig. 5.5). Even allowing the exchange field to assume much lower values fails to capture the behaviour observed experimentally. For H_E two orders of magnitude lower, in fact, the SMR only becomes positive at about 6 T, as the sublattices tilt towards the easy axis direction. Reducing H_E even further, produces a positive SMR at all fields, but its amplitude is saturated (spin-flip phase).

When the applied field rotates outside of the film plane, the sublattices, in addition to the in-plane rotation, also start to tilt out-of-plane (fig. 5.6e,h), but the tilt is limited to a few degrees. When $\beta = 90^\circ$ and $\gamma = 90^\circ$, corresponding to the same out-of-plane field orientation, the in-plane configuration of the two sublattices is not identical: in the first case (fig. 5.6e) the spins align along the easy axis ($\theta_1 = 0^\circ$, $\theta_2 = 180^\circ$), as expected, while in the second case (fig. 5.6h) they are perpendicular ($\theta_1 = -90^\circ$, $\theta_2 = 90^\circ$). This is due to the small value of H_{Ay} , that makes the energy minima of these two configurations very close to each other. As a result, a very

Figure 5.6: Simulation of the sublattices equilibrium positions for $H_E = 287$ T, $H_{Ay} = 0.044$ T, $H_{Az} = 0.338$ T and $H_0 = 7$ T. Plot of **a** θ_1 and θ_2 , **b** φ_1 and φ_2 and **c** field-dependent longitudinal SMR as a function of α when the field rotates in the (easy) $i-t$ plane. Plot of **d** θ_1 and θ_2 , **e** φ_1 and φ_2 and **f** field-dependent longitudinal SMR as a function of β when the field rotates in the $t-n$ plane. Plot of **g** θ_1 and θ_2 , **h** φ_1 and φ_2 and **i** field-dependent longitudinal SMR as a function of γ when the field rotates in the $i-n$ plane. Sketches of the rotation geometry and of the two AF sublattices (as blue and red arrows) are shown in the inset for fields angles of 0° and 90° .

small modulation (compared to the in-plane modulation) is observed in the β scan, in contradiction with our experiments. A modulation in this direction is instead typical of ferromagnets or paramagnets.

In addition, no modulation in the γ scan is expected from the simulations (fig. 5.6i). Again this is different from what is observed experimentally (fig. 5.4b), where a modulation with maximum at $\gamma = 90^\circ$ is found. Assuming a larger H_{Ay} value, that could be plausible given the shape anisotropy of the needle-like crystals, the configuration with $\gamma = 90^\circ$, $\theta_1 = 0^\circ$ and $\theta_2 = 180^\circ$ would be energetically favoured, resulting in a rotation of the sublattices in the $i-t$ plane. This can lead to an ADMR with maximum at $\gamma = 90^\circ$, as observed experimentally. However, in this case the amplitude of the SMR would decrease with increasing applied field, as the sublattices tilt towards the easy axis from the spin-flop configuration at $\gamma = 0^\circ$, raising the

value of the low resistance state. This is also inconsistent with our experimental measurements, that show an increase of the out-of-plane modulation with increasing applied field (not shown).

5.6 Discussion

From these simulation, it is evident that the positive SMR response measured experimentally cannot be explained by the spin canting of a uniaxial antiferromagnet with exchange and anisotropy field values as reported in literature for CaFe_2O_4 . For the external magnetic field to be able to induce a large enough canting of the AF sublattices in the spin-flop state that results in a positive SMR amplitude, its value has to be comparable to H_E . However, this cannot be the case for CaFe_2O_4 films, given the T_N of 185 K. In addition, even in a scenario with lower H_E , the model would not completely capture the measured behaviour in the field-dependence of the SMR and in the field rotation in the $n-i$ plane. Therefore, the observed positive contribution to the SMR cannot be intrinsic to the AF ordering, arising from a tilt of the sublattices with the magnetic field, and instead a different source for such positive contribution needs to be taken into account to explain the observed ADMR.

One possibility is that the material displays additional spins that are not accounted for in our theoretical model. This would be in good agreement with the observed opening of the $M-H$ loops at around 130 K in both bulk [32] and thin films [28], which is proposed to originate from “orphan spins” at the magnetic antiphase boundaries [31, 34]. In addition, short-range 1D interactions and up to 350 K [33] and a even higher Curie-Weiss temperature [31] have been reported in CaFe_2O_4 single crystals and could also explain the persistence of the positive SMR modulation at temperatures above T_N .

Another possible origin for this positive contribution would be surface and shape effects [35]. It is well-known [36–38], that due to surface magnetic anisotropy and magneto-elastic strain at the surface, the magnetic structure of the the top few nm can largely differ from that of bulk. These becomes particularly relevant in AF nanoparticles, even up to 500 nm in size, due to the finite-size and shape constraints. For example, loss of long-range ordering or another type of structure or a change of easy axis can occur at the surface [39], as well as different reorientation behaviour with an applied magnetic field[40]. In our case, due to the needle-shape of the crystals with large aspect ratio and a width in the 100 nm range, these effects may play an important role. To include such effects in the SMR model, a much more complex approach to the simulation of the spin structure of CaFe_2O_4 thin films, beyond the scope of this work, is required.

We also considered, but excluded, that the positive modulation arises from effects other than the SMR. In particular, the Hanle magnetoresistance, originating from the precession of edge spin accumulation [41, 42], is a common source of artefacts in SMR measurements as it is also characterized by a resistance modulation with period 180° and a phase similar to positive SMR. The modulation induced by the Hanle effect is analogous to the SMR response of a FM and only appears when the field rotates in the $i-t$ and $n-t$ planes. In order to distinguish between the contributions from

the Hanle and spin-Hall magnetoresistances, the field dependence resistance can be studied for a fixed direction of the applied field, as shown in figure 5.5. For the Hanle effect, a positive quadratic increase of R_L and R_T with $\vec{H}$ is expected, and this differs from what is measured for both small and large devices, where a linear increase at low fields and a quadratic negative saturation at higher fields always occurs. In addition, a modulation arising from this effect would show a monotonic trend with temperature, which is different from our observations in both single- and multi-domain devices.

Anisotropic magnetoresistance arising from the magnetic proximity effects has also been observed in FM/Pt bilayers, that can compromise the use of thin Pt as a detector of pure spin current [43, 44]. However, the magnitude of this effect is expected to be much lower in compensated antiferromagnets where a net magnetization can only appear locally due to uncompensated domain boundaries [44]. This effect is known to induce a ADMR when $\vec{H}$ rotates in the $n - i$ plane and, thus, cannot explain the positive modulation observed in the β scan [45, 46].

Therefore, we believe that the most likely explanation for the observed ADMR is the SMR arising from the rotation of the Néel vector of the AF structure and an additional positive contribution that originates from uncompensated spins at the antiphase boundaries. These spins, which do not generally interact with each other, will give rise to a linear, paramagnetic-like, field-induced magnetization but they will, generally, not order at a finite temperature, as it is observed in CaFe_2O_4 . However, interactions between orphan spins could emerge thanks to the large correlation lengths that develop around the second-order antiferromagnetic phase transition [28]. This would explain the appearance of a net magnetization in a limited temperature range. However, the possibility of surface effects due to the small size of the crystals composing the films cannot be excluded.

5.7 Conclusions

We have measured the ADMR in $\text{Pt}/\text{CaFe}_2\text{O}_4$ bilayers for both multi and single structural domain devices. The sinusoidal modulation of the Pt resistance for both in-plane and out-of-plane field rotations and the magnetic field dependence indicate the presence of two contributions to the SMR: a negative and a positive one. The former depends quadratically on the magnetic field and its intensity decreases with increasing temperature, corresponding to the rotation of the Néel vector of the antiferromagnetic ordering. The latter depends linearly on the magnetic field, occurs at all temperatures and is consistent with the presence of uncompensated spins that are uncoupled from the AF ordering. These observations support the scenario in which spin fluctuations create antiphase boundaries in the B phase ($\uparrow\downarrow\uparrow\downarrow$ ground state), that locally display $\uparrow\uparrow\downarrow\downarrow$ spin ordering characteristic of the A-phase. At the antiphase boundaries, uncompensated moments, that are free to rotate with the applied magnetic field, are present, leading to a positive contribution to the SMR. We hypothesize that, in the proximity of the critical phase transition, when long-range correlations emerge, the coherent effect of these antiphase boundaries gives rise to the observed net magnetic moment. Finally, additional effects from confinement and anisotropy at the

surface cannot be ruled out, and they could play a role in the difference between the behaviour of single and multi-domain devices. Although such a difference is not fully explained yet, the experiments show the potential of multiscale SMR measurements to extract unique information from complex magnetic samples. To further investigate this aspect, we have initiated a collaboration with the ISIS Neutron and Muon Source (UK) where the magnetic structure of our CaFe_2O_4 will be investigated by means of neutron diffraction. Aligning the beam with respect to the magnetic easy axis, will allow to address the response of the different domains individually. In addition, the possibility of applying a magnetic field during the collection of the diffraction pattern will also provide new insight into the behaviour of this material especially in relation to the spin-flop transition.

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Chapter 6

CaFe₂O₄-CaCr₂O₄ solid solutions

Abstract

In this work the effects of substitution of Fe by Cr in CaFe₂O₄ thin films are investigated. We report that with increasing amount of Cr the crystal structure of the films and their epitaxial relationship with the substrate change, going from well-defined oriented domains in the case of undoped CaFe₂O₄ to textured polycrystals in CaFeCrO₄. Such changes can be explained by the partial amorphization of the native CaTiO₃ at the interface between film and substrate. Characterization of the magnetic properties shows that the substitution by Cr promotes the stability of the B phase and decreases the ordering temperature in the oriented crystals. On the other hand, the behaviour of the polycrystalline Cr rich films largely deviates from that of the undoped material.

Selected content from this chapter is part of the Master theses of Rick Scholtens and Ivar Dijk.

6.1 Introduction

Because of the deep interconnection between magnetic and crystal structure in solids, modifications of the lattice by means of epitaxial strain or chemical substitution can have a large impact on the magnetic properties of a material. This is especially true in the case of systems where bonding geometry of the magnetic spins is close to the threshold between ferromagnetic and antiferromagnetic coupling, as in the case of CaFe₂O₄.

Solid solutions of CaFe₂O₄ with other isostructural oxides have been studied before. Specifically, Zouari *et al.* [1] have investigated the replacement of Fe in the CaFe₂O₄ structure by Mn atoms. Here, Mn³⁺ preferentially occupies Fe(2)³⁺ sites changing significantly their environment geometry due to the Jahn-Teller distortion. Increasing axial elongation upon increasing Mn concentration has been correlated to the enhancement of both the low temperature magnetization and the Néel temperature of the material. In this case, no solid solution in the Mn-rich side of the phase diagram has been found, where a even more distorted structure is expected.

On the other hand, solid solutions between CaFe₂O₄ and CaCr₂O₄ form in a broader compositional range. CaCr₂O₄ is a $S = 3/2$ magnet that displays spatially long-ranged incommensurate cycloidal magnetic ordering below 21 K [2, 3] in its stable β polymorph. The first magnetic phase diagram of the system was investigated by

Corliss *et al.* [4] up to 50% substitution and is depicted in figure 6.1a. Interestingly, they found that only in certain broad temperature and composition ranges, the two distinct magnetic phases, A and B, coexist in thermal equilibrium with the A magnetic arrangement being stable at low temperature in the undoped CaFe_2O_4 and B being preferred at higher Cr concentrations [5].

Figure 6.1: **a** Magnetic phase diagram of the $\text{CaFe}_2\text{O}_4\text{-CaCr}_2\text{O}_4$ solid solution, reprinted with permission from Ref.[4]. **b** Temperature evolution of the FC and ZFC magnetization in 100 Gauss (top) and of the magnetic site ordered moment value (bottom), for CaFe_2O_4 (left panels, in blue) and $\text{CaFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ (right panels, in red), reprinted with permission from Ref.[6].

Similar results have been obtained more recently by Songvilay *et al.* [6], who have studied polycrystalline samples of CaFe_2O_4 and $\text{CaFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ by means of elastic and inelastic neutron scattering. Here, magnetoelastic effects are invoked to explain the stabilization of the ferromagnetic inter-chain exchange in the A-type magnetic ordering, while the random Cr distribution on the magnetic Fe sites is

responsible for the stabilization of pure B down to low temperature. This also results in a decrease of the T_N observed upon increasing Cr concentration and a difference in the macroscopic magnetic properties (see fig. 6.1b). Interestingly, in this study short-range order expected in the case of incomplete stacking of the A and B structures and the dynamical effects originating from such defects, that were reported before [7], were not observed. This is inconsistent with the scenario in which there is nucleation of A ($\uparrow\uparrow\downarrow\downarrow$) at the domain boundaries of B ($\uparrow\downarrow\uparrow\downarrow$) in a first order-type transition and suggests instead a picture where magnetic exchange disorder leads to magnetic excitations (A phase) of the thermodynamic ground state (B phase). Following these interesting reports we decided to combine both the effect of epitaxial growth and Cr substitution in $CaFe_2O_4$ thin films and the results are discussed in the present chapter.

6.2 Ceramics

As discussed in Chapter 3 the first stage for PLD growth of oxide thin films is the preparation of suitable targets with the desired stoichiometry. Therefore, we synthesized several polycrystalline pellets with general chemical formula $CaFe_{2-x}Cr_xO_4$ where $x = 0.2, 0.5$ and 1 , by means of solid state synthesis [8–10]. The process was the same as described for the undoped $CaFe_2O_4$ ceramics, with the only addition of stoichiometric amounts of Cr_2O_3 to the precursors mix. Furthermore, in this case the thermal treatment was conducted in a tube furnace under a constant flow of 100 ml/min of Ar gas to prevent oxidation of the Cr^{3+} in air.

Characterization of the ceramics by means of powder XRD (see fig. 6.2) revealed pure phase products with orthorhombic $Pnma$ structure. The lattice parameters were extracted from the refinement of the powder diffraction pattern and are listed in table 6.1. As it can be seen, the unit cell volume decreases upon increasing Cr concentration, as expected given the smaller size of this atom. Specifically, the a and b parameters show an almost linear decrease with x , while c displays a limited change up to $x = 0.2$, after which it also starts to decrease linearly. This could be attributed to a slight preferential occupation by Cr of the $Fe(2)$ sites only at low doping concentrations.

The magnetic properties of the samples were investigated by means of SQUID magnetometry and shown in figure 6.3, with the most relevant parameters also reported in table 6.1. First of all, an overall decrease of the susceptibility values is observed with respect to the undoped $CaFe_2O_4$. Moreover, in accordance with the literature [4, 6], a shift of T_N towards lower temperature was observed upon increasing Cr concentration, as well as a gradual disappearance of the maximum in the susceptibility curve that is attributed to the formation of magnetic antiphase boundaries with local A structure. This is also accompanied by the suppression of the splitting between field-cooled (FC) and zero field cooled (ZFC) curves upon increasing the amount of Cr . However, the two curves seem to always converge at the maximum measurement temperature (400 K). This is probably indicative of the presence of a magnetic impurity with high ordering temperature, which however was not detected by means of powder XRD. Finally, the hysteresis in the $M - H$ loop at 130 K is also

not observed at high *Cr* doping concentrations.

Figure 6.2: Powder XRD of the $CaFe_{2-x}Cr_xO_4$ PLD targets. Plot of the measured intensity as a function of 2θ from 18° to 65° for samples with $x = 0.2$ (black), $x = 0.5$ (red) and $x = 1$ (blue).

Table 6.1: Unit cell and magnetic parameters of $CaFe_{2-x}Cr_xO_4$ ceramics.

parameter	$x = 0$	$x = 0.2$	$x = 0.5$	$x = 1$
a [Å]	9.2345(55)	9.22014(28)	9.19229(23)	9.1694(5)
b [Å]	3.0230(17)	3.01817(10)	3.00772(6)	2.99890(16)
c [Å]	10.7014(22)	10.6895(4)	10.68019(26)	10.6724(6)
V [Å ³]	298.743(21)	297.468(11)	295.284(18)	293.442(59)
R / wR	0.0359 / 0.0515	0.0216 / 0.029	0.0225 / 0.0311	0.0418 / 0.0538
T_N [K]	175	170	125	35
χ max [K]	155	110	no	no

A decrease in the density of the ceramics is also noticed that is consistent with the change of grain size and shape observed by SEM (see inset of fig. 6.3). This could be due to the different synthesis conditions and makes these targets less ideal for PLD growth than those of $CaFe_2O_4$.

Figure 6.3: Plot of the magnetic susceptibility (χ) as a function of temperature (T) of **a** $\text{CaFe}_{1.8}\text{Cr}_{0.2}\text{O}_4$, **b** $\text{CaFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ and **c** CaFeCrO_4 measured in a 100 Oe field after FC (full dots) and ZFC (open dots). Scanning electron microographies of the sample surface are show in the inset. **d** Plot of the magnetization (M) as a function of T measured at 130 K of undoped CaFe_2O_4 (black) and CaFeCrO_4 (red).

6.3 Thin films

6.3.1 Growth and structure

$\text{CaFe}_{2-x}\text{Cr}_x\text{O}_4$ thin films were grown by means of PLD on TiO_2 (110) substrates. The growth parameters were optimized starting from those found for calcium ferrite. Laser energy, repetition rate, number of pulses and process pressure were kept constant. In general it was observed that at higher Cr amounts growth at higher temperature promoted the formation of particles on the samples surface, while too low temperatures prevented the crystallization of the material. Therefore, the Cr containing films are optimally grown in a temperature window between 720 $^\circ\text{C}$ and 770 $^\circ\text{C}$.

Moreover, we investigated the effect of the annealing atmosphere on the oxidation state of the Cr . Samples were grown under identical conditions and then cooled down under a pressure of 200 mbar O_2 , 1 mbar O_2 , 1 mbar Ar and in vacuum. No significant

difference was observed in the topography and crystal structure of the films. We also performed XPS measurements on the samples annealed in 200 mbar O_2 and 1 mbar Ar pressure (see Appendix A). Here, we observed that the Cr oxidation state is not affected by the large O_2 pressure during annealing, but the oxygen stoichiometry is [11, 12]. Therefore, we decided to maintain 200 mbar of O_2 as standard annealing conditions.

After growth, the quality of the surface was assessed by means of AFM and it is shown in figure 6.4. A clear change in the surface morphology is found upon addition of Cr . In the samples with composition $CaFe_{1.8}Cr_{0.2}O_4$ the needle-like crystals observed in the undoped calcium ferrite were reduced in size and only present in small amounts, while most of the surface displayed a flatter morphology (fig. 6.4a). Upon increasing the Cr content, the needle-like crystals became abundant again, but mostly displayed a single orientation not seen in the undoped films, with the long axis parallel to the substrate $[001]$ direction, thus rotated of 90° with respect to domains $T1$ and $T4$ of $CaFe_2O_4$ (fig. 6.4c). In some of the $CaFe_{1.5}Cr_{0.5}O_4$ samples, larger crystals with the original orientations were also still present (fig. 6.4b). Longer annealing at relatively low temperatures seemed to promote the growth of the new type of crystals at the expense of the old ones. EDS analysis of the elemental composition in the $x = 0.5$ and $x = 1$ films, shows that the $Cr:Fe$ stoichiometry is close to the expected 1:2 and 1:1 ratios in all domains.

Figure 6.4: AFM topography images of **a** $CaFe_{1.8}Cr_{0.2}O_4$, **b** $CaFe_{1.5}Cr_{0.5}O_4$ and **c** $CaFeCrO_4$ thin films.

Figure 6.5 shows the specular XRD diffraction patterns of the films. Here, the most apparent effect of increasing Cr concentration is the dramatic drop of the intensity of the main film peak at $2\theta = 33.6^\circ$. In addition, a slight shift of the peak towards larger angles is observed, consistently with the decrease in the lattice parameters. Moreover, an extra peak for the $x = 0.2$ samples, often found at $2\theta = 31.9^\circ$, has not been identified yet.

To further study the orientation and domain structure of the $CaFe_{2-x}Cr_xO_4$ films we also utilized EBSD. Figure 6.6 shows a scan of a $CaFe_{1.5}Cr_{0.5}O_4$ film. Most of the surface of the sample can be indexed as the $CaFe_2O_4$ orthorhombic phase (coloured areas), with only some areas where the quality of the Kikuchi pattern was not sufficient to identify the phase. As it can be seen from the comparison with the SEM micrograph in figure 6.6a, these areas correspond to the layer underneath the needle-like crystals. In this sample the majority of the crystals display the same two

Figure 6.5: XRD 2θ - ω scans of $\text{CaFe}_{2-x}\text{Cr}_x\text{O}_4$ films with increasing Cr concentration from $x = 0$ to $x = 1$. Plot of the measured intensity as a function of 2θ from 15° to 75° . The unidentified peak at $2\theta = 31.9^\circ$ is indicated with a star.

out-of-plane orientations, (302) (blue) and (004) (red), as in the undoped calcium ferrite (fig. 6.6b). By contrast, the most abundant in-plane orientation has the [010] direction of the CaFe_2O_4 lattice parallel to the substrate [001] direction (gray), corresponding to a domain type that is not present in the undoped samples and will be hereafter denoted as $T7$ (fig. 6.6c). Crystals with the $T1$ - $T6$ type orientations (see Chapter 3) were also found (orange, purple, teal).

Similar measurements were also performed on samples with $x = 0.2$ and $x = 1$ (not shown). In the samples with $x = 0.2$ only the needle-like crystals visible in figure 6.4a belong to the orthorhombic CaFe_2O_4 phase, while the majority of the sample is composed by a phase that is crystalline but could not be identified. The quality of the Kikuchi pattern was not sufficient for indexing probably due to the low thickness. It is however clear that it is not CaFe_2O_4 nor CaTiO_3 . Conversely, the CaFeCrO_4 samples are almost entirely composed of CaFe_2O_4 orthorhombic phase with $T7$ domain orientation. These measurements confirm the expected correspondence between the AFM topography and the unit cell orientation: the long axis of the needle-like crystals is the b -axis and at high Cr concentration it mostly lays parallel to the substrate [001] direction. Interestingly, in all films the same elemental composition was found for all domain types, thus the different epitaxial relation can not be ascribed to a difference in Cr content.

The characterization of the domain structure of the $\text{CaFe}_{2-x}\text{Cr}_x\text{O}_4$ films also reveals a connection between the crystal orientation and the specular XRD scan (fig. 6.5): the more abundant domain $T7$ is, the lowest the intensity of the out-of-plane

Figure 6.6: EBSD scan of a $91\ \mu\text{m} \times 50\ \mu\text{m}$ area of the surface of a $\text{CaFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ film. **a** Map of the SEM (secondary electrons) contrast. Maps highlighting in solid colours **b** the 2 out-of-plane and **c** the 4 in-plane orientations. The unit cell is depicted in red. Image taken by Ir. Dr. Václav Ocelík.

peak at 33.5° . Initially, this was surprising, as domain $T7$ is crystalline and displays the same out-of-plane orientation as the other domains. Therefore, we hypothesized that the decrease in intensity could be caused by a misalignment of the film crystal lattice with respect to that of the substrate, which is used for the alignment of the 2θ - ω scan.

To verify this hypothesis and gain more insight into the local structure of the $\text{CaFe}_{2-x}\text{Cr}_x\text{O}_4$ samples we resorted to STEM measurements. Two lamellas were cut from a thin film sample with $x = 0.5$ perpendicular (1) and parallel (2) to the substrate's $[001]$ edge. In addition, in-situ EDS was performed to determine the elemental composition throughout the films thickness.

Figure 6.7 shows an image of the cross-section of the film from lamella 1 and the results of the EDS analysis. In order from bottom to top, the following layers can be seen:

- The regular TiO_2 Rutile lattice viewed from the $[001]$ zone axis. The lattice parameters extracted from the FFT of the HAADF image are $d_{110} = 3.25\ \text{\AA}$, $d_{1\bar{1}0} = 3.24\ \text{\AA}$ and, from lamella 2, $d_{001} = 2.94\ \text{\AA}$ in perfect agreement with the known TiO_2 crystal structure [13].
- A darker (indicating lower atomic number) and rough layer approximately 10-15 nm thick. From EDS the composition of this layer results to be $\text{Ca } 14.7 \pm 0.7\ \text{at\%}$, $\text{Ti } 15.6 \pm 0.3\ \text{at\%}$ and $\text{O } 67.9 \pm 1.2\ \text{at\%}$, corresponding to a native

Figure 6.7: HAADF-STEM image of the cross-section of a CaFeCrO_4 thin film. **a** Overview and **b** overlay of the elemental distribution (solid colour) from in-situ EDS analysis. Image taken by Dr. Majid Ahmadi.

CaTiO_3 . The formation of such layer was expected as it also occurs at the interface between CaFe_2O_4 and TiO_2 , as discussed in Chapter 3. However, in this case, crystalline areas alternate with amorphous regions and, thus, there is no structural match with the underlying TiO_2 substrate. This, in turn, results in loss of proper epitaxial relation between film and substrate. We believe that this lack of crystallization is due to the lower temperature used during the deposition of the Cr containing films compared to those of the undoped calcium ferrite (770° and 820° respectively).

- The CaFeCrO_4 film, approximately 50 nm thick, that already from the overview image (fig. 6.7a), appears not to be single-crystalline and epitaxial, but is instead composed of multiple grains. Clear atom positions are visible within the grains, indicating that they are crystalline in nature. From compositional analysis it results that the cations distribution is also not uniform in this layer. The majority of the grains (green regions in fig. 6.7b) display a $\text{Ca} : \text{Fe} : \text{Cr}$ stoichiometry close to the target 1 : 1 : 1 ($14.5 \pm 0.5 \text{ at\%}$, $15.9 \pm 0.3 \text{ at\%}$, $17.3 \pm 0.8 \text{ at\%}$). However, some isolated grains are also found (blue regions in fig. 6.7b)

with very low *Ca* content ($4.6 \pm 0.8 \text{ at\%}$) and especially rich in *Fe* ($23.6 \pm 0.5 \text{ at\%}$) compared to *Cr* ($15.1 \pm 1.1 \text{ at\%}$). This is possibly an unwanted *Fe* – *Cr* Oxide whose magnetic properties will be discussed in the next section. The size of the grains is in the order of 50 nm, well below the resolution of EDS maps in the SEM of 1 μm and, thus, they could not be observed with the previous characterization.

- *C* (dark) and *Pt* (light) layers that have been deposited over the film to protect it during the cutting and thinning of the lamella. Figure 6.8 shows the depth-profile of the elemental composition across the thickness of lamella 1 in two selected areas of the sample.

Figure 6.8: Depth profile of the elemental composition of a *CaFeCrO₄* film in two selected lines **a** excluding and **b** including the *Fe* – *Cr* oxide impurity phase. The insets show the position of the line scans in the HAADF-STEM image.

In the first (fig. 6.8a), *Fe* (blue), *Cr* (green) and *Ca* (red) are present in approximately the same amount in the main phase of the film. Moving towards the interface, the amounts of *Cr* and *Fe* decrease drastically while that of *Ti* (orange) increases, until it reaches the level of *Ca* in the intermediate *CaTiO₃* layer. The second profile in the figure is chosen to cross one of the Iron-Oxide grains (fig. 6.8b). Here, the *Fe*:*Cr* stoichiometry is close to 4:3, while the other elements are essentially absent. Differently from the undoped calcium ferrite samples described in Chapter 3, here all

the interfaces between the various layers are very rough and large regions with mixed composition can be found, which makes the study of the magnetic properties more difficult.

Figure 6.9: **a** HAADF-STEM image of the crystal lattice of CaFeCrO_4 and **b** its FFT. **c** HAADF-STEM image of the boundary between two grains and **d** its FFT. **e** Simulation of the reciprocal lattice based on the CaFe_2O_4 structure of Ref.[14] viewed from the $[010]$ zone axis. **f** Overview HAADF-STEM image of multiple grains with FFT in the inset. The green lines are guide-to-the-eyes to identify the hexagonal pattern and the $[004]$ peak. Image taken by Dr. Majid Ahmadi.

Using the high-resolution HAADF-STEM images, we have studied the crystal structure and orientation of the CaFeCrO_4 grains. In figure 6.9 the hexagonal pattern

that the *Fe* atoms form in the *a*–*b* plane of the *Pnma* structure is clearly recognizable. The hexagonal geometry is also reflected in the FFT of figure 6.9b. Here the brighter spots are the [302] and [004] reflections, that form an hexagon around the middle of the beam. The values of the lattice spacing extracted from the FFT are: $d_{302} = 3.25$ Å, $d_{004} = 3.25$ Å. Figure 6.9e shows a simulation of theoretical pattern viewed from the [010] zone. The position of the [004] and $[00\bar{4}]$ spots can be used to determine the tilt of the crystal lattice within the *a* – *b* plane, that for this particular grain results to be 8° off with respect to the (302) out-of-plane orientation.

Analysis of many other similar patterns (as exemplified in fig. 6.9f) allows to calculate the local misorientation between grains that ranges between fractions of a degree to approximately 20°. The transition between two adjacent grains occurs through a discontinuous crystal rotation, as shown in figure 6.9c. Here, an area is chosen that contains two adjacent crystal grains and the boundary between them. As it can be seen in the FFT in figure 6.9d, two well-defined lattice orientations are present with no smearing of the peaks, that would indicate a continuous rotation. Therefore, even if the crystal structure of *CaFe₂O₄* is maintained, the misalignment between adjacent grains explains the absence of the out-of-plane peak in the XRD specular scans, as the intensity of the (302)-(004) reflections gets spread over a relatively broad range of angles. On the other hand, in EBSD measurements, where the tolerance angle for the out-of-plane orientation is larger (1-2°) and the resolution not enough to distinguish between individual grains, indexing the Kikuchi pattern gives a mean value between the orientations of the small grains.

6.3.2 Magnetic properties

The magnetic properties of *CaFe_{2-x}Cr_xO₄* films have been investigated by means of SQUID magnetometry. Figure 6.8a-c shows the temperature dependent magnetic susceptibility of the three compositions. All the measurements were performed aligning *H* parallel to the magnetic easy-axis ([010]) of domain *T7*, unless otherwise specified. The plot of the susceptibility as a function of temperature of the sample with $x = 0.2$ (fig. 6.10a) is characterized by a unique transition at $T = 73$ K where FC/ZFC splitting also occurs. Above this temperature, the χ displays first an almost linear and then Curie-Weiss decay and reaches zero at about 350 K. This indicates that the main phase in these samples, although non identified yet, is magnetic in nature.

Among the prepared compositions, only the samples with $x = 0.5$ (fig. 6.10b) display the characteristic behaviour of *CaFe₂O₄*, albeit the relevant features are shifted towards lower temperatures. In fact, the Néel temperature is here found at 145 K and the maximum in the FC curve (correspondent to a minimum in the ZFC one) appears at 60 K. Moreover, like in the undoped samples, the susceptibility is non-zero up to 400 K. This is consistent with the expected effect of *Cr* addition and not dissimilar to what is observed in the ceramic targets.

The behaviour of the sample with $x = 1$ and single domain (*T7*) is very different: here a monotonous decay of χ with *T* is observed from 5 to 400 K. No clear transition temperature is observed within the measurement range. However, upon varying the direction of $\vec{H}$ with respect to the long axis of needle-crystals (not shown), a different

response is measured, which suggests the presence of some magnetic anisotropy. At Cr concentrations above 0.5 a large FC/ZFC splitting is observed that persists above T_N , similarly to what is found for the ceramic pellets and for the samples with $x = 0.5$. This is indicative of the presence of a magnetic impurity with high ordering temperature, possibly the $Fe - Cr$ oxide seen in STEM measurements. Further measurements at higher applied magnetic fields could help increase the signal of the target phase over that of the impurity phase at high temperatures, if the latter is present in small amounts.

Figure 6.10: Magnetic properties of $CaFe_{2-x}Cr_xO_4$ films. Plot of the magnetic susceptibility (χ) as a function of temperature (T) from 5 to 400 K in a 100 Oe magnetic field for samples with **a** $x = 0.2$, **b** $x = 0.5$ and **c** $x = 1$. The field-cooled (FC) data are plotted in red while zero-field-cooled (ZFC) ones in black. Plot of the magnetization (M) as a function of field (H) from -7 to 7 T at 3 selected temperatures for samples with **d** $x = 0.2$, **e** $x = 0.5$ and **f** $x = 1$.

Figure 6.10d-f also shows the hysteresis loops of the 3 compositions at 20 K, 120 K and 220 K. As it can be seen, most of the loops are closed and display the linear increase up to high fields typical of antiferromagnetic spin-flop phase. Only the loop at 20 K of the $\text{CaFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ composition displays some magnetic hysteresis. Recalling that the presence of net magnetic moment has been associated to the coexistence of the A and B structures [7], this is consistent with the lowering of temperature range in which the A and B structures coexist induced by Cr addition.

From these experiments a correlation emerges between the relative amount of *T7* domains and the magnetic properties. Comparing the response of samples grown with the same amount of Cr, the presence or absence of a XRD peak at 33.5° correlates with the presence or absence of a maximum in the $\chi - T$ plot, characteristic of A/B phase coexistence. Whereas when the amount of *T7* is larger the magnetic transition disappears. This is unexpected since there is no detectable difference in composition or crystal structure between domain *T7* and the other domain types, that only differ in crystal orientation. The cause of this drastic change of properties as well as the phase of $\text{CaFe}_{0.2}\text{Cr}_{1.8}\text{O}_4$ samples require further investigation. To this end, we have planned Mössbauer spectroscopy measurements on ^{57}Fe enriched samples, which will be object of further work. This technique, being sensitive to different iron sites, may allow to distinguish between the contributions of the $\text{CaFe}_x\text{Cr}_{2-x}\text{O}_4$ and impurity phases.

6.4 Conclusions

Thin films with various compositions in the solid solution between CaFe_2O_4 and CaCr_2O_4 can be grown by means of PLD on TiO_2 (110) substrates. Upon increasing the amount of Cr, the structure of the films and their epitaxial relationship with the substrate change, from well-defined oriented domains in the case of undoped CaFe_2O_4 to textured polycrystals in CaFeCrO_4 . The intermediate composition $\text{CaFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ displays a mixture of the two extremes. This can be attributed to the structural change in the native CaTiO_3 intermediate layer that is fully crystalline in the undoped samples and partially amorphous in CaFeCrO_4 , possibly due to the lower growth temperature used. Interestingly, even in the samples grown with higher Cr concentrations, the epitaxial relationship with the substrate is not completely lost. In fact, the CaFeCrO_4 grains are all oriented with the CaFe_2O_4 [010] direction parallel to the substrate's [001]. This is also reflected in the morphology of the sample, characterized by needle-like crystals parallel to the substrate edge (domain *T7*), as seen in figure 6.4c.

The macroscopic magnetic properties of the films have also been investigated. The samples with $\text{CaFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ composition display the characteristic features of the coexistence of A/B magnetic structures, but shifted towards lower temperature, as expected with addition of Cr. On the other hand, the magnetic properties of samples consisting mostly of *T7* domains largely deviate from those of the other domain types, despite displaying no detectable difference in composition or structure. It is possible that, given the delicate equilibrium between competing interactions in $\text{CaFe}_{2-x}\text{Cr}_x\text{O}_4$, even a small change in the magnetoelastic effect induced by the

different grain size is responsible for large changes in the magnetic properties. This would confirm that CaFe_2O_4 is an ideal candidate for the study of frustration and “spatial chaos” in magnetic systems.

In addition to the main orthorhombic phase, a $\text{Fe} - \text{Cr}$ oxide impurity phase is also found in these films, that is ordered magnetically with T_N above 400 K. This unfortunately complicates the interpretation of magnetic data and prevents the use of these samples in devices or for other applications. Therefore, we conclude that the addition of Cr is a viable way to tune the magnetic properties and epitaxial growth of CaFe_2O_4 thin films. However, further optimization of the films is needed to obtain single-phase samples.

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Chapter 7

Periodicity-doubling cascades: direct observation in ferroelastic materials

Abstract

Very sensitive responses to external forces are found near phase transitions. However, transition dynamics and pre-equilibrium phenomena are difficult to detect and control. We have observed that the equilibrium domain structure following a phase transition in ferroelectric/ferroelastic BaTiO₃, is attained by halving of the domain periodicity multiple times. The process is reversible, with periodicity doubling as temperature is increased. This observation is reminiscent of the period-doubling cascades generally observed during bifurcation phenomena and, thus, it conforms to the “spatial chaos” regime earlier proposed by Jensen and Bak [1] for systems with competing spatial modulations.

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7.1 Introduction

Current interest in adaptable electronics calls for new paradigms of material systems with multiple metastable states. Functional materials with modulated phases bring interesting possibilities in this direction [1]. Ferroic materials are good prospective candidates because the modulation can be controlled by external magnetic, electric or stress fields. In magnetic materials, the presence of competing interactions can lead to wealth of modulated structures, exemplified by the axial next-nearest-neighbor Ising (ANNNI) model [2]. In ferroelectrics, interesting modulations in the form of domain patterns involve not only domains with alternating up and down polarization but also vortices [3] and ferroelectric skyrmions [4]. Ferroelectrics are often also ferroelastic [5] and display modulations of the strain.

When ferroelastic materials are grown in thin film form on a suitable crystalline substrate, they can be subjected to epitaxial strain, which typically relaxes by the formation of ferroelastic domains [6, 7]. In the simple case of ferroelastic systems with orthogonal lattices grown on a cubic substrate, different types of 90° domain configurations form, either so-called a/c domains (with the long c -axis alternating in-plane and out-of-plane) or a/b domains (long axis fully in-plane), depending on the sign of the strain imposed on the film by the substrate [8]. In the absence of

dislocations or other defects, ferroelastic domains in epitaxial films are expected to alternate periodically [6–8]. The periodicity of this modulation, or the domain width (w), is determined by the competition between the elastic energy in the domains and the formation energy of domain walls and is a function of the thin film thickness (d). For $d > w$, the relation $w = \beta d^{1/2}$ holds, as a particular case of the Kittel's law [6, 9–11]. The exponent β is primarily a function of the saturation value of the order parameter and anisotropy and, thus, is system dependent [39–41]. Ferromagnetic systems give rise to larger β values ($\approx 10\text{--}100 \text{ nm}^{1/2}$) than those found for ferroelectric systems ($\sim 1\text{--}5 \text{ nm}^{1/2}$), for which a strong crystalline anisotropy exists due to the presence of a polar axis [42].

In the ferroelastic case, geometrical effects are also important and discretization of domain widths, with minimum sizes determined by the need of lateral lattice coherence at the domain wall, have also been shown [12, 13]. Recently, an original hydrodynamics-like approach has been put forward, in which non-equilibrium ferroic domain structures are rationalized with respect to surface folding, wrinkling and relaxation [14]. As both misfit strain and domain wall energies change with temperature, the equilibrium patterns are temperature dependent and the question arises of how does the system evolve towards (global or local) equilibrium. While studies of ferroelectric domain formation and switching are common [15–20], less attention has been paid to microscopy studies of temperature-driven annihilation of ferroelastic nanodomains [21, 22] and it is only recently that experimental developments have allowed the in-situ study of domain dynamics [23–28].

In the present chapter, we report the direct observation of ferroelastic/ferroelectric domain evolution by sequential periodicity halving and doubling on BaTiO_3 thin films. Moreover, we present the results of phase field simulations [29–32] that support the observations showing that domain wall nucleation takes place in the center of existing domains. Period doubling cascades, associated to the proximity of order-to-chaos transitions, have been often observed as frequency doubling sequences in the time regime, but they have not yet been reported in spatially modulated systems. The results, thus, present strong evidence that ferroelastic systems with competing modulations are at the edge of chaos, as predicted for magnetic materials by Jensen and Bak [1].

7.2 BaTiO_3 films under low epitaxial strain

The experiments of this study have been performed on BaTiO_3 films grown under low epitaxial strain on SrRuO_3 -buffered NdScO_3 substrates, as described in Ref.[33] and discussed in the Introduction. Here, the low-strain condition flattens the energy landscape such that different ferroelectric domain configurations can be accessed within a moderate temperature range [34]. For small values of strain, the films display a low temperature phase, called ca_1/ca_2 , which is monoclinic [34]. However, since the monoclinic distortion and out-of-plane polarization components are rather small, this state is very close to an a_1/a_2 configuration, for which the c -axis lies in-plane for both domains and rotates by 90° at each domain wall. However, we notice that the in-plane anisotropy of the NdScO_3 substrate (not considered in Ref.[34]),

gives rise to two different in-plane lattice parameters and, thus, this phase is actually orthorhombic (the symmetry would be triclinic if the small out-of-plane component of the polarization was taken into account). Therefore, in this work the domain configuration with the long (polar) axis lying in-plane is named as a/b , instead of a_1/a_2 , as is typical in tetragonal $BaTiO_3$. When the temperature is raised above 50 °C, a phase transition to a pseudo-tetragonal a/c phase occurs. Due to the proximity to the transition point and to the first-order nature of the transition, coexistence of a/b and a/c domain structures at room temperature has been observed in some cases, as reported in Ref.[35]. Thus, for the sake of clarity, the transition at 50 °C can simply be described as a transition from a high-temperature, pseudo-tetragonal a/c domain structure to a low-temperature, pseudo-orthorhombic a/b domain structure [36].

Low strained $BaTiO_3$ films represent an ideal system for the study of the evolution of the domains periodicity because, unlike in other ferroics, here the transformation from a/c to a/b domains in these films is slow enough to be followed with piezoresponse force microscopy (PFM). Typical domain configurations below and above the transition can be seen in figure 7.1a and b, at 25 °C and 70 °C, respectively.

Figure 7.1: LPFM amplitude images showing the domain structure of a 90 nm thick $BaTiO_3$ film at **a** 25 °C and **b** 80 °C where the a/b and a/c domain structures are stable, respectively. **c** Drawing of the a/b matrix (black diagonal lines) with the a/c domain walls (green/purple dashed and green/white dashed lines are the two types of domain walls), adapted from Ref.[37].

Investigation of a large number of samples with thickness ranging from 30 nm to 330 nm confirms the robustness of the domain configurations and the expected $w = \beta d^{1/2}$ scaling law, with $\beta \sim 10 \text{ nm}^{1/2}$ for both the a/b and a/c domains. Here, the a/c structure refers to the domains generated while cooling from the paraelectric phase (above $T_C \approx 120$ °C). However, when the a/c domain configuration is reached upon heating from the a/b configuration, β is reduced to about $7 \text{ nm}^{1/2}$. We name this domain pattern with a slightly different domain periodicity, a/c' . A possible explanation for this observation is that the domain walls for the new a/c' domains preferably nucleate at the existing a/b domain walls. Since these domain walls are rotated by 45° (around the azimuthal axis) with respect to each other, the domain width relationship between these two domain structures is governed by a $\sqrt{2}$ factor. This would explain the approximately same ratio of the observed β values for the a/b

($\beta = 10 \text{ nm}^{1/2}$) and a/c' ($\beta = 7 \text{ nm}^{1/2}$) domain sizes. So pre-existing walls acting as nucleation and pinning sites will still give rise to a quadratic law if they are sufficiently periodic with a modified β scaling factor (see Supplementary Information of Ref.[38]).

Differences in β pre-factors within a single type of material can also be found when the sample morphologies produce different domain wall widths [43]. For ferroelastic domains in the very thin film limit (for $d < w$), Roytburd's approximations are not valid and a rigorous calculation of the elastic energy of the system leads to an approximate linear dependence of w with d [7, 8, 44, 45]. This law, thus, describes the optimal average domain size in thermodynamic equilibrium and in the absence of defects. When kinetic effects affect the final domain configuration, $w = \beta d^n$ scaling laws with $\frac{1}{2} < n < 1$ have been observed [46, 47]. Our observation thus reflects the important role of pre-existing domain walls in the nucleation of new domain walls and the balance between kinetic and thermodynamic effects (see Supplementary Information of Ref.[38]).

7.3 PFM

PFM experiments have been performed using Dual AC Resonance Tracking mode (DART) in an Asylum AFM system, which provides a natural signal amplification mechanism by following the cantilever mechanical contact resonance. The coexistence of two different domain structures in the samples, related to the first-order character of the transition, enhances the complexity of the structure and is responsible for the relatively weak contrast and the need for resonance tracking to observe the domains in the PFM images. Since for these samples the polarization is mainly in-plane, we performed Lateral-PFM measurements (LPFM) and used the lateral deflection to extract the corresponding lateral cantilever contact resonance, which is sensitive to the in-plane ferroelectric polarization perpendicular to cantilever axis. In this mode, b -domains are observed as dark lines since their in-plane component is parallel to the cantilever axis. After collecting PFM images of the films at room temperature, the samples were heated to the paraelectric phase at 200 °C for 5 minutes and then cooled down in steps of 10°. Measurements were performed at each temperature between 70 °C (about 20° above the nominal transition temperature) and 30 °C. The same measurement procedure has been followed to study the domains evolution upon heating. The analysis of the PFM images was performed by means of the Gwyddion software and domains periodicities have been extrapolated from the Fast Fourier Transform (FFT) of the LPFM Images for more accurate quantification.

In order to investigate the evolution of the domain formation, the films were heated to 200 °C and measured during cooling from 90 °C to 30 °C at steps of 5°. Figure 7.2 shows images of four stages of the domain evolution. During the cool-down process, the a/c structure arises below the para-ferro transition (fig. 7.2a). At a temperature of 45 °C (fig. 7.2b), the first b -domains start appearing inside the a/c matrix and increase in number as the temperature lowers. The a/b domain walls, signalled with white lines, reveal a domain periodicity of approximately $4w_0 = 400 \text{ nm}$ for this 90 nm thick film. Further cooling down to 35 °C (fig. 7.2d) shows new b -domains appearing halfway in between the existing domain walls, halving the domain

periodicity to about $2w_0 = 200$ nm. This value is, in turn, approximately double that found at room temperature, after the sample has equilibrated for several hours and the high-temperature domain configuration has disappeared $w_0 = 100$ nm (fig. 7.2d). Thus, two sequential periodicity halving events take place during the transition from the a/c to the a/b domain configuration on cooling.

Figure 7.2: LPMF amplitude images of the temperature evolution of the domain structure of a 90 nm thick $BaTiO_3$ film upon cooling. Images taken at **a** 55 °C, **b** 45 °C, **c** 35 °C and **d** 30 °C after allowing the equilibrium domain period ($w_0 = 100$ nm) to be reached. The white solid lines indicate the a/b domain walls.

A similar mechanism, albeit shifted in temperature due to thermal hysteresis, is observed when heating the samples through the phase transition, as shown in figure 7.3. The transition from a/b to a/c domains is followed on heating from 30 °C to 70 °C at 5° steps. The initial a/b domain periodicity at 30 °C is again $w_0 = 100$ nm (fig. 7.3a). Upon heating, the domain walls start to rearrange and at 55 °C (fig. 7.3b), domains with $w = 2w_0$ appear. With increasing temperature up to 65 °C (fig. 7.3c), $w = 4w_0$ becomes the most abundant period. Finally at 60 °C (fig. 7.3d), a domain with a size of $w = 8w_0$ can also be observed within the area of the image. This process is reversible and can be observed multiple times upon cooling and heating below and above T_C .

Figure 7.3: LPFM amplitude images of the temperature evolution of the domain structure of a 90 nm thick $BaTiO_3$ film upon heating. Images taken at **a** 30 °C, with the equilibrium domain period ($w_0 = 100$ nm), **b** 55 °C, **c** 60 °C and **d** 65 °C. The white solid lines indicate the a/b domain walls.

The periodicity values are obtained by performing the Fast Fourier Transform (FFT) of the LPFM images, as shown in figure 7.4. In the line scans, symmetrical peaks around the middle position are clearly visible that corresponds to the periodic domains. From these images the wall-to-wall distance is calculated. Therefore, the transition to the a/c phase takes place by sequentially annihilating one every other b -domain and, thus, the apparent domain periodicities follow a Cantor set sequence with $w = 2^n w_0$ ¹. Pre-fractal domain patterns following Cantor set sequences have also been observed in ferroelectrics under electric field [48].

Our experiments also reveal the self-repairing of “wrongly” nucleated domain walls, indicating that the center of existing domains is the equilibrium position for new domains. Figures 7.5a and b show b -domains right after their formation, displaying unequal widths, probably due to pinning by the local defect structure (it is well known that defects act as preferred nucleation points for new domains [11, 41]). Due to the random nature of these defects, we have occasionally observed deviations from the apparent 2^n domain evolution law. However, the elastic forces in this situation

¹This is an apparent rule because it ignores the finite width of the b -domains not properly resolved in PFM images.

Figure 7.4: Line profiles of the FFT transform (in the inset) of the LPFM amplitude images of figure 7.3. Images taken at **a** 30°C , **c** 60°C and **d** 65°C .

lead to a movement of the b -domains with respect to each other to reach a position equidistant between the neighbouring b -domains (fig. 7.5a-d). This sideways rearrangement of the domain walls to achieve a periodic configuration is not possible in the presence of larger defects, as shown in figure 7.5e-f.

7.4 Simulations

Theoretical simulation of the domain evolution in PFM experiments have also been conducted by our collaborators Jacob Zorn and Long-Quing Chen at the Department of Materials Science and Engineering at the Pennsylvania State University. Phase-field simulations are performed using the time-dependent Ginzburg-Landau equations for BaTiO_3 under strain. Details of the theoretical methods are not described here and can be found in Ref.[38].

The results of the simulations are shown in figure 7.6. Here, it can be seen that

Figure 7.5: Self-repair of the domain periodicity in a 90 nm thick $BaTiO_3$ film at 30 °C. LPFM amplitude images of **a** newly formed a/b domains and **c** after waiting for 1 hour. The initial irregular separation and final periodic one are shown in **b** and **d** as the height profile of the white lines in the LPFM images. **e** LPFM amplitude image of the same sample in the presence of a large particle signalled by a white arrow. **f** The domains are not able to re-arrange even after 12 h.

the alternating pseudo- a/b phase appears at low temperatures and an a/c tetragonal structure predominates at high temperatures. Figure 7.6a shows that the domain structure of the high temperature phase, a/c , agrees with the experimental observations previously captured by Everhardt *et al.* [33] with $\{101\}$ domain walls (thus consistent with the $[010]$ projections on the PFM images). These simulations also demonstrate the change in domain wall orientation from $\{101\}$ to $\{110\}$, also consistent with PFM observations, with the “new” (orthorhombic) domains forming in the middle of the “old” (tetragonal) domains. An analysis of the phase-field simulation results in a β coefficient of $\beta = 7 \text{ nm}^{1/2}$ at high temperature and $\beta = 10 \text{ nm}^{1/2}$ at low temperature, supporting our experimental observations in figure 7.2).

Investigation of the elastic energies agrees with the experimental observation of stress relaxation being achieved by the formation of new domains at the center of old domains. To increase the simulation areas, we have also performed 2D simulations (fig. 7.6b). In this case, the orientation of the polarization in the two phases does not fully agree with the experiment due to the simplicity of the model, but successive nucleation of new domains halfway between existing domain walls is clearly observed as the temperature is decreased. In addition, it is shown that the “new” domains nucleate near the film-substrate interface, at the 90° (100) domain wall and along the

$\langle 110 \rangle$ directions.

Thus, periodicity changes take place by the formation of new stress-relieving elements (singularities) exactly in the center of the old domains, as already predicted by dynamic pattern formation [49, 50]. In the current measurements, a new b -domain (thus, a pair of domain walls) conforms such singularity, but other types such as single domain walls, dislocations, cracks, etc. are governed by similar physics. In the case of ferroelastic domains, increasing the strain (e.g. by decreasing the temperature) would repeat the process between a first-generation singularity and a second generation singularity, and so on.

Figure 7.6: **a** Three-dimensional and **b** two-dimensional domain structures generated by the phase field method, indicating the misfit strain conditions that led to their formation. In **a**, as the temperature decreases from 100°C to 25°C , a change in domain wall orientation from 101 to 110 takes place signalling the phase transition. It is also apparent that the new domains form at the half-way point between the original domain walls. In **b**, subsequent nucleation of a new domain halfway between existing domain walls (shown by the open vertical arrows) is also shown to take place as the temperature decreases from **ii** 80°C to **ii** 60°C and to **iii** 25°C . Domain notation: $a_1 = (P_0, 0, 0)$, $a_2 = (0, P_0, 0)$, $c = (0, 0, P_0)$, $O_{1+} = (P_0, P_0, 0)$, $O_{1-} = (-P_0, -P_0, 0)$, $O_{2+} = (P_0, -P_0, 0)$, $O_{2-} = (-P_0, P_0, 0)$, $O_{4+} = (P_0, 0, -P_0)$, $O_{5+} = (0, P_0, P_0)$, $O_{5-} = (0, -P_0, -P_0)$, $O_{6+} = (0, P_0, -P_0)$, $O_{6-} = (0, -P_0, P_0)$ and $R_1 = (P_0, -P_0, -P_0)$.

More generally, in addition to boundary conditions and the effect of substrates, effective interactions between domain walls and evolution of domain wall structures can come from other physical processes. If several order parameters are activated to generate a domain wall, the energy landscape is complex with several minima, which combine to define the domains and the wall structures. Lateral extensions of domain walls would favour the wall-wall interactions and such phenomena have been explored in bi-quadratic or linear-quadratic coupling between order parameters [51–56]. Atomistic approaches are very limited [57, 58] so far and no firm conclusions

can be reached for direct interactions. If no such wall-wall interaction existed and no external constraints occur, then the pattern energy density would depend only on the total number of domain walls and their self-energy.

Periodicity can also originate from nucleation. Domains nucleate from the surface or an interface and the nucleation centres repel each other. The periodicity and deviations from a periodic array stem from the mistakes in distribution of nucleation sites, which would often form Cantor sets leading to phenomena like period doubling and local periodicity disorder [59–61]. Finally, we mention that in free crystals periodicity of domain walls, period doubling and disorder can be induced by the sideways movement of domains in terms of front propagation [50, 55, 62, 63].

7.5 Conclusions

In conclusion, in this chapter we have discussed the direct observation of spatial period doubling/halving sequences consistent with those found as part of the clock-model calculations [64]. This behaviour belongs to a class of scaling phenomena known as period-doubling cascades that are mathematically investigated by means of bifurcation theory and characterize systems at the “edge-of-chaos”. Even though a link with spatially modulated phases of matter has been made [1], spatial period doubling cascades had not yet been observed experimentally. Thus, our observation of domain periodicity halving should not be exclusive of the system under investigation, but represents a more general mechanism of transformation in materials with competing periodic structures. Interestingly, the presence of different coexisting domain widths in epitaxial thin films is ubiquitous in the literature [46, 47, 65–67]. Careful analysis shows that these widths often appear to be governed by the 2^n relationship expected from periodicity halving/doubling. As examples we can point to the $PbZr_{0.2}Ti_{0.8}O_3$, thin films grown on $SrTiO_3$ by Ganpule *et al.* [65], which have c -domain sizes of 22, 44, 88 and 172 nm, related by period doubling. Other examples are figures 1a and b in Ref.[68], where the different sizes of c -domains that coexist along the b -axis of a $PbTiO_3$ thin film grown on a $DyScO_3$ substrate are 75, 150 and 300 nm. More examples of discretization of domain sizes in various ferroelastic can be found [12, 13], suggesting a similar temperature evolution of the domain periodicity sometimes disrupted most likely due to the presence of local defects.

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Appendix A

X-ray photoelectron spectroscopy

The oxygen stoichiometry determination in PLD grown films is a delicate issue that is often under debate. In general, oxygen vacancies can form during the sample synthesis, however we expect it to be limited in our case due to the use of relatively high oxygen pressure (0.2 mbar) during growth and annealing (200 mbar). If oxygen vacancies were present, the requirement of charge neutrality would induce a change in the oxidation state of Fe from 3+ to 2+, which as mentioned in the main text, is not observed in Mössbauer experiments. Moreover, we have analysed our samples by means of x-ray photoelectron spectroscopy (XPS) to better determine the oxidation state and chemical environment of the Fe and O . Despite XPS is a surface technique and, thus, it cannot be used alone to draw conclusions about the stoichiometry of the full film, we could rule out the presence of Fe^{2+} and oxygen vacancies at the surface.

Figure A.1a shows the $Fe\ 2p$ peaks, with an enlargement of the low binding energy region (fig. A.1b). Here, we observe two peaks at 0.715 and 0.728 KeV, corresponding to the $Fe\ 2p_{3/2}$ and $2p_{1/2}$, respectively. These values are consistent with Fe in the 3+ oxidation state. Moreover, the full area best fitted by the G-S multiplet characteristic of Fe^{3+} (fig. A.1d). If Fe^{2+} was present it would appear as a shoulder at lower binding energy. The broad peak (yellow in fig. A.1d) is at a too low energy to belong to Fe^{2+} and it is not well fitted by characteristic G-S multiplet of Fe^{2+} . Therefore, this is most likely a shake-off peak or due to some metallic Fe^0 . To properly fit this region of the spectrum we also took into account the typical satellite peak, between the the $Fe\ 2p_{3/2}$ and $2p_{1/2}$ peaks, as well as the so-called surface peaks and pre-peaks that are due to atoms with slightly different bonding environments located at the surface and in proximity of defects respectively.

Figure A.1c shows the XPS spectrum in the O region. As it can be seen, the oxygen peak can be properly fitted with a single peak at 0.533 keV (consistent with $O\ 1s$), indicating that the element is present in a single oxidation state and uniform environment. In case of oxygen vacancies or interstitial oxygen defects additional peaks would be expected at higher binding energies. The $Ca\ 2p$ region of the spectrum (fig. A.1d) is deconvoluted into four peaks, a pair at 0.349 keV and 0.353 keV belongs to the majority of Ca atoms and a second couple, shifted to slightly larger energies (0.352 keV and 0.356 keV), probably belongs to Ca atoms at the surface. The fitting of this region is also complicated by the superposition of the $Au\ 3d_{3/2}$ peak at 0.352 keV that is caused by a Au coating layer evaporated on the sample surface to be used as a reference for calibration of the XPS energies. All the parameters extracted from the fitting of the XPS spectra are reported in table A.1. From the areas of the peaks and taking into account the atomic sensitivity factor (ASF) for each atom we

calculated the stoichiometry of the sample that results to be: $CaFe_{1.5}O_8$.

Table A.1: Fit parameters of the XPS spectrum¹ of a 90 nm thick $CaFe_2O_4$ film.

Peak	Position (eV)	FWHM (eV)	ASF (eV)	A/ASF
Pre-peak	710.169	3.090	2.957	758.5164018
Fe 2p3/2	714.700	3.983	2.957	3324.645587
Satellite	723.118	3.796	2.957	797.142374
Fe 2p1/2	728.320	3.983	2.957	1662.322624
Shake-off	710.678	3.13	2.957	574.3287115
Pre-peak	712.790	1.511	2.957	182.5701725
G-S multiplet Fe^{3+}	713.794	1.400	2.957	583.2742645
G-S multiplet Fe^{3+}	714.694	1.355	2.957	478.2847481
G-S multiplet Fe^{3+}	715.508	1.492	2.957	387.4108894
G-S multiplet Fe^{3+}	716.408	1.502	2.957	244.0686507
Surface-peak	717.523	1.240	2.957	79.67500845
Pre-peak	530.315	1.883	0.711	651.5822785
O 1s	533.080	2.315	0.711	6287.171589
Surface-peak	536.127	1.506	0.711	125.7552743
Pre-peak	347.786	1.1614	1.833	125.6726678
Ca 2p3/2 (1)	349.380	1.864	1.833	470.4909984
Ca 2p3/2 (2)	352.133	1.583	1.833	53.38352428
Au 4d3/2	352.376	4.066	6.25	175.80096
Ca 2p1/2 (1)	353.478	1.864	1.833	235.2454992
Ca 2p1/2 (2)	356.133	1.583	1.833	26.69176214

¹The Fe portion of the spectrum reported here is obtained from the sum of multiple scans in order to increase the signal to noise ratio. Therefore the areas of the peaks are not the ones used for the stoichiometry calculation.

Figure A.1: XPS spectrum of a 90 nm thick CaFe_2O_4 film. **a** $\text{Fe } 2p$ and **b** enlargement of the low binding energy region fitted by the characteristic G-S multiplet of Fe^{3+} , **c** $\text{O } 1s$ and **d** $\text{Ca } 2p$.

We also performed XPS measurements on two samples with nominal composition $\text{CaFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ annealed in O_2 atmosphere and a mixture of O_2 and Ar respectively. Similar XPS peaks and peaks position are observed in both cases, but a different stoichiometry is calculated from the peaks areas: $\text{CaFe}_{1.1}\text{Cr}_{0.3}\text{O}_8$ and $\text{CaFe}_{1.3}\text{Cr}_{0.6}\text{O}_{3.2}$. This indicates that the cation stoichiometry is close to the desired one and the Oxygen content is largely influenced by the annealing atmosphere. Therefore we choose the Oxygen reach atmosphere as the standard growth condition for the rest of our samples. Moreover, differently from the undoped samples, here the $\text{O } 1s$ area of the spectrum (fig. A.2c) is deconvoluted into two almost equally large peaks at 0.529 and 0.532 keV, indicating two types of bonding environments. Similarly the $\text{Fe } 2p$ (fig. A.2a) and $\text{Cr } 2p$ (fig. A.2b) regions are also optimally fitted with two kinds of each atomic species. Both the $\text{Fe } 2p$ (0.725 keV and 0.711 keV) and $\text{Cr } 2p$ (0.585 keV and 0.575 keV) peaks are at relatively large energies, indicating that the atoms are most likely in the 3+ oxidation state. Differently from the undoped ferrite here the $\text{Ca } 1s$ region of the spectrum (fig. A.2d) is much simpler (C was used as a reference instead of Au) and only shows one type of bonding environment. This results are in good

Table A.2: Fit parameters of the XPS spectrum² of a $\text{CaFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ film annealed in 200 mbar of O_2 .

Peak	Position (eV)	FWHM (eV)	ASF (eV)	A/ASF
Cr 2p3/2 (1)	575.431	2.55	2.427	6116.596621
Cr 2p3/2 (2)	578.703	4.087	2.427	1307.189534
Cr 2p1/2 (1)	585.266	2.879	2.427	4719.229501
Cr 2p1/2 (2)	588.215	2.371	2.427	336.4911413
O 1s (1)	529.524	2.005	0.711	4720.589311
O 1s (2)	531.661	2.755	0.711	5177.018284
Fe 2p3/2 (1)	711.248	3.029	2.957	496.8285424
Fe 2p3/2 (2)	713.715	3.341	2.957	358.7544809
Shake-off	719.689	6.238	2.957	247.8018262
Fe 2p1/2 (1)	725.219	3.971	2.957	356.6374704
Fe 2p3/2 (2)	728.693	2.721	2.957	58.53297261
Pre-peak	733.080	4.644	2.957	194.7007102
Ca 2p3/2 (1)	346.238	1.779	1.833	854.1091107
Ca 2p1/2 (2)	349.702	1.779	1.833	401.8166939

agreement with the presence of an Iron-Chromium oxide impurity phase discussed in Chapter 6.

The fit parameters relative to the scans of the sample annealed in O_2 atmosphere are listed in table A.2.

We believe that the information extracted from the fitting of the XPS data alone is not conclusive for the determination of the stoichiometry and oxidation state of the atomic species in our films. This is because the analysis of the data is subject to some systematic errors:

- the technique is only sensitive to the surface layer and due to the impossibility of performing XPS in-situ without breaking the vacuum we can not prevent the absorption of moisture from the atmosphere.
- the ASF used are obtained from the literature but refer to a beam-sample geometry that is not exactly the same as in our experimental setup.
- in the fitting process there is no standard procedure for the attribution of the position and width of extra peaks (satellites, pre-peaks, surface peaks, shake-off peaks) if not by comparison with previous reports. This can easily lead to overfitting issues that can largely affect the extracted parameters.

Therefore, we decided not to include the XPS data in the main body of this thesis but only append it to complement the data from other experimental techniques.

²The *Fe* and *Cr* portions of the spectrum reported here are obtained from the sum of multiple scans in order to increase the signal to noise ratio. Therefore the areas of the peaks are not the ones used for the stoichiometry calculation.

Figure A.2: XPS spectrum of a $\text{CaFe}_{1.5}\text{Cr}_{0.5}\text{O}_4$ thin film annealed in 200 mbar of O_2 . **a** Fe 2p, **b** Cr 2p, **c** O 1s and **d** Ca 2p.

Appendix B

Raw data and fit parameters of the electrical measurements

Table B.1: Raw data and fit parameters multi-domain device with H rotating in the $i - t$ plane

T (K)	A_a	B	y_0	ϕ_a	ϕ_{OH}	w	Adj. R^2	R_{0T} (Ω)	R_{0L} (Ω)	g
5	-4.64983E-5	1.6051E-5	-5.57191E-7	4.74723	116.61412	180	0.99848	2.4736E-4	7.65636	1
20	-5.74579E-5	1.64489E-5	-2.4783E-7	5.59422	117.57278	180	0.99876	1.76431E-4	7.73707	1
50	-5.43766E-5	1.64639E-5	9.92253E-6	5.24293	117.98595	180	0.99847	-8.20165E-4	7.73665	1
80	-2.77024E-5	1.3994E-5	4.08E-6	4.3914	117.33723	180	0.99439	-0.00221	8.66416	1
100	-7.20989E-6	1.07609E-5	9.73378E-6	-6.70202	116	180	0.9844	-0.00321	9.98882	1
120	1.19407E-5	9.65247E-6	8.2972E-6	7.7654	116	180	0.99803	-0.00409	10.87195	1
150	3.62701E-5	9.86304E-6	1.82809E-5	4.35902	116	180	0.99538	-0.00542	10.87256	1
180	7.08157E-5	8.85893E-6	1.81277E-5	3.89305	116	180	0.99833	-0.00671	11.72906	1
200	9.04709E-5	7.28038E-6	1.16866E-5	3.98655	116	180	0.99791	-0.00748	14.95138	1
240	1.20265E-4	6.52736E-6	2.39356E-5	3.72623	116	180	0.99549	-0.00899	16.49915	1
270	1.34207E-4	6.56413E-6	2.08598E-5	4.0477	116	180	0.9984	-0.01008	17.62032	1
300	1.41335E-4	6.54266E-6	1.24804E-5	3.95631	116	180	0.99833	-0.011	18.7156	1

Table B.2: Raw data and fit parameters single-domain device with H rotating in the $i - t$ plane

T (K)	A_a	B	y_0	ϕ_a	ϕ_{OH}	w	Adj. R^2	R_{0T} (Ω)	R_{0L} (Ω)	g
5	1.84526E-4	-2.96774E-6	1.22196E-5	1.01603	70.71162	180	0.99241	-0.51915	13.42397	2/3
20	1.42046E-4	-4.98684E-6	1.22556E-5	0.73967	70.70014	180	0.99219	-0.52243	14.36561	2/3
50	1.12921E-4	-4.92743E-6	1.00898E-5	0.90898	70	180	0.9862	-0.55504	15.38991	2/3
100	1.58735E-4	-6.24356E-6	-8.99756E-6	1.03101	70	180	0.9822	-0.48313	16.37646	2/3
130	1.91831E-4	-7.09376E-6	-1.06997E-5	0.65451	70	180	0.98598	-0.52968	17.74936	2/3
160	2.06387E-4	-5.71469E-6	-1.77286E-7	0.081	70	180	0.99199	-0.5743	20.40537	2/3
200	2.86646E-4	-6.41679E-6	-1.81072E-5	-0.54502	70	180	0.99492	-0.62828	21.98629	2/3
250	2.85596E-4	-5.47176E-6	-1.86608E-5	-0.37834	70	180	0.99636	-0.69122	24.22041	2/3
300	2.90175E-4	-5.42033E-6	-1.96993E-5	-0.43332	70	180	0.99665	-0.75041	25.77561	2/3

Table B.3: Raw data and fit parameters multi-domain device with H rotating in the $n - t$ plane

T (K)	A_b	C	y_0	ϕ_b	w	Adj. R^2	$R_{0L}(\Omega)$	g
5	3.01651E-4	1.28345E-8	-1.3279E-4	180	93.83072	0.91963	7.13122	1
10	3.22494E-4	-5.22562E-8	-1.30117E-4	180	93.54357	0.91587	7.14386	1
15	3.22733E-4	9.79661E-8	-1.58906E-4	180	94.10282	0.93541	7.1363	1
22	3.35693E-4	2.19881E-7	-1.88869E-4	180	94.01499	0.92983	7.21778	1
25	3.31701E-4	5.55742E-9	-1.45349E-4	180	92.07374	0.94032	7.29515	1
40	3.03108E-4	2.71646E-7	-1.85325E-4	180	93.54851	0.91312	7.71909	1
45	2.7044E-4	-3.43123E-7	-4.7976E-5	180	95.03319	0.94006	7.8855	1
50	2.58711E-4	-5.51117E-8	-1.0105E-4	180	93.22224	0.91613	8.07166	1
55	2.84181E-4	5.28664E-8	-1.32598E-4	180	95.84543	0.92808	8.30684	1
60	2.73283E-4	2.93443E-7	-1.77373E-4	180	92.09834	0.93607	8.50311	1
70	2.46206E-4	5.29471E-7	-2.27149E-4	180	95	0.94637	8.90082	1
85	2.72514E-4	2.56035E-7	-1.68202E-4	180	95.6153	0.94364	9.56233	1
100	2.5297E-4	1.92869E-7	-1.47464E-4	180	94.82507	0.9236	10.21547	1
115	2.7722E-4	-1.07401E-6	9.37867E-5	180	92.19913	0.95631	10.84254	1
130	2.67138E-4	7.31915E-7	-2.8139E-4	180	95.81585	0.963	11.44728	1
145	2.66122E-4	4.75995E-7	-2.24577E-4	180	95	0.95702	12.03774	1
160	2.60942E-4	3.58725E-7	7.57746E-5	180	91.77083	0.86131	12.62634	1
175	2.77653E-4	4.0818E-7	-2.15072E-4	180	95	0.93788	13.20293	1
190	2.79829E-4	-2.25398E-8	-1.16039E-4	180	94.87607	0.92215	13.77063	1
197	3.06914E-4	-2.61678E-7	-7.98337E-5	180	95.26717	0.93587	14.01142	1
203	3.0923E-4	-8.93929E-8	-1.26453E-4	180	94.21647	0.95538	14.45532	1
209	3.06335E-4	-8.37264E-8	-1.2502E-4	180	95.40099	0.94118	14.67893	1
220	3.18568E-4	-5.41645E-8	-1.2776E-4	180	92	0.93274	15.45218	1
250	3.36532E-4	-4.23329E-8	-1.36959E-4	180	93.92344	0.94093	16.003	1
275	3.43646E-4	4.28903E-8	-1.58032E-4	180	92	0.95925	16.89473	1
300	3.08641E-4	1.20147E-6	-3.75881E-4	180	95.02626	0.97003	17.75115	1
325	3.21585E-4	-3.20475E-7	-7.55559E-5	180	92.76755	0.94715	18.65087	1
350	3.13847E-4	-1.47666E-6	1.58397E-4	180	92	0.97689	19.46428	1

Table B.4: Raw data and fit parameters multi-domain device with H rotating in the $n - i$ plane

T (K)	A_b	C	y_0	ϕ_b	w	Adj. R^2	$R_{0L}(\Omega)$	g
5	2.17834E-4	6.15101E-7	-1.52683E-4	91.61495	180	0.93149	7.76752	1
10	2.7929E-4	-5.47644E-8	-1.2741E-4	91.60394	180	0.93272	7.79137	1
20	3.14918E-4	1.28809E-7	-1.63873E-4	89.38364	180	0.93434	7.86239	1
30	2.99108E-4	-1.68219E-8	-1.39958E-4	90.77885	180	0.95026	8.0544	1
45	3.26324E-4	1.05939E-7	-1.65803E-4	91.15064	180	0.97332	8.90423	1
60	2.81656E-4	1.68629E-7	-1.52181E-4	89.12628	180	0.9353	9.557	1
75	2.2758E-4	3.70235E-7	-1.47069E-4	90.9572	180	0.9091	10.62427	1
85	2.30436E-4	1.17195E-7	-1.2191E-4	88.58138	180	0.89679	10.60789	1
95	1.95287E-4	5.63232E-7	-1.52078E-4	90	180	0.90794	10.64069	1
105	1.95287E-4	5.63232E-7	-1.52078E-4	90	180	0.93149	11.74109	1
120	1.70841E-4	5.05096E-7	-1.34367E-4	89.55238	180	0.92307	13.68218	1
130	1.31889E-4	4.05796E-7	-1.05423E-4	89	180	0.95211	14.09963	1
140	9.71424E-5	3.74412E-7	-8.54699E-5	90.64919	180	0.90261	14.09246	1
150	1.4491E-4	4.15506E-7	-1.12626E-4	89.48314	180	0.90464	14.09181	1
160	1.08733E-4	4.1536E-7	-9.53285E-5	89.59176	180	0.90081	14.08696	1
170	1.05633E-4	3.54961E-7	-8.75779E-5	92.75691	180	0.7453	14.08207	1
180	9.67924E-5	5.40546E-7	-1.03001E-4	94.34094	180	0.92053	14.06899	1
190	1.07706E-4	4.708E-7	-1.00612E-4	90	180	0.82186	14.07053	1
200	7.88766E-5	6.51494E-8	-4.45126E-5	88.54054	180	0.56418	14.06983	1
215	7.70151E-5	8.90693E-8	-4.58256E-5	90	180	0.71277	17.23194	1
230	9.36628E-5	-1.0716E-7	-3.36089E-5	87.78266	180	0.69394	17.11007	1
245	5.3812E-5	4.83002E-7	-1.09409E-4	99.00143	180	0.73193	17.67556	1
275	2.29837E-5	-2.82559E-7	3.32873E-5	90	180	0.40831	17.67613	1
300	5.31526E-5	1.66111E-8	-2.69713E-5	90	180	0.36531	19.23116	1

Summary

The aim of this thesis is to investigate the coexistence and evolution of modulated structures in ferroic materials. Periodic structures and patterns are ubiquitous in nature and similar morphologies develop in very different systems, regardless of their microscopic structure and the nature of their interactions. The period of the modulation is determined by the relative strength of competing interactions acting on the system and corresponds to a minimum in the energy landscape. The way in which systems evolve out of equilibrium towards metastable configurations is also common between different systems, suggesting an underlying universal mechanism. At the boundary between stable states, where a phase transition occurs, systems can display anomalous behaviour characterized by either phase coexistence and hysteresis or large fluctuations of macroscopic parameters and long-range correlations, depending on the order of the transition. Mathematically, this is described by the theory of phase transition and critical phenomena. A better understanding and control of systems at the edge of a phase transition can allow for designing materials with enhanced response to external stimuli and novel functionalities, making modulated structures promising candidates for application in electronic devices.

In this thesis I study *two exemplary systems* with competing modulated structures. *The first one is the antiferromagnet CaFe_2O_4* , in which two magnetic spin arrangements, termed A and B, coexist over a certain range of temperature below approximately 200 K, where the material orders magnetically. Full agreement on the mechanism of the A/B phase coexistence has not been reached yet, but recent work from Lane *et al.* (Physical Review B 104, 104404, 2021) suggests that the A phase finds its origin in the freezing of antiphase boundaries created by thermal fluctuations of the B phase. However, large variations of behaviour have been observed in different samples (eg. powders or single crystals), calling for the need to obtain high quality samples that are key for decoupling the intrinsic properties of the material from the effect of defects and disorder.

In this work, first the synthesis of thin films of CaFe_2O_4 grown epitaxially on TiO_2 (110) substrates is optimised (Chapter 3). The films are crystalline and single phase and display a complex domain structure consisting of two out-of-plane orientations each with three in-plane crystal directions. Careful characterization of the structure by means of complementary techniques, reveals that such domains form due to the epitaxial relation of the CaFe_2O_4 film with a native CaTiO_3 layer at the interface with the substrate. Although relaxation of the crystal lattice occurs and, thus, epitaxial strain cannot be used as a means to tune the structure of the material in this case, my results open the way for further investigation of the epitaxial growth of strained CaFe_2O_4 films on CaTiO_3 -buffered substrates.

The magnetic properties of the CaFe_2O_4 films are also investigated both globally and locally (Chapters 4 and 5). Here I show that, macroscopically, the samples

display long-range antiferromagnetic ordering below 185 K, with a single magnetic transition, that is second-order type with critical exponent $\beta \approx 1/3$. A net in-plane magnetization is also present, revealed by hysteresis loops and microscopy images, that peaks at around 120 K and that was attributed before by Stock *et al.* (Physical Review Letters 119, 257204, 2017) to magnetic antiphase boundaries. Signs of irreversible processes are also evident from the large splitting between the field-cooled and zero-field-cooled susceptibility that persists up to high temperatures and does not follow the expected Curie-Weiss behaviour. This is also reflected in the persistence of a large positive modulation in the spin Hall magnetoresistance measured, for the first time, at the interface between *Pt* and *CaFe₂O₄* up to 400 K. These measurements indicate the coexistence of both an antiferromagnetic ordering and uncompensated, uncoupled moments over a large temperature range. Although the origin of the net magnetization is not fully understood yet, I hypothesize that it can arise from the coupling of the antiphase boundaries in proximity of the critical transition, where long range correlations occur. Thus this work strongly indicates that, in *CaFe₂O₄* thin films, the one of the two magnetic orderings (possibly A) is not a thermodynamically stable phase but rather a double modulation that arises from local variations consistent with antiphase boundaries. The stability of the two magnetic structures can also be influenced by doping and, in particular, substitution by *Cr*. In Chapter 6 it is shown that this is the case in the thin films too, as the addition of *Cr* promotes the stability of the B phase and decreases the ordering temperature of the material. Furthermore, upon *Cr*-substitution changes in the domain structure of the films also occur.

The second system studied in this work are *BaTiO₃* thin films where low epitaxial strain induces a rich phase diagram of periodic stripe domain patterns. In particular, I focus on the transition between a purely in plane (*a/b*) ferroelectric and ferroelastic domain configuration at room temperature and an alternating in-plane out-of-plane one (*a/c*) at higher temperature (Chapter 7). The transition is first order and, thanks to the slow dynamics of domains formation, can be followed with piezoresponse force microscopy upon heating and cooling. Here the equilibrium periodicity is obtained by sequential period doubling/halving events, reminiscent of period doubling cascades in dynamical systems. This, not only may represent a more general mechanism of transformation in materials with competing periodic structures, but is also one of the first direct reports of the route to “spatial chaos” in a condensed matter system.

Samenvatting

Het doel van dit proefschrift is om de evolutie en het naast elkaar bestaan van gemoduleerde structuren in ferroïsche materialen te onderzoeken. Periodieke structuren zijn alomtegenwoordig in de natuur en vergelijkbare morfologiën ontwikkelen zich in zeer verschillende systemen, ongeacht hun microscopische structuur en de aard van hun interacties. De periode van de modulatie wordt bepaald door de relatieve sterkte van de concurrerende interacties die inwerken op het systeem en komt overeen met een minimum in het energielandschap. De manier waarop systemen evolueren vanuit evenwicht naar metastabiele configuraties is ook vergelijkbaar voor verschillende systemen, wat een onderliggend universeel mechanisme suggereert. In het grensgebied tussen stabiele toestanden, waar een fase overgang plaatsvindt, kunnen systemen afwijkend gedrag vertonen. Afhankelijk van de orde van de overgang, wordt deze gekenmerkt door fasecoëxistentie, hysteresis, of grote fluctuaties van macroscopische parameters en langeafstandscorrelaties. Wiskundig gezien wordt dit beschreven door de theorie van faseovergangen en kritische verschijnselen. Een beter begrip en controle over systemen op de rand van een faseovergang, kan het mogelijk maken om materialen te ontwerpen met een verbeterde respons op externe stimuli en nieuwe functionaliteiten. Hierdoor kunnen gemoduleerde structuren veelbelovende kandidaten zijn voor toepassingen in elektronische apparaten.

In dit proefschrift bestudeer ik *twee voorbeeldsystemen* met concurrerende gemoduleerde structuren. *De eerste is de antiferromagneet CaFe_2O_4* , waarin twee magnetische structuren, A en B genaamd, naast elkaar bestaan, beneden ongeveer 200 K, waar het materiaal magnetisch ordent. Er is nog geen volledige overeenstemming bereikt over het mechanisme van het naast elkaar bestaan van de A/B-fase, maar recent werk van Lane *et al.* (Physical Review B 104, 104404, 2021) suggereert dat de A-fase zijn oorsprong vindt in het bevriezen van de antifase-grenzen gecreëerd door thermische fluctuaties van de B-fase. Er zijn echter grote verschillen waargenomen in het gedrag van verschillende monsters (bijv. poeders of eenkristallen), waardoor het noodzakelijk is om monsters van hoge kwaliteit te verkrijgen. Deze monsters zijn essentieel om de intrinsieke eigenschappen van het materiaal te ontkoppelen van het effect van defecten en wanorde.

In dit werk wordt eerst de synthese geoptimaliseerd van dunne CaFe_2O_4 films die epitaxiaal op $\text{TiO}_2(110)$ substraten worden gegroeid (hoofdstuk 3). De films zijn kristallijn, enkelfasig en vertonen een complexe domeinstructuur, die bestaat uit twee domeinoriëntaties die haaks op het vlak staan, elk met drie kristalrichtingen in het vlak. Zorgvuldige karakterisering van de structuur, door middel van complementaire technieken, onthult dat dergelijke domeinen worden gevormd door de epitaxiale relatie van de CaFe_2O_4 film met een natieve CaTiO_3 laag op het grensvlak met het substraat. Hoewel er een relaxatie van het kristalrooster optreedt, en in dit geval epitaxiale spanning dus niet gebruikt kan worden als een middel om de structuur van het

materiaal te beïnvloeden, openen mijn resultaten de weg voor verder onderzoek van de epitaxiale groei van gespannen CaFe_2O_4 films op CaTiO_3 gebufferde substraten.

De magnetische eigenschappen van de CaFe_2O_4 films worden zowel globaal als lokaal onderzocht (hoofdstukken 4 en 5). Hier laat ik zien dat de monsters macroscopisch een lange-afstand antiferromagnetische ordening vertonen beneden 185 K, met een enkele magnetische overgang van de tweede orde en een kritische exponent $\beta \approx 1/3$. Er is ook een netto magnetisatie aanwezig in het vlak, onthuld door de observatie van hystereselussen en met behulp van microscopie beelden, met een maximum rond 120 K die eerder werd toegeschreven aan magnetische antifasegrenzen door Stock *et al.* (Physical Review Letters 119, 257204, 2017). Teken van onomkeerbare processen zijn ook duidelijk uit de grote splitsing tussen de veldgekoelde en nul-veldgekoelde magnetische susceptibiliteit, die aanhoudt tot hoge temperaturen, en die niet het verwachte Curie-Weiss gedrag volgt. Dit gedrag is ook terug te vinden in de aanhoudende grote positieve modulatie in de spin Hall-magnetoweerstand, dat voor de eerste keer gemeten is op het grensvlak tussen Pt en CaFe_2O_4 tot 400 K. Ook deze metingen duiden op het naast elkaar bestaan van een antiferromagnetische ordening en niet-gecompenseerde, ontkoppeld momenten over een groot temperatuurbereik. Hoewel de oorsprong van de netto magnetisatie nog niet volledig wordt begrepen, veronderstel ik dat deze kan ontstaan door de koppeling van de antifasegrenzen in de buurt van de kritische overgang, waar lange-afstandscorrelaties optreden. Dit werk geeft dus sterk aan dat, in CaFe_2O_4 dunne films, een van de twee magnetische ordeningen (mogelijk A) geen thermodynamisch stabiele fase is, maar eerder een dubbele modulatie is die voortkomt uit lokale variaties die consistent zijn met antifasegrenzen. De stabiliteit van de twee magnetische structuren kan ook worden beïnvloed door dotering en in het bijzonder door substitutie met Cr . In hoofdstuk 6 wordt aangetoond dat dit ook het geval is in de dunne films, aangezien de toevoeging van Cr de stabiliteit van de B-fase bevordert en de ordeningstemperatuur van het materiaal verlaagt. Bovendien treden bij Cr -substitutie ook veranderingen in de domeinstructuur van de films op.

Het tweede systeem dat in dit werk wordt bestudeerd zijn BaTiO_3 dunne films, waarbij lage epitaxiale spanning een rijk fasediagram van periodieke streepdomeinpatronen induceert. In het bijzonder concentreer ik mij op de overgang tussen een puur in het vlak (a/b) ferro-elektrische en ferro-elastische domeinconfiguratie bij kamertemperatuur naar een configuratie die alterneert in het vlak en uit het vlak (a/c) bij hogere temperatuur (hoofdstuk 7). De eerste orde overgang kan, dankzij de langzame dynamiek van domeinvorming, gevolgd worden met piezorespons-krachtmicroscopie bij verwarming en afkoeling. Hier wordt de evenwichtsperiodiciteit verkregen door opeenvolgende periodeverdubbelings- en halveringsgebeurtenissen, die doen denken aan periodeverdubbelingscascades in dynamische systemen. Dit kan een algemener mechanisme van transformatie vertegenwoordigen in materialen met concurrerende periodieke structuren. Daarnaast is het ook een van de eerste directe rapporten van de route naar “ruimtelijke chaos” in een systeem van gecondenseerde materie.

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Grants and awards

2021

American Ceramics Society (ACerS)

Student Travel Grant to the Electronic Materials and Applications Meeting and One-year ACerS membership

2020

European Magnetic Association (EMA)

Student Travel Grant to the Joint European Magnetic Symposia

2017

Royal Netherlands Chemical Society (KNCV)

Honorable Mention for the Golden Master Award for the best (bio)chemistry master thesis in the Netherlands

List of publications

1. Damerio, S.; Kaverzin, A.; Ocelík, V.; Hoogeboom, G.; van Wees, B.; Noheda, B., *Antiferromagnetic ordering and uncoupled spins in CaFe_2O_4 thin films probed by spin Hall magnetoresistance* (Accepted at Advanced Electronics Materials)
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3. Huisman, R.; Bruijn, M.; Damerio, S.; Eggens, M.; Kazmi, S.N.R.; Schmerbauch, A.E.M.; Smit, H.; Vasquez-Beltran, M.A.; van der Veer, E.; Acuautila, M.; Jayawardhana, B.; Noheda, B., *High pixel number deformable mirror concept utilizing piezoelectric hysteresis for stable shape configurations*, Journal of Astronomical Telescopes, Instruments, and Systems, 7(2), 029002, (2021) doi: 10.1117/1.JATIS.7.2.029002
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