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Spin-like polar textures in ferroelectrics

by

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Thesis

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Declarations

I declare that the contents of this thesis represent my own work carried out at the Department of Physics, University of Warwick, between October 2017 and October 2021 under the supervision of Prof. Marin Alexe. The research results reported here have not been previously submitted, either wholly or in part, at this or any other academic institution for admission to a higher degree.

The transmission electron microscopy samples used in Chapter 4 and 6 were prepared by the author, Dr. Jonathan J.P. Peters and Dr. James Gott. STEM analysis and displacement mapping on these samples were performed by Dr. Jonathan J.P. Peters and Dr. James Gott. The strain mapping analysis was done by the author, using a code written by Dr. Jonathan J.P. Peters. The diffraction contrast simulations were computed by Dr. Richard Beanland. All other sample growths, specimen preparation, characterisation, and theoretical simulation were carried out by the author.

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3. Samuel D. Seddon, Daniela E. Dogaru, Sam J. Holt, **Dorin Rusu**, Jonathan J. P. Peters, Ana M. Sanchez, and Marin Alexe. Real-space observation of ferroelectrically induced magnetic spin crystal in SrRuO3. *Nat Commun* **12**, 2007 (2021)

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Acronyms

ADF	Annular Dark Field
CCD	Charged Coupled Device
CW	Clockwise
DF-TEM	Dark-Field Transmission Electron Microscopy
DFT	Density Functional Theory
DMI	Dzyaloshinskii-Moriya interaction
DSO	DyScO_3
FeRAM	Ferroelectric Random Access Memory
FIB	Focused Ion Beam
FTJ	Ferroelectric Tunnel Junction
FWHM	Full width at half maximum
HDR	High Dynamic Range
HW	Howie-Whelan
LSMO	$(La_{0.7}, Sr_{0.3})MnO_3$
PC	Primitive Cell
PCBZ	Primitive cell Brillouin Zone
PIPS	Precision Ion Polishing System
PLD	Pulsed Laser Deposition
РТО	$PbTiO_3$
PZT	$Pb(Zr_{20},Ti_{80})O_3$
RHEED	Reflective High Energy Electron Diffraction
RSM	Reciprocal Space Map
SAED	Selected Area Electron Diffraction
\mathbf{SC}	Supercell
SCBZ	Supercell Brillouin Zone
STEM	Scanning Transmission Electron Microscopy
STO	$ m SrTiO_3$
SRO	$SrRuO_3$
T _c	Curie Temperature
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction

Abstract

The bulk properties stemming from the polar nature of the ferroic materials makes them suited for a wide range of devices such as piezoelectric actuators, non-volatile memories, pyroelectric sensors. In thin film form, the physical properties of these materials (polarization, domain topologies, Curie temperature etc.) become highly susceptible to the electrical and mechanical boundary conditions imposed by the boundary layers. The interface coupling between the ferroelectric and its boundary layers can give rise to unique phenomena which is unobserved in bulk ferroelectrics. The objective of this thesis is to pursue a recently observed ability of ferroelectric materials to display, under specific boundary conditions, complex polar topologies that resemble magnetic spin textures induced by non-collinear spin interactions (i.e. Dzyaloshinskii–Moriya interaction).

First, several PTO/STO superlattice architectures were grown, in order to re-create the polar vortex topology. This allowed us to capture the ferroelectric domains, going from a monodomain state to polar vortices and to flux-closure domains. X-ray diffraction studies have revealed that the polar topologies inside the PTO layers are composed of two perpendicular modulations, co-existing in the sample. In the second part of this study we focus on the sample showing polar vortices, and follow the evolution with temperature of all periodicities. It is shown that any form of periodic arrangement dissolved at around 150 °C, with the exception of the vortex array, which disappears at approximately 350 °C. Because of this we were able to study the nature of the vortex phase transition and concluded that it can be described within the mean field theory as a second order phase transition.

Next, we performed DFT calculations on metal-ferroelectric-metal structures in order to find a conductive substitute for STO, which could allow for polar vortices to form within PTO. LSMO and SRO were chosen due to their good lattice match to PTO and because of their electrical properties. Here, atomic relaxations were performed and the interface physics was described. LSMO, depending on the interface termination, was shown to have either a screening or an enhancing effect on the ferroelectric polarization, depending on its orientation. This can be detrimental to the formation of polar vortices, as one interface termination favors a specific polarization direction. On the other hand, SRO was shown to sustain the vortex topology, by confining the polarization to PTO.

Finally, the results of the DFT calculations done on the SRO/PTO/SRO systems were tested by producing such architectures using PLD. It is shown that polar vortices do indeed form inside PTO, however the XRD results hint towards a more complex polar topology. Using a combination of electron microscopy techniques such as DF-TEM, STEM, diffraction contrast simulations, complemented by XRD studies and circular dichroism measurements, it is shown the emergence of a complex polar topology which resembles a unique spin texture called incommensurate spin crystals, recently found in ferromagnets.

Chapter 1

Introduction

In this technological era, computation generally requires a random access memory, which is continuously supplied with power in order retain data. Ferroelectrics, due to their retention properties and the inherent switchable polarization which can be associated with "0" and "1" data bits, have proven to be the ideal component for such computer memory applications [1]. This culminated with the realization of FeRAMs, which are radiation resistant [2], not affected by power disruption, require low operating voltages and provide a long data retention ($\sim 10 \text{ yrs} [3]$). While such devices use ferroelectric (typically PZT) layers already $\sim 100 \,\mathrm{nm}$ thin [4], the necessity to produce smaller devices and increase the storage capacity has pushed for further research into the characteristics of nanometer-sized ferroelectric films. This thickness regime enables the use of new physics such as quantum tunneling. Devices that operate based on this principle are the ferroelectric tunnel junctions (FTJ), where the ferroelectric layer acts as a barrier whose height can be modulated by altering the polarization state [5]. Further control over the domain state, proved that the ferroelectric can also play the role of a memristor, where the resistance can be continuously altered by means of fractional domain switching [6].

For a ferroelectric thin film, the polarization state is strongly dependent on its strain state [7] and boundary layers [8], i.e. the atmosphere or another material. Clarifying the polar textures at this thickness is an ideal task for electron microscopybased techniques such as scanning transmission electron microscopy (STEM), which are capable of mapping the polarization state with unit-cell resolution. As proof, researchers have observed that thin ferroelectric films of $PbTiO_3$ (PTO), under specific strain and boundary layers, can display polarization vortices [9], a state previously observed in magnetic materials as spin topologies [10].

Starting from a need to reduce the size of the storage devices, the ferroelectrics were pushed into an environment where polar topologies mimic the magnetic spin topologies, despite the difference in the origins and strengths of the electric and magnetic forces. Pursuing this fact, it is the objective of this thesis to advance the understanding of the mechanisms that are behind the emergence of spin-like polar topologies in ferroelectric thin films.

To this end, various sample architectures were grown, ranging from ferroelectric/insulator superlattices to metal/ferroelectric/metal structures, all with their own unique characteristics and domain structures. Several invasive and non-invasive techniques were employed to peer into the structural characteristics of these systems, starting form high resolution XRD, to X-ray dichroism; from STEM to diffraction contrast TEM etc. DFT calculations were employed to analyze some of the physical characteristics of the systems of interest. The ferroelectric material used is PTO, due to its good lattice match to the substrates used and because of its large polarization and other properties which allow for a straight-forward interpretation of the observed results.

In the up-coming chapter (3), a number of pages are dedicated to describing the materials used in this study, techniques which allowed for a nearly perfect growth (with unit cell precision), as well as the key parameters one needs to be aware of when diving into sample growth via PLD. Next, all major experimental and theoretical techniques are presented, starting with XRD, where the physical principles and operations are highlighter along with the circular dichroism. As TEM emerged as one of the pillars of this thesis, time is spent on describing the image formation mechanisms as well as the some of the imaging techniques (diffraction contrast, STEM imaging). This chapter ends with details about the DFT method and its workflow principles, along with some technical details useful in Chapter 5. The next chapter (4) starts with a revision of the work done in [9], which consists of PTO/STO superlattices grown on DSO substrates, shown to be hosts of polar vortices (within PTO). Then, a more in-depth analysis is presented, where the thickness of PTO was varied inside an interval which contains polar vortices. Consequently, the domain topologies were analyzed with respect to the thickness of the PTO layer. Here, the STO thickness was carefully chosen so the ferroelectric layers are electrically decoupled. In the second part of this chapter, reciprocal space maps of the sample showing polar vortices were recorded at various temperatures, in order to track the periodicities through their phase transition. These were measured in-situ at a synchrotron beamline.

Knowing that PTO develops polar vortices with STO as boundary layers, chapter (5) is dedicated to a fully theoretical study into the possibility of replacing the STO layer with a conductive electrode and still have polar vortices. Two materials were chosen, LSMO and SRO due to their good in-plane lattice match and their conductive properties. Furthermore, both can be grown in-situ along with PTO. The interface of LSMO with PTO displays interesting physics which, ultimately, could inhibit the formation of polar vortices in a LSMO/PTO/LSMO structure, due to the charged atomic planes of LSMO. On the other hand, SRO possesses no charged planes and despite its large number of free carriers, it seems to allow for polar vortices to form in specific SRO/PTO/SRO systems.

Finally, the results of chapter 5 are put to the test in chapter 6. Heterostructures comprised of SRO/PTO/SRO were grown on STO buffered DSO substrates. STEM cross sectional displacement mapping shows polar vortices forming along one of the crystallographic directions. XRD reciprocal space mapping reveals two overlapping periodicities running along perpendicular directions, possibly hinting at a new form of polar ordering. Further plan-view dark field studies, supported by additional plan-view STEM imaging and Howie-Whelan diffraction contrast simulations confirm a new polar phase, similar to the newly discovered incommensurate spin crystals [11]. Further DFT studies support the hypothesis of this new type of ordering in PTO.

Chapter 2

Background

2.1 Ferroelectrics-general aspects

2.1.1 Spontaneous polarization and ferroelectricity

The term *ferroelectric* is reserved for a special class of insulating or semiconducting materials which are polar under zero electric field, and possess two or more metastable states [12, 13]. These can be described by a vector with specific magnitude and angles, relative to the crystallographic axes of the polar material. If, for simplicity, the system has two metastable states, they will be energetically equivalent and symmetry equivalent (see Figure 2.1), so the two vectors usually point along opposite directions! These vectors are referred to as "spontaneous polarization", and a crucial characteristic of a ferroelectric (which separates it from piezoelectrics and pyroelectrics) is that its polarization can be switched from one state into the other by applying an electric field.

A typical as-grown ferroelectric displays domains. Within a domain, the polarization points in the same direction, however the direction can differ between domains. The domains are separated by domain walls which can move, allowing the domains to shrink/grow [14–18]. This phenomenon causes the ferroelectrics to display a hysteretic behaviour during the switching process [19, 20]. In the ideal case, a typical hysteresis loop is symmetric w.r.t. the origin (Figure 2.2), which allows



Figure 2.1: **Phenomenological description**. Free energy representation of the two-state ferroelectric system. The two polarization orientation are energetically equivalent one can change its orientation by applying an electric field. The high energy state at zero polarization corresponds to a centrosymmetric (e.g. cubic) state.

one to extract relevant parameters such as saturated and remnant polarization, and the coercive field.

Extreme care is imposed when measuring hysteresis loops [21] as it needs to be accompanied by current-voltage measurements. A spontaneous polarization emerges only in crystals with a polar space group. However, unless the polarization can be switched, the crystal is not ferroelectric (e.g. wurtzite-type insulators). One condition that can lead to the presence of multiple, switchable polarization orientations is that the polar structure (e.g. tetragonal) is obtained as a distortion of a higher-symmetry, non-polar structure (cubic). This principle was evolved into a "structural criteria" for finding ferroelectricity in inorganic crystals, first by Abrahams [22–24]), and then by others [25, 26]. It also serves as a systematic approach within the first-principles theoretical framework. By computing the phonons of the high-symmetry structure, the unstable modes (i.e. imaginary frequencies [27]) are used to search for symmetry lowering ferroelectric distortions.

The notion of a spontaneous polarization is the keystone of understanding



Figure 2.2: Hysteresis loop. P_r is the remnant polarization, when the electric field is turned off; E_c is the coercive field and P_{sat} is the saturated polarization.



Figure 2.3: Electronic density. (Left) Idealized case where the electronic density of the crystal can be split into well defined individual contributions. (Right) The electronic density in a real system, where it can not be split into individual cells.

ferroelectrics, therefore a few lines will be dedicated to it. There are two contributions to the polarization of a system: electronic and ionic. The ionic one is given in terms of bare ionic displacements. The classic Clausius-Mossotti (CM) image of the polarization considers the charge density of the whole system as a superposition of non-overlapping localized charge distribution, each having its own polarization, as shown in Figure 2.3(left).

In real systems, this in not the case. The electronic charge distribution is continuous and periodic and cannot be unambiguously partitioned into cells[13] (Figure 2.3(right)), which is why the CM image breaks down. The solution was found by Resta, King-Smith and Vanderbilt, where the polarization is defined as an integrated current (density) when the ferroelectric system goes from one polar state into the other (switches) and the polarization is expressed in terms of a Berry phase [28–30]. This approach yielded a new technical detail. The polarization is not single values, but is a *lattice*, with values $\vec{P}_0 + e\vec{R}/V_{cell}$. Here, \vec{R} is the lattice Bravais vector. Why is this important? The multivaluedness of the polar lattice allows for a more visual representation, in terms of Wannier functions, which are essentially the Fourier transform of the electronic Bloch waves. Using this method Baldereschi *et al.* [31] reached a very important conclusion, that the linearity of the phenomenological expression of polarization, given in terms of Born effective charges is valid. This provides a Clausius-Mossotti-like image, where one needs to compute the dynamical Born effective charges and the ionic displacements to find the polarization. A direct experimental use of this result is that it enables one to directly estimate the polarization in a ferroelectric film by performing STEM displacement mapping [32–35].

2.1.2 Origin of ferroelectricity in perovskite oxides

The first ferroelectric crystal discovered in 1930 was the Rochelle salt [20]. For a while, it was believed that a complex crystal structure is necessary for ferroelectricity. This was until BaTiO₃ was discovered, a simple perovksite-type crystal which showed ferroelectric behavior [36]. PbTiO₃ is another simple perovksite, similar to BTO. Both crystal structures are described by an ABO₃ unit cell formula, with the basis composed of 5 atoms. A typical representation is the B-site cation having an oxygen cage octahedra, and the A-site anion filling the space in between, as shown in Figure 2.4.

The polar distortions involve the simultaneous movement of the oxygen cage centre of mass and of the B-site cation. This seems to be in accordance with the above-mentioned principle that the polar state is a distortion of a highersymmetry reference state (usually cubic symmetry). The transition from a high temperature non-polar state to a lower temperature polar state is accompanied



Figure 2.4: **Typical polar perovskite unit cell**. (Centre) The projection of the perovskite unit cell showed in its centrosymmetric state. The spontaneous polarization is zero. (Right) The off-centering of the titanium (Ti) and oxygen (O) atoms induces a dipolar moment at the unit cell level.

by a divergence in the dielectric constant. Furthermore, because the transition involves a physical movement of ions, the lattice parameters will experience a step discontinuity, associated with a divergent dielectric response [37].

As mentioned, ionic displacements within the crystal unit cell can lead to a spontaneous polarization, but this does not mean that the crystal is ferroelectric. Looking into the origin of ferroelectricity in perovskite oxides, it seems that it is the result of a delicate balance between short-ranged repulsion (Coulomb)-which favor a symmetric structure, and orbital bonding which act as a stabilizing agent for the distortions necessary for ferroelectricity [13, 38, 39]. Because the orbital bonding stabilizes symmetry lowering distortions the degeneracy of orbital energy levels is lifted, and this phenomenon is know as the pseudo-Jahn-Teller effect [40].

2.2 Size effects

In the previous section, the notion of a *ferroelectric* material was introduced and the *spontaneous polarization* was described. An ideal (infinite) ferroelectric crystal displays a spontaneous polarization which is spatially homogeneous. There are no domains, as any disruption of the polarization field is energetically costly. As soon as the translational symmetry is broken, i.e. by the introduction of surfaces, the situation changes drastically. In BTO for example, the unscreened surface bound charges generate a depolarizing field which approaches 300 MV/cm [41]. This cannot be sustained by the ferroelectric without reverting to a paraelectric state, unless, it breaks the polarization field into smaller homogeneous regions of uniform polarization (domains) separated by domain walls [42]. While the creation of domain walls is energetically unfavorable, the cost is compensated by the reduction of the total energy of the crystal.

Considering the technological trend, to miniaturize all devices, simple questions arise. What happens to a ferroelectric when its made into a film (e.g. less than 200 nm), or even approaching the 2D limit? Nowadays, tunneling devices utilize ferroelectric barriers that are a few nanometers in size [43–45].

As one is aware already, the surface plays a crucial role in the observed properties, even more so in a film. In order to conceptually understand the size effects associated with a reduction of the ferroelectric dimensionality, Landau theory was employed in the '90s. Within this framework, the surface physics and its contribution is made through a so-called extrapolation length (ξ) [46, 47], which is not dependent on the thickness, and can be positive of negative. Furthermore, the thickness (and shape) of the film influences the energetics of the system, as the total energy is defined as a volume integral. These effects were shown to cause a size-driven phase transition [48, 49]. If the thickness of the films is smaller than a threshold. This threshold is dictated by the extrapolation length. The sign of the extrapolation length tells if the polarization decreases towards the surface (screened [50]) or is enhanced at the surface [51]. Therefore, below this threshold, the film can suffer a phase transition to a paraelectric state or remain in an enhanced polar state. These size effects can also alter the Curie temperature, usually by decreasing it. As a note, the above arguments were made in the absence of depolarizing fields. If considered, they can severely reduce the polarization of the film [52], further alter the Curie temperature [53], or even change the order of the phase transition [54]. Such are some of the effects one has to consider when a ferroelectric material is made into a thin film.

Given the size effect problem, what are the limits of ferroelectricity? For example, the extrapolation length for $BaTiO_3$ and $PbTiO_3$ is evaluated at 4 nm

and 3 nm, respectively [48]. In a more recent study [55] on PZT, ferroelectricity was detected in thin films down to 4 nm. Below this value, PTO thin films were shown to still possess ferroelectricity however, the polarization is severely reduced [56]. In PTO, ferroelectricity itself was shown to exist down to three unit cells [57] - basically, as long as there exists at least one unit cell that compositionally represents the ferroelectric (the surface unit cells are excluded).

Because of their usefulness as non-volatile memories [58] or tunneling junctions [45], ferroelectrics are usually sandwiched between insulators, metals, or they can have hybrid interfaces (metal/insulator). As Landau theory is a phenomenological approach, it makes no assumptions on the microscopic nature of the system. Meanwhile, the computational capabilities have evolved enough to allow the *abinitio* investigation of ferroelectric thin films. One of the successes of this approach is that it predicts the presence of ferroelectricity down to a few unit cells [59]. Furthermore, realistic DFT simulations of a capacitor-like SRO-BTO-SRO system show that the main problem is the unscreened depolarization field which suppresses the ferroelectricity [60], and not the size effect as described by the Landau theory.

2.2.1 Polar domains

A ferroelectric material necessarily creates domains in order to reduce its total energy. In a ferroelectric thin film, the surface effects become more and more relevant, the thinner the film is. The unscreened surface bound charges generate a depolarization field, which can suppress the ferroelectricity, if uncompensated.

In order to lower the depolarization field, the electric dipoles close to the interface rotate in such a way that they become parallel to the interface. In this way there are no surface bound charges, and no depolarization field, while the film is still in its polar state [61]. Unfortunately, ferroelectric films are grown on a host crystal, usually in a strained state, which takes such a scenario out of the equation. Alternatively, it can form strain releasing polar pattern, such as a/c domains (Figure 2.5a), which reduce the depolarization field as well as the strain field [62]. Even in the ultrathin limit (few unit cells) the ferroelectric material can



Figure 2.5: **Domains**. Sketch of some of the typical domain topologies inside a ferroelectric thin film. **a**, a/c pattern. **b**, 180° domains. **c**, Flux-closure domains. **d**, Polar vortices.

still avoid the ferroelectricity suppression by adsorbing ions from the atmosphere, which in particular were shown to stabilize the polar structure into 180° domains [63] for PTO ultrathin films (Figure 2.5b).

Another scenario would be to grow metallic contacts in order to forcefully screen the depolarization field [8]. In principle, the ferroelectric would be in a monodomain state if the screening were perfect. However, the reality is different. Even if the metal-ferroelectric contact is ideal, there is a non-zero screening length over which the free charges redistribute themselves to screen the surface bound charges. This screening length is in the range of one - to several Angstrom [64].

Because depolarizing fields are always present, the ferroelectric film necessarily needs to form domains. The periodicity of the domains is not arbitrary and is dependent on the square root of the film's thickness:

$$w = \sqrt{\frac{\sigma d}{U}}, \qquad (2.2.1)$$



Figure 2.6: **Domain size scaling**. For ferroelectric materials, it is shown that the relation between the periodicity of the domain structure and the thickness is shown to be described by the Kittle's law. Reproduced from reference [65].

where σ is energy density of the domain walls, U is the energy density of the domains and w is the domain period [65]. The above equation is also called the Kittel law and was shown to describe the experimental domain periodicities for a wide range of materials and thicknesses (Figure 2.6).

Charles Kittel (1946) was the first to outline that the similarity between ferroelectrics and ferromagnets is also reflected by the domain structure, namely 180° domains. He also emphasized the "domains of closure" for surface domains – also referred to as Landau-Lifshitz, which form in ferromagnets [66] and have the advantage of minimizing the demagnetization fields (Figure 2.5c). At the time, closure domains in ferroelectrics had not been observed.

A growing number of theoretical works [67–70] predicted polarization topologies in ferroelectric systems, previously observed only in ferromagnets, such as vortices [71–73], pushing the ferro-electric/magnet analogy even further. Using PFM techniques, ferroelectric vortices were indeed detected in micron-sized [74] and nano-sized [75] PZT disks. It was in 2011 when the first observation of magneticlike closure domains was reported in PTO [76] and BiFeO₃ (BFO) [77] specimens using cross-sectional TEM. These flux-closure domains are located at the interface between a ferroelectric and an insulator, minimizing the depolarization field, in a similar manner to the ferromagnetic Landau-Lifshitz domains. It is noteworthy to mention that the flux-closure domains in ferroelectric introduce a vertex - defect in the polarization field where three different domains meet. In ferroelectric thin films, the strain gradient and the strain fields in the vertex region can be so large that it can cause the crystal lattice to rupture [78]. Flux closure domains were observed not only in ferroelectric thin films (nanometer-sized), but also in micron-sized crystals of BTO, proving that the scale of the ferroelectric material is not necessarily a factor [79].

An epitaxial ferroelectric film grown in a strained state does not adopt a fully in-plane monodomain state, due to clamping effects, and it needs to develop rather typical domain patterns e.g. 180°, a/c or a1/a2. This information, coupled with the fact that the ferroelectric can form closure domains at the interface where the depolarization field is deliberately maximized (by being in contact with an insulator), lead to the discovery of polar vortices (Figure 2.5d) in ferroelectricinsulator superlattices of PTO-STO in 2016 [80]. This polar topology is different than the flux-closure domains as it is described by a continuous Néel winding of the local dipole. This was certainly unexpected for several reasons. PTO has a tetragonal unit cell with two possible directions for the electric dipole: Parallel or anti-parallel to the long c-axis. If the polarization is perpendicular to the interface, the c-axis is perpendicular as well. In closure domains however, the unit cell is distorted so the c-axis is parallel to the interface. This does not happen in PTO thin films with polar vortices. The lattice does not have enough room to relax into regions with a homogeneous polarization. Second, continuous rotations of the electric dipole of any kind, Néel or Bloch, are not inherent to the ferroelectric crystal as the energy penalty is too large. Nevertheless, a phenomenological approach based on free energy minimization yielded valuable information regarding the interplay between the strain energy, strain gradient and the depolarization field [81], which is responsible for the emergence of polar vortices in such systems.

Chapter 3

Methods

The search for new polar phases in ferroelectrics begins with an overview of the experimental and theoretical techniques that are capable of providing accurate information about the possible emergent polarization topologies. The materials used and the sample preparation is a crucial part of the process, therefore, time is spent on describing the crystalline and electronic properties (insulating/conducting) of each material used in this thesis. Thin crystalline films of these materials are grown on an atomically flat host crystal, called a substrate. Throughout this work, all films are grown using the pulsed laser deposition technique and necessary details about the growth process are given.

Structural investigations at the atomic level are performed using aberration corrected scanning transmission microscopy (STEM), as well as conventional TEM diffraction techniques such as dark field imaging. Non-invasive x-ray diffraction techniques are applied to extract information about the periodicities within the sample, which are otherwise unattainable by electron microscopy. Further density functional theory (DFT) is employed in order to gain insight into the physical properties of specific systems, and due to its important role, a section is dedicated to the fundamental notions and workflow of DFT.

3.1 Materials

3.1.1 Substrates: DyScO₃

DyScO₃ is a band insulator with an orthorhombic unit cell described by the space group Pbnm. Its lattice parameters are a = 5.449 Å, b = 5.726 Å, c = 7.913 Å, with



Figure 3.1: \mathbf{DyScO}_3 oxygen octahedra. Tilt pattern of DSO. Reproduced from reference [82].

the angles between the crystallographic axes equal to 90° [82]. The oxygen octahedra surrounding the B-site (Scandium) ion displays a complex rotation pattern described by $a^{-}b^{-}c^{+}$ in Glazer notation [83], as shown in Figure 3.1. The valence states of both Dy and Sc is 3+ so the DyO and ScO₂ planes have a non-zero valence sum, therefore, these planes are charged.



Figure 3.2: Ortho-cubic relation. **a**, Stacking relation of cubic on top of an orthorhombic substrate. **b**, DSO crystal structure projected along $[010]_{pc}$. **c**, DSO crystal structure projected along $[100]_{pc}$.

The substrates used in this thesis have a $(110)_{\rm o}$ terminated surface, with a miss-cut angle of about 0.05°. The necessity of a miss-cut angle is imposed by the thin film growth mechanisms, which will be described later on. Because the surface cut is the $(110)_{\rm o}$ plane, it provides a favorable base for the growth of cubic structures with closely matched in-plane lattice constants. In this geometry, the pseudocubic notation is favorable (Figure 3.2a), with mention that the projected crystal structure along the $[010]_{\rm pc}$ and $[100]_{\rm pc}$ is not the same (Figures 3.2b, c). This helps to



Figure 3.3: **AFM topography of DSO annealed surface**. The steps are ~ 4 Å high (one unit cell). Along the tarrace, the contrast does not vary, which is a consequence of the surface being atomically flat.

unambiguously identify the pseudocubic directions relative to an absolute reference system (the orthorhombic axes). In the pseudocubic system, the in-plane lattice constants are evaluated to about 3.953 Å, from geometrical considerations.

In order to ensure an atomically flat surface (necessary for thin film growth), the substrate needs to be processed. In particular, the DSO substrate was annealed at $1030 \,^{\circ}$ C for 2 hrs at atmospheric pressure, in a flow of 99.9% O₂, which creates a ScO₂ single terminated surface. The DSO surface after annealing is shown in Figure 3.3.

Films grown on a substrate will experience either a compressive or a tensile strain. This is quantified by the formula: $s=(a_{sub}-a_{film})/a_{sub}$, where a is the inplane lattice parameter. The reason for choosing DSO as a substrate is that it imposes a tensile strain on the ferroelectric material of interest (PTO), influencing its polarization state [84] (unlike SrTiO3, which imposes a compressive strain).

3.1.2 Boundary layers: (La_{1-x},Sr_x)MnO₃, SrRuO₃, SrTiO₃

 $(La_{1-x},Sr_x)MnO_3$ is a perovskite oxide whose properties can be tuned from an antiferromagnetic insulator to a conducting ferromagnet by varying the doping level. At x=0.33 the $(La_{0.7},Sr_{0.3})MnO_3$ crystal symmetry is described by the space group R3c with lattice constants a = 5.503 Å, b = 5.503 Å, c = 13.34 Å [85]. The oxygen cage around the B-site ion is tilted according to an a⁻a⁻c⁻ pattern. At this doping concentration, the magnetic transport properties are maximized, reaching a near complete spin polarization of the conduction electrons and a Curie temperature of ~370 K [86]. Doping the LaMnO₃ with Sr causes the Mn ions to have mixed valence states, 3+ and 4+, along with La³⁺ and Sr²⁺. This causes the (La,Sr)O and MnO₂ planes to be charged, similar to DSO.

Unlike LSMO, SrRuO₃ is a material with charge neutral SrO and RuO₂ planes. Its crystal structure belongs to the space group Pnma with lattice parameters a = 5.568 Å, b = 7.845 Å, c = 5.532 Å, and displays the oxygen cage tilting pattern $a^{-}b^{+}c^{-}$ [87]. At room temperature it behaves like a metal and goes through a phase transition to a ferromagnetic state below ~150 K. Because it has similar in-

plane lattice constants to DSO, SRO is a good conductive candidate for an epitaxial film on the substrate.

SrTiO₃ is an insulator with crystal symmetry described by the Pm $\bar{3}$ m space group and lattice constants a = b = c = 3.905 Å [88]. The in-plane lattice constant makes the STO a lattice matched material to the DSO substrate, enabling a defectfree epitaxial growth. Because of this property, it is used as a buffer layer of a few nanometers to shield the layers from the effect of the charged planes of the DSO substrate. Also, the thickness is low enough so the substrate strain can be properly carried to the rest of the layers. Furthermore, STO has a large dielectric constant [89], which makes it easily polarizable, especially if it is in contact with PTO.

3.1.3 Ferroelectric film: PbTiO₃

The ferroelectric material which is used throughout this thesis is PbTiO₃. Its space group symmetry is P4mm with lattice parameters a = b = 3.90 Å and c = 4.135 Å [90]. The high temperature paraelectric state is a cubic structure, and it goes through a single phase transition to its polar tetragonal ferroelectric state below the bulk Curie temperature of 490 °C. In ferroelectric perovskite oxides, the polarization is usually given by the shift of the B-site ion relative to its oxygen cage. For PTO, the A-site also contributes to the polarization, which is the main reason that PTO possesses a larger polarization (~100 μ C/cm²) than BTO, for example. However, as a thin film, at the interface between the PTO and another material the polarization can locally rotate. The A-site ion is hardly displaced and the polar rotation can be approximated by knowing the position of the B-site atom. This means that STEM displacement mapping will provide a relatively straight-forward check of the local polar state. It is for these reasons that the PTO is the ideal ferroelectric to be tested under various extreme mechanical and electrical boundary conditions.

3.2 Sample preparation

3.2.1 Pulsed laser deposition with RHEED capabilities

Since the 1980s the pulsed laser deposition (PLD) has established itself as a unique technological process for creating both thin and thick films, with the ability to produce functional materials with device quality. Its popularity reached its peak due to the technique's inherent flexibility and the speed with which a process is completed, which can be applied to any material, from insulators, semiconductors, to metals, polymers, or even biological materials [91].



Figure 3.4: Sketch of a PLD system. The chamber is under vacuum (typically 10^{-6} mbar). The laser beam hits the desired target and ablates the material, which reaches the substrate. The substrate is mounted on a substrate heater, as oxide films require growth temperatures of about 600°. If necessary, the chamber can be filled with custom gases. Reproduced from reference [92].

PLD is a physical vapor deposition technique, the schematic of which is shown in Figure 3.4. A high-powered laser pulse (typically in the nanoseconds) is directed and focused on the target material to be deposited. The laser used in this thesis is a KrF excimer laser in pulsed mode, at 248 nm. The laser energy (tens of mJ) is absorbed by the target and if the energy density is high enough, the material is vaporized forming a so called plasma plume (ablation). The target is mounted on



Figure 3.5: Rheed. a, Diffraction process. b, Ideal layer-by-layer growth. c, 3D grwoth. d, Example of rheed spot intensity oscillations. e, Schematic of the layer-by-layer growth process. Here, the integrated intensity of three diffraction spots is shown (red, blue, green). a, b, c, e, reproduced from reference [93].

a rotating holder in order to evenly ablate the target. The plasma plume, made up of electrons, ions, diatomic species etc. expands within microseconds. If a substrate is placed in its path, these species will adhere to the surface and the process of reconstructing a thin film starts. The ablation process is usually done in high vacuum, or under a specific partial pressure of a high purity gas (e.g. 99.999% O_2). Oxide materials usually require a certain partial pressure of O_2 for two main reasons. First, the collisions between the plasma species and the ambient gas reduce the kinetic energy of the species, ensuring a higher adhesion probability to the substrate surface. Second, it oxidises the species in the plume, enabling the control over the stoichiometry of the deposited film. Typically the substrate is mounted on a heater, as the oxide films used in this thesis require growth temperatures above 500 °C.

The PLD system can be enhanced with a reflective high energy electron diffraction (RHEED) gun, which enables precise control over the thin film thickness, with unit-cell precision. RHEED, as the name suggests, is a grazing incidence diffraction technique involving energetic electrons ($\sim 30 \text{ keV}$). Because of this, RHEED

is a surface sensitive technique with a depth resolution of about 1 nm, making it ideal for tracking the growth process. The physics behind RHEED is relatively straightforward, as show in Figure 3.5(A). The small depth resolution coupled with a large, milimeter sized beam, leads to a sampled volume which appears almost 2D. The reciprocal lattice of a 2D-like crystal is a set of extended rods and the intersection of the Ewald sphere with these rods is recorded on the fluorescent screen as diffraction spots (Figure 3.5(B), (C)).

The time evolution of the growth process is then tracked by integrating the intensity around one of the diffraction spots at every time step. In the case of a layer-by-layer growth it results in a graph of the form shown in Figure 3.5(D). The maximum intensity corresponds to a completely covered surface. When species from the plasma plume adhere to the surface (start of a new layer), nucleation centers are formed and the intensity drops because the electrons randomly scatter from the surface, reaching a minimum (Figure 3.5(E), ϑ =0.5). The nucleation sites extend and coalesce and the percentage of coherently scattered electrons increases as the new layer is formed (ϑ =1).

3.2.2 Thin film growth modes

If the growth of thin films is done by PLD, four growth modes can be distinguished, the schematics of which are shown in Figure 3.6. For a layer-by-layer (Frank-van der



Figure 3.6: **Growth modes**. **a**, Frank-van der Merwe growth. **b**, Stranski-Krastanov growth. **c**, Volmer-Weber growth. **d**, Step-flow growth. This requires vicinal surfaces.

Merwe) the nucleation sites laterally extend and coalesce to form a new complete layer. The growth on a new layer is done only when the underlayer is complete. In the Stranski-Krastanov regime, the overlayer starts to form before the underlayer is complete, resulting in a step-bunching effect. Volmer-Weber growth occurs when the cohesion forces exceed the adhesion forces, causing an island formation instead of a uniform layer. Lastly, in the step-flow growth, the adatoms diffuse and nucleate on the vicinal surfaces. This causes the steps to propagate during growth, forming the thin film layers.

Throughout this thesis, heterostructures involving multiple thin films of different materials are of interest. This imposes the need for layer-by-layer or stepflow growth mode. In order to achieve the right growth mode, several key parameters need to be considered. The laser fluence (energy surface density) controls the nucleation rate during growth. The repetition rate influences the flux of the incoming species, therefore controlling the growth rate. The substrate-target distance impacts the homogeneity of the film as well as the deposition rate. The partial atmosphere controls the deposition rate by reducing the kinetic energy of the adatoms; it also oxidises the species and alters the stoichiometry. The temperature affects the diffusion of the adsorbed species and thus, the nucleation behaviour.

3.3 X-ray diffraction techniques

3.3.1 High Resolution XRD

Before going into the relevant information necessary for understanding the XRD results in this thesis, the appropriate background is established. Ideally, a crystal is represented by an infinite 3D array of lattice points, called a "Bravais lattice" and a group of atoms called a basis (Figure 3.7). The Bravais lattice symmetry is described by the so called point group symmetry. This group contains rotations, reflections, and translations which are multiple integer of the lattice vectors. When the internal symmetry of the basis is considered, the point group is expanded into a space group. There are 32 point groups and 230 space groups. It is further shown that the diffraction condition depends only on the Bravais lattice, but the peak intensity can only be calculated if the basis (hence, space group) is known.



Figure 3.7: Constitutive elements of a crystal. Basis represents the elements that are periodically repeated at every single lattice point. a, b are the lattice basis and T represents a lattice vector, with integer parts of a and b.

The 3D lattice array is a discrete space, where all vectors are of the form:

$$\vec{T} = u\vec{a} + v\vec{b} + w\vec{c}, \qquad (3.3.1)$$

with u, v, $w \in \mathbb{Z}$. In diffraction, the notion of planes is important. A plane can be defined using three lattice points (vectors). The orientation of a plane is defined using Miller indices (details are given in [94]). An example of such planes (described by specific Miller indices) are shown in Figure 3.8. One can already observe that the distance between the planes defined by different Miller indices is dependent on the (hkl) values. The higher the values, the smaller the inter-planar distance, and the more densely packed the planes are. Therefore, it is useful to define the inter-planar distance in terms of (hkl). The formula is dependent of the Bravais lattice and can have a complex form, especially if the lattice is e.g. monoclinic. As a simple example, we reproduce the relation for a cubic crystal:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2}$$
(3.3.2)

The x-ray diffraction process can be thought of as an interference effect among the scattered electromagnetic waves off of the atomic planes (Figure 3.9),



Figure 3.8: **Crystallographic planes**. The description of the crystallographic planes is achieved using Miller indices (hkl). The value of these indices describe the point of intersection of the crystallographic axes and the plane.

described by specific Miller indices. W. L. Bragg and his father W. H. Bragg [95] have shown that if a certain geometric condition is satisfied, diffraction can occur. This condition is:

$$m\lambda = 2d_{hkl}\sin\vartheta, \qquad (3.3.3)$$

where ϑ is the Bragg angle, d_{hkl} is the interplanar distance, λ is the wavelength and m is interference order. An important conclusion of this relation can be expressed as $\vec{Q} = \vec{k}_{in} - \vec{k}_{out}$, and it states that the scattering vector is perpendicular to the scattering planes.

This allows for a more geometrical view over the diffraction phenomenon, called the Ewald construction. It states that diffraction occurs if and only if $\Delta \vec{k} = \vec{Q}$, where \vec{Q} is a lattice vector. This is represented in Figure 3.10 and mathematically as:

$$|\vec{\mathbf{Q}}| = 2|\mathbf{k}|\sin\vartheta = \frac{4\pi}{\lambda}\sin\vartheta.$$
 (3.3.4)


Figure 3.9: **XRD mechanism**. (Left) X-rays are elastically scattered off of the crystallographic planes which satisfy the Bragg law. (Right) Laue condition in vector representation.

Considering Bragg's law we can link the magnitude of the diffracted spot's \vec{Q} -vector to the inter-planar distance by:

$$|\vec{\mathbf{Q}}| = \frac{2\pi}{\mathbf{d}_{hkl}} \tag{3.3.5}$$

The Bragg's law and its consequent relations are reflected by the crystal lattice symmetry (point group), however, no information about the basis is contained within these relations. The basis symmetry impacts the intensities of the Bragg peaks, as it will be shown.

In order to understand how the scattering of the x-rays off of the atomic planes leads to diffraction we first look into how the x-rays scatter off a single atom. The frequency of x-rays ranges from 10^{16} to 10^{20} Hz. At this frequency, the nucleus will not oscillate in the the electromagnetic (EM) field of the x-rays. The electrons, however, do. Electrons radiate EM waves when subjected to an accelerated motion. This process is called Thompson scattering. Without going into details [96], the scattering amplitude of x-rays by a single electron is described by:

$$f_{e} = \int \rho(\vec{r}) e^{\frac{2\pi i}{\lambda} (\vec{s} - \vec{s}_{0})\vec{r}} \, dV, \qquad (3.3.6)$$

where $\rho(\vec{r})$ is the charge density of the electron; \vec{s}_0 and \vec{s} are the incident and scattered wave vectors. Keep in mind that the electron is not point-like, but spread



Figure 3.10: **Ewald contruction** Diffraction is achieved at all lattice vectors where the Ewald sphere intersects the lattice points.

around the nucleus. If the atom has n electrons, then the scattering amplitude is

$$f = \sum_{j=1}^{n} f_{en} = \sum_{j=1}^{n} \int \rho(\vec{r})_{j} e^{\frac{2\pi i}{\lambda} (\vec{s} - \vec{s}_{0})\vec{r}} \, dV, \qquad (3.3.7)$$

where f is usually called "x-ray atomic scattering factor". This is nothing more than the Fourier transform of the electron charge density. Considering what a crystal is, the diffraction pattern is the Fourier transform of the electronic charge density of the crystal:

$$\{F_{hkl}\} = FT[\rho(\vec{r})] \tag{3.3.8}$$

$$I_{hkl} = |F_{hkl}|^2,$$
 (3.3.9)

where $\{F_{hkl}\}\$ is the set of scattering amplitudes, and I_{hkl} is the intensity for a particular (hkl) reflection corresponding to a particular set of planes $\{hkl\}$.

In the beginning we mentioned that the Bravais lattice gives the diffraction pattern, but not the peak intensities. To calculate the latter we need to have knowledge about the basis of the crystal structure. If the basis is known, the scattering amplitude is the vector sum of the individual atomic scattering factors:

$$F_{hkl} = \sum_{j} f_{j} e^{-i2\pi(hx_{j} + ky_{j} + lz_{j})}, \qquad (3.3.10)$$

where the sum is performed over the basis atoms; f_j is the atomic scattering factor and x_j, y_j, z_j are the position of the basis atoms.

3.3.2 Reciprocal Space Mapping

Having a basic knowledge about the origin of the diffraction pattern, the focus is set on the type of samples that will be studied in this thesis. That is, epitaxial multilayers grown on the vicinal surface of a crystalline substrate. In order to study the quality and the various periodicities that arise in these samples we employ the use of a diffractometer in the Bragg-Brentano geometry. The simplified schematic is shown in Figure 3.11(left). Here, the sample is mounted on a stage whose position is controlled by 6 motors: 3 positional (x, y, z) and 3 which are used to align the sample's Bragg spots to the beam (ω , φ , χ). Any trajectory in real space is accompanied by a corresponding path in reciprocal space. The detector sweep is called a 2ϑ scan. If the detector is fixed and the sample-incident beam angle is varied, an ω (or rocking curve) scan is performed. The third mode is a coupled scan where both the detector and the sample rotate simultaneously, called a $\vartheta - 2\vartheta$ scan. As mentioned, each scan probes the reciprocal space along specific paths. An example is shown in Figure 3.11(right). A $\vartheta - 2\vartheta$ scan probes the so-called Crystal Truncation Rod (CTR), which contains the collective reflections from all the layers. An ω scan can provide information about the mosaic spread of the crystalline planes and their lateral correlation length. φ and χ scans are typically involved in aligning the sample to the beam.

When multiple thin films are grown on a crystalline substrate, its corresponding reciprocal space changes accordingly, therefore, it is important to understand these specific changes. A useful strategy is to construct reciprocal space maps, which are 2D slices of the reciprocal space. If the detector is 1D, for every single ω point,



Figure 3.11: **Operating principles**. (Left) Schematic representation of the constitutive elements of a diffractometer. (Right) Paths in the reciprocal space laid down by the different real space scans (ω, ϑ etc.).

the detector performs a sweep between specified angles, thus constructing a 2D map. If the detector is 2D, a reciprocal space volume can be reconstructed, as for every ω point, the detector records a 2D image. Regardless of the detector capabilities, the reciprocal space map is an invaluable tool when studying the periodicities within a multilayer. Depending on the epitaxial relation between the grown film and the substrate, the film can be relaxed, partially relaxed, or fully strained. This is reflected in the reciprocal space by the relative peak position of the substrate to the film (Figure 3.12). The symmetric reflection (001) is insensitive to any in-plane periodicities, and will not reveal any information about the strain state. On the other hand, an asymmetric reflection (hkl) has information about the periodicities along all h, k, l directions. Therefore, the strain state of the film can be deduced from the asymmetric reflections. If the position of film's diffraction peak relative to the substrate diffraction spot is the same as for a symmetric reflection, the film is fully strained to the substrate. Experimentally, it is a requirement for all grown films to be fully strained to the substrate. Any other lateral shift means that there is some degree of relaxation, which is usually accompanied by the formation of structural defects.

The film thickness we are interested in is in the nanometre range. At this scale the diffraction peak suffer from finite size effects, which means that the width of the



Figure 3.12: Film - substrate stacking. (Left) The film has relaxed so the inplane lattice parameters are different from the substrate's. (Right) Epitaxial relation between the film and the substrate. No in-plane relaxation has occured.

film's diffraction spot is larger than that of the substrate (Figure 3.13-left). One can deduce the thickness of the film from the inverse of the Full-Width at Half Maximum of the corresponding peak. If the crystal lattice planes are arranged in a mosaic pattern, the lateral spread of the peak is increased, as shown in Figure 3.13(centre). In case of a superlattice Figure 3.13(right), several features can be distinguished. First, the superlattice is composed of A+B pairs, repeated a certain number of times. This periodicity is reflected by the superlattice peaks. The position of the zeroth order superlattice peak contains information about the lattice parameters of the constitutive A and B materials. The interference between the x-rays reflected by the top surface and bottom surface of the superlattice creates interference fringes in-between the superlattice peaks, from which the total thickness can be estimated.

Ferroelectric materials normally develop specific domain patterns, which depend on the mechanical and electrical boundary conditions. These domains usually have well defined periodicities. The periodic polar domains inevitably give rise to periodic strain fields, which enables the use of x-rays to probe the periodic lattice perturbation. It will be shown that this leads to so-called diffraction satellites,



Figure 3.13: **Real space - Reciprocal space equivalence**. (Left) The film peak is extended along the vertical axis due to its small thickness (few nanometers), as compared to the substrate (0.5 mm). (Centre), If the film displays mosaicity, its peak will show lateral broadening. (Right), Description of a superlattice reciprocal space.

which are usually present next to the superlattice peaks, or the grown film's peak. In order to understand how the diffraction satellites emerge, the scattering amplitude is considered in the case of a standing sinusoidal strain wave [97]. In this case, the "unit cell" is extended to include a full period of the periodic strain wave (instead of just the basis atoms). The electronic charge density is approximated to:

$$\rho(\vec{r}) = \sum_{\vec{r}_n} \delta(\vec{r} - \vec{r}_n - \vec{A} \sin(\vec{Q} \cdot \vec{r}_n)), \qquad (3.3.11)$$

where $\vec{A}\sin(\vec{Q}\cdot\vec{r}_n)$ represents the lattice perturbation, and \vec{r}_n is the atomic position vector. The scattering amplitude of the scattering vector \vec{k} is just the Fourier transform of the charge density:

$$\rho(\vec{k}) = \sum_{\vec{r}_n} \int \delta(\vec{r} - \vec{r}_n - \vec{A}\sin(\vec{Q} \cdot \vec{r}_n)) e^{i\vec{r}\vec{k}} \, d\vec{r} = \sum_{\vec{r}_n} e^{i\vec{k}(\vec{r}_n) + \vec{A}\sin(\vec{Q} \cdot \vec{r}_n)}$$
(3.3.12)

Using the Jacobi-Anger expansion for the exponential with the sine term

$$e^{iz\sin(n\phi)} = \sum_{n=-\infty}^{\infty} e^{in\phi} J_n(z)$$
(3.3.13)

gives the following form to the scattering amplitude:

$$\rho(\vec{\mathbf{k}}) = \sum_{\vec{\mathbf{r}}_n, n} e^{i(\vec{\mathbf{k}}+n\,\vec{\mathbf{Q}})\cdot\vec{\mathbf{r}}_n} \mathbf{J}_n(\vec{\mathbf{k}}\cdot\vec{\mathbf{A}})$$
(3.3.14)

Because the Bessel function does not depend on the atomic positions, the sum over \vec{r}_n is non-zero only if $\vec{k} + n \vec{Q}$ is a multiple of a lattice vector, \vec{G} . This means that $\vec{k} = \vec{G} - n \vec{Q}$. It results in the scattering factor having the form:

$$\rho(\vec{k}) = J_0(\vec{k} \cdot \vec{A}) \,\delta(\vec{k} - \vec{G}) + J_1(\vec{k} \cdot \vec{A}) \,\delta(\vec{k} \pm \vec{Q} - \vec{G}) + \dots \tag{3.3.15}$$

Experimentally, by performing an ω scan, the scattered wave-vector (k) orientation is varied. When the condition $\vec{k} = \pm \vec{Q} + \vec{g}$ is met, the scattering is coherent and it gives rise to diffraction satellites.



Figure 3.14: Angle space - Q space coordinate transform. (Left), Incident and scattered vectors general geometry. (centre) Side view. (Right, Top view).

Technically, the ω , $\vartheta - 2\vartheta$ or the RSM scans etc. are cuts of the reciprocal space performed in angle space. For example, a 2D RSM map is a surface embedded in a 3D space of curvilinear coordinate axes (ω , $2\vartheta_{\rm H}$, $2\vartheta_{\rm V}$). In order to analyze the real space periodicities, a coordinate transform from the curvilinear system (ω , $2\vartheta_{\rm H}$, $2\vartheta_{\rm V}$) to the rectangular system (Q_x , Q_y , Q_z) needs to be performed. With the help of the schematics shown in Figure 3.14 the deduction of the transforms is straightforward and the formulas are shown below:

$$Q_{x} = \frac{2\pi}{\lambda} \left(\cos(2\vartheta_{V} - \omega) \cos 2\vartheta_{H} - \cos \omega \right)$$
(3.3.16)

$$Q_{y} = \frac{2\pi}{\lambda}\cos(2\vartheta_{V} - \omega)\sin 2\vartheta_{H}$$
(3.3.17)

$$Q_{z} = \frac{2\pi}{\lambda} \left(\sin(2\vartheta_{V} - \omega) + \sin \omega \right)$$
(3.3.18)

3.3.3 Circular Dichroism

Dichroism is a scattering phenomenon, where the scattering cross-section of a photon in a medium is dependent on the polarization state of the incident photon. Circular/linear dichroism involves incident photons which are circularly/linearly polarized. Polarization domains can be observed by x-ray diffraction. Moreover, the domains can possess a left/right handedness, which cannot be detected by standard x-ray diffraction. This property is called chirality. Most common in magnetism (because the magnetic moment breaks time reversal symmetry), circular dichroism experiments can distinguish between e.g. flux-closure domains and Ising type domains [98]. Without going into details, to measure the dichroic signal one proceeds as follows. The diffraction signal of the domains is measured for both left and right circularly polarized x-rays. If the domains possess chirality, left/right x-rays have different scattering cross-sections, therefore, the quantity $(I_{left} - I_{right})/(I_{left} + I_{right})$ will have non-zero values for the diffraction satellites. When considering ferroelectric domains, the polarization does not break time symmetry, however, a dichroic signal can still be measured. For an experiment performed at resonance, Lovesey has shown that it can be traced to the x-ray scattering by a chiral arrangement of charge density quadrupolar moments [99]. Off-resonance, the source of the dichroic signal can be something like a natural dichroism. Finding the source for a dichroic signal is not trivial and is beyond the scope of this thesis.

3.3.4 Data acquisition

X-ray diffraction studies were performed at several synchrotron facilities. The synchrotron storage rings at Brookhaven National Laboratory and Advanced Light Source, Argonne National Laboratory use "undulators", causing the electrons to oscillate and emit electromagnetic waves. This ensures a high photon flux, of approximately 10^{15} ph/s. The storage rings at Diamond Light Source and the European Synchrotron Radiation Facility use bending magnets instead of "undulators", resuling in a lower photon flux (~ 10^{12} ph/s).

Superlattices of PTO/STO were studied at Brookhaven National Laboratory, NSLS-2, beamline 8-ID, at 8 keV beam energy. Reciprocal space mapping as well as temperature dependent XRD on the PbTiO₃/SrTiO₃ superlattices were performed at the European Synchrotron radiation Facility, XMaS-Grenoble, beamline BM28, at 7.7 keV beam energy. Diffraction studies were carried out on SRO/PTO/SRO at the I16 beamline of the Diamond Light Source using an energy of 8.04 keV and a spot size of 200 μ m×60 μ m. Dichroism experiments were performed at 7.7 keV on beamline 4-ID-D at the Advanced Light Source, Argonne National Laboratory with the circular polarised light generated using a diamond phase retarder. Lab based XRD studied were also performed using a Panalytical X'Pert Pro MRD diffractometer with Cu K_α radiation and a 1D PiXcel detector.

3.4 Electron microscopy

3.4.1 Conventional TEM

The basic idea behind TEM is that it uses electrons to "see" structures with a resolution down to a few picometers. This feat is possible via de Broglie's waveparticle duality. Technically, the sample is under a beam current of electrons and due to the distance between the electron source and the specimen, the electrons behave like plane-waves. The interaction of the plane-waves with the specimen results in an exit-wave which is projected onto a detector (charged-coupled device (CCD) camera / phosphor screen). In this way, an image of the specimen is formed and the contrast within this image is rooted in two mechanisms: amplitude contrast and phase contrast. In the case of an amplitude contrast, the sample need to be thick enough in order to sufficiently alter the scattering of the electrons. On the other hand, the phase contrast implies that the sample only alters the phase of the incident wave (thin samples).



Figure 3.15: Sketch of a TEM operating principle. The incident wave interacts with the specimen, considered thin enough to only change the phase of the incident beam. The optics system, can construct either a magnified image of the specimen, or its reciprocal space. The resulted information is recorded by the detector (fluorescent screen, CCD camera etc.).

Electron microscopy studies are an important part of this thesis and it is worth going through the basics of how the image is formed in a microscope. For this purpose, the weak phase object approximation [100] is a good starting point. It assumes a thin specimen, which only alters the phase of the incident wave. The specimen is under parallel illumination. If the incident plane-wave is ψ , the interaction with the specimen changes only the phase of the incident wave. In the weak limit it has the form:

$$\psi_{\text{exit}}(\vec{\mathbf{r}}) = \psi_{\text{inc}} e^{i\sigma V(\vec{\mathbf{r}})} \approx \psi_{\text{inc}}(1 + i\sigma V(\vec{\mathbf{r}})), \qquad (3.4.1)$$

where σ is an interaction constant and V(\vec{r}) is the projected potential of the specimen. In its back focal plane, the objective lens forms the Fourier transform of the specimen exit wave:

$$\psi_{\text{exit}}(\vec{q}) = \text{FT}[\psi_{\text{exit}}(\vec{r})] \tag{3.4.2}$$

The exit wave then passes through magnetic lenses and apertures before reaching the detector. The objective lens introduces aberrations, while the objective aperture contributes with its own transfer function. Thus, at the detector, the wave function has the form:

$$\psi_{\text{exit}}(\vec{q}) = \psi_{\text{exit}}(\vec{q}) t_{\text{aperture}}(\vec{q}) e^{-i\chi(\vec{q})}, \qquad (3.4.3)$$

where $t(\vec{q})$ is the transfer function of the objective aperture, and $\chi(\vec{q})$ describes the objective lens aberrations. If, for simplicity, the lens system has cylindrical symmetry, then $\chi(\vec{q}) = \chi(\alpha)$ and:

$$\chi(\alpha) = \frac{2\pi}{\lambda} \left(\frac{1}{2} C_1 \alpha^2 + \frac{1}{4} C_3 \alpha^4 + \frac{1}{6} C_5 \alpha^6 \right), \tag{3.4.4}$$

where $C_1 = \Delta f$ is the defocus and C_3 is the spherical aberration. Higher order or asymmetric aberration functions are beyond the scope of this thesis and will not be further considered.

The detector records the square modulus of the exit wave, $I = |\psi_{exit}(\vec{r})|^2$, which by virtue of the above rationale is:

$$I = |\psi_{exit}(\vec{r})| = \psi_{exit}(\vec{r}) \circledast FT^{-1}[t_{aperture}(\vec{q}) e^{-i\chi(\vec{q})}] = \psi_{exit}(\vec{r}) \circledast t(\vec{r}), \quad (3.4.5)$$

where \circledast is the convolution operator.

The ray optics for two typical TEM operational modes is shown in Figure



Figure 3.16: **Ray paths in a TEM**. (Right) In imaging mode. (Left) In diffraction mode

3.16. In the imaging mode, an objective aperture is inserted in the *back-focal plane* of the objective lens (Figure 3.16a). In the diffraction mode, a selected area diffraction aperture is inserted in the *image plane* of the objective lens (Figure 3.16b). In this mode the reciprocal space of the specimen is projected onto the detector. More details can be found in the referenced book [101].

3.4.2 Selected area diffraction pattern

As mentioned in the previous section, a transmission electron microscope can be operated in diffraction mode, which means that the reciprocal space of the specimen is projected onto the detector (Figure 3.16b). The strength of this method, as far as diffraction techniques go, lies in the very short wavelength associated with the electrons. As an example, for an electron accelerated at a voltage of 200 keV the de Broglie wavelength is 2.5 pm, compared to the wavelength of a photon at 8 keV, which is ~154 pm. Compared to x-ray diffraction, the Ewald sphere of electrons is

much larger, and considering that the sample is thin, is also intersects more points of the specimen's reciprocal space. Unlike XRD, where the scanned reciprocal space volume is restricted to a region around the Bragg peak, TEM diffraction can capture the projected symmetry of the specimen. This makes it ideal for investigations into the crystalline stacking of superlattices or the possible periodic domains in ferroelectric films. Nevertheless, it has certain drawbacks. One of them is that one cannot identify the position of the Bragg peaks with the same precision as in XRD. Even if the geometrical (Bragg) condition is perfect, the lens system inevitably introduces aberrations. The second reason is related to the high dynamic range of the electrons. In order to record less bright peaks such as diffraction satellites, a higher acquisition time is required. However, this will saturate the brighter peaks such as the direct beam. On the other hand, a low acquisition time will not capture the less intense spots. To compensate for the limited dynamic range of the detector, the diffraction image is acquired by taking multiple shots with different exposure times, ranging from minutes (for the weak peaks) to miliseconds (for the bright peaks). The final image, referred to as a High Dynamic Range (HDR) electron diffraction image, is created by overlapping all images in such a way that the saturated peaks are removed [102].

3.4.3 Diffraction contrast imaging

As mentioned, in diffraction mode the reciprocal space of the specimen is projected onto the detector. The pattern always has one spot, called the direct beam, formed by electrons which are scattered along the beam trajectory. All other spots are formed by electrons scattered by specific (hkl) planes. One can form an image using only the direct beam (Bright Field - BF, Figure 3.17a) or the electrons scattered by one set of hkl planes (Dark Field - DF, Figure 3.17b). This type of the contrast is an *amplitude contrast*, which normally occurs because of two reasons: there is a thickness variation within the sample which means that the amount of material which scatters the electrons can vary locally, and/or the diffraction can differ locally due to the inhomogeneities in the specimen. Because of these reasons, it is also called mass-thickness contrast.



Figure 3.17: Bright Field and Dark Field imaging. (Top), Example of a difftaction pattern where specific peaks are excited. A, Bright field mode utilizes the transmitted beam, by selecting the central spot using the objective aperture. B, Dark Field mode selects the scattered electrons.

There is a special type of amplitude contrast, called *diffraction contrast*, where most of the incoming electrons are scattered by a single set of {hkl} planes. This is achieved by tilting the sample so that we bring the hkl planes into the Bragg condition. The other diffracted beams do not disappear, but they become faint. Therefore, in this geometry, only two beams are strong, the direct beam and the {hkl} diffracted beam. This technique is called *two-beam* condition, and is sketched in Figure 3.18a. In order to image the scattering {hkl} planes, we need to select the strong diffracted beam. Imaging the off-axis diffracted beam will induce aberration-related artifacts in the final image, therefore, the beam needs to be tilted so that the strong beam is brought on-axis (Figure 3.18b). By doing so, the strong diffracted beam becomes weak, and we obtain an image in the *weak-beam* regime. This imaging technique is useful when studying dislocations, because the contrast is rather insensitive to the location of the defect in the specimen; it is also useful when studying defects that are close to each other ($\sim 4 \text{ nm apart}$).



Figure 3.18: **Beam-specimen specific geometries**. **a**, Sample is tilted to the diffraction condition is satisfied by a specific set of (hkl) planes. **b**, The beam is tilted keeping the sample in the same position as in (a). In this case, the previously strong \vec{g} becomes weak. This is the weak-beam contrast. **c**, The beam is tilted so the $-\vec{g}$ becomes strong, hence strong-beam condition. **d**, Sketch of the positive and negative excitation error.

Another imaging approach to bring the weak, off-axis hkl reflection into the optical axis (Figure 3.18c). This causes it to become strong, giving the technique its name, *strong-beam* condition. In the final image, the excited beam appears bright in the areas where the Bragg condition is satisfied, making it useful when studying lattice perturbations which normally take the lattice planes in and out of the Bragg condition. Such lattice perturbations can be the ferroelectric domains. It is worth mentioning that the Bragg condition is not normally satisfied in an ideal sense. The amount of deviation from the ideal condition is quantified by the *excitation error* (\vec{s}), so $\vec{K} = \vec{g} + \vec{s}$, where \vec{g} is the diffraction vector (Figure 3.18d). As a rule, to maximize the contrast in the strong beam condition, one should form the image under positive excitation error.

3.4.4 Diffraction contrast simulations

The Howie-Whelan set of equations provides a phenomenological approach to understanding the observed diffraction contrast. As the electron beam passes through the specimen, the direct and the diffracted beams are recorded on the detector. The exit-wave amplitude can be written as a sum of contributions from every \vec{g} -vector:

$$\psi_{\text{total}} = \varphi_0 e^{2\pi i \vec{\mathbf{g}}_0 \cdot \vec{\mathbf{r}}} + \varphi_{g_1} e^{2\pi i \vec{\mathbf{g}}_1 \cdot \vec{\mathbf{r}}} + \varphi_{g_2} e^{2\pi i \vec{\mathbf{g}}_2 \cdot \vec{\mathbf{r}}} + \dots, \qquad (3.4.6)$$

where ϕ_g is the diffracted beam amplitude.

If we consider that only one diffracted beam is strong (corresponding to a \vec{g} -vector), then we are in the two-beam approximation (the second strong beam is the direct beam) and the Howie-Whelan equations are:

$$\frac{\mathrm{d}\varphi_{\mathrm{g}}}{\mathrm{d}z} = \frac{\pi i}{\xi_{\mathrm{g}}} \varphi_{0} \mathrm{e}^{2\pi i \mathrm{s} z} + \frac{\pi i}{\xi_{0}} \varphi_{\mathrm{g}}$$
(3.4.7)

$$\frac{\mathrm{d}\varphi_0}{\mathrm{d}z} = \frac{\pi i}{\xi_0}\varphi_0 + \frac{\pi i}{\xi_g}\varphi_g \mathrm{e}^{2\pi i \mathrm{s} z},\tag{3.4.8}$$

where ξ is the extinction distance and s is the excitation error. An important aspect of these equations is that any change in the amplitude of either the direct (φ_0) or diffracted (φ_g) beams depends on both beams, and the fact that the amplitude changed with distance results in a diffraction in the dynamical regime. For more information the reader is referred to the textbooks of William and Carter [103].

3.4.5 Scanning transmission electron microscopy

The description of the image formation in conventional TEM assumed a parallel illumination of the specimen. In scanning transmission microscopy, the incident beam is convergent on the specimen, and rastered across the area of interest. The scattered electrons are collected by annular detectors located at various angles. A typical imaging detector is the Annular Dark Field (ADF) detector, centered on the optical axis between ~ 50-150 mrad. Because of the high collection angle, the scattered intensity is roughly proportional to ~ Z^2 . The resulting Z-contrast makes the images relatively straight-forward to interpret where regions with brighter signal correspond to the position of the column of atoms, while the lack of signal indicates

a vacuum region. This enables the accurate determination of the position of the column of atoms, which is used to approximate the local orientation of the polar displacements within the epitaxially grown layers.

3.4.6 Specimen preparation

STEM and cross-sectional DF-TEM samples were prepared using a TESCAN FIB-SEM system. The sample was flat-polished starting with an ion energy of 30 keV and 2 nA beam current, before decreasing it down to 2 keV and 50 pA for the final polish. Plan-view DF-TEM samples were flat polished on an Allied High Tech Multiprep using a series of diamond abrasive sheets with 30 μ m down to 1 μ m roughness. The sample was thinned to a thickness of about 30 μ m, followed by further thinning in a Gatan Precision Ion Polishing System with a starting energy of 6 keV and 60 μ A which decreased to 100 eV 20 μ A for final cleaning.

3.4.7 Microscopes

STEM images were recorded in a double CEOS-corrected Schottky emission JEOL ARM-200F microscope operating at 200 keV. Annular Dark Field signals were collected in the range between 45-180 mrad, with a probe forming a convergence semi-angle of 21 mrad. For accurate position/displacement measurements, each image is reconstructed from several orthogonal fast scans which were aligned for rigid and non-rigid distortions using the SmartAlign routines55. Atomic positions were then found using nonlinear least squares fitting of 2D Gaussian functions including contributions from nearest neighbours. Diffraction contrast images were recorded with two beam conditions on a JEOL 2100 with a LaB6 filament operating at 200 kV.

3.5 Density Functional theory

3.5.1 Fundamentals

The density functional theory (DFT) approach is widely used by both experimentalists and theoreticians for *ab initio* investigations into the structural and electronic properties of matter, and to make predictions of novel materials and experimental outcomes.

DFT is a theory of correlated many-body systems. In 1964 P.Hohenberg and W.Kohn [104] have shown that the density of particles of a quantum manybody system found in its ground state can be considered as a "basic variable". This means that all the properties of the system are functionals of the ground state density, giving the technique its name (DFT). It is worth stating the Hohenberg-Kohn theorems that are at the basis of the modern formulation of DFT (the proofs can be found in [105]):

1. For any system of interacting particles in an external potential $V_{ext}(\vec{r})$, the potential $V_{ext}(\vec{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\vec{r})$.

2. A universal functional for the energy E[n] in terms of the density $n(\vec{r})$ can be defined, valid for any external potential $V_{ext}(\vec{r})$. For any particular $V_{ext}(\vec{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\vec{r})$ that minimizes the functional is the exact ground state density $n_0(\vec{r})$.

The density functional theory is an exact theory of many-body systems. If the ground state density is known, all properties (static susceptibilities, specific heat, band structure, fermi surface etc.) can be derived. However, solving the Schrödinger equation of a system of interacting particles, is too difficult. For such a system, the Hamiltonian is:

$$\hat{H} = -\frac{\hbar}{2\,m_e} \sum_{i} \nabla_i + \sum_{i} V_{ext}(\vec{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$
(3.5.1)

Without going into details, the total energy functional associated with the Hamiltonian is:

$$E_{HK}[n] = T[n] + E_{int}[n] + \int V_{ext}n(\vec{r}) d\vec{r},$$
 (3.5.2)

where T[n] is the kinetic energy. Fortunately, in 1965, W.Kohn and L.J. Sham have proposed a replacement of the many-body problem (described by the beforementioned Hamiltonian) with an auxiliary system of independent particles, which is more easily solved [106]. The *ansatz* set up by Kohn and Sham assumes that the ground state density of the original system is the same with one describing a system of independent particles. All the many-body effects of the original system are contained within a term called the *exchange-correlation functional*. Therefore, in the Kohn-Sham approach, the energy functional has the form:

$$E_{HK}[n] = T_s[n] + \int V_{ext}n(\vec{r}) d\vec{r} + E_{Hartree}[n] + E_{xc}[n],$$
 (3.5.3)

where
$$E_{\text{Hartree}}[n] = \frac{1}{2} \int d^3(\mathbf{r}) d^3(\mathbf{r'}) \frac{n(\vec{r})n(\vec{r'})}{|\vec{r} - \vec{r'}|}$$
 (3.5.4)

In principle, if the exchange-correlation functional is known, the ground state densities of the many-body system can be found by solving the Kohn-Sham equations [105].

The accuracy of the Kohn-Sham approach is dependent on how well the $E_{xc}[n]$ term describes the true exchange-correlation energy. Kohn and Sham pointed out in the early days that solids can often be considered to be close to the limit of an homogeneous electron gas. In this approximation the exchange-correlation functional is local in character, which means that $E_{xc}[n]$ depends of the local density. This approximation is called the Local Density Approximation, or LDA, and works best for systems close to a homogeneous electron gas, such as metals. An improvement over LDA is a functional which takes into account the magnitude of the gradient of the density, as well as the density itself. This results in the Generalized-Gradient Approximation (GGA). For crystalline materials, it these two

types of functionals that have constantly been adjusted in order to better describe the exchange-correlation energy. One can also consider the Laplacian of the density, along with its gradient and the density, resulting in meta-GGA. There are various degrees of complexity, and more details can be found here [107].



Figure 3.19: Total energy minimization workflow.

As a final point of the DFT overview, it is necessary to describe the workflow (Figure 3.19) that leads to the ground state density. The Kohn-Sham *ansatz* replaces the many-body system with an auxiliary system of independent particles. The

resulting set of Kohn-Sham equations of independent particles needs to be solved under the condition that the effective potential $V_{eff}(\vec{r}) = V_{ext}(\vec{r}) + V_{Hartree}[n] + V_{xc}[n]$ and the density are consistent. The process starts from an initial guess of the density. For example, the initial guess for a crystal can be the sum of the atomic charge densities of all the basis atoms. Using this density, the effective potential is constructed and the Kohn-Sham system is solved for the new density. The new density is likely to differ from the initial guess, so a new one is calculated from mixing the initial guess and the newly obtained density. Then another external potential is constructed and the process is repeated until the input density differs from the output density by a set amount. This is called a self-consistent (SCF) cycle. A non self-consistent (NSCF) calculation involves a single run of the described scheme. This is usually performed to process the ground state density found from a selfconsistent cycle.

3.5.2 Simulated systems

In this subsection, the focus is on the different types of systems which are simulated in this thesis using the Quantum ESPRESSO code [108, 109], as well as to describe their own particular characteristics. A typical DFT code, which uses plane-waves as the basis functions necessarily has a unit cell which is periodically repeated along all three direction, forming an infinite crystal. This is because a plane-wave code solves the Kohn-Sham equations in Fourier space.

There are three main types of system architectures. The first one consists of a single unit cell of the material of interest (Figure 3.20a). This architecture is chosen when the structure of the material needs to be optimized (atomic and cell relaxation) with the purpose of finding its bulk properties (density of states, electronic band structure, polarization etc.). The second type of architecture is called a supercell (Figure 3.20b). It involves stacking together multiple unit cells, in order to form a larger block. This allows one to artificially reduce the symmetry of the unit cell by e.g. creating point defects, or displacing the atoms by hand. The main advantage of this architecture is that it allows the user to stack different



Figure 3.20: System architecture. a, The unit cell is representative of an infinite crystal. This is used in bulk calculations. b, Supercell architecture, where the representative unit is constructed using multiple unit cells (a) of possible various materials. Slab, Here, vacuum is introduced in an attempt to separate the supercell from its periodic image.

materials, enabling the study of interfaces. Because the system is periodically repeated along all three directions, the system is under short-circuit boundary conditions. The third, and final type of system is a supercell which contains vacuum. This is called a slab (Figure 3.20c). It has the particular advantage of completely decoupling the materials within the slab from their periodic images (at least along one direction). This means that one can independently study materials that are necessarily part of a periodic system, e.g. isolated molecules, isolated 2D layers, isolated heterostructures, adsorption of molecules by various surfaces etc.

Most of the interests in this thesis revolve around utilizing supercells and slabs, consisting of crystalline insulators and/or conductors. In section 3.5.1, the workflow of a DFT simulation was briefly described, and two key points were emphasized: the density and the exchange-correlation functional. The initial density is approximated using the so-called pseudopotential files, which contain information about the charge distribution around the nucleus. In this thesis, ultrasoft [110] and projector-augmented wave [111] pseudopotentials were used. The exchangecorrelation functional is crucial in obtaining the experimentally observed bulk properties. For crystalline insulators and conducting oxides, PBEsol [112, 113] has been shown to reproduce (within an acceptable error) the experimentally observed lattice constants of the materials simulated in this thesis [114].

A final procedural point is made regarding the calculation of the density of conduction electrons, and the real-space representation of the wavefunctions, using the Quantum ESPRESSO code. First, a self-consistent calculation (SCF) is performed over a Monkhorst-Pack k-mesh [115] to get the effective potential and the wavefunctions corresponding to the ground state of the system. Due to the size of the slab, the k-states are folded, so the k-mesh can be coarse. Next, a non self-consistent calculation (NSCF) with a denser k-mesh is run to obtain the wavefunctions (density) with a higher degree of accuracy and to better describe the charge density at the Fermi level (if there is a conducting material in the slab). At the third step, a band-type calculation is run, where you can directly specify the k-points or the k-path in the reciprocal space. This will calculate the eigenvalues for each band at the specified k-points. The real-space wavefunctions depend explicitly on the band index and the k-point. Therefore, the aim is to use the band calculation to extract k(band index, energy). This is possible as the dispersion relation E(k) can be reversed for each band. The real-space wavefunctions are given by a routine called wfck2r.x whose output is a complex valued block of data structured as follows: n_x , n_y , n_z , N_{bands} , $N_{k-point}$. Each k-point contains all N_{bands} and each band contains $n_x \times n_y \times n_z$ data entries. At this point it clear why we needed k (energy) for each band. For the calculation of the conduction electrons, or to plot the wavefunctions in real space, one needs only to select the energy window and use the following formula:

$$\rho_{\rm free}(\vec{r}) = \sum_{E > E_{\rm Fermi} - E_{\rm min}} w_{n\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\vec{r})|^2, \qquad (3.5.5)$$

where $w_{n\mathbf{k}}$ is the k-point weight and $f_{n\mathbf{k}}$ is the occupancy number.

Chapter 4

$PbTiO_3$ -SrTiO₃ superlattices

4.1 Introduction

Pulsed laser deposition techniques augmented by RHEED capabilities have enabled the growth of thin films with sub-unit cell precision, and a better control over the interface sharpness. This led researchers to experiment with ferroelectric thin films under specific mechanical and electrical boundary conditions [116–118]. As a result, strained ferroelectric films with insulating boundary layers, such as PbTiO₃/SrTiO₃ superlattices were shown to be an ideal environment for hosting topological entities, now known as polar vortices. This is a significant progress in the field of ferroelectrics, because such structures were known to exist only in ferromagnets as spin textures. Since the discovery of polar vortices in PTO/STO superlattices, efforts were made to interact with these structures via mechanical stress [119], light pumping [120] and electric fields [121].

Nevertheless, a number of questions remain unanswered. How does the polarization texture change with varying PTO thickness? In a superlattice, all layers are coupled by mechanical boundary conditions. Does this impact the polar ordering, be it in-plane or out-of-plane? What kind of phase transition do polar vortices go through by changing the temperature? The purpose of this chapter is to answer these questions, enriching our knowledge of this exotic form of polar ordering. In the following section electron microscopy is used to reveal the domain type within the PTO films for two thickness regimes and highlight the main differences between them. Dark Field imaging is employed, where the information is given in terms of a diffraction contrast, to observe any long-ranged ordering, which is limited to a field of vision of about 200 nm). Second, aberration-corrected Scanning Transmission Electron Microscopy (STEM) is used to map the displacements at the unit cell level and reveal the local polar ordering.

In the follow-up section, detailed X-ray reciprocal space mapping is performed on a range of samples with the PTO thickness varied inside the interval 7-20 uc. The simultaneous emergence of two perpendicular periodicities is shown along the principal axes, as well as an out-of plane ordering as thickness of the PTO is increased. Furthermore, all diffraction features around the substrate Bragg peak are linked to their real space correspondent.

The final section is focused on the system showing polar vortices, where an in-depth analysis of the behavior with temperature of the various periodicities present in the system is performed. In other words, of interest is the type of the phase transition the vortices go through.

4.1.1 Sample growth

The DSO substrate is $(110)_{\rm o}$ oriented with a miss-cut angle of about 0.05°. The stacking direction of the grown films is along $[110]_{\rm o}//[001]_{\rm pc}$ with the in-plane directions given by $[001]_{\rm o}//[100]_{\rm pc}$ and $[1-10]_{\rm o}//[010]_{\rm pc}$. This geometry is shown in Figure 3.2a. Because the DSO lattice parameters are $a_{\rm DSO} = 5.449$ Å, $b_{\rm DSO} = 5.726$ Å and $c_{\rm DSO} = 7.913$ Å, it implies that the in-plane directions $[1-10]_{\rm o}//[010]_{\rm pc}$ and $[110]_{\rm o}//[001]_{\rm pc}$ are not symmetry equivalent, (under C₄ rotation). This may have an effect on the domain distribution in the epitaxially grown ferroelectric layer.

In the literature [121–123] we find the superlattices grown on DyScO₃ substrates with an SrRuO₃ buffer layer, to improve the growth. In this study no buffer layer is used, and the SrTiO₃/PbTiO₃ superlattices were grown directly on the substrate by pulsed laser deposition with RHEED, so the thickness of the films



was precisely controlled. The temperature and the laser fluence for STO/PTO are

Figure 4.1: **Superlattice architecture**. **a**, Structural characteristics of the grown superlattices. **b**, Cross sectional ADF-STEM image of a STO-PTO superlattice. The electron beam is parallel to $[010]_{\rm pc}$. Bottom left inset shows that the interface between the STO and PTO is sharp down to the atomic level.

600/590 °C at 1 J cm^{-2} . The pulse frequency was 3 Hz for all layers and the partial oxygen pressure was kept at 0.1 mbar throughout the growth. The cooling rate was set at 20 °C min^{-1} in 200 mbar of O₂. The PbTiO₃ target is an in-house compressed and sintered pellet with 10% lead excess to compensate for the high lead volatility during growth.

 $m SrTiO_3/PbTiO_3$ superlattices were grown under these conditions, with architectures shown in Figure 4.1a. STO is highly polarizable (large dielectric permittivity [89]) and DFT studies have shown that the polarization from the PTO layer extends into the STO over ~3-4 uc from the interface [124]. To make sure that the PTO layers are electrically decoupled, the STO thickness increases accordingly. In order to verify that the interfaces are atomically flat, we perform STEM imaging on the PTO₁₆/STO₂₀ superlattice, as shown in Figure 4.1b. The contrast shown within the PTO layers arises from the local lattice perturbations induced by the polar domains.

A basic requirement for a superlattice studies in this thesis is that all layers are epitaxially strained and there is no strain relaxation through the generation of



Figure 4.2: **Reciprocal Space Map**. **a**, RSM around DSO $103_{pc}=332_{o}$ for the PTO₁₂ - STO₁₄ superlattice. **b**, PTO₂₀ - STO₂₀.

defects. In order to assess this at the macroscopic level, we perform X-ray Reciprocal Space Mapping (RSM) around the substrate's asymmetric reflection $332_0=103_{pc}$ (Figure 4.2) for two superlattice systems: 14 and 20uc PTO. In this geometry $[001]_0=[100]_{pc}$ is in the scattering plane. Among the many features present in this map, which will be explained later on, the crystal truncation rod is at the same Q_x value, regardless of the Q_z . This means that macroscopically, the superlattice shows no in-plane relaxation, therefore, is it in a strained state (clamped to the substrate). Here, and later on, the Q_x and Q_y directions are set along the $[h00]_{pc}$ and $[0k0]_{pc}$ directions respectively.

4.2 Cross-sectional electron microscopy studies

It was shown in the the previous section that the STEM image for the PTO_{16}/STO_{20} shows contrast within the PTO layers. This is due to the local strain fields generated by the polar distortions. If the lattice is disrupted by periodic/non-periodic modulations dark field (DF) imaging under two-beam condition can provide the contrast to highlight the polarization pattern. Therefore, DF-TEM imaging was performed on the PTO_{16}/STO_{20} superlattice, with the electron beam along the [010]_{pc} direction.

Because the DF-TEM signal is a diffraction contrast, if the atomic displacements satisfy the condition $\vec{g} \cdot \vec{R} > 0$, that region will appear as bright (otherwise, dark [125, 126]). Here, \vec{g} is the excited diffraction spot, and \vec{R} is atomic displacement direction of the atoms within the excited atomic planes. As a note, the direction of the displacements \vec{R} gives the direction of the polarization. First, the sample is tilted so the diffraction spot with $\vec{g} = [001]_{pc}$ is excited (Figure 4.3a). A doubling in the number of spots is observed along the $[100]_{pc}$ direction, because the selected area aperture isolates a region that has both the substrate and the film in it. Figure 4.3b shows the diffraction pattern corresponding to the substrate, revealing the same doubling of spots. Under these conditions, we observe an alternating bright/dark periodic contrast confined to the PTO layers, with a periodicity of ~11 nm, as shown in Figure 4.3c. If the illuminating conditions are changed so that $-\vec{g}$ is excited, the contrast in inverted. This means that there are regions with non-zero displacements along the $[001]_{pc}$ direction. The alternating bright/dark contrast shows that this component alternates between being parallel and anti-parallel to $[001]_{pc}$. Moreover, the contrast within the individual layers of PTO seems to align along the vertical axis, which implies that the PTO layers are coupled, most likely through the strain field.

Next, the $\vec{\mathbf{g}} = [100]_{\rm pc}$ vector is excited (Figure 4.3d). Here, clear diffraction satellites are observed, as a result of the superlattice periodicity (PTO and STO amount to about 15 nm), as highlighted in Figure 4.3d-inset. Such satellites are visible under the $\vec{\mathbf{g}} = [001]_{\rm pc}$ excitation as well. Furthermore, the diffraction contrast changes drastically. A wave-like pattern is present in all PTO layers with a heavy contrast of triangles along the $[100]_{\rm pc}$ direction, with a periodicity of about 11 nm. Again, when $\vec{\mathbf{g}} \rightarrow -\vec{\mathbf{g}}$ the contrast is inverted, which points towards the displacements having an additional component which is parallel to the interface. The bright/dark regions suggest the local orientation of the displacements: parallel (bright) and antiparallel (dark) to the $[100]_{\rm pc}$ direction. With this data alone, one cannot define the precise underlying polarization texture, as previous studies have shown that both polar vortices and flux-closure domains have a similar dark field contrast [119, 127]. To obtain information about polar displacements at the unit-cell level, we perform aberration-corrected STEM and focus on two thickness regimes: 12 and 16uc PTO. In Figures 4.4a and b we show a high magnification ADF-STEM image



Figure 4.3: Cross-sectional Dark Field TEM. a, Diffraction image showing the excited g-vector. b, Kinematic simulation of the DSO substrate, projected along the $[010]_{pc}$. Note the doubling of diffraction peaks along the $[100]_{pc}$ direction. c, Twobeam conditions diffraction contrast, with g=001 excitation vector. d Diffraction image showing the excitation vector. (Inset) The diffraction contrast periodicity along [001] can be observed as satellites around the films diffraction spots. e, Twobeam conditions diffraction contrast, with g=100 excitation vector.

of the superlattices' area of interest. As expected, the interfaces are atomically flat, with the PTO layers evidenced by a brighter contrast. In a ferroelectric, strain and polarization are always coupled. Therefore, different polar patterns should result in different strain textures. With this in mind strain analysis and STEM displacement mapping was performed on the 12 and 16uc PTO superlattices. As expected, polar vortices and flux-closure domains have different strain fingerprints, shown in Figures 4.4c and d. Vortices show a tilted rhombohedral pattern, while the flux-closure domains display a wave-like shape. This subtle difference is linked to the fundamental difference between vortices and flux closure domains. The former

shows a continuous rotation of the polarization, while the latter is made up of regions where the polarization is homogeneous [128].



Figure 4.4: Strain/displacement mapping. a, b, ADF-STEM image of the PTO-16 (a) and PTO-20 (b) superlattices. c, d, Strain mapping highlighting the out-of-plane strain variation throughout the PTO layers. Note the different strain textures between the vortex (c) and the the flux-closure (d). Insets 1 and 2 reveal the displacement mapping within the grown PTO layers corresponding to the boxed areas in (c) and (d), respectively.

To further emphasize this, STEM displacement mapping on regions highlighted by 1 and 2 are shown at the bottom of Figure 4.4. Pairs of clockwise (CW) and counter-clockwise (CCW) vortices form (1), with the vortex core aligned along a horizontal line. On the other hand, the flux closure pattern (2) is composed of regions with homogeneous polarization, with cores that are clearly misaligned, displaying a strong zig-zag pattern. As we will find further on, these differences will impact the alignment of the polar textures between the PTO layers in the superlattice.

Pursuing such an analysis for all samples might not yield conclusive results about the changes in the domain morphologies with respect to the PTO thickness, for the following reasons. The dark field image under two-beam conditions shows diffraction contrast based on the electron scattering off the atomic planes that satisfy the diffraction condition. The thickness of the sample influences such contrast, which means that any additional modulation that can be present along $[010]_{pc}$ (parallel to the beam path, in this geometry) will add to the diffraction contrast. Furthermore, the STEM image shows, to some extent, the average position of a column of atoms. This averages out any possible modulation that occurs in the thickness of the sample, i.e. parallel to the beam. Because of this, electron microscopy techniques do not provide a full picture of the polarization in PTO. On the other hand, the observed polar pattern is periodic, making the X-ray diffraction studies invaluable in providing complementary information about the periodicities in all three directions.

4.3 X-ray diffraction analysis of polar topologies

As was briefly revealed in the XRD asymmetric scans shown in Figure 4.2, the DSO Bragg peak is decorated by a number of features. The goal in this section is to analyze the behavior of these features with respect to the thickness of the PTO layer, as well as create a link between them and the real space polarization texture. As a note, the polarization itself is invisible to the X-rays, however, any polarization pattern will generate a strain on the crystal lattice. As was shown in the methods section a periodic strain wave generates satellite decorations (incommensurate or not) around the substrate Bragg peak.

Rocking curves were taken at azimuth angles 0° and 90°. At 0°, $[001]_0 = [100]_{pc}$ is in the scattering plane and we designate this direction as Q_x . When the azimuth is 90°, the $[-110]_0 = [010]_{pc}$ is in the scattering plane and we call this direction Q_y . In



Figure 4.5: Reciprocal space maps around DSO 002_{pc} . a, $[100]_{pc}$ is in the scattering plane. b, $[010]_{pc}$ is in the scattering plane.

Figure 4.5, the reciprocal space maps taken for the 7uc up to 12uc-PTO superlattices are shown, along the two azimuth directions, $Q_x = [100]_{pc}$ (a) and $Q_y = [010]_{pc}$ (b). The superlattice with 7uc of PTO does not show any diffraction satellite along Q_x and Q_y , meaning that there are no periodic structures, i.e. possibly monodomain. Superlattices with $N_{PTO} > 10uc$ show diffraction satellites along both Q_x and Q_y directions however, along Q_y the periodicity not as well defined. This asymmetry is maintained for superlattices with $N_{PTO} > 12uc$, as shown in Figures 4.6a, b along with new features becoming more visible as the PTO thickness is increased. These are labelled in Figure 4.6c as F1, F2 and F3. In the following sections their meaning will be made clear.

4.3.1 Preliminary quality analysis

Cross-sectional STEM imaging has revealed atomically flat interfaces over 100 nm length scale. Given the fact that one randomly cuts a FIB specimen from the grown



Figure 4.6: Reciprocal space maps around DSO 002_{pc} . a, $[100]_{pc}$ is in the scattering plane. b, $[010]_{pc}$ is in the scattering plane. c, Diagram of relevant features as observed in the RSM.

sample, it imposes the need to verify the interface roughness over a larger area. We employ the use of XRR (x-ray reflectivity) to obtain information about the surface roughness, films density and thickness. This is performed for all superlattice architectures, but in Figure 4.7a only the 10, 14 and 16uc of PTO are shown. Interference oscillations are present at all scattering angles and the slow decay of the signal implies low surface roughness. Data fitting was done in order to extract information about the thickness of the PTO (assuming the STO thickness known) and the density of the layers. The PTO thicknesses for the 10, 11, 12, 14, 16 and 20uc PTO systems, from the data fit, are 38.9, 39.3, 45.6, 55.2, 64.0, 77.4 Å. In Figure 4.7b, the real part of the scattering length density reproduces the behaviour of the PTO and STO material density. This is represented with respect to the distance from the substrate, with coloured boxes marking the PTO layers. Up to 14uc PTO thickness, the density shows similar values, however, it shows an increase above 16uc PTO. This could be linked to the change in the domain morphology, however, it is difficult to prove without further evidence. Finally, the thickness of the layers matches the values given in the table of Figure 4.1a, with ± 1 uc (~ 4Å) error.



Figure 4.7: **Sample quality**. **a**, Reflectivity data for superlattices with different PTO thicknesses. The intensity oscillations are evidence of sharp interfaces. **b**, Parameter fit of the reflectivity data shown in (**a**), showing the materials density throughout the superlattice and the thickness of the individual layers. the PTO has a higher density than PTO, represented by the blue rectangles.

A different aspect of the superlattice growth quality can be assessed from the crystal truncation rod (CTR) of the film present around the substrate Bragg peaks. Here, we image around the DSO $002_{\rm pc}$ peak, as shown in Figure 4.8a. Several features can be distinguished, aside the substrate $220_{\rm o}=002_{\rm pc}$ diffraction spot. There are indexed peaks, which we will deal with in a moment, and in between these peaks the intensity has an oscillatory behavior as a result of thin film interference. This interference phenomenon is heavily dependent on the interfaces being flat. The oscillation period gives the inverse of the full superlattice thickness.

$$d_{ml} = \frac{t_{STO}c_{STO} + t_{PTO}c_{PTO}}{t_{STO} + t_{PTO}}$$
(4.3.1)

$$d_{\rm ml} = \frac{4\pi}{Q_{\rm zero}} \tag{4.3.2}$$

where t and c are the thickness and the average out-of-plane lattice parameters and Q_{zero} is the zeroth order superlattice peak. The thickness of the PTO layers were refined thought the XRR measurements. Because the system is epitaxially strained to the substrate, the in-plane lattice constant is set to DSO, 3.953 Å. Assuming that the tensile stress on the STO unit cell is volume preserving, it gives $c_{STO} = 3.88$ Å. Hence, all parameters for d_{ml} are known, except for c_{PTO} , which means we can directly link the average out-of-plane lattice parameter of PTO to the zeroth order superlattice peak. Because the zeroth-order superlattice peak is hidden under the



Figure 4.8: **CTR scans a**, $\vartheta - 2\vartheta$ scans along the crystal truncation rod around the DSO 002_{pc} reflection. The indexed superlattice peaks are used to calculate the average out-of-plane lattice parameter of PTO. **b**, Out-of-plane lattice parameter of PTO within the various superlattice architectures.

DSO $002_{\rm pc}$, we need to use the other orders to interpolate the value at index zero, as shown in the inset of Figure 4.8a. Consequently, Figure 4.8b shows the evolution of the PTO average out-of-plane lattice parameter, with respect to the thickness of the PTO. Its values are around 4.01 Å (~ 4.18 Å for bulk), due to the tensile strain imposed by the substrate. While this value does not change significantly within the range of studied PTO thicknesses, it presents a decreasing trend with increasing thickness. The "kink" at 16uc PTO is possibly due to a change in domain morphology, as was previously hinted by the XRR data.

4.3.2 Polar topologies investigation - thickness dependence

Earlier, we have observed features (diffraction satellites) in the vicinity of the DSO Bragg peak, which were referred to as F1, F2 and F3 (Figure 4.6). As a reminder, the $[h00]_{pc}$ and $[0k0]_{pc}$ directions are labelled as Q_x and Q_y . First, we focus on feature F1 and its dependence on the PTO thickness (Figure 4.9). In order to extract the position of the F1 satellite, we integrate the signal inside a superlattice Brillouin zone, which is bounded by two adjacent superlattice peaks. The results are shown in centre and right panels of Figure 4.9. For the 16uc PTO superlattice, the F1 satellite is found at $Q_x = 0.06 \text{ Å}^{-1}$, corresponding to a real space periodicity of about 11 nm. We know from the previous section that polar vortices form along $[100]_{pc}=[001]_{o}$. Therefore, along the Q_x direction, the F1 features probe the same type of periodicity as observed in the dark field images of Figure 4.3, i.e. the vortex/flux-closure periodicity.

By varying the PTO thickness, several specific characteristics can be observed. The first one is the linear dependence of the real space periodicity on the thickness of the PTO layer, along both Q_x and Q_y directions. Kittel's law for ferromagnetic domains, translated to ferroelectrics, states that the domain size scales as the square root of the thickness [62]. This law, however, does not account for exogenous effects like strain gradient, which are present given the domain topologies, and will cause a deviation from the square root law [129]. Furthermore, the film thickness range in our studies is a few nanometers, up to ~10 nm, an interval too narrow to properly test for domain scaling law. Second, the periodicities along Q_y are slightly larger than along Q_x , however, much weaker. This is evident as the intensity of the F1 satellite along Q_x is constant w.r.t. the thickness, while the intensity along the Q_y direction decreases with increasing PTO thickness.

As we image around the substrate 002_{pc} , the vertical periodicities **do not** contain any in-plane component. The F2 satellites possess an internal structure along the Q_z direction, which points to some ordering along the out-of-plane direction. In order to understand the origin of this, we compare its Q_z line profile to the $Q_z = 0$ scan. (Figures 4.10a, b). The superlattices have different architectures, so


Figure 4.9: (Feature F1). **a**, (Left) RSM in the $Q_z - Q_x$ plane. (Centre) Line profiles along the Q_x direction, as a result of integrating the red boxed area along Q_z . The red box Q_z size represents one Brillouin zone of the superlattice. (Right) The real space periodicities and their dependence on the thickness of the PTO. **b**, Same processing performed along the perpendicular Q_y direction.

the corresponding superlattice peaks shown in the center panels (1) have different Q_z positions. These are tracked by dotted lines. On the right panels (a2) the line profile for Q_x satellites shows intensity modulations, most obvious for the systems with thicker PTO layers. The intensity peaks follow the same behavior as the superlattice peaks (dotted line). As mentioned, the superlattice peaks at $Q_z = 0$ are present due to the periodic repetition of PTO+STO layers, and the lateral position of the *F1* feature strictly represents the in-plane periodicity of the domains. Therefore, we conclude that it is the vertical alignment of domains between the different PTO layers of the superlattice which causes the before-mentioned internal structure of the *F1* satellite.





Figure 4.10: Internal structure of Feature F1. a, (Left) Boxed area include the CTR of the grown films (1) and the first order satellite (2). (Centre) Line profiles as a result of integrating the red boxed area (1) along the Q_x direction. Dotted lines mark the superlattice peaks. (Right) Line profiles of the first order satellite, showing features that are linked to the superlattice peaks observed in the crystal CTR. b, Similar treatment is carried out along the Q_y direction. c, Dark field TEM under g=001 excitation, showing the vertical alignment of polar regions, which is observed as the Q_z modulation of Feature F1.

To summarize the data so far, the F1 satellite along the Q_x direction displays similar intensity values regardless of the PTO thickness. The situation is different along the Q_y direction where the vertical alignment of the ferroelectric domains and intensity of the F1 satellite are dependent on the PTO thickness.

Features F2 and F3 are fundamentally different. They do not possess any internal structure, nor are they aligned to the superlattice peaks. Feature F2 forms a rhombohedral pattern with the superlattice 0 and +1 index peaks, and it is present in all samples along both the Q_x and Q_y directions. Because of this specific geometry, we calculate this angle for each PTO thickness along Q_y (Figure 4.11a) and Q_x (Figure 4.11b). For the systems up to 14uc of PTO, the angle value is rather constant (~55° - within measurement error) for both azimuths. Above 14uc, there is a jump of about 3°, observed along both directions, which is not present in the behaviour of feature F1, but was observed in the estimation of the PTO c lattice parameter and of the layers' density from the XRR data. We link such a jump to a change in polar topology from a vortex pattern, where the polarization rotates continuously (low strain gradient), to a flux-closure pattern where the polarization forms homogeneous closure domains (large strain gradient at the walls).



Figure 4.11: Angle of feature F2 and F3 relative to the zeroth order superlattice peak. a, Feature F2 angle dependence of the thickness of the PTO layers, along the Q_y direction. b, Similar treatment to (a) is carried out for feature F2 along Q_x . c, The thickness dependence of the feature F3 angle, relative to the zeroth order superlattice peak.

Feature F3 is found at twice the Q value (from the CTR) of feature F1, regardless of the azimuth angle. However, it is not its second order diffraction satellite, as it does not possess an internal structure, nor is it centered on the same Q_z value as feature F1. Again, we calculate the angle of the segment that passes through it's maximum and the zeroth order superlattice peak. The results shown in Figure 4.11c reveal a value of about 48°, and does not display any particular thickness dependence. Features F2 and F3, though they share some similarities (no internal structure, not centered on superlattice peaks), they ultimately act on different length scales.

In the case of feature F1, the distance between it and the CTR is the relevant quantity to analyze since we know it corresponds to the **real space periodicity** of polar textures within the individual PTO layer. The real space periodicities that emerge as features F2 and F3 cannot be defined in the same way, and to get a sense of the length scales we plot the distance (in real space) between these features and the zeroth order superlattice peak, as shown in Figures 4.12a - c. The length scale for feature F2 is between 14 and 20 nm and it shows the same jump characteristic between the 14 and 16 uc PTO superlattices, as expected from the behaviour of its angle. On the other hand, the length scale of satellite F3 is between 6 and 9 nm with no jump (angle does not show a jump either - Figure 4.11c).



Figure 4.12: Feature F2 and F3 in real space. a, The relevant quantity is the distance from the respective features to the zeroth order superlattice peak, shown with green and red. b, c, Length of the red/green segment with increasing PTO layer thickness. d, Dark field-TEM under g=100 excitation shows the origin of the observed features (F2 and F3).

In order to connect the angles and the length scales of features F2 and F3 to their corresponding real space periodicities, we analyze the 16uc superlattice

(Figure 4.12d). Red segments correspond to feature F2 and green to F3. For this PTO thickness (16uc) the F2 angle and segment length are $\sim 58^{\circ}$ and 19-20 nm. These are generated by the vertical stacking of PTO polar textures. On the other hand, feature F3 reproduces features on the 6-9 nm scale, located within one PTO layer, as evidenced in the inset of Figure 4.12d.

Both F1 and F3 are sensitive to the polarization textures within one layer of PTO. Their dependence on the PTO thickness shows a linear dependence with no discontinuity. Only when observing the vertical alignment of domains (feature F2) do we observe a discontinuous behaviour in its characteristics (angle, periodicity), when transitioning from 14 and 16uc PTO thickness. As mentioned earlier, we attribute this to a change in polarization topology, from vortex to flux-closure. The latter induces a better vertical stacking though strain fields due to the strong wavelike lattice deformation.

Because the polar textures within single PTO layers are periodically reproduced, we ask ourselves what kind of thermodynamic phase transition is such a system subjected to? Unique among the studied polar phases, vortices constitute a thermodynamic system with a phase transition that has not yet been analyzed.

4.4 Polar vortices - temperature evolution

In order to study the evolution of the PTO vortices with the temperature, data was gathered from a synchrotron beam source at XMaS-Grenoble, beamline BM28 at 7.7 keV energy. The beam intensity being several orders of magnitude brighter than the lab-based sources ensures that relatively faint features can be tracked during heating/cooling. The sample was oriented such that the $[001]_o=[100]_{pc}$ direction is in the scattering plane (parallel to the beam) and corresponds to 0° azimuth. Scans were performed at 0° and 90° azimuth angles. At each angle, rocking curves within the scattering plane were used to determine the position of the diffraction satellites along the $[h00]_{pc}$ and $[0k0]_{pc}$ directions. Such scans were performed around the symmetric $220_o=002_{pc}$ (both 0° and 90° azimuths), the asymmetric $332_o=103_{pc}$ (0°



Figure 4.13: **3D RSM**. Reciprocal space volume scan around the DSO substrate 002_{pc} Bragg peak.

azimuth) and $240_{\rm o}=013_{\rm pc}$ (90° azimuth) substrate reflections. These sets of scans were measured during heating/cooling between 50-510 °C.

An example of the reciprocal space volume sampled around the $220_{o}=002_{pc}$ for the PTO_{10}/STO_{10} superlattice is shown in Figure 4.13. From this viewing perspective, an obvious set of diffraction satellites is visible, which corresponds (as we have seen in the previous section) to the polar vortex ordering. In order to extract information about the position and the intensity of the diffraction satellites, the 3D volume was projected onto 2D maps by integrating along the third dimension, producing Q_x-Q_z , Q_y-Q_z and Q_x-Q_y maps. The evolution of the individual diffraction satellite intensities was tracked through their phase transitions.

An example of the evolution of the diffraction satellites with temperature is shown in Figure 4.14 as Q_x - Q_y maps around the 220_o reflection. Out of all the diffraction satellites present at 50 °C, only the signal corresponding to polar vortices (feature *S1*) remains at 250 °C, before completely disappearing at 510 °C. After cooling the sample down to 250 °C the polar vortices reform, confirming them as a stable phase in the studied STO₁₀/PTO₁₀ superlattice.

Beside features S1 and S2, which describe the polar ordering along $[100]_{pc}$



Figure 4.14: **DSO 002_{pc} Q**_{xy} **maps**.(Left) The evolution of the 2D RSM as a function of temperature. (Right) Relevant features. The colorbar is for all figures.

and $[010]_{pc}$, a sharp feature, S3, can be seen close to the DSO Bragg 220_o peak in Figure 4.14. It was shown, in the previous section, that these satellites emerge as a consequence of the vertical alignment of domains across the superlattice. In order to find the maximum intensity of the satellites from the 2D maps, the signal is integrated inside the red box as shown in Figure 4.14(right). From the resulted signal, the baseline was subtracted in order to create a common reference between the data sets at different temperatures. The new set of points were fit using a power Lorentzian from which the maximum intensity was extracted.

The temperature evolution of the satellites is shown from two different perspectives: integrated over the satellite projection (Q_x vs Q_y maps) and integrated over a superlattice Brillouin zone (Q_z vs $Q_{x(y)}$ maps). The reason for this is technical in nature, because the reciprocal space volume has missing data points in the satellite regions, which can change their position as the sample is heated/cooled.

Around a symmetric reflection, the satellite S1 represents the ordering of the vortex structure, along a plane parallel to the PTO/STO interface. By increasing the



Figure 4.15: **DSO 002**_{pc} - Feature S1. a, Q_x - Q_y map. Boxed area shows the integration limits. b, Maximum intensity vs temperature plot for phi = 0° beam-sample geometry. c, The same plot, but for phi = 90° beam-sample geometry. d, e, f, The same treatment as for (a), (b) and (c).

temperature, the satellite intensity decreases continuously without any step changes, and this can be observed regardless of the azimuth angle (Figures 4.15b, c, e, f). This characteristic is reminiscent of an order parameter which goes through a second order phase transition. Close to the transition temperature (about $350 \,^{\circ}\text{C} - 400 \,^{\circ}\text{C}$), the intensity does not tend to zero in a way that its first derivative is discontinuous, but it behaves as if the transition is made in the presence of an effective field (which is shown to remove the discontinuity in the first order derivative [130]). This is plausible, as there might be residual fields due to non-zero local electric dipoles inside the ferroelectric. During the cooling process the polar ordering is restored and it seems to closely follow the initial curve.

Feature S2 (Figure 4.16a) shows that there exists a periodic perturbation of the crystal lattice in a direction perpendicular to the vortex array. Not only is it weaker, but it is also less stable than the vortex array. Figures 4.16b, e show that the



Figure 4.16: **DSO 002_{pc} - Features S2 and S3**. **a**, Q_x - Q_y map. **b**, Feature S2 dependence on the temperature. Its corresponding real space periodicity dissolves above 150 °C. **c**, Feature S3 shows a similar behavior as S2, disappearing above 100 °C. **d**, **e**, **f**, The same features, as seen from the Q_y - Q_z maps. The colorbar is the same for a and d.

periodicity dissolves at temperatures above 150 °C. Interestingly, the loss of the S2 periodicity cannot be inferred from the temperature dependence of the feature S1. Also, feature S3, also dissolves at a similar temperature to S2 (Figures 4.16 c, f). In the previous section, we attributed the vertical alignment of domains to the strain field, which unlike the electric field, cannot be screened. Polar vortices minimize the strain field, but some degree of vertical alignment still exists. It is possible that by increasing the temperature, the strain is gradually released, thus removing the main drive for the vertical alignment. A complete decoupling of PTO layers creates polar phase described only by polar vortices (S1), without an additional modulation along the perpendicular direction.

So far we have analyzed the satellites around the $002_{pc} = 220_{o}$ reflection, where the diffracting planes are parallel to the interfaces and the satellites S1 and



Figure 4.17: **DSO 103**_{pc} - Feature S1. a, Q_x - Q_y map. Boxed area shows the integration limits. b, Maximum intensity vs temperature plot for phi = 0° beam-sample geometry. c, The same plot, but for phi = 90° beam-sample geometry. d, e, f, The same treatment as for (a), (b) and (c). The colorbar is the same for a and d.

S2 contain information only about the in-plane periodicities. By measuring the diffracting signal around an asymmetric peak $(332_o=103_{pc} - 0 \text{ degree azimuth})$ and $240_o=013_{pc} - 90 \text{ degree azimuth})$, the {hkl} planes necessarily mix the periodicities that are along and perpendicular to the PTO/STO interface. Nevertheless, the temperature dependence should be the same because ultimately, we observe the same structures from different angles.

As expected, the S1, S2 and S3 features show the same temperature dependence as measured in the $220_{o}=002_{pc}$ conditions. The intensity of satellite S1 reaches zero somewhere between $350 \,^{\circ}\text{C} - 400 \,^{\circ}\text{C}$, as revealed by Figures 4.17b, c, e, f. The second modulation (S2), perpendicular to the vortex array (S1), dissolves above $150 \,^{\circ}\text{C}$, and feature S3 is barely visible, even in the line scans.

Except the polar vortices, all other forms of ordering disappear above 150 °C, which allows us to strictly focus on the vortex array and its evolution with temperature. Unfortunately, a proper search for the Curie temperature T_c and the critical



Figure 4.18: **DSO 103**_{pc} - **Features S2 and S3**. **a**, Q_x - Q_y map. **b**, Feature S2 dependence on the temperature. Its corresponding real space periodicity dissolves above 150 °C. **c**, Feature S3 is barely visible around the DSO 103_{pc}. **d**, **e**, **f**, The same features, as seen from the Q_y - Q_z maps. The colorbar is the same for a and d.

exponent, will not be achieved as the current data set only allows for an estimation of these parameters. We want to generate a graph of $\ln(I)$ vs $\ln(T/T_c - 1)$, where I is the intensity and T_c is the transition temperature. If the dependence of the intensity on the temperature close to the transition point is power-law like, then the resulting points should lie on a straight line, with a slope equal to the critical exponent. For this, we need an estimate of the T_c . Regardless of the theoretical framework used to model the critical phenomena (mean field, Ising d=2 or d=3; d - dimension), the T_c seems to be between 340-360 °C, simply by visual inspection. As a starting point we use the mean field theory to estimate the T_c .

We consider the most basic form of energy expansion in terms of an order parameter labelled α , and write the free energy as $F = A(T - T_c)\alpha^2 + B\alpha^4$. Taking the first derivative w.r.t. the order parameter results in an equation which allows one to find the dependence of the order parameter on the temperature (top, Figure



Figure 4.19: **Phase transition**. **a**, (Left) Feature S1 around the asymmetric reflection. Data fit is done using mean-field theory. (Right) Feature S1 around the symmetric reflection. **b**, Contour plot of the Chi-squared with (Tc,p) as variables for the asymmetric (left) and symmetric (right) reflection. **c**, The ln(I) vs ln(T/T_c – 1) plot shows a power law dependence of the satellite intensity on the temperature. **d**, Mean-field theory characteristic when considering a non-zero effective field.

4.19)a. Here, we have two unknowns, p and T_c . In order to find the best fit, we restrict the data set to values close to the transition temperature and calculate the least squares for each curve for a particular set of T_c and p. This is shown in Figure 4.19b for the data set around the asymmetric (left) and the symmetric substrate reflection (right). From this, we estimate the T_c around 348 °C. We can now proceed further and plot the ln(I) vs ln(T/T_c – 1), as shown in Figure 4.19)c. One already realizes that the present phase transition can be described by a critical exponent of 0.5. Other critical exponents such as 1/8 (Ising, d=2) and ~0.325 (Ising, d=3) [131] are shown for comparison. If we vary T_c between $T_c = 348 \pm 1$ °C, the slope varies between 0.48 and 0.52. Again, this is only an estimate as there are few points in the present data set. Nevertheless, the dissolution of the vortex array seems to be described by a phase transition with a critical exponent of 0.5.

Within the mean field theory framework we can address the experimentally observed smooth transition through T_c . As mentioned earlier, this behaviour indi-

cates that the transition is done in the presence of an electric field. We can use the simple energy functional form shown earlier, and add an effective field term. As a note, if the effective field is non-zero, one cannot estimate the critical exponent, as the latter is defined in the limit when the effective field tends to zero. The data fit is shown in Figure 4.19d. The presence of an effective field is plausible, as the vortex phase transition is not associated with any structural phase transition, which means that the PTO is still in its polar state after the vortex array dissolves.

4.5 Conclusions

In summary, PTO/STO superlattices were analyzed with PTO thicknesses between 10 and 20 uc. We have shown that superlattices with PTO thicknesses less than 14 uc (STO thick enough to electrically decouple the PTO layers) constitute a favorable environment for polar vortices. This polar arangement minimizes the degree of vertical alignment of the domains between the individual PTO layers. If the PTO thickness is greater than 14 uc, features that indicate a vertical alignment of domains emerge, signaling the transition to flux-closure domains. This implies that the polar vortices minimize the strain field, which drives the vertical alignment of the domain between the different PTO layers, while flux-closure domains do not. Nevertheless, the lateral periodicities of these polar textures (vortex/flux-closure) vary continuously, obeying a linear dependence on the thickness of the PTO.

The PTO_{10}/STO_{14} superlattice was chosen as a prime example to study the phase transition of polar vortices. Because the vertical alignment of domains is minimal in this system, at a temperature of ~150 °C all other forms of ordering are dissolved and only the vortex array remains, which was shown to disappear at about 350 °C. The behaviour of the satellite intensities with temperature can be described as a phase transition with a critical exponent of 0.5 (mean field theory).

Chapter 5

Ab initio studies of metal ferroelectric structures

5.1 Introduction

In the previous chapter we have studied how the domain morphology is influenced by the thickness of the ferroelectric (PTO) layer within a ferroelectric-insulator superlattice. We also tracked the phase evolution of the polar vortices as a function of temperature, and found that the phase transition can be understood within the mean-field framework.

With such exotic polarization topologies formed in ferroelectric-insulator heterostructures, it is natural to ask ourselves if these could emerge in a metalferroelectric-metal trilayer, or even be stable at all. If possible, it could lead to directly manipulating these polar topologies by means of a device, instead of necessarily measuring the collective effect of all layers within a ferro-insulator heterostructure [122]. Achieving this feat poses a possibly insurmountable difficulty as the metallic contacts could provide enough free electrons to screen the surface bound charges induced by the polarization, thus stabilizing the polar domains in the ferroelectric layer [8].

As was shown in the previous chapter, the polarization morphology strongly depends on the thickness of the PTO film, and polar vortices were found in the 10-14 uc thickness range. At this thickness the interface plays an important role in the stability of these polar topologies. From a practical point of view, an intimate contact at both interfaces can be achieved by epitaxial growth of both conductive oxides and ferroelectric materials. This requires the use of materials with a good in-plane lattice match, to avoid 3D growth processes and/or the creation of defects. Therefore, we focus on metallic oxides such as $(La_{0.7},Sr_{0.3})MnO_3$ and $SrRuO_3$. However, replacing the insulator with a metal requires an in-depth study of the interfacial effects such as interface metalicity caused by charge injection, suppressed or enhanced polar distortions and oxygen cage tiltings, all of which might be detrimental to the sought after polar topologies.

The first part of this chapter is dedicated to the *ab-initio* study of the interface between the LSMO and PTO. Here we analyse the structural distortions that extend in both materials, with respect to the polarization orientation, and the screening properties of LSMO.

In the second part we perform a similar analysis, but replace LSMO with SRO. Here, we analyse two system geometries. One which assumes a polarization monodomain (as reflected by the geometry of the supercell), where we are interested to find out if the thickness of PTO is sufficient in order to avoid charge spillage from SRO into PTO, which invalidates any result. This study sets up the second simulated system, where we allow for domain formation and relaxation within the PTO layer. In both cases the thickness of the PTO and SRO layers are equal.

5.2 $PbTiO_3$ -(La_{0.7},Sr_{0.3})MnO₃ heterostructures

 $(La_{0.7}, Sr_{0.3})MnO_3$ is an ABO₃ - type metallic oxide with R3c space group symmetry, and B-site oxygen cage tilting described by a⁻a⁻a⁻ in Glazer notation. Under the compressive/tensile strain induced by a substrate, the tilt pattern becomes a⁻a⁻c⁻. To account for octahedral tiltings in PTO and LSMO, it is necessary to construct the supercell in a $\sqrt{2} \times \sqrt{2}$ geometry as shown in Figures 5.1a, b.

We relax the atomic positions of both materials using the Quantum Espresso



Figure 5.1: Simulation slab architecture. a, Lateral view of the $((La_{0.7},Sr_{0.3})MnO_3)_{10}$ - $(PbTiO_3)_7$. b, Top view of the same slab. Bottom, The studied interface terminations and the polarization orientation.

plane-wave code, within the Generalized Gradient Approximation formalism (GGA). The exchange-correlation functionals are in the Perdew-Burke-Ernzerhof parametrization, adapted for solids (PBEsol). In order to properly reproduce the structural characteristics for both the PTO and LSMO in their bulk forms, we use Projector Augmented Wave pseudopotentials with the constituent elements having the semicore and valence state as follows: La $5s^2$ $6s^1.5$ $5p^6$ $6p^0.5$ $5d^1$ $4f^0$; Mn $3s^2$ $4s^2$ $3p^6$ $3d^5$; O $2s^2 2p^4$; **Pb**: $6s^2 6p^2 5d^{10}$; **Ti** $3s^2 4s^2 3p^6 4p^0 3d^2$. Doping is achieved using the Virtual Crystal Approximation (VCA), which mixes the pseudopotentials of two species with a set amount of percentage. In this way (La,Sr) virtual atoms are created with the right amount of mixing to result in $(La_{0.7}, Sr_{0.3})MnO_3$. The same technique is used to create virtual species at the surface of PTO. The termination is (PbX), with X composed of 40%N – 60%O or 40%F – 60%O, which creates a displacement field $D = \pm 40 \,\mu C \,\mathrm{cm}^{-2}$. The integration in the Brillouin zone is performed over a computer generated Monkhorst-Pack k-mesh and a Gaussian smearing of 0.01 eV. The kinetic energy cut-off value is 80 Ry and for the charge density, 320 Ry. The calculations are spin-polarized, except when we calculate the conduction charge distribution.

Within these approximations, the oxygen cage tilt for LSMO has a simulated value of $\sim 5.2^{\circ}$, compared to the experimental [132] of $\sim 7.8^{\circ}$, as it might be expected

given the strain state. PTO has a calculated c/a ratio of about 1.06, close to the experimental 1.07 [114] (~ 1% error). We use the individually relaxed (with the in-plane lattice parameter of STO) PTO and LSMO unit cells to construct the slab; 7uc of PTO and 10uc of LSMO are enough to regain the bulk properties away from the interface. The slabs were relaxed until the Hellmann-Feynman forces were below $0.07 \,\mathrm{eV/\AA}$.

5.2.1 Interface relaxation

The calculation results are grouped according to the interface termination. The scenarios where the polarization points up or down are treated for both type of interfaces: $(La,Sr)O_2 - TiO_2$ and PbO - MnO₂. LSMO is a metallic oxide which shows charge imbalance within its MnO₂ and $(La,Sr)O_2$ atomic planes due to the non-zero valence sum over the respective constituent atoms. Thus, the MnO₂ plane possesses -0.7*e* and the $(La,Sr)O_2$ plane, +0.7*e*. These charges create an effective polarization of $\pm 0.35e$ per 2D unit formula [133]. This has a drastic impact on the polarization at the interface, as depending on its orientation, LSMO can stabilize or suppress it. Furthermore, the oxygen cage displays an anti-phase tilting pattern. If viewed along the crystallographic axes, the projection of the oxygen column will amount to a net zero tilt. In order to observe the tilt, the viewing direction must be set to $\langle 110 \rangle$ (see Figure 5.1). Also, the polar displacements are calculated by finding the difference between the position of the B-site and the oxygen cage centre of mass.

Before going into details, one should notice that the relaxed configuration of the studied systems show that the polar displacements in PTO reach bulk-like values far from the interface, and zero inside LSMO, as expected (Figures 5.2a, b top). Furthermore, the oxygen cage tilts [134] are zero inside the PTO, while in LSMO they reach a constant value of ~ 5.1° again, as expected (Figures 5.2a, b bottom). It is at the interface where significant changes occur.

We consider the $(La,Sr)O_2$ - TiO_2 interface first. With the polarization oriented "up", there will be a corresponding negative surface bound charge density



Figure 5.2: **Rumpling and tilt. a, b**, Full atomic relaxation of $(La,Sr)O_2 - TiO_2$ interface for both P_{up} and P_{down} polarization orientations. In the top figure the displacement of the B-site (Ti/Mn) ions relative to its oxygen cage shows the impact the polarization orientation has on the local atomic arrangement. The bottom figure represents the oxygen cage tilt behaviour throughout the system. A larger polarization value reduces the tilt angle.

at the PTO/LSMO interface. Alternatively, it becomes positive when the polarization is "down" oriented. Therefore, the $(La,Sr)O_2 - TiO_2$ interface should have a screening effect for P_{up} and a reinforcing effect for P_{down} .

Indeed, our simulations indicate that the $(La,Sr)O_2 - TiO_2$ interface screens the P_{up} surface bound charge, indicated by a displacement value at the interface of about 15 pm - significantly lower than the displacement value inside the PTO (~ 28 pm). Interestingly, the electric field caused by the PTO polarization induces polar displacements in LSMO within the first ~ 2 uc from the interface, which acts as a screening mechanism. On the other hand, the tilt pattern of LSMO is continued in PTO, via inter-cage connectivity. However, it rapidly decreases to zero, as expected from PTO becoming bulk-like away from the interface. A coupling between polar displacements and oxygen cage tilting is possible and can lead to a slight rotation of the polarization [135]. Needless to say, the DFT calculations are performed with all atoms being allowed to move along all three directions. The presented results have such an effect accounted for.

The interface chemistry should have a significant effect on the effectiveness of LSMO to screen/enhance the polarization. Unfortunately, we cannot compare the P_{up} to the P_{down} scenario for the $(La,Sr)O_2 - TiO_2$ interface. The GGA approximation underestimates the PTO band gap (~ 1.5 eV), which causes the Fermi level for the P_{down} system to be in the conduction band, which triggers charge spillage from LSMO into PTO. In turn this influences the atomic relaxation process, leading to artifacts, as observed in the displacement and the tilt pattern shown in Figure 5.2a, bottom. In this particular system, this might not have happened if the band gap was close to the experimental value (~ 3.4 eV).

Unlike the $(La,Sr)O_2$ - TiO₂ interface, the PbO - MnO₂ termination does not suffer from such artifacts (Figure 5.2b). The MnO_2 plane is negatively charged, therefore it should reinforce the "up" oriented polarization. Far from the interface the polar displacement values in PTO are similar between the two polarization orientations, ~ 25 pm. With an interfacial displacement of about 19 pm for P_{up}, this interface has a reinforcing effect, as expected. However, the cost of this is the polar distortions induced in LSMO, which extend up to 3-4 uc away from the interface in order to attenuate the electric field caused by the surface bound charges. When the polarization is in the opposite direction, the interface has a screening effect, reflected by a low interfacial polar displacement of about 5 pm. Consequently, the induced Bsite polar displacements in LSMO are confined to the first unit cell from the interface. Additionally, the competition between the polar distortions and the oxygen cage tilting, is reflected in these results. If the interfacial polarization is reinforced, the cage tilt is suppressed, while a screened polarization favors the tilting of the oxygen cage. Furthermore, the spatial extent over which the PTO layer produces polar shifts in LSMO can also be observed in the tilt pattern (Figure 5.2b, bottom). The tilt values decrease as soon as the LSMO shows polar displacements, which occur 3-4 uc away from the interface for P_{up} and about 1uc for P_{down} . In PTO, the B-site displacements reach their bulk value two unit cells away from the interface, which causes the oxygen tilt to rapidly reach almost zero within this spacial length.

So far, the structural relaxation of the LSMO-PTO system were analyzed, focusing on the interface. We maintain this focus, but observe the interface from the perspective of electronic charge redistribution.

5.2.2 Interfacial charge redistribution

In DFT simulations, the final electron density is as much a cause of the ionic positions as it is an effect of these (self-consistency). Therefore, the electronic charge density can be processed to provide a different perspective into the physical properties of the interface. Here, we focus on the PbO - MnO₂, which is artifact-free, and we ask ourselves what are the changes in the magnetic properties of LSMO at the interface, induced by the polarization orientation? We have already found that the oxygen cage tilt pattern changes drastically close to the interface. Because the magnetic properties of LSMO depend on the Mn-O bond length (Mn - 3d and O - 2p orbitals overlap), a decrease in the tilt angle could cause an increase in the magnetic moment. DFT calculations performed on bulk LSMO with a⁻a⁻c⁻ and a⁰a⁰c⁰ and 3.35 $\mu_{\rm B}$ for a⁻a⁻c⁻ tilt pattern.

LSMO is a half-metal (Figure 5.3a), which means that the conduction electrons have a certain degree of spin polarization. Also, the states close to the Fermi level are composed mostly of Mn 3d orbitals. By manipulating the electronic charge density close to the interface, the local magnetic properties can be altered.

As seen from the structural relaxations, opposite polarization orientations have a specific effect on how far the polar distortions extend in LSMO. The PbO - MnO_2 termination is negatively charged and reinforces the "up" orientation. Intuitively, the electron charge concentration needs to decrease in the vicinity of the interface. Because the electrons are spin polarized, the net magnetic moment is affected, showing a decrease of about 10% over the first 2 uc from the interface, as



Figure 5.3: **Magnetisation**. **a**, Spin resolved density of states in bulk $(La_{0.7}Sr_{0.3})MnO_3$. **b**, Average magnetic moment per Mn in the vicinity of the interface for different polarization orientations. At the interface, the strongest deviation of the magnetization from its bulk value is achieved when the surface bound charges in PTO are negative (P_{up}).

seen in Figure 5.3b. If the polarization is "down" oriented, the PbO - MnO_2 plane has a screening effect and in this scenario, it causes an electronic charge accumulation which increases in the local net magnetic moment by about 7%. Unlike the "up" polarization orientation, the effect is confined to the first unit cell at the interface, corroborating the polar distortion observations (Figure 5.2b).

While the behavior of the electronic charge density in the vicinity of the interface is intuitively understood, we want be to more precise. Because LSMO is a half-metal, it has a non-zero density of sates in a region around the Fermi level. The Fermi-Dirac distribution implies that there is an interval of energies centered on the Fermi level, with non-zero occupation probabilities, the width of which depends on the thermal energy (kT). The electrons within this energy interval are called conduction electrons. The relaxed positions obtained in section 5.2.1 were used, and the calculation is **not** spin - resolved. There are specific paths in reciprocal space which have the property that all other k-points map onto them by applying the space group symmetry elements to the k-points. Therefore, by analyzing the behavior of the electronic band structure along these paths, we fully describe the electronic properties of the system. For a tetragonal unit cell the k-paths, shown in Figure 5.4, are G - X - M - G - Z - R - A - Z | M - A | X - R. At this point one



Figure 5.4: Tetragonal Brillouin zone high-symmetry points and paths.

needs to proceed with care. The k-path shown above is for the tetragonal Brillouin zone. Because we constructed the slab to account for possible oxygen tilts, this tetragonal Brillouin zone ceases to be a good representative of the system. Due to the geometry of the system, the regular tetragonal unit cell is contained within the slab unit cell as shown in Figure 5.5a, where PC refers to primitive cell (Brillouin) and SC refers to the slab cell. Furthermore, the PTO and LSMO layers are stacked along the *c-axis* direction, meaning that the states along the Z - R - A -Z path will be mixed with the states along the G - X - M - G path. Considering that the slab Brillouin zone is almost 2-dimensional, it is sufficient to analyze the G - X - M - G | M - A | G - Z | X - R paths.

The task we are facing is what path needs to be chosen in the slab cell in order to be mapped onto the primitive cell G-X-M-G path? In Figure 5.5b the projection of the reciprocal space is shown, along with the relationship between the SCBZ and PCBZ. A \vec{k} state which lies outside the SCBZ, but inside the PCBZ is folded onto the \vec{K} state via a SCBZ translation vector, \vec{G}_0 . This is a injective operation. The process of unfolding is not unique, meaning that a \vec{K} -state can have more than one vector which is unfolded onto it. Folding and unfolding is described in [136]. In order to find what k-points from the SCBZ are unfolded onto the G-X-M-G path in the PCBZ, we look at how the path is folded in the first place. The process is described in Figure 5.5c. Considering the geometrical relationship between the SCBZ and the PCBZ, a \vec{K} state can be unfolded into 2 vectors, with $\vec{G} = \vec{G}_0$ and



Figure 5.5: **Projection of cells. a**, Real-space geometrical relation between the supercell (SC) - primitive cell (PC). **b**, First Brillouin zone of the supercell (SCBZ) and primitive cell (PCBZ). The folding of states from PCBZ to SCBZ is shown. **c**, Steps taken to find the SCBZ path that unfolds onto the G-X-M-G path of the PCBZ.

 $\vec{G} = 0$ (see [136]). Therefore, the path shown in the last panel of Figure 5.5c will be unfolded onto itself and onto G-X-M-G, which is what we are interested in.

Now that the k-points are known, the band structure can be computed. Considering the Fermi-Dirac distribution, only states with energy above $E_{Fermi} - 0.2 \text{ eV}$ are considered as "conduction electrons". The 0.2 eV value is not arbitrary, and represents the value at which the occupancy number starts to change if we consider a thermal energy kT of about 0.026 meV (room temperature). Lastly, the conduction charge density is calculated using the relation

$$\label{eq:rho} \rho_{free}(\vec{r}) = \sum_{E > E_{Fermi} = 0.2} w_{n\mathbf{k}} f_{n\mathbf{k}} |\psi_{n\mathbf{k}}(\vec{r})|^2, \qquad (5.2.1)$$

where $w_{n\mathbf{k}}$ is the k-point weight and $f_{n\mathbf{k}}$ is the occupancy number. The system is periodic along the directions parallel to the interface, and of interest is the planar

average of $\rho_{free}(\vec{r})$,

$$\bar{\rho}_{free}(z) = \frac{1}{S} \int_{S} \rho_{free}(\vec{r}) dx dy$$
 (5.2.2)

This quantity is represented in Figure 5.6 for the PbO - $\rm MnO_2$ interface.



Figure 5.6: Free charge density. **a**, The polarization is up oriented. The black line is the planar averaged charge density as per formula above. The red dotted line takes the quantity shown in black and averages it in a one unit cell window (nano-smoothing [137]). **b**, Same as (**a**) for polarization down.

As previously mentioned most of the states in the vicinity of the Fermi level originate from the 3d orbitals of Mn. Therefore, a higher concentration of free charges are present in the PbO - MnO₂ planes, compared to the (La,Sr)O -TiO₂ planes, as seen in Figure 5.6 far from the interface. In metals e.g. copper, the electrons are delocalized and the single-electron wavefunction can extend over nearest neighbours. While this is not the case here, one can notice the nonzero electronic charge density between the atomic planes within LSMO, owing to its metallic nature, while it is zero inside PTO. Depending on the polarization orientation, the electrical boundary conditions at the interface change: the interface has a reinforcing effect for P_{up} and a screening effect for P_{down} , and the free electron density redistributes itself according to the local electric field. Therefore, P_{up} causes a depletion of free charges at the interface, as seen in Figure 5.6a. Quantitatively, we observe a noticeable decrease in the free charges of about 100% from its average bulk value (far from the interface). Alternatively, for P_{down} , there is an increase in charge density at the interface, however, due to its native screening properties, the increase is less substantial ($\sim 20\%$). This confirms the analysis of LSMO magnetisation behaviour as a function of the polarization orientation. For both polarization orientations, the free charge density is shown to be perturbed from across approximately 2 uc, consistent with the variation of the local magnetic moment. Also, within PTO there is a sharp decay of the charge density. This corresponds to the so called metal-induced gap states and is a quantum mechanical effect caused by having an interface between a metal and an insulator.

The fact that the PbO - MnO_2 and the (La,Sr)O - TiO_2 planes possess a net charge was shown to greatly affect the polarization of PTO in the vicinity of the interface. While this is a fascinating effect it is ultimately detrimental when searching for metallic contacts that can allow for polarization vortices to form in the PTO layer. This is because the topology of polar vortices includes regions where the polarization points "up" or "down" (perpendicular to the interface). The native charge of the LSMO termination will favor one orientation over the other which, as mentioned, is detrimental to the formation of polar vortices. For this reason we substitute the LSMO layer with SRO, which is a good lattice match for PTO and does not possess charged RuO₂ planes. We follow with a similar study.

5.3 PbTiO₃-SrRuO₃ heterostructures

In the previous section, the PTO in-plane lattice constant was matched to that of STO. Strain is an important ingredient in the formation of polar vortices, so the following simulations consider the tensile strain imposed by lattice matching the system to the $DyScO_3$ substrate. The results obtained in the previous sections indicate that the oxygen tilt pattern throughout the system closely follows the polar distortions, as a consequence rather than their main drive. Therefore, we first consider an SRO-PTO supercell (no vacuum present) whose geometry does **not** allow for oxygen cage tilt. The effect of SRO on polarization "up" and "down" is studied, and an analysis of the charge redistribution is made to confirm that no charge spilling occurs. Here, SRO and PTO are both 6uc thick (Figure 5.7a). This was shown to be enough to decouple the interfaces from their periodic images [138]. Also, these simulations are a set up for the next system, where we allow all atoms to move freely, and account for tilt propagation in PTO (Figure 5.7b).



Figure 5.7: Supecell geometry. a, This geometry simulates a polarization monodomain. b, We allow for domain relaxation.

The calculations were performed using the Quantum Espresso suite, a planewave code employing the Generalized Gradient Approximation. The exchangecorrelation functional is in the Perdew-Burke-Ernzerhof parametrization adapted for solids, PBEsol. As the magnetic properties are not of interest at this point, Vanderbilt ultrasoft pseudopotentials were used with elements having their valence states composed of: **Pb** 5d¹0 6s² 6p², **Sr** 4s² 4p⁶ 4d¹ 5s¹ 5p⁰, **Ti** 3s² 3p⁶ 4s² 3d¹, **Ru** $4d^7$ $5s^1$ $5p^0$, **O** $2s^2$ $2p^4$. The integration over the Brillouin zone is performed over an automatically generated Monkhorst-Pack k-mesh with a Gaussian smearing of $0.01 \,\mathrm{eV}$. The kinetic energy cut-off is 70 Ry and 450 Ry for the charge density. Atomic relaxations of bulk PTO and SRO were done under the strain imposed by the substrate with the resulting unit cells used to construct the supercell. Using the PBEsol functional, the relaxed unstrained bulk PTO unit cell yields lattice constants equal to a = 3.873(1) Å and c = 4.218(1) Å, which results in a c/a ratio of 1.089 (within 1.7% error of the experimental value). Spin orbit coupling is very weak for PbTiO₃ and was not considered. Hubbard corrections were not used. The supercell forces converged to less 80 meV/Å per atom (600 atoms).

5.3.1 $1 \times 1 \times N$ supercell geometry. Structural and electronic analysis

Realistically, PTO thin films grown via PLD between SRO electrodes have slightly different interfaces. One is sharp, with single termination, while the other is most likely the result of mixed terminations (see Chapter 6). To account for this in our simulations, we design the system with asymmetric interfaces namely, PbO - RuO₂ and SrO - TiO₂. Note that unlike the (La,Sr)O and MnO₂ planes, the SrO and RuO₂ planes are charge neutral, so the surface bound charges created by the polarization are mostly screened through the redistribution of free charges within SRO.

We compute the polar distortions throughout the entire supercell for both "up" and "down" polarization orientations, as shown in Figure 5.8. The thickness of SRO is indeed properly chosen to decouple the PTO layer from its periodic images, as shown in Figure 5.8(left) by the polar displacement reaching zero in the centre of SRO. The system is not symmetric with respect to polarization reversal (it would



Figure 5.8: **Structural relaxation**. (Left) Oxygen cage - B site centre of mass displacements. (Right) Oxygen cage - A site centre of mass displacements. For both polarization orientations, PTO retains its polar displacements, by polarizing the SRO unit cells which are in direct contact with PTO.

have been, were the interfaces symmetric) therefore, the polar displacements (δ_{B-O})

for P_{up} and P_{down} differ by a slight amount in the centre of PTO: about 25 pm for P_{up} , and 0.22 pm for P_{down} . This value is retained throughout the PTO film, even in the vicinity of the interfaces. Figure 5.8(right) shows the offset of the oxygen cage centre of mass w.r.t. to the A-site ions. In PTO, the contribution of the δ_{A-O} type offsets to the polarization magnitude is greater than in BTO for example. However, the Pb atoms barely move were the polarization to rotate. Nevertheless, the δ_{A-O} displacements behave in a similar manner to δ_{B-O} .

The polar displacements in SRO are confined to the first unit cell for the SrO - TiO_2 termination, while the PbO - RuO_2 interface needs two unit cells to shield the polarization. This is valid for both polarization orientations. Nevertheless, this shows an improvement over the LSMO electrode, whose charged planes can significantly alter the polarization state at the interfaces, requiring a larger screening length too.

As was shown in the previous section, the final ionic positions are intimately connected to the electronic charge density. Again, of interest is the free charge density, which can redistribute itself according to the local electric field. Unlike the LSMO-PTO system, which posed complications due to the geometry of the slab (relative to the primitive cell), the situation is simpler for this system. In plan projection the SC and the PC are the same, therefore, the G-X-M-G paths coincide. The stacking direction of SRO-PTO is along the G-Z path, which means that the states along the Z-R-A-Z path will be mixed with the states along G-X-M-G (Figure 5.9a). Therefore, it is sufficient to calculate the bands along one path. Needless to say, the bands along G-Z, M-A and X-R are still needed. In Figure 5.9b the bands along the mentioned paths are shown. Keep in mind that the bands correspond to the SRO-PTO supercell. Similar to LSMO, the states in the vicinity of the Fermi level are mostly Ru (4d). They also contain hidden information about the interface, such as MIGS (metal induced gap states). Most of the bands along G-Z, M-A, X-R are flat bands, because of the folding process, which mixes the electronic states. This does not pose an issue as an integral over all states is performed. Following the rationale presented in the previous section, we calculate the free charge concentration



Figure 5.9: Charge redistribution. **a**, High-symmetry points and path in the tetragonal Brillouin zone. **b**, Band structure along the paths shown in red in (**a**). **c**, Free charge concentration for P_{down} scenario. **d**, Same as (**c**), but for P_{up} .

around the Fermi level, as shown in Figures 5.9c and d, for polarization "down" and "up", respectively. In all scenarios, similar to LSMO, the free charge density does not reach zero between the atomic planes in SRO, while it rapidly decays to zero inside PTO. Furthermore, it shows maximal values at the RuO₂ planes, as expected from the nature of the bands in the vicinity of the Fermi level (the interface is an exception). The P_{down} orientation creates positive surface bound charges at the SrO - TiO₂ interface (left), and negative at the PbO - RuO₂ interface (right), while P_{up} does the opposite. At the SrO - TiO₂ termination (left), the positive bound charges trigger a clear increase in the free charge density, while the negative bound charges lead to a depletion. In both scenarios, the chemistry of the interface causes the free charge density to penetrate the first 1.5 uc of PTO before reaching zero. At the other interface (PbO - RuO₂), regardless of the polarization orientation, the free charge density in PTO decays rapidly and is confined to 0.5 - 1 uc. Again, there is a charge accumulation/depletion, depending on the sign of the surface bound charges.



Figure 5.10: Allowed states. 2D plot of the squared modulus of the wavefunctions in terms of energy and position. Colored regions represent allowed electronic states, and dark regions outline the forbidden states. This is done for polarization down (a) and up (b). In this way, we highlight the ferroelectric potential barrier.

From an experimental point of view, one is interested in the ferroelectric potential barrier and its shape, which is dependent on the polarization orientation. The problem of band alignment is tricky, but we can avoid all the pitfalls [139–141] by directly plotting the wavefunctions in real space. The results are shown in Figures 5.10 for P_{down} (a) and P_{up} (b). Coloured regions show the allowed states for electrons meaning that, if given the energy (thermally or by voltage bias), they can occupy these states. Dark regions represent the forbidden states, i.e. they cannot be occupied by electrons. These can be clearly observed within PTO, which is an insulator. Furthermore, these forbidden states outline the shape of the potential barrier, whose height and width are dependent on the polarization orientation. As observed in Figure 5.8, the polar displacements in PTO have the same value throughout the film, generating a uniform polarization. This uniformity causes the slope of the potential barrier to be almost constant, resulting in a trapezoidal shape. The MIGS can impact the width of the potential barrier, having a diminishing effect.

The barrier heights are on average $0.5 \,\mathrm{eV}$ for $\mathrm{P}_{\mathrm{dwn}}$ and $0.8 \,\mathrm{eV}$ for P_{up} .

The fact that the free charge density reaches zero inside PTO is crucial, as it leads to relaxation results which are valid and not prone to artifacts, as we have seen with LSMO. This sets up the next simulations, where the supercell geometry allows the atoms to relax into forming complex polarization topologies.

5.3.2 $1 \times 10 \times N$ supercell geometry. Domain relaxation and electronic analysis

In this section, the goal is to find the relaxed structure for SRO-PTO superlattices and consequently, the polarization pattern. The problem is broken down into two steps. First, we look at a single layer of PTO with perfect insulating boundary conditions (vacuum). This provides a starting point for the second step, in which the boundary conditions are changed and the vacuum is replaced with electrodes.

For the first step we assume a $1 \times 10 \times 4$ slab geometry, shown in the left panel of Figure 5.11. The PTO bulk unit cell was relaxed in its polar state. We used this relaxed cell to build the initial polarization pattern. The initial polarization pattern shown in Figure 5.11a may be favorable for the system to relax into polar vortices. This is because the large depolarization fields need to be minimized, and it does this via two mechanisms. Either it goes through a structural change, where the unit cell symmetry changes from tetragonal (polar) to cubic (non-polar) [59] or, the surface dipoles rotate in order to minimize the surface bound charges. The second mechanism is favorable towards polar vortices. In order to avoid the bias set by starting from such a polar state, the system was forced to start from various initial states. This was done in two ways: one domain was made highly inhomogeneous (Figure 5.11c); the percentage of dipoles oriented in the opposite directions (Figure 5.11c) was altered. Even though the relaxation procedure started from completely different states, the end result is that PTO forms polar vortices as a mechanism to minimize the total energy of the system (instead of a structural transition to a nonpolar state). This is shown in Figures 5.11b, d and f. All the relaxed topologies have similar structural characteristics: the lateral size of the vortex is about the same as



Figure 5.11: **Domain relaxation**. (Left) The slab used to search for the domain structure which minimized the slab's total energy. **a**, **c**, **e**, Initial polar states. Several starting points are chosen in order to avoid a possible bias towards the final relaxed atomic configuration. **b**, **d**, **f**, Final polarization configuration, after the full atomic relaxation process.

the thickness of the PTO; clockwise (CW) - counter-clockwise (CCW) vortex pairs are formed.

Using this vortex pattern, the vacuum boundary layer is substituted with SRO (Figure 5.12a). Because SRO has a free charge density that is comparable to that of metals [64], we expect the polar pattern to dissolve into a simpler domain topology such as 180° domains [142]. However, the simulations point towards a different scenario. Figure, 5.12b shows the relaxed atomic positions. The initial vortex structure is retained, with polar displacements induced in SRO in the vicinity of the interface. Furthermore, the vortex pattern does not change its characteristics: the vortex lateral size is similar to the PTO thickness, with pairs of CW and CCW vortices. These results imply that without the complicating effects of charged planes, and owing to a large free charge concentration, SRO confines the polar distortions to the vicinity of the PTO layer.

One might argue that these results are a consequence of the procedure followed so far. To show that this is not the case, the conductive SRO electrode was replaced with an insulating STO layer. In a similar way, the calculation starts with PTO showing polar vortices. STO is highly polarizable, which means that the polarization within PTO can extend into STO, possibly destabilizing the vortex pattern. The results shown in Figure 5.12c, reveal that the vortex pattern is not



Figure 5.12: **Domain relaxation**. **a**, Supercell containing PTO and SRO/STO. **b**, Relaxed structure for the PTO/SRO supercell, showing polar vortices. The SRO confines the polarization within the PTO. **c**, Relaxed structure when PTO is sandwiched between STO layers. The large dielectric constant of STO make it highly polarizable, and polar distortions can be observed well within STO. **d**, Polar distortions within SRO (top) and STO (bottom), outlined by the boxed areas in (**b**) and (**c**).

as clear as in the SRO case. Here, the in-plane rotated dipoles are reduced in strength, almost forming a simple 180° domain wall. On the other hand, the polar displacements in STO are significant and they form a wave-like pattern, in strong contrast with the displacements shown in SRO (Figure 5.12d). This polarizing effect in STO has also been shown to occur even with softer ferroelectrics, such as BTO [124], which has a bulk polarization of $30 \,\mu\text{C/cm}^2$, compared to $90 \,\mu\text{C/cm}^2$ for PTO. In the simulations presented in this chapter the STO layer is 5uc thick, which is not enough to completely decouple the interfaces. In order to achieve this, an STO layer twice as thick is needed however, this is beyond the available computational capability.



Figure 5.13: **Potential barrier**. 2D plot of the allowed states in terms of energy and position. The top figure shows a profile of the simulated SRO/PTO system. The physical potential barrier obtained by representing in real space the wavefunctions is shown to correspond to the region where the PTO resides.

From an experimental point of view, of interest is how does the polar vortex pattern influence the ferroelectric potential barrier. A simple view of polar vortices is that they can be thought of as regions with polarization up, polarization down and polarization in-plane. It was shown in the previous section that for a monodomain PTO the potential barrier is trapezoidal, has different heights and polarization switching reverses the slope. On average, per supercell, the effect of these two regions counteract each other, possibly leading to a more rectangular barrier. In Figure 5.13 we represent the allowed (coloured) and forbidden (dark) states in terms of energy and position. At both interfaces there are states present at the Fermi level within the PTO. These are the MIGS caused by the decay of the wavefunctions from the metal into the insulator. Indeed, the barrier is almost rectangular with an average height of about $0.75 \,\mathrm{eV}$. The potential barrier height values obtained in this and the previous section are not quantitatively accurate, due to the intrinsic underestimation of the PTO band-gap within the DFT formalism. However, all values were obtained in a systematic way, which allows one to compare the average potential barriers of the different polar topologies: up- 0.8 eV, down- 0.5 eV, vortex- $0.75\,\mathrm{eV}.$

The geometry of the supercell allows for tilt propagation analysis. The DFT

simulations show that the oxygen cage tilts induced by SRO are localized within the first 2uc in PTO. These are in-phase tilts of about 2.5°, which are superimposed on the Neel winding of the dipoles due to the vortices themselves. In the regions where



Figure 5.14: **Tilt map**. **a**, Oxygen tilt behaviour along a row of unit cells. In the first/last row (PTO unit cell) the alternating positive-negative values indicate in in-phase tilt of the oxygen cage. This behaviour is most pronounced in the first two PTO unit cells from the interface, showing how the native tilt within the SRO electrodes propagates into the polar PTO. **b**, 2D tilt map throughout the PTO layer. Around the region of the vortex core, the tilt shows higher values that the regions with quasi-homogeneous polarization. This occurs due to the large strain fields which locally distort the lattice.

the polarization points up or down, the tilt value tends to zero, as one expects from the incompatibility of octahedra tilting and polar distortions. However, in the core region, the high strain fields locally distort the unit cell, leading to an apparent non-zero tilt.

The overlap of the interfacial tilt pattern with the rotation of the local dipole within the PTO layer, could lead to possible non-linear couplings, the form of which is reminiscent of the magnetic Dzyialoshiinski-Moriya interaction. This was recently studied by Zhao, et.al. in the case of ferroelectrics/anti-ferroelectrics [143], however, this discussion follows in the next chapter.

5.4 Conclusions

In our search for metallic substitutes for STO, two metallic oxides were considered: LSMO and SRO. Part of the choice was the good lattice match to the substrate and their electrical properties. LSMO has charged (La,Sr)O and MnO₂ planes, which were shown to significantly impact the polarization state at the interface, regardless of the polarization orientation. Furthermore, LSMO was shown to be susceptible to polar distortions over a few unit cells from the interface with PTO. This behaviour is reminiscent of STO, which under similar conditions was shown to become polarized over several unit cells due to its large relative dielectric constant. This behaviour is detrimental when searching for vortex stabilizing conductive electrodes.

SRO was then considered, which does not possess charged planes to disrupt the polarization, therefore, the screening is done via strict polar movement of the Ru atoms or by the free charges. Indeed, it was shown that the polar distortions in SRO are localized within ~ 1.5 unit cells from the interface. This confinement effect proves necessary to stabilize the polar vortex phase in PTO in a metal-ferroelectric environment. Furthermore, the oxygen cage tilting induced by SRO in PTO, could couple to the Neel dipole pattern at the interface, leading to energy terms similar to the ones recently described in [143]. If true, this could trigger the emergence of a new polarization phase in ferroelectrics.
Chapter 6

Polar topologies in PbTiO₃-SrRuO₃ heterostructures

6.1 Introduction

In this chapter we will take an in-depth look into a particular and special form of topological structure that emerges in ferroelectric thin films, under specific electrical and mechanical boundary conditions. Why call them topological structures? Essentially, there is no continuous mapping (twists and cuts are not allowed) that can remove the discontinuity in the vector field - the vortex core. In other words, such structures represent forms of topological defects in the polarization field.

Despite the fundamental difference in the origin and strengths of internal magnetic and electric fields, similar dipolar topologies manifest in both ferroelectrics and ferromagnets. The current understanding of what drives these topologies is based on the complex interplay between strain, strain gradient and depolarizing fields [81]. For example, polar vortices have been discovered in thin ferroelectric films and extensively studied in an environment which maximizes the depolarization field generated by the surface charges in ferroelectric-insulator superlattices [119–121, 144, 145]. The use of insulating layers hinders the integration of such heterostructures into devices that could make use of the electronic characteristics of the complex topologies [146, 147]. However, ferroelectric heterostructures with metallic contacts, which are significantly easier to incorporate into technological devices, have to date been shown only to stabilize more common topologies, such as 180° domains with localized polar vortices at the domain walls [117] or flux-closure type domains [116, 118].

In magnetism, noncolinear spin interactions such as DMi can trigger complex spin topologies which are incommensurate relative to the crystal structure of the host material. Such spin textures are described by multiple magnetic moment windings coexisting along multiple directions. Examples include chiral skyrmion lattices (double [148] or triple [149] - \vec{Q}) or the recently observed incommensurate spin crystal phases (isotropic/anisotropic double - \vec{Q}) [150]. Following the link between the topological dipole textures of ferroelectrics and ferromagnets, can this analogy be extended to multiple - \vec{Q} incommensurate polarisation textures? If possible, such a feat could hint towards the physical manifestation of an electric Dzyaloshinskii–Moriya interaction, which has recently been shown to be allowed by symmetry in ferroelectrics [143].

Here, as a follow-up to the previous chapter, ordered arrays of polar vortices are shown to form in a single thin ferroelectric film with metallic boundary layers. Unlike the vortex phases in PbTiO3/SrTiO3 superlattices, which have a translational symmetry along the vortex core, a new topology is presented, which displays an additional periodic perturbation along the vortex core. This is an analogue of the double - \vec{Q} magnetic spin crystal phase.

An assessment of the growth quality is given by AFM and low-magnification STEM. The cross-sectional polarization topologies was analysed using STEM and DF-TEM methods. However, electron microscopy provides limited information as the 3D information of the polarization topology is encoded into a 2D image. To help fill in the knowledge gap, we measure volumes in the reciprocal space which shows the 3D distribution of periodicities in the sample. Due to the complexity of the polarization textures, we complement the x-ray diffraction data with circular dichroism measurements. This helps in revealing the presence or absence of chirality within the polar textures. Furthermore, we augment these findings with plan view electron microscopy studies. Finally, all knowledge is brought together into a 3D polarization model that reflects the experimental data.

6.1.1 Sample growth

DyScO₃ (110)_o oriented substrates with a miss-cut angle $< 0.05^{\circ}$ were prepared by thermal annealing at 1030 °C for 2 hrs in an oxygen rich atmosphere. Epitaxial SrRuO₃/ PbTiO₃/ SrRuO₃ film structures were deposited onto the SrTiO₃buffered DyScO₃ (110)_o substrates using reflective high energy electron diffractionassisted pulsed laser deposition, which enabled precise control of the layer thickness. The thickness, growth temperature and laser fluence for STO/SRO/PTO/SRO are 10uc/11uc/13uc/11uc, 600/ 670/ 600/ 600 °C and 1.0/ 0.8/ 1.0/ 0.8 J cm⁻², respectively. The laser repetition rate was 3 Hz for all layers, at 0.1 mbar oxygen pressure. The cooling rate was 20 °C/min in 200 mbar of O₂.

The surface of the PLD deposited films were studied using Atomic Force Microscopy (AFM) which showed atomically flat layers as seen in Figure 6.1a. The vicinal structure imposed by the substrate miscut angle ($\sim 0.003^{\circ}$) is retained through all the component layers. The vertical step between adjacent terraces is about 4 Å(1 unit-cell) and the roughness below 1 Å.

A low magnification cross-sectional STEM image of the sample is shown in Figure 6.1b. The STEM data shows the well-defined and smooth layers with layer thicknesses as expected from the nominal structure.

6.1.2 Film stacking geometry

The DSO crystal has an orthorhombic unit cell, which allows one to unambiguously define the directions. In order to set up the reference system, high-magnification STEM imaging was performed on the SRO/PTO/SRO sample along two perpendicular directions, namely $[100]_{pc}$ (Figure 6.2) and $[010]_{pc}$ (Figure 6.3). At the bottom



Figure 6.1: Structural characterization. a, Atomic Force Microscopy (AFM) topography of the surface of our $(SrRuO_3)_{11}/(PbTiO_3)_{13}/(SrRuO_3)_{11}$ tri-layer sample. b, Low magnification cross-sectional Scanning Transmission Electron Microscopy (STEM) of the sample. The scale bar is 10 nm.

of the image the substrate pattern is enlarged, which has distinctive features, unique to the direction of observation. If the electronic beam travels along $[100]_{\rm pc}$, the Dy atoms are arranged in such a way that the resulting columns of atoms is elongated into an ellipse. Furthermore, in this geometry, the DSO unit cell parameters are not equal and the angle formed by its diagonals is not 45°. It is because of this reason that we notice an angular offset of about 3° between the films growth direction, $[001]_{\rm pc}$, and the substrate axis, $[110]_{\rm o}$, as sketched in Figure 6.2. Nevertheless, for simplicity, we will use the $[110]_{\rm o}$ and $[001]_{\rm pc}$ interchangeably, as the 3° angular offset does not trigger any structural changes. On the other hand, if the beam travels along $[010]_{\rm pc}$, the substrate has a clearly defined zig-zag shape, shown in Figure 6.3. One can notice that in this geometry, the stacking direction is perpendicular to the $[-110]_{\rm o} = [010]_{\rm pc}$ direction, but also parallel to $[110]_{\rm o} = [001]_{\rm pc}$. This eliminates the angular offset shown in the perpendicular geometry. In this way one can precisely label the direction, removing the ambiguity introduced by the pseudocubic notations.



Figure 6.2: Grown films stacking geometry. **a**, The stacking of materials as seen along the $[001]_0$ direction. The DSO (substrate) column of atom forms an angle of about 3° with the column of atoms of the growth films (STO,SRO...). **b**, A higher magnification of the substrate shows that the column if atoms is similar to an ellipsoid, a unique characteristic of DSO substrate crystal structure. **c**, The offset can be explained using geometrical means alone. The 3° offset is caused by the geometrical stacking of the different unit cells along this viewing direction.



Figure 6.3: Grown films stacking geometry. **a**, The stacking of materials as seen along the $[010]_0$ direction. Along this viewing direction the previously seen offset is absent. **b**, A higher magnification of the DSO substrate show a zig-zag arrangement of atoms, a characteristic feature of the crystal structure along viewing direction. **c**, Similarly, geometric considerations of the substrate-films stacking can explain the absence of an offset as seen in Figure 6.2.

An important note is that rough interfaces might interfere with the formation

and stabilization of polar textures, which are absent in this study.

6.2 Cross sectional polar textures

6.2.1 Displacement mapping

Early theoretical results have shown that closure domains are highly effective in minimizing depolarization fields in ultrathin films of $BaTiO_3$ (BTO) with SrRuO₃ (SRO) electrodes [151]. Here, these studies were extended within the Density Functional Theory (DFT) framework and applied to the similar PbTiO₃/SrRuO₃ system in which in-plane lattice strain is introduced through epitaxial matching to $DyScO_3$. The details of the study are elaborated in Chapter 5. Bulk PTO has a significantly larger unit cell dipole (~ $90 \,\mu C \, cm^{-2}$) compared to BTO (~ $30\,\mu\mathrm{C\,cm^{-2}}$) suggesting a higher energy cost is associated with any dipole rotation. However, the polar map within the PTO layer, after relaxing the cation – oxygen octahedra, reveals a continuous rotation of the local polarization which assembles into an ordered array of polar vortices, as seen in Figure 6.4a. Thus, the large electrostatic energy is minimised by local rotations of surface dipoles, similar to ferromagnetic Kittel domains [151, 152]. The DFT results suggest that this energy minimisation pathway is adopted even for metal-like boundary conditions introduced by the SRO layer which has a high charge density of $\sim 2 \times 10^{22}$ electrons/cm² and a screening length of only $\sim 1 - 2$ Å [64]. In principle, SRO should provide better screening than SrTiO₃, but our theoretical models reveal that it is still unable to screen the large bound surface charges of the ferroelectric layer which forces the polarisation to develop a complex vortex array in SRO/PTO/SRO systems.

Motivated by these promising predictions of the DFT results showing ordered arrays of vortices in $SrRuO_3/PbTiO_3/SrRuO_3$, cross sectional FIB samples were prepared along the principal pseudocubic crystallographic axes, $[100]_{pc}$ and $[010]_{pc}$, respectively. Since PTO is a displacive ferroelectric, the polarization direction can be determined by knowledge of the relative positions of the B-site cations and oxygen atoms [153]. Thus, the polarization can be mapped, at the unit-



Figure 6.4: Unit-cell scale electric dipole topologies. a, Relaxed cation – oxygen octahedra displacements map of the $(SrRuO_3)_6/(PbTiO_3)_6$ system from DFT, where 6 refers to the number of unit cells of the respective layer. b, Annular Dark Field STEM (ADF-STEM) image showing the distortions within the PbTiO₃ layer. c, Unit cell polarization map of the ADF-STEM image revealing the local structure of the polarization pattern. d, Enlarged region marked by dashed lines in (c), showing the vortices formed by the polar structure. The scale bar for b and c is 2.5 nm.

cell level, using aberration corrected STEM (Figure 6.4b). The experimentally determined polarization map, taken when the beam travels along $[100]_{pc}$, reveals an ordered array of polar vortices (Figure 6.4c) within the ferroelectric layer, with a periodicity of about 8 - 8.5 nm - about half the film thickness. The main topological characteristics, i.e., periodicity, off-centre core, clockwise/anti-clockwise pairs, etc., are in good agreement with the DFT studies, despite the almost doubled thickness of the PTO layer in the experimental sample. The observed vortex pattern has a non-zero toroidal moment $\vec{G} = (2N)^{-1} \sum_{i=1}^{N} \vec{r_i} \times \vec{P_i}$ which is parallel to the vortex core. Here P_i is the local dipole moment located at r_i , and N is the number of dipoles in the summation [73, 154]. The formation of polar vortices, as highlighted in Figure 6.4d, in which the local dipoles rotate in such a way as to reduce both the depolarization and stray fields avoid the suppression of the ferroelectricity in the thin films [60]. Furthermore, the STEM data also shows that the polarization topology is characterized by periodic pairs of clockwise (CW) – counter CW vortices, with a periodicity of about twice the thickness of the PTO film (~9 - 10 nm).

While the DFT supercell does predict relaxation into polar vortices with characteristics similar to the experimental ones (off-centered cores, periodicity) it has an important limitation. It can only produce structures that must have translation symmetry along one direction. This means that the produced vortex structure is homogeneous along $[100]_{pc}$. In order to check if this occurs in the SRO/PTO/SRO sample, STEM displacement mapping was performed on a sample cut perpendicular to the one showing polar vortices. In Figure 6.5 the STEM displacement map is taken when the electron beam travels along $[010]_{pc}$. The polar texture shows periodic adjacent regions with polarization forming 180° domains and a periodicity of about 7 - 10 nm. Close to the interface there is a "closure" effect which causes the polarization to be parallel to the interface, resulting in a reduced depolarization field. Furthermore, the polarization does not present the same continuous rotation effect as the vortices seen in the perpendicular direction, but shows a more step-like transition between domains (homogeneous polarization regions). This observation is not predicted by the DFT simulation, nor does it invalidate the DFT results. It is still possible that the pattern observed in Figure 6.5 is globally periodic, which could explain the fact the vortices retain their structure (periodic displacements will average to zero). Nevertheless, two periodic textures are observed along perpendicular directions. At this point it is not clear whether or not a coupling between these periodicities exists, nor if they are long-ranged.



Figure 6.5: Unit-cell scale displacement mapping. a, ADF-STEM image taken from a cut 90° relative to figure 6.4. b, Unit-cell polarization map of the ADF-STEM image, revealing a pattern fundamentally different from polar vortices, which involve continuous dipole rotation. The scale bar is 4 nm.

6.2.2 Dark Field-TEM

In ferroelectrics, which are also piezoelectrics, the polarization and strain are coupled. It is natural to assume that the polarization textures observed in the previous section generates a characteristic strain field, which acts as a lattice perturbation. To provide such evidence, we use the DF-TEM method which can make use of thicker samples, as the signal is a diffraction signal of the crystalline planes. Similar to the STEM displacement mapping, DF-TEM diffraction contrast imaging was performed on samples cut at 90° to each other. A two-beam condition is used, where one relevant diffraction peak is excited along with the transmitted beam.

In Figures 6.6a and b, we show dark field images of a $[100]_{pc}$ cross section specimen under $g=020_{pc}$ and $g=002_{pc}$ excitation conditions. Under the $g=020_{pc}$ excitation, the dark field contrast shows a sine wave-like pattern along $[010]_{pc}$, which is produced by a modulation of the in-plane component of the internal strain field (and hence polarization). Furthermore, under $g=002_{pc}$ condition, we see that the dark field contrast shows features of alternating bright/dark regions, corresponding to a modulation of the out-of-plane component of the internal strain fields. These characteristics are consistent with the ones found in PTO/STO superlattices, which



Figure 6.6: **Cross-sectional DF-TEM**. **a**, Image of a $(100)_{pc}$ cross section taken under $g=020_{pc}$ excitation condition. **b**, Image of the same $(100)_{pc}$ cross section taken under $g=002_{pc}$ excitation. **c**, Image of a $(010)_{pc}$ cross section (i.e. cut at 90° from a and b) taken using $g=002_{pc}$. The scale bars are 20 nm.

show pairs of clockwise/anti-clockwise vortices. Along the perpendicular $[100]_{pc}$ direction (Figure 6.6c), the diffraction contrast (g=002_{pc}) shows short ranged periodic features, with periodicities that match the STEM data.

The dark field diffraction contrast shown above is clear evidence of a periodic lattice perturbation induced by the polar textures. This opens the possibility of using non-invasive methods such as X-ray diffraction which allows us to study these periodic structures over a wide area.

6.3 X-ray studies

6.3.1 High resolution XRD. Reciprocal space mapping

Any HR-TEM analysis required to reveal domains on the nanometre level necessarily has a very limited field of view. To explore the macroscopic ordering of the polar domains more widely, we employed X-ray diffraction. The periodic structural distortions caused by the polar domains will manifest as satellite peaks in the vicinity of the layer Bragg peaks. Since these domains are within a thin PTO layer, any satellites will be extended in the reciprocal space direction normal to the substrate. The sample was aligned on all instruments with the Q_x , Q_y and Q_z directions coincident with the [h00]pc, [0k0]pc and [001]pc crystallographic directions. Volumes of reciprocal space were mapped during scans of the sample using a two-dimensional area detector and provide simultaneous information about long-range periodic structures along all crystallographic axes. A three-dimensional reciprocal space map (RSM) was recorded in the vicinity of the $(002)_{pc}$ DSO reflections (Figure 6.7a), with Q_x , Q_y and Q_z co-incident with the $[h00]_{pc}$, $[0k0]_{pc}$ and $[001]_{pc}$ directions. Furthermore, to confirm the epitaxy relation between the substrate and the grown films, reciprocal space maps were taken in the vicinity of 103_{pc} on our laboratory source, while the maps around the 002_{pc} were taken at I16 at Diamond Light Source.

Crystal truncation rods (CTR) around the substrate peaks contain the collective reflections from all the layers. Around both the symmetric $(002)_{pc}$ and the asymmetric $(103)_{pc}$ reflections the CTR is found at the same in-plane \vec{Q} as the substrate peak, showing that all layers are fully strained to the substrate, with identical in-plane lattice constants for all the layers.

In order to extract the real-space periodicities from the location of satellite peaks, the three-dimensional scattering volume was first collapsed into two dimensional maps by integrating along the third reciprocal lattice to produce $Q_z - Q_x$, $Q_z - Q_y$ and $Q_x - Q_y$ RSMs (Figure 6.7a). Then, we plot the intensity distribution along the relevant directions as shown in figure 6.8.

For this SRO-PTO-SRO multilayer, we start by considering the collapsed



Figure 6.7: **3D** Reciprocal Space Map. **a**, 3D reciprocal space map around the DSO 002_{pc} Bragg peak. The facets of the volume show the integrated signal along normal direction to the respective plane. **b**, RSM around the asymmetric reflection $(103)_{pc}$.

 $Q_z - Q_x$ full reciprocal space map (figure 6.8a) which contains the surface CTR at $Q_x = 0$ and streaks of intensity centred on $Q_x = 0.07 \text{ Å}^{-1}$ arising from the periodic structure. Extracted one dimensional Q_z scans determined at $Q_x = 0$ and the 1st order satellite peak ($Q_x = 0.07 \text{ Å}^{-1}$) are shown in figure 6.8b. The surface CTR is dominated by the substrate reflection at $Q_z = 3.191(2) \text{ Å}^{-1}$ but the layer peaks can be seen as shoulders at $Q_z = 3.108(2) \text{ Å}^{-1}$ and $Q_z = 3.224(2) \text{ Å}^{-1}$. The extracted CTR recorded at the satellite reflection scan shows two peaks: the first and most intense peak is centred at $3.108(2) \text{ Å}^{-1}$, with the second the first order interference fringe. The zero order peak shows that the periodic structures are contained in a layer which has an out-of-plane lattice constant of about 4.05(2) Å. The width of the peak is broad and about $0.120(5) \text{ Å}^{-1}$ and is a direct measure of the layer thickness from which the satellite originates, which is a 5.25(15) nm thick layer. Both the average out-of-plane lattice constant and the layer thickness match the structural characteristics of the PTO layer, indicating that the host layer to the diffraction

satellites is PTO. More detailed analysis of the periodic functions along the $[100]_{pc}$ direction can be gleaned by considering extracted scans in Q_x . To improve the signal to noise, the Q_x line scans shown in Figure 6.8c were calculated by integrating a region of Q_z as shown by the highlighted box in Figure 6.8a. The resulting onedimensional plot of the diffraction intensity along the Q_x direction shows the 1st and 2nd order satellite peaks and their widths, as seen in figure 6.8c. The extent of the long-range order can be gleaned from the width of the satellite peaks. Along the Q_x ([100]_{pc}) direction we estimate the domains to have a coherent length of approximately 45 nm. However, as the 2nd order satellites have a width roughly twice that of the first order there must also be some dispersion in the periodicity giving rise to additional peak broadening. There are also indications of additional periodicities in the tails of the central Bragg peak around 0.02 Å^{-1} , corresponding to a periodicity of about 30 nm.

Exploring the periodicities along the $[010]_{pc}$ direction follows a similar process, but this time the intensity is initially integrated in Q_x to produce a $Q_z - Q_y$ (Figure 6.8d) before extracting a cut in Q_y by integrating Q_z , as shown in Figure 6.8e. This cut in reciprocal space reveals broad satellite peaks with a spacing of about $\Delta Q_x = 0.078(5) \text{ Å}^{-1}$ and periodicities of approximately 8 nm. Second order satellites are absent indicating that along this direction the ordering is less well ordered than in Q_x . Nevertheless, the Full Width at Half Maximum (FWHM) of the satellite peaks is approximately 0.03 Å^{-1} revealing a coherent length of about 20 Å^{-1} in the Q_y direction. As in the Q_x scan, hints of additional periodicities can be seen in the tails of the central peak at reciprocal space values of $0.022(5) \text{ Å}^{-1}$ corresponding to features with periodicities in the 22 - 28 nm range.

Synchrotron X-ray diffraction is ideal for analyzing ferroelectric domains due to the strain-polarization coupling. However, there are complexities that a regular RSM map will not shine light on. Complex ferroelectric textures could possess such a property, called chirality. Within the XRD realm, circular polarized photons could couple to the chirality of the periodic textures, resuting in a measurable signal. It is important to know if chiral domains are present as it could lead to phases that



Figure 6.8: **RSM data**. **a**, Reciprocal space map Q_z vs Q_x . **b**, Comparison plot of the extracted Q_z scan at $Q_z = 0$ and $Q_z = 0.07 \text{ Å}^{-1}$. **c**, Integrated (boxed area) line profile showing the 1st and 2nd order satellite peaks and their widths. **d**, Reciprocal space map Q_z vs Q_y . **e**, The integrated (boxed area) line profile shows weak first order satellite peaks corresponding to a periodicity of about 8.05 nm. **f**, Plan view Q_x vs Q_y RSM map and line scans (boxed areas) showing the in-plane distribution of the satellite peaks.

are incommensurate to the crystal structure.

6.3.2 Circular Dichroism

Information about possible helicities within the 2D array can be extracted from a non-resonant study of the samples using circularly polarized photons. The sample was orientated such that the $[100]_{pc}//[001]_{o}$ direction is in the scattering plane and along the beam direction at the azimuthal angle 0°. Experiments were performed at four azimuthal angles 0°, 90°, 180°, 270°. At each azimuth, rocking curves within the scattering plane were used to measure the satellite reflections along the H and K directions. The experimental results are shown in Figures 6.9a, b. At each point in the scan, the intensity was recorded separately for each beam helicity and for a fixed monitor count. The resulting "Sum" signal is obtained by averaging the measured intensities for the two helicities and the "Flip ratio" determined from the difference signal, normalized to the sum signal. Any breaking of time-reversal symmetry within the scattering process causes a signal to be present in the flip ratio which reverses in sign when the sample is rotated by 180°. Thus, by comparing the



Figure 6.9: Raw XCD data. a, $([100]_{pc}//[001]_o)$ in the scattering plane) and b, $([010]_{pc}//[-110]_o)$ in the scattering plane). The first row of graphs represents the sum of the dichroic signal; the second row shows the flip ration and its behavior upon 180° rotation of the sample. The last set shows the dichroic signal at the same in-plane Q as the satellites indicating that these structures are the source of the dichroic signal.

data recorded at 0° and 180° with that from 90° and 270° one can probe for symmetry breaking due to the polarization configurations along the $[100]_{\rm pc}$ (0° and 180°) and $[010]_{\rm pc}$ (90° and 270°) directions. The dichroic signal is determined by calculating the difference between the flip ratios recorded after a sample rotation of 180° (the flip ratio is determined from the difference signal, normalized to the sum signal). Such an operation removes any signals that do not break time reversal symmetry. The sum data in Figures 6.9a, b are fully consistent with x-ray diffraction studies reported previously, with the satellite reflections stronger when the $[100]_{\rm pc}//[001]_{\rm o}$ direction is in the scattering plane. The flip ratio is noisier, but there is a signal that appears to reverse sign in the data upon sample reversal when recorded in the $[100]_{\rm pc}//[001]_{\rm o}$ direction, which is more clearly visible in the dichroic signal.



Figure 6.10: **Processed XCD data**. **a**, $([100]_{pc}//[001]_o$ in the scattering plane) and **b**, $([010]_{pc}//[-110]_o$ in the scattering plane). The first row of graphs contain the signal from the two $\pm Q$; the second one show the average of the two.

In Figures 6.10a, b we show the processed results. As the data from the two satellites are in excellent agreement, we can consolidate the data and reduce the uncertainties. We focus first on the dichroic signal. When the sample is orientated with $[100]_{pc}$ in the scattering plane we observe a (weak) dichroic signal which disappears upon rotation of the sample by 90° which brings the $[010]_{pc}$ into the scattering plane. The lack of a dichroic signal in the $[010]_{pc}$ direction is either the result of no symmetry breaking terms, or two terms of equal but opposite sign which cancel completely. In contrast, the flip ratio sum is remarkably consistent for the two sample orientations. As the measured linear polarization content was very small, we rule out the flip sum being the result of linear dichroism or a simple

polarization factor effect. One possible explanation for the flip sum signal is that it originates from natural chiral dichroism which preserves sign upon 180° rotation. Since the flip sum dichroism is identical for both orientations but the dichroic signal is only manifest when the sample is orientated with $[100]_{pc}$ in the scattering plane, one would have to conclude that the modulation along the $[010]_{pc}$ direction in the 2D array results in a purely chiral signal but the periodicity along $[100]_{pc}$ is both chiral and polar.

6.4 Plannar view electron microscopy studies

6.4.1 Dark Field-TEM

In order to study how the two cross-sectional periodicities are interwoven, plan view dark field studies were performed on samples with most of the substrate milled away to allow the sample to be electron transparent. The XRD reciprocal space maps have shown that there are periodic features co-existing along $[100]_{pc}$ and $[010]_{pc}$ axes. In order to reveal these features we record the plan-view TEM image when the sample is tilted so that the $g = [110]_{pc}$ is excited. With no objective aperture in, we observe a labyrinthine pattern [155, 156] (Figure 6.11a) with features along $[100]_{pc}$ and $[010]_{pc}$. Furthermore, the contrast shows a preferential ordering axis, in the same way that the RSM maps show peaks with different intensities along Q_x and Q_y . Figures 6.11b and c show the crystallographic orientation of the substrate relative to the labyrinth structure. Along the $[001]_o$ axis, the DSO unit cell shows a clear zig-zag pattern, which helps identify the plan-view directions.



Figure 6.11: **Diffraction contrast orientation**. **a**, TEM image (objective aperture retracted) reveals a labyrinthine pattern with periodicities matching along the principal $[100]_{pc}$ and $[010]_{pc}$ axes, in agreement with the Q_x vs Q_y RSM map. **b**, Simmulated diffraction pattern of the DSO substrate, corresponding the observation direction of (**a**). **c**, The DSO crystal structure, which shows a zig-zag pattern along $[100]_{pc}$. This feature causes the doubling of the diffraction peaks observed in (**b**).

Figure 6.12a shows a low magnification image of the periodic structures under two-beam conditions and $\mathbf{g_1} = 110_{\mathrm{pc}}$ excitation. The labyrinth pattern is comprised of interwoven domains that run along the principal axes $[100]_{\mathrm{pc}}$ ($\mathbf{Q_x}$) and $[010]_{\mathrm{pc}}$ ($\mathbf{Q_y}$) with periodicities of about 9 - 10 nm. The discrepancy between X-ray and TEM periodicities is likely to come from a slight strain relaxation due to having milled away most of the substrate. Nevertheless, from the X-ray analysis we determined that the periodic structures (periodicities of ~ 9 - 10 nm) along $\mathbf{Q_x}$ and $\mathbf{Q_y}$ have a coherent length of about 45 nm and 22 - 28 nm, respectively. The plan-view DF-TEM displays the real space domain pattern, and these values are shown to relate to the average length of the individual domains running along $[010]_{\mathrm{pc}}$ and $[100]_{\mathrm{pc}}$ directions (inset Figure 6.12a).

Conveniently, the $\mathbf{g_2}$ -vector can be decomposed into orthogonal components, $\mathbf{g_2} = 100_{\mathrm{pc}}$ and $\mathbf{g_3} = 010_{\mathrm{pc}}$ (Figures 6.12b and c). Plan-view dark field image taken under $\mathbf{g_2}$ and $\mathbf{g_3}$ excitation vectors show periodic structures of about 10 nm perpendicular to the excitation vector. The periodic character is reflected by the satellite decorations of the diffraction peaks as seen in the inset of Figures 6.12b, c.

Contrast in dark field TEM images is primarily produced by the internal



Figure 6.12: **Plan-view DF-TEM**. **a**, Low magnification plan view of the complex domain pattern take under the $g_1 = 110_{pc}$ condition. The figure inset shows the enlarged boxed area. **b**, Plan-view dark field image taken under $g_2 = 100_{pc}$. **c**, Plan view diffraction contrast take under $g_3 = 010_{pc}$ excitation. The scale bars are: 100 nm for (**a**), 30 nm for (**b**) and (**c**).

strain field of the vortex structures. Some insight into these strain fields can be obtained by choosing different g-vectors, since the only components that contribute to contrast are parallel to g. A vortex, with displacements perpendicular to its line direction u, appears as a line of contrast perpendicular to g and becomes invisible when g is parallel to u. The coexistence of two modulations is thus confirmed by the dark field $\mathbf{g} = 100_{\rm pc}$ and $\mathbf{g} = 010_{\rm pc}$ images, which show continuity of structures in both directions.

To improve the signal/noise ratio, a bandpass filter is used on the 2D Fourier transform. In this way we impose a frequency cut off for the random high frequency signal which is related to the noise in the system. Ultimately, we allow for frequencies of $0.015 < |\vec{Q}| < 0.16 \text{ nm}^{-1}$, which corresponds to real space periodicities $67 < |\vec{R}| < 6.3 \text{ nm}$. This allows for periodicities within this interval to manifest in the real-space image. The 2D Fourier Transforms show that all Fourier satellites are well within the band-pass filter. As seen in the succession of images from Figures 6.13a-c, the bandpass filter cleans the data revealing intensity modulation along the individual domains. To further check that this is not an artifact introduced by the filtering



Figure 6.13: Noise filter. a, 2D-Fourier transform (FT) of the plan view image taken under g1 = 110 excitation. b, Bandpass filter which removes the noise and retains the signal for $|\vec{Q}| < 0.16 \,\mathrm{nm^{-1}}$. c, Bandpass filter which also removes the central spot and the signal for $|\vec{Q}| < 0.015 \,\mathrm{nm^{-1}}$. The scale bar is 30 nm.

method, we convolve the image with a gaussian function which will have a smoothing effect. Similar to the Fourier filtered image, the blurred image shown in Figure 6.14 reveals that there is an additional periodicity, superimposed on the labyrinth, which gives the diffraction contrast a bead-like texture.

Line profiles along the brighter contrast pattern (Figure 6.15) and darker contrast structures (Figure 6.16) reveal periodic intensity modulations in both unfiltered and filtered data. Such intensity modulations are present regardless of the local structure and have the same periodicity in both the filtered and unfiltered data. This shows the effectiveness of the band-pass filter used to clean the signal and provides further evidence that the filtering process does not induce additional artifacts, but only removes the high frequency noise.



Figure 6.14: **Gaussian smoothing**. (Left) Raw image. (Right) same area after gaussian smoothing. Bead-like features decorating the contrast can be observed, similar to a Fourier filtered image (figure 6.13). The scale bar is 40 nm.



Figure 6.15: Filtered/Unfiltered Bright areas comparison. The bandpass filter improves the signal/noise ratio without introducing artifacts. Both the filtered and unfiltered images display, aside from the labyrinth pattern, a periodic contrast modulation along the individual domains.



Figure 6.16: Filtered/Unfiltered dark areas comparison. The second modulation permeates the labyrinth pattern. All regions bright/dark show periodic contrast intensity oscillations.

As mentioned before, the labyrinth structure imaged under the $g_1 = 110_{pc}$ excitation, at first glance, appears to consist of uniform domains oriented along $[100]_{pc}$ and $[010]_{pc}$. The filter process has shown that the individual domains within the labyrinth pattern contain additional periodic perturbations running along the domains. These perturbations produce modulations in the diffraction contrast intensity regardless of the domain orientation (Figure 6.17b). There is a slight directional dependence of the modulating period, with the domains ordered in the $[010]_{pc}$ having periodicities of about 9.2 nm (inset Figure 6.17b) and those along the $[100]_{pc}$ a period of about 8.2 nm. Comparisons with the DF-TEM and X-ray data suggest that these modulations are the projection of the polar vortex array. The juxtaposition of the labyrinth and the modulations within the domains themselves generates a local rectangular lattice of alternating contrast, but due to the complex domain pattern, square lattice ordering is only short range (Figure 6.17c).

To give some indication of the likely contrast of an array of vortices in dark field TEM we performed diffraction contrast simulations within the 2-beam Howie-Whelan formalism. For details about the simulation, the reader is referred to the



Figure 6.17: **Plan-view TEM imaging**. **a**, Plan-view dark field TEM imaging of $(SrRuO_3)_{11}/(PbTiO_3)_{11}/(SrRuO_3)_{11}$ tri-layers which shows the intricate domain pattern formed by two coexisting periodicities along $[100]_{pc}$ and $[010]_{pc}$. The inset shows the SAED pattern with the excited $g1 = 110_{pc}$ vector. Close inspection of the diffraction spots (boxed area) reveals satellite decorations, similar to the X-ray data Q_x vs Q_y RSM. **b**, Noise filtered image showing intensity modulations along the individual domains. The inset graph shows the probability distribution of finding a certain modulating period of the individual domains parallel to $[100]_{pc}$ (red) and $[010]_{pc}$ (green) respectively. **c**, Magnified area shows the locally ordered modulated domains. The scale bars are: 100 nm for (**a**), 30 nm for (**b**) and 10 nm for (**c**).

Appendix section. While this does not reproduce contrast in images taken with a significant deviation from the Bragg condition – i.e. weak beam dark field images – it gives an indication of the strength of the contrast and its sensitivity to different choices of diffraction vector. We simulate a two-dimensional array of perfect vortices with displacement, R, given by $R = Ad^n e^{-\alpha d^n}$, where d is the distance from the vortex core, with parameters n=1.15 and α =0.6 chosen to match those observed in our cross-section atomic resolution ADF-STEM images. See appendix for more information.

As shown in Figure 6.18, the simulated contrast of a vortex array produces



Figure 6.18: **Plan-view diffraction contrast simulations**. (Left) Experimental plan-view dark field TEM images of the vortex array. Note that the $g = 110_{pc}$ image is at higher magnification and Bragg filtered. (Right) Two-beam Howie-Whelan diffraction contrast simulations of contrast from the strain fields of a 2D array of vortices as described above (deviation parameter s = 0.01 nm). The scale bars are 30 nm for g=010, 30 nm for g=100 and 10 nm for g=110.

the essential characteristics such as an alternating bright/dark arrays along g=100 modulated along the g=010, producing the observed bead-like features. Experimentally, we observe vortex arrays visible in both $g = 100_{pc}$ and $g = 010_{pc}$ directions, but those running along $[100]_{pc}$ give weaker contrast than those running along $[010]_{pc}$. We thus choose the magnitude of the displacement to be chosen as A=0.03 for vortices along $[010]_{pc}$ and A=0.003 for vortices along $[100]_{pc}$. This gives a modulated contrast in a Fourier-filtered $g = 110_{pc}$ image which is a reasonable match to experiment. The simulations were performed using an in-house script which can be found on GitHub [157]. For further details regarding the simulations, see the Appendix section.

6.4.2 Plan-view STEM

In order to extract further information regarding the plan-view polarization texture, we performed STEM displacement mapping on the plan-view sample. Considering the plan-view geometry, the DSO axes $[001]_0 = [100]_{pc}$ and $[-110]_0 = [010]_{pc}$ are anisotropic which allows us to unambiguously identify directions. Plan-view displacement mapping was performed along both the grown layers and the substrate zone axis as shown in Figures 6.19 and 6.20. As was presented in section 6.1.2, Figure 6.2, due to geometrical reasons there is an angle offset between the substrate $[110]_0$ and the $[001]_{pc}$ axis, in the $[001]_{pc} - [010]_{pc}$ plane. In Rochigram mode, the angular offset between the substrate and the films zone axis is obvious (Figure 6.19a), which allows us to identify the directions, as shown in Figure 6.19b. When we record a STEM image along the zone axis of the substrate, we indeed observe the zig-zag pattern characteristic of the substrate. As expected, STEM displacement mapping does not show any features (Figure 6.19c).



Figure 6.19: **Plan-view STEM**. **a**, Ronchigram. **b**, The ADF-STEM image is taken along the zone-axis of the substrate. As a result the clear zig-zag pattern can be observed (boxed area), which helps identify the crystallographic directions. **c**, The displacement map, however, does not show any features, as expected.

On the other hand, when we image along the zone axis of the grown films, stripes parallel to $[010]_{pc}$ can be observed, with the local displacement vectors



Figure 6.20: **Plan-view STEM**. **a**, Ronchigram. **b**, The ADF-STEM image is taken along the zone axis of the grown films. The zig-zag pattern is absent (boxed area). **c**, The displacement map shows clear head-to-head and tail-to-tail domain topologies. Their periodicity is about 10 nm, similar to the values from XRD and previous EM studies.

forming head-to-head and tail-to-tail domain topologies. The periodicity of the stripes is about 10 nm, consistent with the periodicities extracted from the X-ray diffraction RSMs and plan-view Dark Field TEM. Therefore, we identify the displacements as originating mainly form the ferroelectric thin film. The character of the polar orientation indicated that the second modulation shows displacements that run along the vortex core. Because we image through five layers, it is difficult to draw precise conclusions about the polarization topology within the ferroelectric film. Nevertheless, the head-to head- and tail-to tail topology seen in the plan-view STEM is in agreement with the previous plan-view DF-TEM observations (Figure 6.12).

6.5 Emergent polar ordering

6.5.1 Magnetic-like DMI

The complex contrast texture revealed in Figure 6.17c shows that the domain pattern in the ferroelectric layer needs to be characterized not by one, but by two periodic components each described by a \vec{Q} vector. Thus, one \vec{Q} vector determines the periodicity of vortices, given by the alternating bright/dark segments (Figure 6.12c), and a second \vec{Q} vector which breaks the uniformity of the domains in the perpendicular direction, leading to a state described by a double- \vec{Q} modulation. Such incommensurate phases, triggered by multiple \vec{Q} vectors, are found in magnetic materials [149, 158]. For example, chiral skyrmions [159] are described by triple- \vec{Q} cycloidal modulations. The interplay of only two orthogonal periodic modulations results in the so-called incommensurate spin crystals [11, 148, 150], whereby the periodicities are interwoven such that they permeate all space within the magnetic material and no region can be described by one periodicity alone. Whilst the spin crystal phases are stabilized by the non-colinear spin interactions, i.e. Dzyaloshinskii-Moriya interaction, the anisotropy energy will produce different variants of the spin crystal phase [150].

The possibility of an electric DM-like interaction has been put forward by Zhao et al. [143], where the authors have analysed the possibility of specific couplings that can result in non-zero DM-like energies. Such couplings have the form of trilinear products between oxygen octahedra tilts and nearest-neighbour displacements. Due to the displacive nature of PTO, the displacement direction of the B-site cation relative to its oxygen octahedra approximates very well the direction of the polarization, fundamentally linking the two parameters.

As we know, polar vortices form as a result of the interplay between strain, strain gradient and electric energies and thus they can be readily observed in STO/PTO/STO heterostructures. Unlike STO, SRO is metallic perovskite which displays significant oxygen octahedra rotations. Earlier works [133, 160, 161] have experimentally shown that tilted structures of perovskite electrodes induce octahe-



Figure 6.21: **Tilt map**. **a**, Oxygen tilt behaviour along a row of unit cells. **b**, Tilt map throughout the PTO layer (Adapted from Figure 5.14).

dra tilting in non-tilted ferroelectrics across the interface between the two materials. We performed further detailed analysis of the present DFT results which revealed similar behaviour, as can be seen in Figure 6.21. At the interface with SRO, the PTO shows pronounced in-phase octahedra tilts localized at the interface. These tilts superimposed onto the Néel-like dipole winding of the vortices may generate the DMI energy term. This interface induced effect would be analogous to the DM interaction induced by interfacial symmetry breaking in magnets [162].

While the DFT supercell does not allow tilting along all three directions, we can use the current simulation results to further analyse the possible couplings between the oxygen octahedra tilting and the B-site displacements. As imposed by the geometry of the DFT supercell and the periodic boundary conditions, the system is homogenous along the X-axis, which is identical to the $[100]_{pc}$ crystallographic direction. Out of all the possible DM-like couplings, a coupling similar to the E5 coupling shown in Figure 1 of [143] can be considered. Accordingly, the direction of the DM vector \vec{D}_{ij} has components dependent on the rotation axis of oxygen octahedra. In other words, the in-phase oxygen tilting about the X-axis induces a DM vector along the same X-axis. If the B-site displacements induced by the Neel-like dipole winding $(\vec{u}_i \times \vec{u}_i)$, forming the other term of the DMI energy, are parallel to this DM vector, a helical modulation is induced. If they are mutually perpendicular a cycloidal modulation is imposed. However, in a real system we expect PTO to experience at the SRO/PTO interface even more complex structural distortions, with oxygen tilts along both X and Y directions [163], both coupling to the polar distortions. In this case, the direction of the DM vector should point along the [110]_{pc} direction if the tilts have equal strengths, or an arbitrary direction if the tilt strength along X and Y is different. In order to precisely answer this question further detailed theoretical and experimental investigations must be performed.

6.5.2 Polarization model

Based on the TEM and XRD data presented above, we hypothesize that the ferroelectric polarisation orders itself in a domain pattern similar to the magnetic incommensurate spin crystal phases given by two perpendicular periodicities, namely the incommensurate spin crystal 1 (SC1) [164].

While it is very clear that the structure that we observe has two coexisting modulation vectors, a complete model of the variation of polarisation and strain in three dimensions still remains to be determined, because we can only observe periodicities using diffraction and a projection of the structure using transmission electron microscopy. The plan view TEM data indicates that the weaker modulation produces periodic displacements that are parallel to the vortex core, but it remains to be determined whether this occurs by cycloidal-like modulations such as $\vec{Q}_c = C_c \sin(qx)\vec{e}_{[100]} + C_c \cos(qx)\vec{e}_{[001]}$ (x is the $\vec{e}_{[100]}$ coordinate component of the position vector), or is some other more complicated structure. For example, using our DFT to build a 3D vortex array (Figure 6.22a), we obtain identical plan-view projections by adding either a helical-like modulation, given by $\vec{Q}_h = C_h \sin(qx)\vec{e}_{[010]} + C_h \cos(qx)\vec{e}_{[001]}$ (Figure 6.22b) or cycloidal-like modulation (Figure 6.22c).



Figure 6.22: **Double modulation**. **a**, Pseudo 3D representation showing plan and front view through a regular polar vortices. **b**, Vortex arrays with a second helical modulation along the vortex core. **c**, Vortex arrays with a second cycloidal modulation along the vortex core. The color bar maps the projection of the dipole along [001]: white regions contain dipoles oriented parallel to [010], while red and blue regions describe dipoles oriented parallel (red) and anti-parallel (blue) to [001].

To further check the validity of our models we compare the projected polarization pattern along both $[100]_{pc}$ and $[010]_{pc}$ direction with the experimental STEM polarization maps. The projection is achieved by averaging the polar vectors in the direction perpendicular to the projection plane.

Figures 6.23a, b show the displacement maps for samples along the $[100]_{pc}$ -and $[010]_{pc}$ directions. Similar to the X-ray data along the $[010]_{pc}$ direction, well defined polarization topologies (vortices) are formed. The projected map of both the helical-like and cycloidal-like projections reveal that the vortex structure is retained, with a slight difference between the two manifested as an elongation of the vortex



Figure 6.23: Cross-sectional polar maps. a, Polarization maps along the ordered [010]pc direction. The projection of a cycloidal and helical modulated vortex array into the $[001]_{pc}$ - $[010]_{pc}$ plane shows that the domain topology is retained. b, The projection of the modulated vortex array into the $[001]_{pc}$ - $[100]_{pc}$ plane shows that the cycloidal modulation allows the polar vector to rotate in-plane, similar to the experimental polar map, while the helical modulation does not.

cores along $[010]_{pc}$. In the perpendicular direction, however, the disorder throughout the thickness of the sample is reflected as regions of mostly up/down domains. Nevertheless, some areas show that the polarization continuously rotates between these domains. This behaviour is shown by the cycloidal modulated vortices, in detriment to the helical-like modulation which does not allow for in-plane rotation of the polarization vector. If the second modulation is given by another ideal array of vortices perpendicular to the first, the projected displacements maps show that vortices should form along both $[100]_{pc}$ and $[010]_{pc}$.



Figure 6.24: **Plan-view STEM**. **a**, 3D model of the polarization with helical (left) and cycloidal (right) modulation and the projected structure into the three orthogonal planes. **b**, Plan-view STEM displacement map reveals head-to-head and tail-to-tail displacement topologies.

Furthermore, in the $[100]_{pc}$ - $[010]_{pc}$ plane (plan-view geometry), our model best matches the experimental observation when the second modulation has displacements running along the vortices (cycloidal-like, see Figure 6.24). While a helical modulation would also show displacement stripes, the relative orientation of the displacement would be similar 180° domains, in disagreement with the experimental STEM displacement map. These results provide evidence that the periodic intensity oscillations along the domains shown in Figures 6.12 - 6.16 are likely to emerge from an ordered array of polar vortices modulated by a second \vec{Q} -vector characterized by a cycloidal displacement pattern.

6.6 Conclusions

In summary, we have shown that polar vortices also form in a ferroelectric environment where the depolarization field is minimized by the choice of metallic SrRuO₃ electrodes. Moreover, the ferroelectric polarisation generates a new ordered phase described by a double- \vec{Q} modulation that combines a vortex state with a cycloidal modulation. This exhibits textures that mimic, in detail, the incommensurate spin crystal phase SC1 recently found in magnetic materials. The presence of such a double- \vec{Q} structure, mediated by incommensurate interactions, would require an electric counterpart of the magnetic DMi, which has been suggested by Zhao et al. to be permitted by symmetry. Such an electric Dzyaloshinskii-Moriya interaction could provide the phenomenological explanation of the emergence of magnetic-like phases in ferroelectric systems.

Our findings provide a potential pathway for technological exploitation and a fertile framework for further fundamental studies exploring physical phenomena. Such studies would pave the way for the exploration of complex ferroelectric topologies triggered by the electric DMi, similar to topological spin textures found in ferromagnets. Along with the discovery of polar vortices and skyrmions, our findings further blur the border between emergent ferromagnetic and ferroelectric dipole topologies. Understanding the fundamental similarities between the manifestation of spin textures across multiferroics is still lacking, however our findings provide further evidence for the potential of the ferroelectric systems to mimic their magnetic counterparts. Complex topological structures are not native to magnetism, manifesting themselves throughout the sciences [165–167]. The understanding gained from investigations of the fundamental mechanisms within multiferroics extend far beyond applications in condensed matter physics.

Summary and future prospects

This final chapter highlights the main results of the performed investigations and offers some perspectives for further experimentation into domain topologies, which are shown to form in ferroelectrics and ferromagnets alike.

The first part of the thesis builds upon a previous work on PTO/STO superlattices, where polar vortices form within PTO layers [9]. We have analyzed the various periodicities with respect to a range of PTO thicknesses. It was shown that the polar ordering is much more complex than originally portrayed. There are sets of diffraction satellites arising from the domain periodicities inside PTO, located along the film's crystallographic axes. This shows that additional to the vortex array, there is another modulation which runs along the perpendicular direction. Furthermore, the periodic repetition of PTO (superlattice architecture) triggers a vertical alignment of the domains between the individual layers of PTO, which is more pronounced the thicker the PTO layers are. Furthermore, a connection between the diffraction satellites and the real space domains was made. In the second part of this chapter, we tracked the temperature evolution of all the periodicities within the 10 uc thick PTO superlattice. Besides the polar vortex ordering, which dissolves at around 350 °C, all other forms of periodicities were shown to disappear above ~ 150 °C. This enabled a phase transition study of the vortex pattern individually, which revealed itself as a second-order type, with a critical exponent of ~ 0.5 , as predicted by mean field theory.

The second part of the thesis was dedicated to analysing whether metallic oxides such as LSMO and SRO could allow for polar vortices to form. These materials are to substitute STO as boundary layers, feat which could enable the direct manipulation of vortices, instead of the insulator/ferroelectric/insulator system as a whole. It was shown that the polarization of PTO induces polar distortions into LSMO on a length scale which depends on the interface chemistry. These polar distortions further affect the interfacial magnetic moments on Mn atoms via an interfacial free charge redistribution. Depending on the LSMO/PTO interface termination and the polarization orientation, the polarization is heavily suppressed or maintained at a similar value as it is away from the interface. This behavior is not ideal for polar vortices as one polar orientation is promoted, while the other is not. SRO, on the other hand, the polar distortions induced by PTO were shown to be confined to the first one-two unit cells from the interface. This effect helps to confine the polarization within the ferroelectric film, which can possibly promote the formation of polar vortices. Indeed, it was shown that vortices are stable in SRO/PTO/SRO heterostructures. Furthermore, the oxygen cage tilts inherent to SRO propagate into PTO, overlapping with the Néel rotation of the dipoles. This alone can provide the basis for non-colinear interactions, similar to the magnetic Dzyaloshinskii–Moriya interaction.

In the last part of this thesis, the theoretical investigations of the second part were tested. SRO/PTO/SRO trilayers were grown and the polarization texture inside the ferroelectric was studied. A recent work done on a PTO/SRO superlattices [118], with PTO thickness of about 15 nm (5 nm - this thesis) has revealed that a supercrystal phase - not unlike what was presented here, takes shape in these systems. The supercrystal phase, formed by the polarization domains within PTO, displays periodicities along the principal crystallographic axes, bearing close resembles to our ferroelectric incommensurate spin crystal phase. Possibly due to the large thickness of PTO, the real space structures that are periodically repeated along the crystallographic axes are polar domains. Within a domain the polarization is uniform, and it was shown in [118] that the labyrinthine structure is formed by such domains. XRD studies performed on our SRO/PTO/SRO trilayers have shown that two periodic modulations, perpendicular to each other, co-exist along the film's crystallographic axes. One of these modulations is the polar vortex ordering, confirming the earlier theoretical predictions. Further plan-view TEM and STEM investigations have revealed that the observed cross-sectional vortex pattern is a projection of a more complex polarization topology, which is the result of interwoven perpendicular modulations. One which is the vortex array, and a second one which is cycloidal-like in nature. Circular dichroism studies support the nature of the second modulation. While similar to a supercrystal phase, there is a subtle, yet important difference. In a ferroelectric incommensurate spin crystal phase, there are no domains, no region where the polarization is uniform. One can imagine a volume of the spin crystal phase, and within this volume, one will always find the two periodic components. Such a phase was never observed before in a ferroelectric thin or thick film, and it is similar to a newly observed magnetic phase, called incommensurate spin crystal [11].

Although the domain periodicities and topologies in PTO/STO superlattices were analyzed for a range of PTO thicknesses, and the temperature phase transition of the vortex system was described, more work is still required. It would be useful to obtain a complete set of data which involves the temperature evolution of all samples presented in this study. The reason is that it would improve the predictive power of phenomenological-based approaches. The analysis of the temperature phase transition requires more points, especially close to the transition temperature, to allow for a better characterisation of the critical phenomena.

The prediction of stable polar vortices using DFT and their experimental realisation was a significant achievement, however, these were shown to be part of a more complex topology resembling a magnetic phase called incommensurate spin crystal. The DFT analysis hinted at the possibility of a DMi-like interaction, but due to code and resource limitations, a larger system could not be simulated. Using a different DFT code, such as ONETEP, systems of several thousands of atoms can be simulated. This feat could enable the ferroelectric to relax into such


Figure 6.25: Ferroelectric tunnel junction. a, The architecture of the FTJ. b, Tunneling current measurements.

double- \vec{Q} phases. The next step is to fabricate actual devices out of SRO/PTO/SRO trilayer system. This will enable us to directly probe the response of the double- \vec{Q} texture to the electric/magnetic fields. Preliminary tunneling-current measurements performed on $3 \times 3 \,\mu\text{m}^2$ ferroelectric tunnel junctions reveal that the initial state is clearly distinctive of the poled states (Figure 6.25). Furthermore, upon heating to $\sim 350 \,^{\circ}\text{C}$ the initial current characteristic is regained, which hints at the double- \vec{Q} phase being re-established. This claim is further supported by preliminary in-situ temperature dependent dark-field TEM, showing the double- \vec{Q} phase reforms upon cooling down to room temperature.

Appendix A

Howie-Whelan diffraction contrast simulations of the imcommensurate spin crystal

A.1 Mechanisms giving rise to diffraction contrast

The displacements around a vortex give rise to diffraction contrast in two distinct ways. First, the lattice strain produces a change in crystal orientation and a local change in the deviation parameter s, which describes the proximity of the crystal to the Bragg condition employed for imaging. The contrast in TEM images produced by the local tilt of the crystal is familiar from images of dislocations and can be modelled as a local change in s,

$$ds = \frac{d(\vec{g} \cdot \vec{R})}{dz}$$
(A.1.1)

where \vec{g} is the diffraction vector, \vec{R} is the displacement of the crystal from an ideal, unstrained lattice, and the electron beam is propagating along z. The second contrast mechanism arises from the relative displacements of the atoms on a sub-unit

cell scale, which changes the structure factor F_g:

$$F_{g} = \sum_{j} f_{j} e^{2\pi i \vec{g} \cdot \vec{r}_{j}}$$
(A.1.2)

where the sum is performed for all atoms in the unit cell and f_j is the scattering factor for atom j with fractional coordinates r_j . This results in a local change in the extinction distance ξ_g :

$$\xi_{g} = \frac{\pi V_{c} k \cos \vartheta_{g}}{F_{g}}$$
(A.1.3)

where V_c is the volume of the unit cell, k is the magnitude of the electron wave vector and ϑ_g is the Bragg angle.

These equations are well-known and can be found in textbooks such as Hirsh et al. [168], Williams and Carter [101] and many more. In our model we follow a simplified version of the approach taken by Head et al. [169] in which the parameters s and ξ_g are a function of position, s(x,y,z) and ξ_g (x,y,z). These feed into the two-beam Howie-Whelan equations, which can be used to calculate the electron amplitude as the wave propagates through the crystal. Using the column approximation, which assumes that for any given pixel in the image we may neglect any scattering from/to adjacent pixels, we may divide the material into a set of slices and use the electron amplitude as calculated from the Howie-Whelan equations for one slice as the input to the next, until the exit surface of the crystal is reached. At the exit surface, the bright field (BF) and dark field (DF) intensity can then be calculated. This has been implemented using Python/C++ code running on a GPU using pyOpenCL (seehttps://github.com/WarwickMicroscopy/Howie-Whelanpolarisation-vortex), with scattering factors from Kirkland [170]. Although a full many-beam simulation is required for accurate results, the simple two-beam calculation is expected to be correct to first order, apart from weak-beam imaging conditions where coupling into a third beam changes intensities very significantly.

A.2 The structure to be simulated

Cross sectional-STEM images of the PTO layer embedded between SRO layers show vortex structures running along [100] (Figure A.1). Adjacent vortices have opposite senses, clockwise and anticlockwise, and have a spacing between 6 and 8 nm in Figure A.1. The PTO layer is 5.25 nm (13 unit cells) thick and the SRO above and below is 4.4 nm (11 unit cells) thick. There is a 4 nm DyScO₃ (DSO) layer below the SRO and a SrTiO₃ substrate.



Figure A.1: Cross sectional magnitude and quiver plot. Vortices as seen in cross section.

Plan view dark field TEM shows a striped labyrinthine structure with a slight additional modulation along the stripes that may be caused by additional cycloidal or helical distortions (Figure A.2). The spacing of the stripes is about 10 nm – this is slightly bigger than that in Figure A.1 but presumably we have one dark (or bright) stripe per vortex, and vortices of opposite senses give the same contrast. Contrast is quite strong; for the dark field (DF) g = 110 images it is around 25% and for DF g = 100 images it is around 50%.



Figure A.2: **Plan-view dark field contrast**. **a**, **b**, **c**, Vortices seen in plan-view using diffraction contrast imaging.

From Figure A.1, the sub unit-cell displacements around a vortex are a maximum at about 5-6 unit cells from the vortex core and have a magnitude there of about 0.033 nm. We can fit the magnitude of the displacement, R, as a function of distance from the vortex core, d, using a model of the form:

$$\mathbf{R} = \mathbf{A} \, \mathbf{d}^{\mathbf{n}} \, \mathbf{e}^{-\alpha \mathbf{d}^{\mathbf{n}}},\tag{A.2.1}$$

where R is perpendicular to d. This function can be matched to the data using the three fitting parameters A, n and α . A fit to the data in panel 2 of Figure A.2 is shown in Figure A.3 with A=0.055, n=1.15 and α =0.6. In addition to the sub-unit cell displacements there is lattice strain. Although in the sample examined here



Figure A.3: Vortex fit. Fit to experimental polarisation displacements (Figure A.1 panel 2) using equation A.2.1 with A= 0.055, n= 1.15 and $\alpha = 0.6$.

these displacements can vary from place to place, we use a simple vortex of the same form as given in equation A.2.1, with a displacement field perpendicular to the free surface as shown in Figure A.4. Although this does not take into account the relaxation that takes place due to the presence of the free surfaces of the TEM specimen, we expect that it is sufficiently close to reproduce the essential features of the images. We use n=1.15 and α =0.6, but a magnitude of A=0.03, which gives



Figure A.4: The ε_{xx} strain component for a vortex.

a maximum strain of 0.018 perpendicular to the electron beam, similar to that measured from geometric phase analysis of ac-STEM images [171].

A.3 Results

We first consider the case where there is no strain in the material and the only contribution is due to the sub-unit cell (polarisation) displacements. The vortices are 7 nm below the surface of the sample. The thickness of the specimen is not known but if it has just the top three layers it is 4.4+5.25+4.4 = 14 nm thick. We neglect the difference in scattering of the SRO above and below the PTO layer. As shown in Figure A.5 all vortices have the same contrast irrespective of sign, and

appear as a diffuse band of dark contrast. However, the contrast is extremely low and is essentially invisible in the simulation (Figure A.5 left, in which vacuum has intensity zero and the maximum intensity in the image has unit intensity). The plot (Figure A.5right) gives the calculated intensity in absolute units (intensity of the incident beam = unity) and the contrast can be calculated as roughly 0.5%. This is extremely small and the lines of are only visible in an image with enhanced contrast (Figure A.5centre). There is zero contrast when the diffraction vector g is parallel to the vortex line direction. Although the contrast changes (and can



Figure A.5: Simulated diffraction contrast $\mathbf{g} = \mathbf{100}$, $\mathbf{s} = \mathbf{0}$. Dark field image of an array of polarisation vortices (no strain) running along [010] (vertically), with spacing 8 nm and sub-unit cell displacements described by equation A.2.1 with A= 0.055, n= 1.15 and $\alpha = 0.6$ in a 14 nm thick plan-view specimen. The field of view is 100x100 nm. Left: without contrast enhancement the vortices are essentially invisible; centre: with contrast enhancement; right: absolute intensity plot.

even reverse) depending upon specimen thickness, diffraction vector g and deviation parameter s, this does not change its strength sufficiently to allow polarisation to be visualised in diffraction contrast TEM or 4D-STEM. We may thus conclude that polarisation is essentially invisible in diffraction contrast TEM images. We also note that the same argument applies to 4D-STEM measurements, where the intensity in a diffraction pattern is mapped over a scanned area, with the caveat that multiple scattering near a zone axis makes unequivocal interpretation of this contrast rather more difficult. We now consider strain contrast and give a simulated image in Figure A.6 for an array of vortices with strain (A= 0.03, n= 1.15 and α = 0.6) using g = 100, but with the parameter s varying from top to bottom of the image. This



Figure A.6: Simulated diffraction contrast $\mathbf{g} = 100$. Dark field image of an array of vortices running along [010] (vertically), with spacing 8 nm and sub-unit cell displacements described by equation A.2.1 with A= 0.03, n= 1.15 and $\alpha = 0.6$ in a 14 nm thick plan-view specimen. Contrast is due to local strain and the field of view is 100x100 nm. Left: image with a deviation parameter s varying vertically (the exact Bragg condition at s=0 is half way up the image). Clockwise and anticlockwise vortices give different contrast, which depends on s, illustrated by the plot on the right for s = 0.01 nm.

corresponds to a crystal that bends through the Bragg condition and shows how the contrast varies due to this effect. Here the contrast is very strong, which would make the vortices readily visible experimentally. However, we see that clockwise and counter-clockwise vortices have different contrast. When s is positive and the vortex has counter-clockwise displacements when viewed along [100] the contrast is weak, whereas for clockwise displacements the contrast is strong. This strong/weak contrast reverses for opposite signs of s and g. There is zero contrast when the diffraction vector g is parallel to the vortex line direction.

As noted in the first section, the two-beam simulation is unreliable for large deviations from the Bragg condition, i.e. at the top and bottom of Figure A.6 where weak-beam conditions apply. By analogy with dark field weak-beam images of the strain field of a dislocation, we would expect the actual contrast here to become a sharp bright line. This does not change the invisibility of the vortices when g is parallel to their line direction. Adding a modulation of the displacement



Figure A.7: Simulated diffraction contrast $\mathbf{g} = 100$. Dark field image of an array of vortices running along [010] (vertically), with spacing 8 nm and sub-unit cell displacements described by equation A.2.1 with A= 0.03, n= 1.15 and $\alpha = 0.6$ plus a sinusoidal variation of 10%, in a 14 nm thick plan-view specimen. Contrast is due to local strain and the field of view is 100x100 nm. Left: image with a deviation parameter s varying vertically (the exact Bragg condition at s = 0 is half way up the image). Right: image with constant s = 0.01 nm.

magnitude along the vortex changes the width of the line of contrast as shown in Figure A.7. This also tends to even up the contrast between vortices of different chirality. However, it doesn't change the direction of the stripes and the vortices still have no contrast when the diffraction vector g is parallel to their line direction.

The modulation of Figure A.7 does not produce a very good match to the experimental images (Figure 6.18), in which images taken with g = 100 or g = 010 give lines of contrast of fairly constant width. The double modulation we observe is only present when g = 110. We may thus exclude a modulation of the helical component of displacement. Experimentally we observe lines of contrast in both [100] and [010] directions that each become invisible when g is parallel to their line direction. Figure A.8 shows that clockwise and anticlockwise vortices can have different contrast and their crossing can increase or decrease contrast, depending upon their sign. For closely spaced vortices (Figure A.9), the lines of contrast may



Figure A.8: Simulated diffraction contrast $\mathbf{g} = 100$, 010 and 110. Dark field images of two widely-spaced arrays of vortices running along [010] (vertically) and [100] (horizontally), and deformation field described equation A.2.1 with A = 0.03 (vertical), A = 0.15 (horizontal), n = 1.15 and $\alpha = 0.6$. Contrast is due to local strain and the field of view is 100x100 nm.



Figure A.9: Simulated diffraction contrast $\mathbf{g} = 100$, 010 and 110. Dark field images of two widely-spaced arrays of vortices running along [010] (vertically) and [100] (horizontally), and deformation field described by equation A.2.1 with A = 0.03 (vertical), A = 0.15 (horizontal), n = 1.15 and $\alpha = 0.6$. Contrast is due to local strain and the field of view is 100x100 nm.

overlap. There is some resemblance to the experimental images.

A.4 Summary

Two-beam diffraction contrast simulations reproduce some aspects of the experimentally observations. Most importantly they confirm that a vortex becomes invisible when the g-vector is perpendicular to their displacements. Also, they show that strain contrast is much stronger than polarisation contrast. However, they fail to reproduce the observations exactly, due to the limitations of the twobeam calculation and uncertainty about the detail of the displacement field. A more accurate simulation would require the inclusion of multiple scattered beams, which may allow a comparison between different models of the displacement fields in this double-modulated structure.

Bibliography

- Scott, J. F. & Paz de Arajuro, C. Ferroelectric memories. Science 246, 1400 (1989).
- Scott, J. F., Araujo, C., Brett Meadows, H., McMillan, L. & Shawabkeh, A. Radiation effects on ferroelectric thinfilm memories: Retention failure mechanisms. *Journal of Applied Physics* 66, 1444 (1989).
- Philofsky, E. FRAM-the ultimate memory. Sixth Biennial IEEE International Nonvolatile Memory Technology Conference, 99–104 (1996).
- Dawber, M., Rabe, K. & Scott, J. F. Physics of thin-film ferroelectric oxides. *Rev. Mod. Phys.* 77, 1083 (2005).
- Pantel, D. et al. Tunnel electroresistance in junctions with ultrathin ferroelectric Pb(Zr0.2Ti0.8)O3 barriers. Appl. Phys. Lett. 100, 232902 (2012).
- Chanthbouala, A. et al. A ferroelectric memristor. Nature Materials 11, 5 (2012).
- Kvasov, A. & Tagantsev, A. Role of high-order electromechanical coupling terms in thermodynamics of ferroelectric thin films. *Phys Rev B* 87, 184101 (2013).
- Lichtensteiger, C., Fernander-Pena, S., Weymann, C., Zubko, P. & Triscone, J.-M. Tuning of the Depolarization Field and Nanodomain Structure in Ferroelectric Thin Films. *Nano Lett.* 14, 4205–4211 (2014).

- Yadav, A. K. *et al.* Observation of polar vortices in oxide superlattices. *Nature* 530, 198–201 (2016).
- Wachowiak, A. *et al.* Direct Observation of Internal Spin Structure of Magnetic Vortex Cores. *Science* 298, 577–580 (2002).
- Seddon, S. D. *et al.* Real-space Observation of Ferroelectrically Induced Magnetic Spin Crystal in SrRuO3. *Nat Commun* **12**, 2007 (2021).
- Lines, M. & Glass, A. Principles and Applications of Ferroelectrics and Related Materials (2001).
- Rabe, K., Ahn, C. H. & Triscone, J.-M. Physics of ferroelectrics A modern perspective (2007).
- Jung, D., Dawber, M., Scott, J. F., Sinnamon, L. & Gregg, J. M. Switching dinamycs in ferroelectric thin films: An experimental survey. *Integrated Ferroelectrics* 48, 59–68 (2002).
- Paruch, P., Giamarchi, T., Tybell, T. & Triscone, J.-M. Nanoscale studies of domain wall motion in epitaxial ferroelectric thin films. *Journal of Applied Physics* 100, 051608 (2006).
- Scott, J. F. et al. Superdomain dynamics in ferroelectric-ferroelastic films: Switching, jamming, and relaxation. Applied Physics Reviews 4, 041104 (2017).
- Sarin Kumar, A. *et al.* High-frequency surface acoustic wave device based on thin-film piezoelectric interdigital transducers. *Appl. Phys. Lett.* 85, 1757 (2004).
- Paruch, P., Tybell, T. & Triscone, J.-M. Nanoscale control of ferroelectric polarization and domain size in epitaxial Pb(Zr 0.2 Ti 0.8)O 3 thin films. *Appl. Phys. Lett.* **79**, 530 (2001).
- Dawber, M., Farnan, I. & Scott, J. A classroom experiment to demonstrate ferroelectric hysteresis. *American Journal of Physics* **71**, 819 (2003).
- Sawyer, C. B. & Tower, C. H. ROCHELLE SALT AS A DIELECTRIC. Phys Rev 35, 269–275 (1930).

- Scott, J. F. Ferroelectrics go bananas. J. Phys.: Condens. Matter 20, 021001 (2008).
- Abrahams, S. Systematic Prediction of New Ferroelectric Inorganic Materials in Point Group 6. Acta Cryst. B46, 311–324 (1990).
- Abrahams, S. Structurally Based Predictions of Ferroelectricity in Seven Inorganic Materials with Space Group Pba2 and Two Experimental Confirmations. Acta Cryst. B45, 228–232 (1989).
- Abrahams, S. Structurally Based Prediction of Ferroelectricity in Inorganic Materials with Point Group 6mm. Acta Cryst. B44, 585–595 (1988).
- Capillas, C., Aroyo, M. & Perez-Mato, J. Search for New Pna21 Ferroelectrics. Ferroelectrics 301, 203–206 (2004).
- Kroumova, E., Aroyo, M. & Perez-Mato, J. Prediction of new displacive ferroelectrics through systematic pseudosymmetry search. Results for materials with Pba2 and Pmc21 symmetry. Acta. Cryst B58, 921–933 (2002).
- Zhong, W., King-Smith, R. & Vanderbilt, D. Giant LO-TO Splittings in Perovskite Ferroelectrics. *Phys Rev Lett* 72, 3618 (1994).
- Resta, R. Theory of the electric polarization in crystals. *Ferroelectrics* 136, 51–55 (1992).
- Resta, R. Macroscopic polarization in crystalline dielectrics: the geometric phase approach. *Rev. Mod. Phys.* 66, 899 (1994).
- Vanderbilt, D. & King-Smith, R. Theory of polarization in crcystalline solids. *Phys Rev B* 47, 1651–1654 (1993).
- Resta, R., Posternak, M. & Baldereschi, A. Towards a Quantum Theory of Polarization in Ferroelectrics: The Case of KNbO3. *Phys Rev Lett* 70, 1010– 1013 (1993).
- Jia, C.-J., Lentzen, M. & Urban, K. Atomic-Resolution Imaging of Oxygen in Perovskite Ceramics. *Science* 299, 870 (2003).

- Jia, C.-J., Urban, K. W., Alexe, M., Hesse, D. & Vrejoiu, I. Direct Observation of Continuous Electric Dipole Rotation in Flux-Closure Domains in Ferroelectric Pb(Zr,Ti)O3. Science 331, 4 (2011).
- 34. Jia, C.-J. *et al.* Unit-cell scale mapping of ferroelectricity and tetragonality in epitaxial ultrathin ferroelectric films. *Nature Mater* **6**, 64 (2007).
- Jia, C.-L. *et al.* Atomic-scale study of electric dipoles near charged and uncharged domain walls in ferroelectric films. *Nature Materials* 7 (2008).
- Kwei, G., Lawson, A., SBillinge, S. & Cheong, S.-W. Structures of the ferroelectric phases of Barium Titanate. J. Phys. Chem. 97, 2368–2377 (1993).
- 37. Devonshire, A. Theory of ferroelectrics. Advances in Physics 3, 85 (1954).
- 38. Cohen, R. Origin of ferroelectricity in perovskite oxides. *Nature* **358** (1992).
- Opik, U. & Pryce, M. Studies of the Jahn-Teller effect I. A survey of the static problem. Proc. R. Soc. Lond. A 238, 425–447 (1957).
- Pearson, R. The second order Jahn-Teller effect. Journal of molecular structure 103, 25–34 (1983).
- Ahn, C. H., Rabe, K. & Triscone, J.-M. Ferroelectricity at the Nanoscale: Local Polarization in Oxide Thin Films and Heterostructures. *Science* 303, 488 (2004).
- Luk'yanchuk, A. I., Lahoche, L. & Sene, A. Universal Properties of Ferroelectric Domains. *Phys Rev Lett* **102**, 147601 (2009).
- Gruverman, A. *et al.* Tunneling Electroresistance Effect in Ferroelectric Tunnel Junctions at the Nanoscale. *Nano Lett.* 9, 3539–3543 (2009).
- 44. Tsymbal, Y. E. & Kohlstedt, H. Tunneling across a ferroelectric. Science 313, 181 (2006).
- Pantel, D. & Alexe, M. Electroresistance effects in ferroelectric tunnel barriers. Phys Rev B 82, 134105 (2010).
- Tilley, D. & Zeks, B. Landau theoru of phase transitions in thick films. Solid State Commun 49, 823–827 (1984).

- Wang, Y., Zhong, W. L. & Zhang, P. Lateral size effects on cells in ferroelectric films. *Phys Rev B* 51, 17235 (1994).
- Shaoping, L. et al. Dimension and Size Effects in Ferroelectrics. Jpn. J. Appl. Phys. 36, 5169–5174 (1997).
- Wang, C. & Smith, S. Landau theory of the size-driven phase transition in ferroelectrics. J. Phys.: Condens. Matter 7, 7163–7171 (1995).
- 50. Nagarajan, N. *et al.* Scaling of structure and electrical properties in ultrathin epitaxial ferroelectric heterostructures. *J. Appl. Phys* **100**, 051609 (2006).
- Stengel, M., Vanderbilt, D. & Spaldin, N. Enhancement of ferroelectricity at metal–oxide interfaces. *Nature Mater* 8, 392 (2009).
- 52. Kim, D. J. *et al.* Polarization Relaxation Induced by a Depolarization Field in Ultrathin Ferroelectric BaTiO3 Capacitors. *Phys Rev Lett* **95**, 237602 (2005).
- Mehta, R., Silverman, B. & Jacobs, J. Depolarization fields in thin ferroelectric films. J. Appl. Phys. 44, 3379 (1973).
- Batra, I., Wurfel, P. & Silverman, B. A new type of First-Order phase transition in ferroelectric thin films. *Phys Rev Lett* **30**, 384 (1972).
- Tybell, T., Ahn, C. H. & Triscone, J.-M. Ferroelectricity in thin perovskite films. Appl. Phys. Lett. 75, 856 (1999).
- Lichtensteiger, C., Triscone, J.-M., Junquera, J. & Ghosez, P. Ferroelectricity and Tetragonality in Ultrathin PbTiO3 Films. *Phys Rev Lett* 94, 047603 (2005).
- Fong, D. D. et al. Ferroelectricity in Ultrathin Perovskite Films. Science 304, 1650 (2004).
- Auciello, O., Scott, J. F. & Ramesh, R. The Physics of Ferroelectric Memories. *Physics Today* 51 (1998).
- Meyer, B. & Vanderbilt, D. Ab initio study of BaTiO3 and PbTiO3 surfaces in external electric fields. *Phys Rev B* 63, 205426 (2001).

- Junquera, J. & Ghosez, P. Critical thickness for ferroelectricity in perovskite ultrathin films. *Nature* 422, 506 (2003).
- Lai, B.-K., Ponomareva, I., Kornev, I., Bellaiche, L. & Salamo, G. Thickness dependency of 180° stripe domains in ferroelectric ultrathin films: A first principles-based study. *Appl. Phys. Lett.* **91**, 152909 (2007).
- G. Catalan, e. Flexoelectric rotation of polarization in ferroelectric thin films. Nat. Mater. 10, 963–967 (2011).
- Gattinoni, C. *et al.* Interface and surface stabilization of the polarization in ferroelectric thin films. *PNAS* 117, 28589–28595 (2020).
- Ahn, C. H. et al. Ferroelectric field effect in ultrathin SrRuO3 films. Appl. Phys. Lett. 70 (1997).
- Catalan, G. Fractal Dimension and Size Scaling of Domains in Thin Films of Multiferroic BiFeO3. *Phys Rev Lett* 100, 027602 (2009).
- Dürr, H. A. et al. Chiral Magnetic Domain Structures in Ultrathin FePd Films. Science 284, 2166–2168 (1999).
- Kornev, I., Fu, H. & Bellaiche, L. Ultrathin Films of Ferroelectric Solid Solutions under a Residual Depolarizing Field. *Phys Rev Lett* **93**, 196104 (2004).
- Ponomareva, I., Naumov, I. & Bellaiche, L. Low-dimensional ferroelectrics under different electrical and mechanical boundary conditions: Atomistic simulations. *Phys Rev B* 72, 214118 (2005).
- Fu, H. & Bellaiche, L. Ferroelectricity in Barium Titanate Quantum Dots and Wires. *Phys Rev Lett* **91**, 257601 (2003).
- Lai, B.-K. *et al.* Electric-Field-Induced Domain Evolution in Ferroelectric Ultrathin Films. *Phys Rev Lett* 96, 137602 (2006).
- Aguado-Puente, P. & Junquera, J. Ferromagneticlike Closure Domains in Ferroelectric Ultrathin Films: First-Principles Simulations. *Phys Rev Lett* 100, 177601 (2008).

- Aguado-Puente, P. & Junquera, J. Structural and energetic properties of domains in PbTiO3/SrTiO3 superlattices from first principles. *Phys. Rev. B* 85, 8 (2012).
- Naumov, I., Bellaiche, L. & Fu, H. Unusual phase transitions in ferroelectric nanodisks and nanorods. *Nature* 432, 4 (2004).
- 74. Gruverman, A. et al. Vortex ferroelectric domains. J. Phys. Condens. Matter 20, 4 (2008).
- Rodriguez, B. et al. Vortex Polarization States in Nanoscale Ferroelectric Arrays. Nano Letters 2009, 5 (2009).
- Jia, C.-J., Urban, K. W., Alexe, M., Hesse, D. & Vrejoiu, I. Direct Observation of Continuous Electric Dipole Rotation in Flux-Closure Domains in Ferroelectric Pb(Zr,Ti)O3. Science 331, 4 (2011).
- Nelson, C. et al. Spontaneous Vortex Nanodomain Arrays at Ferroelectric Heterointerfaces. Nano. Lett. 11, 7 (2011).
- Tang, Y. L. *et al.* Suppl. mat.: Observation of a periodic array of flux-closure quadrants in strained ferroelectric PbTiO3 films. *Science* (2015).
- McQuaid, R., McGilly, L., Sharma, P., Gruverman, A. & Gregg, J. M. Mesoscale flux-closure domain formation in single-crystal BaTiO₃. Nat Commun 2, 404 (2011).
- Yadav, A. K. *et al.* Observation of polar vortices in oxide superlattices. *Nature* 530, 198–201 (2016).
- Hong, Z. et al. Stability of Polar Vortex Lattice in Ferroelectric Superlattices. Nano Letters 17, 2246-2252. ISSN: 1530-6984. https://doi.org/10.1021/ acs.nanolett.6b04875 (2017).
- Leferovich, R. P. & Mitchell, R. A structural study of ternary lanthanide orthoscandate perovskites. *Journal of Solid State Chemistry* 177, 2188–2197 (2004).

- Glazer, A. The clasiffication of tilted octahedra in perovskites. Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. 28, 3384–3392 (1972).
- Highland, M. et al. Interfacial charge and strain effects on the ferroelectric behavior of epitaxial (001) PbTiO3 films on (110) DyScO3 substrates. Appl. Phys. Lett. 104, 132901 (2014).
- Hibble, S., Cooper, S., Hannon, A., Fawcett, I. & Breenblatt, M. Local distortions in the colossal magnetoresistive manganates La0.7Ca0.3MnO3, La0.8Ca0.2MnO3 and La0.7Sr0.3MnO3 revealed by total neutron diffraction. J. Phys.: Condens. Matter 11, 9221 (1999).
- Boschker, H. *et al.* Strong uniaxial in-plane magnetic anisotropy of (001)- and (011)-oriented La0.67Sr0.33MnO3 thin films on NdGaO3 substrates. *Phys Rev* B 79, 214425 (2009).
- Bansal, C., Kawanaka, H., Takahashi, R. & Nishihara, Y. Metal-insulator transition in Fe-substituted SrRuO3 bad metal system. *Journal of Alloys and Compounds* 360, 47–53 (2003).
- Longo, V. *et al.* On the photoluminescence behavior of samarium-doped strontium titanate nanostructures under UV light. A structural and electronic understanding. *Phys. Chem. Chem. Phys.* **12**, 7566–7579 (2010).
- Pontes, F., Lee, E., Leite, E. & Longo, E. High Dielectric Constant of SrTiO3 Thin Films Prepared by Chemical Process. *Journal of Materials Science* 35, 4789–4787 (2000).
- Kuroiwa, Y., Aoyagi, S. & Sawada, A. Evidence for Pb-O Covalency in Tetragonal PbTiO3. *Phys Rev Lett* 87, 217601–217605 (2001).
- Eason, R. PULSED LASER DEPOSITION OF THIN FILMS: APPLICATIONS-LED GROWTH OF FUNCTIONAL MATERIALS. WILEY-INTERSCIENCE (2007).
- Edited by Lawrence, J. Advances in Laser Materials Processing: Technology, Research and Application. Woodhead Publishing (2018).

- Edieted by Pryds, N. & Esposito, V. Metal Oxide-Based Thin Film Structures. Elsevier (2018).
- Fewster, P. X-ray scattering from semiconductors and other materials. New Jersey : World Scientific (2015).
- Bragg, W. & Gragg, W. The Reflection of X-rays by Crystals. Proc. R. Soc. Lond. A 88, 428 (1913).
- Waseda, Y., Matsubara, E. & Shinoda, K. X-Ray Diffraction Crystallography. Springer-Verlag Berlin Heidelberg (2011).
- Hill, J., Helgesen, G. & Gibbs, D. X-ray-scattering study of charge- and spindensity waves in chromium. *Phys Rev B* 51, 10336 (1995).
- 98. Dürr, H. A. et al. Chiral Magnetic Domain Structures in Ultrathin FePd Films. Science 284, 2166-2168. https://science.sciencemag.org/content/ sci/284/5423/2166.full.pdf (1999).
- Lovesey, S. & Van der Laan, G. Resonant x-ray diffraction from chiral electricpolarization structures. *Phys Rev B* 98, 155410 (2018).
- Glaeser, R. Methods for imaging weak-phase objects in electron microscopy. *Rev Sci Instrum* 84, 111101 (2013).
- Carter, C. & Williams, D. Transmission electron microscopy: Basics. Springer (2016).
- Evans, K. & Beanland, R. High Dynamic Range Electron Imaging: The New Standard. Microsc. Microanal. 20, 1601–1604 (2014).
- Carter, C. & Williams, D. Transmission electron microscopy: Diffraction, imaging and spectroscopy. Springer (2016).
- Hohenberg, P. & Kohn, W. Inhomogeneous electron gas. *Phys Rev* 136, 864 (1964).
- Martin, R. Electronic Structure: Basic Theory and Practical Methods. Cambridge (2004).

- Kohn, W. & Sham, L. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys Rev*, 1133 (1965).
- 107. Toulouse, J. Review of approximations for the exchange-correlation energy in density-functional theory. *Chapter in the book Density Functional Theory* (2021).
- 108. Giannozzi, P. *et al.* Advanced capabilities for materials modelling with quantum espresso. *Journal of Physics: Condensed Matter* (2017).
- 109. Giannozzi, P. et al. Quantum espresso: a modular and open-source software project for quantum simulations of materials. Journal of Physics: Condensed Matter, 19 (2009).
- Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys Rev B* 41, 7892 (1990).
- 111. Blochl, P. Projector augmented-wave method. Phys Rev B 50, 17953 (1994).
- Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* 77 (1996).
- Perdew, J. et al. Restoring the density-gradient expansion for exchange in solids and surfaces. Phys. Rev. Lett. 100 (2008).
- Zhang, Y., Sun, J., Perdew, J. & Wu, X. Comparative first-principles studies of prototypical ferroelectric materials by LDA, GGA, and SCAN meta-GGA. *Phys. Rev. B.* 96 (2017).
- Monkhorst, H. J. & Pack, J. D. Special points for brillouin-zone integrations. *Phys. Rev. B* 13 (1976).
- Li, S. et al. Periodic arrays of flux-closure domains in ferroelectric thin films with oxide electrodes. Appl. Phys. Lett. 111, 5 (2017).
- 117. Peters, J. J. P., Apachitei, G., Beanland, R., Alexe, M. & Sanchez, A. M. Polarization curling and flux closures in multiferroic tunnel junctions. *Nat Commun.* 7, 7 (2016).

- 118. Hadjimichael, M. *et al.* Metal–ferroelectric supercrystals with periodically curved metallic layers. *Nat. Mater.* (2021).
- 119. Li, X. *et al.* Atomic-scale observations of electrical and mechanical manipulation of topological polar flux closure. *PNAS* **117**, 18954–18961 (2020).
- Stoica, V. A. *et al.* Optical creation of a supercrystal with three-dimensional nanoscale periodicity. *Nature Materials* 18, 7 (2019).
- 121. Yadav, A. et al. Spatially resolved steady-state negative capacitance. Nature 565, 468–471 (2018).
- 122. Das, S. *et al.* Local negative permittivity and topological phase transition in polar skyrmions. *Nat. Mater.* (2020).
- Das, S. et al. Observation of room-temperature polar skyrmions. Nature 568, 368–372 (2019).
- 124. Aguado-Puente, P. & J.Junquera. Structural and energetic properties of domains in PbTiO3/SrTiO3 superlattices from first principles. *Phys. Rev. B* 85, 184105–184113 (2012).
- 125. Asada, T. & Koyama, Y. Coexistence of ferroelectricity and antiferroelectricity in lead zirconate titanate. *Phys Rev B* 70, 104105 (2004).
- 126. Asada, T. & Koyama, Y. Ferroelectric domain structures around the morphotropic phase boundary of the piezoelectric material PbZr1-xTixO3. *Phys Rev B* 75, 214111 (2007).
- 127. Li, Q. et al. Quantification of flexoelectricity in PbTiO3/SrTiO3 superlattice polar vortices using machine learning and phase-field modeling. Nat Commun 8, 1468 (2017).
- Tang, Y. L. *et al.* Suppl. mat.: Observation of a periodic array of flux-closure quadrants in strained ferroelectric PbTiO3 films. *Science* (2015).
- Bennett, D., Basagoiti, M. & Aracho, E. Electrostatics and domains in ferroelectric superlattices. R. Soc. Open Sci. 7, 201270 (2020).
- 130. Landau, L. & Lifshitz, E. Statistical Physics. Pergamon Press (1980).

- Tong, D. Statistical Field Theory. University of Cambridge Part III Mathematical Tripos (2017).
- 132. Borisevich, A., Kalinin, S. V., Pennycook, S. J. & Pantelides, S. Control of Octahedral Tilts and Magnetic Properties of Perovskite Oxide Heterostructures by Substrate Symmetry. *Phys Rev Lett* **105**, 227203 (2010).
- 133. Peters, J. et al. Polarization Screening Mechanisms at La_{0.7}Sr_{0.3}MnO₃/PbTiO₃
 Interfaces. ACS Appl. Mater. Interfaces 12, 10657–10663 (2020).
- May, S. et al. Quantifying octahedral rotations in strained perovskite oxide films. Phys Rev B 82, 014110 (2010).
- Zhang, S. *et al.* Polarization Rotation in Ultrathin Ferroelectrics Tailored by Interfacial Oxygen Octahedral Coupling. ACS Nano 12, 3681–3688 (2018).
- Popescu, V. & Zunger, A. Extracting E versus k effective band structure from supercell calculations on alloys and impurities. *Phys Rev B* 85, 085201 (2012).
- 137. Junquera, J., Cohen, M. & Rabe, K. Nanoscale Smoothing and the Analysis of Interfacial Charge and Dipolar Densitie. ArXiv (2018).
- Kolpak, A. M., Sai, N. & Rappe, A. Short-circuit boundary conditions in ferroelectric PbTiO3 thin films. *Phys. Rev. B* 74, 054112–054117 (2006).
- 139. M. Stengel P. Aguado-Puente, N. A. S. & Junquera, J. Band alignment at metal/ferroelectric interfaces: Insights and artifacts from first principles. *Phys. Rev. B* 83, 235112–235139 (2011).
- Choe, D.-H., West, D. & Zhang, S. Band Alignment and the Built-in Potential of Solids. *Phys Rev Lett* **121**, 196802 (2018).
- 141. A. Baldereschi, S. & R.Resta. Band Offsets in Lattice-Matched Heterojunctions: A model and First-Principles Calculations for GaAs/AlAs. *Phys. Rev. Lett.* 61, 734–737 (1988).
- 142. Zubko, P., Stucki, N., Lichtensteiger, C. & Triscone, J.-M. X-Ray Diffraction Studies of 180 Ferroelectric Domains in PbTiO3/SrTiO3 Superlattices under an Applied Electric Field. *Phys. Rev. Lett.* **104**, 4 (2010).

- 143. Zhao, H. J., Chen, P., Prosandeev, S., Artyukhin, S. & Bellaiche, L. Dzyaloshin-skii Moriya-like interaction in ferroelectrics and antiferroelectrics. *Nat. Mater.* 20, 341–345 (2021).
- Damodaran, A. R. *et al.* Phase coexistence and electric-field control of toroidal order in oxide superlattices. *Nature Mater* 16, 7 (2017).
- 145. Ponomareva, I., Naumov, I. I. & Bellaiche, L. Low-dimensional ferroelectrics under different electrical and mechanical boundary conditions: Atomistic simulations. *Phys. Rev. B* 72, 5 (2005).
- 146. Sanchez-Santolino, G. et al. Resonant electron tunnelling assisted by charged domain walls in multiferroic tunnel junctions. Nature Nanotech 12, 8 (2017).
- 147. Penthorn, N. E., Hao, X., Wang, Z., Hua, Y. & Jiang, H. W. Experimental Observation of Single Skyrmion Signatures in a Magnetic Tunnel Junction. *Phys. Rev. Lett.* **122**, 6 (2019).
- Kurumaji, T. et al. Néel-Type Skyrmion Lattice in the Tetragonal Polar Magnet VOSe2O5. Phys. Rev. Lett. 119, 237201–237205 (2017).
- Kurumaji, T. *et al.* Skyrmion lattice with a giant topological Hall effect in a frustrated triangular-lattice magnet. *Science* 365, 914–918 (2019).
- 150. Yi, S. D., Onoda, S., Nagaosa, N. & Han, J. H. Skyrmions and anomalous Hall effect in a Dzyaloshinskii-Moriya spiral magnet. *Phys. Rev. B.* 80, 054416– 054421 (2009).
- Aguado-Puente, P. & Junquera, J. Ferromagneticlike Closure Domains in Ferroelectric Ultrathin Films: First-Principles Simulations. *Phys Rev Lett* 100, 177601 (2008).
- Dürr, H. A. et al. Chiral Magnetic Domain Structures in Ultrathin FePd Films. Science 284, 2166–2168 (1999).
- Jia, C.-L. *et al.* Atomic-scale study of electric dipoles near charged and uncharged domain walls in ferroelectric films. *Nature Materials* 7 (2008).

- Dubovik, V. M. & Tugushev, V. V. Toroid moments in electrodynamics and solid-state physics. *Physics Reports* 187, 57 (1990).
- 155. Nahas, Y. *et al.* Inverse transition of labyrinthine domain patterns in ferroelectric thin films. *Nature* **577**, 47–51 (2020).
- Nahas, Y. et al. Topology and control of self-assembled domain patterns in low-dimensional ferroelectrics. Nat Commun 11, 5779 (2020).
- 157. https://github.com/WarwickMicroscopy/Howie-Whelanpolarisation-vortex.
- Seki, S., Yu, X. Z., Ishiwata, S. & Tokura, Y. Observation of Skyrmions in a Multiferroic Material. *Science* 336, 198–201 (2012).
- Yu, X. Z. et al. Real-space observation of a two-dimensional skyrmion crystal. Nature 465, 901–904 (2010).
- 160. Aso, R., Kan, D., Shimakawa, Y. & Kurata, H. Octahedral Tilt Propagation Controlled by A-Site Cation Size at Perovskite Oxide Heterointerfaces. *Cryst. Growth Des.* 14, 2128–2132 (2014).
- Sanchez-Santolino, G. et al. Oxygen Octahedral Distortions in LaMO₃/SrTiO₃
 Superlattices. Microsc. Microanal. 20, 825–831 (2014).
- 162. Udalov, O., Beloborodov, I. & Sapozhnikov, M. Magnetic skyrmions and bimerons in films with anisotropic interfacial Dzyaloshinskii Moriya interaction. *Phys Rev B* 103, 174416 (2021).
- Sepliarsky, M., Stachiotti, M. & Migoni, R. Surface reconstruction and ferroelectricity in PbTiO3 thin films. *Phys. Rev. B.* 72, 014110–014116 (2005).
- 164. Chen, J., Zhang, D. W. & Liu, J. M. Exotic skyrmion crystals in chiral magnets with compass anisotropy. *Sci. Rep.* 6, 29126 (2016).
- 165. Sato, T., Ishiyama, T. & Nikuni, T. Vortex Lattice Structures of a Bose-Einstein Condensate in a Rotating Lattice Potential. *Phys Rev A* 76, 053628 (2007).
- Saw, T. B. *et al.* Topological defects in epithelia govern cell death and extrusion. *Nature* 544, 212–216 (2017).

- Tsesses, S. *et al.* Optical skyrmion lattice in evanescent electromagnetic fields. Science 361, 993–996 (2018).
- Hirch, P., Howie, A., Nicholson, R., Pashley, D. & Whelan, M. Electron microscopy of thin crystals (1965).
- Head, A. Computed electron micrographs and defect identification. North Holland (1973).
- 170. Kirkland, E. Advanced computing in electron microscopy. Springer (1998).
- 171. https://jjppeters.github.io/Strainpp/.