



Domains and functionality in multiferroic BiFeO_3 films

Noah Waterfield Price

Wadham College

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ABSTRACT

For over half a century, the technological promise of spins manipulable by a small voltage has captivated the interest of experimental and theoretical researchers alike. However, if thin-film multiferroics are to be incorporated into future data storage devices, a much greater understanding of their behaviour and how they differ from their bulk counterparts is required. In this thesis, we probe the fundamental multiferroic properties of BiFeO₃ films through a combination of state-of-the-art diffraction and microscopy techniques. We investigate the coupling between magnetic, ferroelectric, and structural order, with a focus on domains, and how the domain structure may be manipulated in order to tailor the multiferroic properties of the material.

Using non-resonant magnetic x-ray scattering (NXMS) and neutron diffraction, we study the magnetic and structural properties of (111)_{pc}-oriented BiFeO₃ films. Contrary to the general belief that they grow as a rhombohedral monodomain, we find that they comprise a sub-micron texture of monoclinic domains. The magnetic structure is found to be intimately coupled to the structure, resulting in the propagation vector being locked to the monoclinic b-axis. This magnetoelastic coupling opens up a route to strain-engineer the magnetic domains via epitaxial strain. By growing BiFeO₃ films on a lower-symmetry, TbScO₃ substrate, we are able to engineer a magnetic, structural and ferroelectric monodomain, coherent over the entire film, constituting an increase in the domain size by over five orders of magnitude.

We directly demonstrate the coupling between ferroelectric and magnetic order parameters of the cycloidal magnetic structure. Using NXMS polarimetry to measure directly the magnetic polarity, we show that upon switching the ferroelectric polarisation, the magnetic polarity switches accordingly—a major rearrangement of the magnetic structure, with each spin rotating by 90° on average. This goes counter to idea that magnetic and ferroelectric order parameters are only weakly coupled in type-I multiferroics.

Finally, using photoemission electron microscopy we are able to directly image the sub-micron magnetostructural domain structure. We further show that there is a strong interfacial coupling between the magnetostructural domains of BiFeO₃ with a ferromagnetic overlayer. The BiFeO₃ domains are found to impose a uniaxial anisotropy in the overlayer, opening up a route to control ferromagnetic domains.

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Definitions of symbols and constants

k_i (k_f) :	Initial (final) wavevector of x-ray photon
E_i (E_f) :	Initial (final) energy of x-ray photon
$\mathbf{K}$:	Scattering wavevector $\mathbf{K} = \mathbf{k}_f - \mathbf{k}_i$
$\mathbf{G}$:	Reciprocal lattice vector
$\mathbf{R}$:	Direct lattice vector
(h, k, l) :	Miller indices
μ_B :	Bohr magneton $\mu_B = e\hbar/(2m_e)$
T_N :	Néel temperature
T_C :	Curie temperature
$\mathbf{a}, \mathbf{b}, \mathbf{c}$:	Basis vectors of the direct lattice
$\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$:	Basis vectors of the reciprocal lattice
$\mathbf{M}(\mathbf{r})$:	Magnetisation at $(\mathbf{r})$
$\mathbf{M}(\mathbf{K})$:	Magnetic structure factor at $(\mathbf{K})$
$\mathbf{q}$:	Magnetic propagation vector
σ :	Pauli spin matrices
J :	Exchange constant
ϵ (ϵ') :	Incident (final) polarisation vector of x-ray photon
$\mathbf{P}$:	Electric polarisation
$\mathbf{H}(\mathbf{r})$:	Magnetic field strength at $\mathbf{r}$
$\boldsymbol{\mu}(\mathbf{r})$:	Magnetic moment at $\mathbf{r}$

Acronyms

BFO :	BiFeO ₃
STO :	SrTiO ₃
SRO :	SrRuO ₃
TSO :	TbScO ₃
NXMS :	Nonresonant x-ray magnetic scattering
PEEM :	Photoemission electron microscopy
XMLD :	X-ray magnetic linear dichroism
XMCD :	X-ray magnetic circular dichroism

Publications

- **Coherent magnetoelastic domains in multiferroic BiFeO₃ films**

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- **Magnetostriction-driven ground-state stabilization in 2H perovskites**

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- **Electrical switching of magnetic polarity in a multiferroic BiFeO₃ device at room temperature**

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INTRODUCTION TO MULTIFERROICS

1.1 Introduction

THE study of electronic and magnetic phenomena in solids is central to the pursuit of cutting-edge technology. Functionality in modern consumer electronics, ranging from touch sensors in mobile devices to nonvolatile data storage in hard disk drives, stems directly from the intrinsic electronic and magnetic properties of their constituent materials. Led by the continued search for novel materials and trend towards device miniaturisation, recent research into what have been termed *multiferroics*¹ has attempted to combine electronic and magnetic properties into a single multifunctional material. Multiferroics are materials in which two or more ‘ferroic’ properties coexist. Below their critical temperature, ferroic materials possess certain macroscopic properties which are both *spontaneous* (i.e. they exist independently of any external fields) and *switchable* (i.e. they can be manipulated by external fields). The interplay between different ferroic properties in multiferroics (fig. 1.1) leads not only to a broad spectrum of rich and fascinating fundamental physics, but also to many novel mechanisms that promise important practical applications.

The principal technological potential of multiferroics lies in lowering the energy cost of computation in data storage and logic devices. Since its invention in 1963,³ the complementary metal–oxide–semiconductor (CMOS) field-effect transistor has driven technological progress at an extraordinary rate. In what has become known as ‘Moore’s Law’,⁴ advances in CMOS technology have approximately doubled the density of transistors in integrated circuits every two years.⁵ However, this scaling down of components has led to increased energy consumption and heat generation to such a degree that these issues have become a serious limi-

¹H Schmid. *Ferroelectrics*, **162**: 317–338, 1994.

³FM Wanlass *Low stand-by power complementary field effect circuitry* US Patent 3,356,858 Dec. 1967

⁴GE Moore. *Electronics*, **38**: 114–117, 1965.

⁵RR Schaller. *IEEE Spectrum*, **34**: 52–59, 1997.

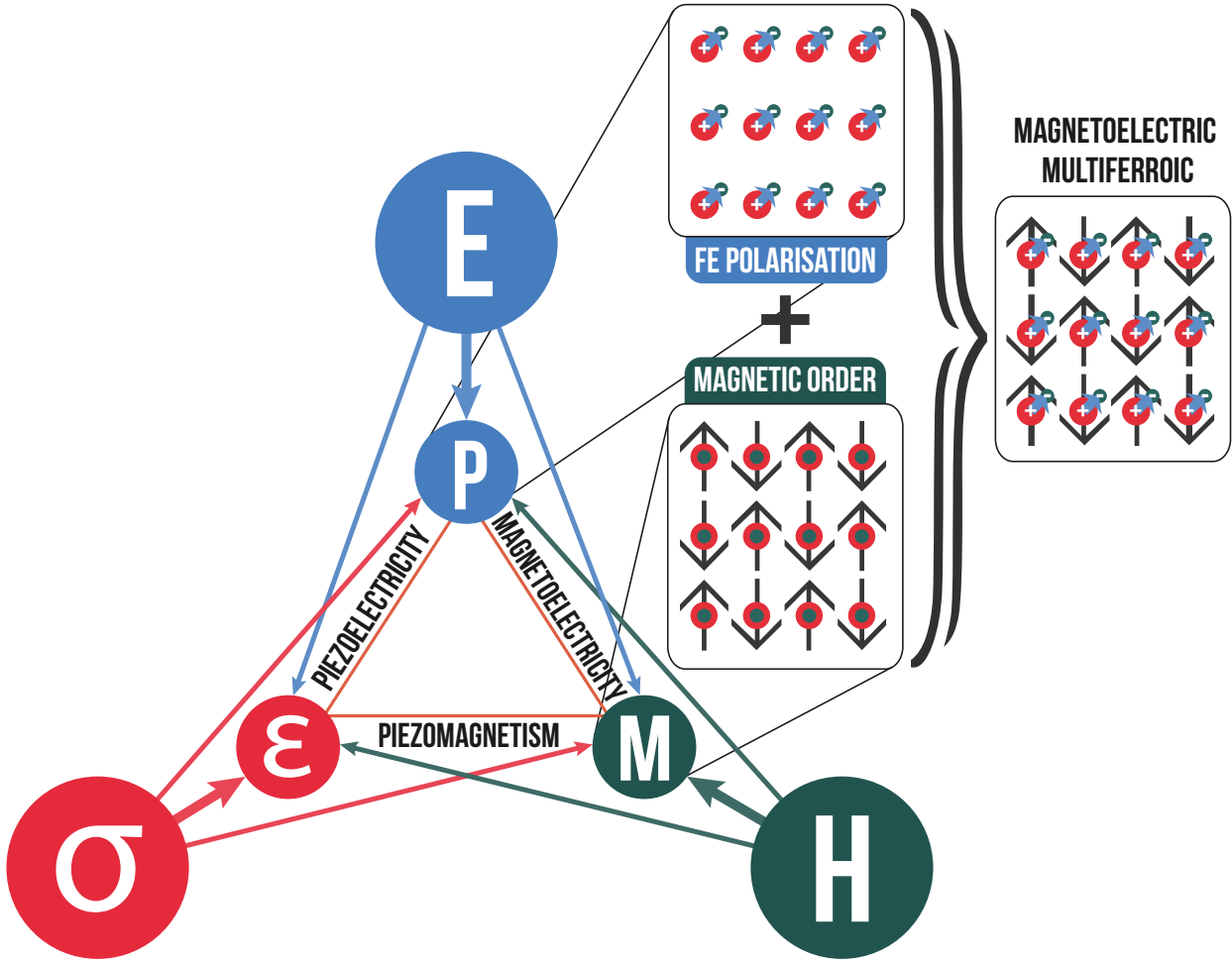


Figure 1.1: **Relationship between different ferroic orders.** In singly ferroic materials, a spontaneous electric polarisation P , magnetisation M or strain ϵ will form below a certain critical temperature. These can be controlled by an electric field E , magnetic field H or mechanical stress σ respectively. In multiferroics there are coupling mechanisms allowing for additional methods of control, for example, switching the electric polarisation with an applied magnetic field. After Spaldin *et al.* (2005).²

tation on device performance.⁶ The current cost of CMOS computation is $\sim 10^{-11}$ J/bit,⁷ many orders of magnitude more than the Landauer limit, which gives a theoretical lower limit of $E = k_B T \ln 2 \sim 3 \times 10^{-21}$ J/bit.⁸ Ferroic materials offer an alternative to the CMOS transistor, storing the binary information in their spontaneous properties. The spontaneous magnetisa-

⁶K Bernstein et al. *P. IEEE*, **98**: 2169–2184, 2010.

⁷RK Cavin, P Lugli, and VV Zhirnov. *P. IEEE*, **100**: 1720–1749, 2012.

⁸R Landauer. *IBM J. Res. Dev.*, **5**: 183–191, 1961.

tion of ferromagnetic materials has already proven an effective medium for non-volatile data storage⁹ and has been the central component of commercial hard disk drives since the 1950s.¹⁰ The persistence of the magnetisation, allowing information to remain even in the ‘off’ state of a device (a property shared by all ferroic materials), is a clear advantage over the volatile state of CMOS-based devices. However, the high energy cost associated with switching the magnetisation of these materials ($\sim 10^{-8}$ J/bit¹¹) prevents them from providing a viable alternative on their own. A multiferroic device, encompassing multiple ferroic orders, offers a different approach. By allowing the magnetic state to be controlled through its coupling to one of the other ferroic properties, a multiferroic device could harness the non-volatile nature of the magnetic state whilst remaining energetically cheap to switch.^{12–14} Although an ordered magnetic moment switchable solely by an applied *electric* field is impossible due to symmetry constraints,¹⁵ there are many other routes to exploiting this coupling. This thesis comprises an investigation into the coupling between magnetic order and other ferroic orders in multiferroic materials, with the view to create prototype logic devices based on electrical and mechanical control of magnetic order.

A key property of ferroic materials, fundamental in both their theoretical and experimental study, is that they conform to definite symmetry principles. All ferroic materials are *crystals*, such that their atoms are ordered in a periodic lattice which is invariant under a group of symmetry operations known as a *space group*. The symmetry elements of a space group consist of some combination of point and translational operations. These include both pure operations i.e. proper and improper rotations, mirror reflection, inversion, and centering and lattice translations, and compound operations i.e. screw axes (translation + rotation) and glide planes (translation + reflection). The 230 space groups can be generated by combining the 32 point groups with the

⁹NA Spaldin. *Magnetic materials: Fundamentals and applications*. Cambridge University Press, 2010.

¹⁰IBM RAMAC 650 announcement Sept. 1956

¹¹PC Lacaze and JC Lacroix. *Non-volatile memories*. John Wiley & Sons, 2014.

¹²JF Scott. *Nat. Mater.*, **6**: 256–257, 2007.

¹³M Bibes and A Barthélémy. *Nat. Mater.*, **7**: 425–426, 2008.

¹⁴F Matsukura, Y Tokura, and H Ohno. *Nat. Nano.*, **10**: 209–220, 2015.

¹⁵SW Cheong and M Mostovoy. *Nat. Mater.*, **6**: 13–20, 2007.

14 Bravais lattices.

The manifestation of ferroic order in a crystal is necessarily associated with the loss of some of these symmetry operations. These broken symmetries put strict constraints not only on the allowed form of any ferroic properties, but also on any potential coupling between them. This is stated succinctly in Neumann's principle:¹⁶

“The symmetry of any physical property of a crystal must include the symmetry elements of the point group of the crystal.”

Thus understanding the symmetry of the ferroic phase enables vital insights into the system. Symmetry analysis is a technique used extensively throughout this thesis, both in designing experiments to probe specific properties of ferroic materials and in interpreting the results of these experiments.

A further consequence of symmetry breaking in ferroics is the existence of *domains*, where different regions of the crystal have ferroically ordered in different orientations (equivalent by the broken symmetry elements of the parent structure). It is this domain structure and its response to external fields that gives ferroic materials their highly non-linear and hysteretic behaviour. From both a technological and experimental perspective, the effects of domains can be problematic since they can obfuscate (or even completely negate) the intrinsic properties of a material. However, if properly understood, domain effects can also be exploited to very finely tune the properties of a material.

The focus of this thesis is thin film BiFeO_3 , its multiferroic domain structure and how this may be manipulated to control its properties. In the remainder of this chapter, I will give an introduction to ferroic and multiferroic materials, their properties and classification, followed by a brief introduction to domains.

¹⁶FE Neumann and OE Meyer. *Vorlesungen über die Theorie der Elasticität der festen Körper und des Lichtäthers: gehalten an der Universität Königsberg*. vol. 5 BG Teubner, 1885.

1.2 Ferroic Materials

Upon changing the environmental conditions of a material, it can undergo a *phase transition*, entailing a spontaneous change of symmetry in which its structure changes. For example, as depicted in fig. 1.2(a), upon cooling a crystal through a certain *critical temperature*, T_c , it will undergo a phase transition from a disordered liquid (point group $\infty\infty m$) to a solid with long-range periodic order (and a discrete point group), thus breaking the isotropic translational and rotational symmetry of the disordered phase.

A ferroic material is a one that can undergo one or more ferroic phase transitions. A ferroic phase transition is defined as a non-disruptive^{17*} phase transition that entails a lowering of the point-group symmetry of the material. For example, in a ferromagnetic phase transition, disordered spins on a lattice will align along a certain direction, which breaks the higher rotational symmetry of the parent phase (fig. 1.2(b)). In contrast, crystallisation is an example of a non-ferroic phase transition, since unlike the ferromagnetic transition, it breaks the non-disruptive condition.

An important consequence of a ferroic phase transition is long-range ordering of at least one macroscopic tensor property. In ferroelectric materials, for example, the appearance of a spontaneous polarisation at the critical temperature can result from a long-range polar distortion of the crystal structure (fig. 1.2(c)). Given that in the parent phase, two or more of the possible orientations of this property are equivalent by symmetry and thus degenerate, this tensor property will in general be inhomogenous (usually discontinuously so) over the material in the ferroic phase. These regions, known as domains, differ in their orientations of the tensor property and

¹⁷M Guymont. *Phys. Rev. B*, **24**: 2647, 1981.

*A phase transition is non-disruptive if the new structure can be described (its symmetry elements, Wyckoff positions of atoms, etc., can be located) in the frame of reference of the old structure after a continuous distortion that does not entail an additional change of symmetry. This requires, for instance, that the high-symmetry axis of the parent phase coincides with the high-symmetry axis of at least one of the domains of the ferroic phase and atomic displacements are small enough that there is a one-to-one correspondence of all atoms and bonds between both phases. See Guymont (1981)¹⁷ for further details.

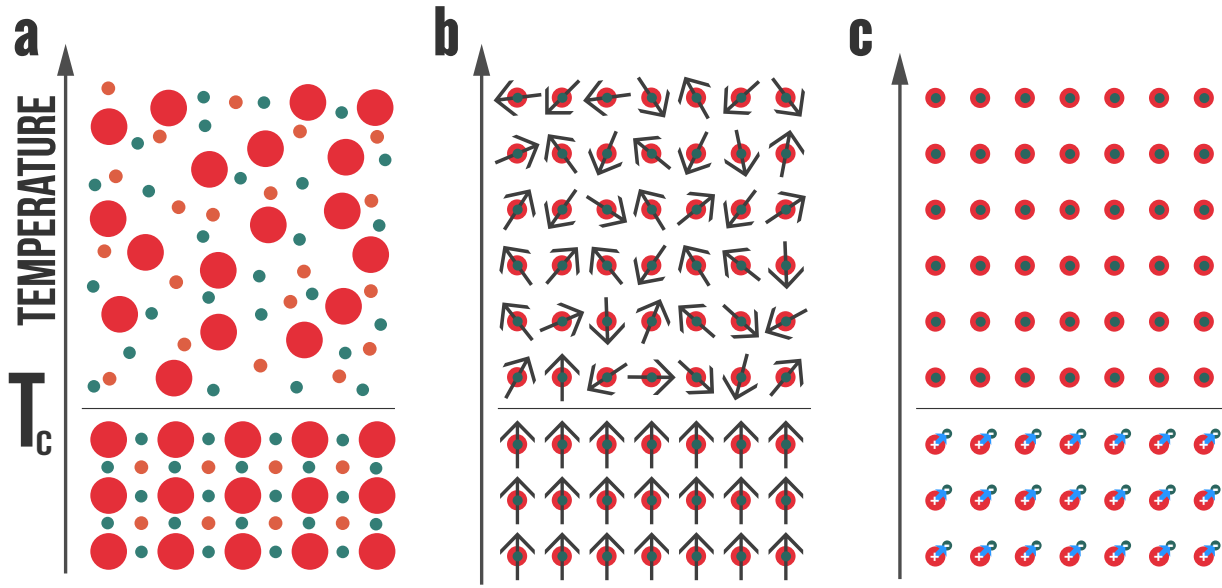


Figure 1.2: **Symmetry breaking phase transitions.** Schematic depictions of the onset of ordering below the critical temperature in the case of **a**, crystallisation, **b**, ferromagnetic ordering and **c**, ferroelectric ordering.

are related to one another by the broken symmetry operators of the parent phase. This domain structure can be modified by its *conjugate field*: an external electric, magnetic or stress field (or some combination of the three) that couples directly to the macroscopic tensor property. In the above example, ferroelectric domains can be modified by the application of an external electric field. There do exist, however, some ferroic materials with conjugate fields that are not so easily experimentally realisable. For example, the conjugate field of an antiferromagnet would be a staggered magnetic field with a periodicity on the atomic length scale.

1.2.1 Thermodynamics of ferroic phase transitions

Phase transitions can be understood in terms of the Gibbs free energy of the involved phases. Consider a ferroic crystal under the influence of an external magnetic field (H_i), electric field

(E_i), and a uniaxial stress (σ_{ij}). The generalised free-energy differential can be written as¹⁸

$$dF = -SdT - H_i dB_i - E_i dD_i - e_{ij} d\sigma_{ij}, \quad (1.1)$$

where S is the entropy, and B_i , D_i , and ε_{ij} are the magnetic flux density, electric displacement, and strain, respectively. We can write the latter three quantities each as a sum of a spontaneous component (denoted by the subscript (s)) and any induced components, due to the presence of external fields. Magnetic flux density may be induced by magnetic fields (magnetic permeability), electric fields (magnetoelectricity) and applied mechanical stress (piezomagnetism). In this case, the magnetic flux density can be written as

$$B_i = B_{(s)i} + \mu_{ij} H_j + \alpha_{ij} E_j + Q_{ijk} \sigma_{ij} + \dots, \quad (1.2)$$

where μ_{ij} , α_{ij} and Q_{ijk} are the coefficients of the magnetic permeability tensor, magnetoelectric tensor, and piezomagnetic tensor respectively. Similarly, for the electric displacement we have

$$D_i = D_{(s)i} + \epsilon_{ij} E_j + \alpha_{ij} H_j + d_{ijk} \sigma_{ij} + \dots, \quad (1.3)$$

where ϵ_{ij} and d_{ijk} are coefficients of the dielectric permittivity tensor and the piezoelectric tensor, respectively. Finally, the strain is given by

$$\varepsilon_{ij} = \varepsilon_{(s)ij} + s_{ijkl} \sigma_{kl} + d_{kij} E_k + Q_{kij} H_k + \dots, \quad (1.4)$$

where s_{ijkl} are the coefficients of the elastic-compliance tensor.

We can obtain an expression for the free energy, F , by substituting the expressions for B_i , D_i and ε_{ij} into eq. (1.1), combining terms and integrating. Since they are equivalent by symmetry, this applies equally for all domains, regardless of their orientation. To classify ferroic materials,

¹⁸VK Wadhawan. *Introduction to ferroic materials*. CRC press, 2000.

we can consider calculating the difference in the free energy for two different domains of a ferroic crystal, $\Delta F = {}^2F - {}^1F$, with reference to a set of measurement axes. Noting that, by definition, $D_{(s)i} = \epsilon_0 E_i + P_{(s)i}$ and $B_{(s)i} = \mu_0 H_i + M_{(s)i}$, we obtain

$$\begin{aligned}
 -\Delta F = & \overbrace{\Delta P_{(s)i} E_i + \Delta M_{(s)i} H_i + \Delta \epsilon_{(s)ij} \sigma_{ij}}^{\text{Primary ferroic terms}} + \\
 \text{Secondary ferroic terms} & \left\{ \begin{aligned} & \frac{1}{2} \Delta \epsilon_{ij} E_i E_j + \frac{1}{2} \Delta \mu_{ij} H_i H_j + \frac{1}{2} \Delta s_{ijkl} \sigma_{ij} \sigma_{kl} + \\ & \Delta \alpha_{ij} E_i H_j + \Delta d_{ijk} E_i \sigma_{jk} + \Delta Q_{ijk} H_i \sigma_{jk}, \end{aligned} \right. \quad (1.5)
 \end{aligned}$$

where tertiary and higher order terms have been omitted since they are outside the scope of this thesis.*

A ferroic crystal will have a finite value for at least one of the terms in eq. (1.5). These can be further categorised into *full* or *partial* ferroics: in a full ferroic, ΔF is non-zero for *all* pairs of orientation states, whereas in a partial ferroic, only a subset of pairs of orientation states give a finite ΔF . We now describe a classification of ferroic materials based on Equation (1.5), classifying them in terms of their tensor properties and their relationships to external fields.

1.2.2 Primary ferroics

The first three terms of eq. (1.5), which are linear in the conjugate fields, describe what are known as primary ferroics. These are ferroelectrics, ferromagnets and ferroelastics, respectively.

Ferromagnetism

If $\Delta M_{(s)i}$ is finite for at least one pair of domains (for any i), i.e. the two domains differ in their spontaneous magnetisation, then the crystal is said to be ferromagnetic. This also includes

*These higher order effects are often difficult to observe as they are easily masked by any primary or secondary effects also present in a system. Two tertiary effects that will be mentioned briefly are magneto- and electro-striction, which correspond to terms $\sim \sigma H^2$ and $\sim \sigma E^2$, respectively.

ferrimagnetic materials and weak ferromagnets. Long range magnetic order may also come in the form of *antiferromagnetism* or more complex, non-collinear structures.

Historically, ferromagnetism is the oldest ferroic property known to science, its study dating back to the ancient Greeks.¹⁹ From its first recorded practical use in the magnetic compass by Chinese mariners²⁰ to its use in the first electric power plant providing power generation to Manhattan, New York,²¹ ferromagnetism has contributed vitally to technological development over the past millennium. Now, magnetic materials play a crucial role in many devices across various sectors including audio technology, telecommunications, energy distribution and generation, and data storage.⁹

Spontaneous magnetic order in crystalline solids is caused by *exchange* interactions between nearby magnetic ions. The exchange interaction is quantum mechanical in nature and arises from the fact that the overall electron wavefunction must be antisymmetric under particle exchange to satisfy the Pauli exclusion principle.²² Consider a system comprising two interacting electrons labelled a and b at positions $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively. Their overall wavefunction can be written as a product of the spatial and spin components such that the symmetric-spin, antisymmetric-spatial (singlet) state is given by

$$\psi_S = \frac{1}{\sqrt{2}}[\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) + \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)]\chi_S, \quad (1.6)$$

and the antisymmetric-spin, symmetric-spatial (triplet) state is given by

$$\psi_T = \frac{1}{\sqrt{2}}[\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2) - \varphi_a(\mathbf{r}_2)\varphi_b(\mathbf{r}_1)]\chi_T, \quad (1.7)$$

where χ_S and χ_T are the symmetric and antisymmetric spin-only wavefunctions, respectively.

¹⁹JF Keithley. *The story of electrical and magnetic measurements: From 500 BC to the 1940s*. John Wiley & Sons, 1999.

²⁰CW Chen. *Magnetism and Metallurgy of Soft Magnetic Materials*. New York: Dover Publications, 1986.

²¹C Sulzberger. *IEEE Power Energy M.*, **11**: 76–85, 2013.

²²W Pauli. *Z. Phys. A*, **31**: 765–783, 1925.

The difference in energy between these two states is what defines the *exchange constant*:

$$J_{ab} = \frac{E_T - E_S}{2} = \int \varphi_a^*(\mathbf{r}_1) \varphi_b^*(\mathbf{r}_2) \mathcal{H} \varphi_a(\mathbf{r}_1) \varphi_b(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (1.8)$$

which quantifies the interaction between the two spins, and whether it is energetically favourable for them to align or antialign. This can be generalised to a many body system, giving an expression for the effective spin-Hamiltonian,²⁴ or, as it is better known, the Heisenberg Hamiltonian:

$$\mathcal{H} = 2 \sum_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1.9)$$

where J_{ij} is the isotropic exchange constant that describes the interaction between spins i and j . Note that if $J_{ij} < 0$ for all neighbouring spins, the system will order ferromagnetically whereas, if $J_{ij} > 0$, they will order antiferromagnetically. If multiple exchange interactions are present or if spins in certain geometries (on a triangular lattice, for instance) are antiferromagnetically coupled, these interactions can result in *magnetic frustration*, which can stabilise more complex,

²⁴SJ Blundell. *Magnetism in condensed matter*. OUP, 2003.

Table 1.1: Classification of primary and secondary ferroics. After Newnham (2005).²³

Ferroic class	Orientation state differ in	Switching force	Example
<i>Primary</i>			
Ferromagnetic	Spontaneous magnetisation M_i	Magnetic field H_i	Co
Ferroelectric	Spontaneous polarisation P_i	Electric field E_i	BaTiO ₃
Ferroelastic	Spontaneous strain ϵ_{ij}	Mechanical stress σ_{ij}	CaAl ₂ Si ₂ O ₈
<i>Secondary</i>			
Ferrobimagnetic	Magnetic susceptibility μ_{ij}	Magnetic field $H_i H_j$	NiO
Ferrobielectric	Dielectric susceptibility ϵ_{ij}	Electric field $E_i E_j$	SrTiO ₃
Ferrobielastic	Elastic compliance s_{ijkl}	Mechanic stress $\sigma_{ij} \sigma_{kl}$	SiO ₂
Ferromagnetoelectric	Magnetoelectric coefficients α_{ij}	Magnetic field and electric field	Cr ₂ O ₃
Ferromagnetoelastic	Piezomagnetic coefficients Q_{ijk}	Magnetic field and mechanical stress	FeCO ₃
Ferroelastoelectric	Piezoelectric coefficients d_{ijk}	Electric field and mechanical stress	NH ₄ Cl

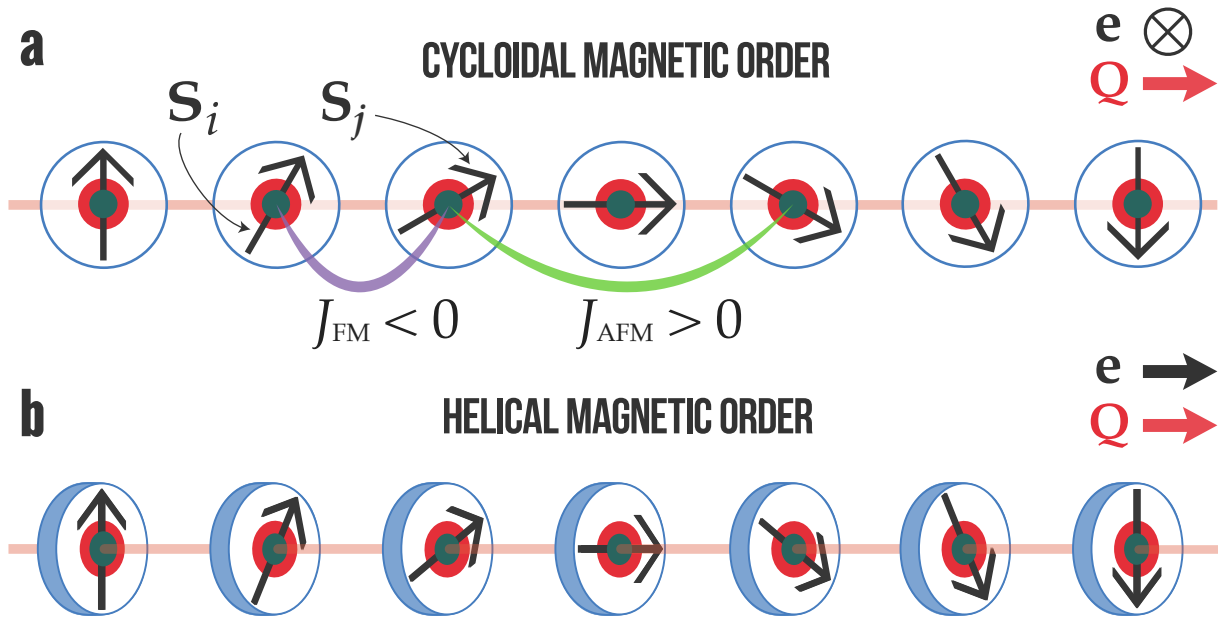


Figure 1.3: **Noncollinear magnetic structures.** Competing exchange interactions can stabilise non-collinear magnetic structures. For example, nearest neighbour, $J_{\text{FM}} < 0$, and next-nearest neighbour, $J_{\text{AFM}} > 0$, can result in a ground-state (a,) cycloidal spin structure where spins rotate in a plane containing the propagation vector ($\mathbf{Q} \perp \mathbf{e}$) or a (b,) helical spin structure in which the spins rotate in a plane orthogonal to the propagation vector ($\mathbf{Q} \parallel \mathbf{e}$). Here $\mathbf{Q}$ is the magnetic propagation vector and $\mathbf{e}$ is the spin rotation axis.

often incommensurate, spin arrangements such as helical or cycloidal magnetic structures as shown in fig. 1.3.

This *direct* exchange interaction is dependent on a spatial overlap of the electron orbitals of neighbouring magnetic ions. However, in many ionic solids, this exchange mechanism does not account for the interaction between magnetic ions since they are separated sufficiently that the orbital overlap is negligible. There is instead an *indirect* exchange interaction, known as *superexchange*, whereby a non-magnetic ion (usually O^{2-}) located between the magnetic ions mediates the exchange.

The nature of the superexchange interaction depends largely on the crystal structure, specifically on the bond angle between the non-magnetic and magnetic ions.^{25,26} This effect, amongst

²⁵JB Goodenough. *Phys. Rev.*, **100**: 564, 1955.

²⁶J Kanamori. *J. Phys. Chem. Solids.*, **10**: 87–98, 1959.

others, allows the crystal structure to influence the magnetic structure, and vice versa. This interaction between magnetic and structural order is particularly important in the context of multiferroics as it provides a mechanism that can couple the magnetic structure to other ferroic properties.

Ferroelectricity

If $\Delta P_{(s)i}$ in eq. (1.5) is finite for at least one pair of orientation states of a crystal, it is said to be ferroelectric. Ferroelectricity, unlike ferromagnetism, is very much a 20th century phenomenon, having been first observed in 1920 by Joseph Valasek.²⁷ In measurements of the material known as Rochelle salt, Valasek demonstrated hysteretic switching of the polarisation with an applied electric field. In the following decades, a new series of ferroelectrics based on a family of hydrogen-bonded compounds was discovered: namely the potassium arsenates and phosphates, including the material KH_2PO_4 (better known as KDP).^{28,29} The polarisation in these compounds results from an order–disorder transition that involves ordering of the H^+ ions in the hydrogen bonds to create ferroelectric domains.³⁰ The first observation of ferroelectrics in non-hydrogen-bonded compounds was in the perovskite oxides in the 1940s.^{31–33} The most notable of these is BaTiO_3 ,^{34,35} a material that now sees common use in modern capacitors and transducers.³⁶ For BaTiO_3 (and several other perovskite oxides with d^0 transition metal ions), the ferroelectric state arises from a polar distortion of the covalently-bonded $\text{O}^{2-}-\text{Ti}^{4+}$ octahedra, lowering its overall bond energy. In recent years, there has been a significant increase in the research interest in

²⁷J Valasek. *Phys. Rev.*, **17**: 475, 1921.

²⁸G Busch and P Scherrer. *Nat. Sci.*, **23**: 737–737, 1935.

²⁹G Busch. *Helv. Phys. Acta*, **11**: 269–298, 1938.

³⁰JC Slater. *J. Chem. Phys.*, **9**: 16–33, 1941.

³¹BT Matthias and JP Remeika. *Phys. Rev.*, **76**: 1886, 1949.

³²BT Matthias. *Phys. Rev.*, **75**: 1771, 1949.

³³G Shirane, S Hoshino, and K Suzuki. *Phys. Rev.*, **80**: 1105, 1950.

³⁴B Wul. *Nature*, **156**: 480, 1945.

³⁵B Wul. *Nature*, **157**: 808, 1946.

³⁶GH Haertling. *J. Am. Ceram. Soc.*, **82**: 797–818, 1999.

ferroelectricity, with many new materials and ferroelectric mechanisms being discovered.³⁷

Ferroelectrics (and in fact all ferroics) can be categorised into *proper* and *improper* ferroics. In a proper ferroelectric, the order parameter is proportional to the spontaneous polarisation* such that the polarisation results directly from a structural phase transition that lowers the point group symmetry to a polar group. For example, some perovskite oxides have a transition metal ion with an electron lone pair in their outer shell (e.g. Bi^{3+} in BiFeO_3). The ferroelectric ordering of the molecular dipoles of these highly-polarisable ions can then lead to a macroscopic polarisation.

The spontaneous polarisation in an improper ferroelectric emerges at a phase transition in which the primary order parameter is *not* the spontaneous polarisation. The polarisation arises instead through some coupling to the primary order parameter, which will have different transformational properties to the polarisation. Improper ferroelectricity was first observed in gadolinium molybdate $\text{Gd}_2(\text{MoO}_4)_3$,³⁸ which, unlike all proper ferroelectrics, shows no anomaly in the dielectric constant at T_C . The order parameter in this case is a soft acoustic mode that couples to the polarisation through the piezoelectric effect.³⁹ Another family of improper ferroelectrics that is particularly relevant to this thesis have a spontaneous polarisation that arises due to a *magnetic* phase transition. The classic example of which is TbMnO_3 , where the low temperature, cycloidal magnetic ordering induces a polar distortion of the crystal structure.^{40,41}

Ferroelasticity

If at least two domains of a crystal differ in their spontaneous strain (i.e. $\Delta\epsilon_{(s)ij}$ in eq. (1.5) is finite), the crystal is said to be ferroelastic. Ferroelastic domains may be thought of as a special case of structural twins that differ from the parent structure only by small atomic displacements

³⁷JF Scott. *Science*, **315**: 954–959, 2007.

*It is possible to further differentiate between proper and pseudoproper ferroelectrics, where, in the latter case, the order parameter has the same symmetry as the polarisation, but is not the polarisation itself.

³⁸LE Cross, A Fouskova, and SE Cummins. *Phys. Rev. Lett.*, **21**: 812, 1968.

³⁹SE Cummins. *Ferroelectrics*, **1**: 11–17, 1970.

⁴⁰T Kimura et al. *Nature*, **426**: 55–58, 2003.

⁴¹H Katsura, N Nagaosa, and AV Balatsky. *Phys. Rev. Lett.*, **95**: 057205, 2005.

such that the non-disruptive condition is not broken. Although proper ferroelastics do exist, most ferroelastic materials are improper,⁴² with their spontaneous strain appearing through coupling to some other primary instability. This instability may also be elastic in character, such as in antiferrodistortive (cell-doubling) phase transitions where the order parameter is a soft mode or it can originate from other forms of ferroic order. For example, although the domains in the orthorhombic phase of BaTiO₃ differ in their spontaneous strain, the order parameter describing the tetragonal–orthorhombic phase transition is in fact a polarisation.^{43*} Magnetic order may also induce (improper) ferroelasticity through magnetostriction or other spin-lattice coupling mechanisms.^{44,45}

1.2.3 Secondary ferroics

Materials for which there are finite terms in eq. (1.5) that are *quadratic* in the external fields (E_i , B_i and σ_{ij}) are known as secondary ferroics. In contrast to their primary counterparts, these exhibit no difference between domains in their spontaneous magnetisation, polarisation or strain. They instead differ in their *induced* magnetisation, polarisation or strain, when an external field is applied. By applying an appropriate combination of external fields, E_i , B_i and ε_{ij} , it is then possible to switch between secondary ferroic domains. From a practical perspective, secondary and higher-order ferroics are of significant interest because they often exhibit coupling between properties that would otherwise behave independently. However, because the coercive fields for switching ferroic domains rise very sharply with the order of the ferroic phenomenon,⁴⁶ it is often not possible to detect secondary and higher-order ferroic effects in materials where the

⁴²JC Toledano and P Toledano. *Phys. Rev. B*, **21**: 1139, 1980.

⁴³YA Izyumov and VN Syromyatnikov. *Phase transitions and crystal symmetry*. vol. 38 Springer Science & Business Media, 2012.

*BaTiO₃ is also an example of a *partial* ferroic as, although 90° domains differ in their ferroelastic tensor, 180° domains do not.

⁴⁴E Ascher et al. *J. Appl. Phys.*, **37**: 1404–1405, 1966.

⁴⁵P Toledano et al. *Jpn. J. Appl. Phys.*, **24**: 179–181, 1985.

⁴⁶VK Wadhawan. *Phase Transit.*, **3**: 3–103, 1982.

corresponding primary effects are also present.

Crystals that have two or more domains with a difference in their free energy $\Delta F \sim E^2, H^2$ and σ^2 are ferrobimagnetic, ferroelectric, and ferrobielastic, respectively. These materials produce a difference in the magnetic, dielectric and elastic susceptibility between domains. For example, α -quartz is a ferrobielastic with two possible ferrobielastic domains, known as Dauphiné twins. The two orientation states have no difference in their spontaneous strain but differ in their elastic susceptibility such that, if an external mechanical stress is applied, a strain difference is induced between them.⁴⁷ By applying a mechanical stress in the appropriate direction, it is then possible to switch between the two ferrobielastic orientation states.⁴⁸

Secondary ferroics with domains differing in their free energy as $\Delta F \sim EH, E\sigma$ and $H\sigma$ (the latter three terms of eq. (1.5)) are ferromagnetoelectric, ferroelastoelectric and ferromagnetoelectric, respectively. These materials are of particular interest since they allow a magnetisation, polarisation or strain to be controlled by a *non-conjugate* external field*. For instance, ferromagnetoelectrics, which are especially relevant to this thesis, allow a magnetisation to be controlled via an electric field.

(Ferro)Magnetoelectricity

A ferromagnetoelectric, more commonly referred to simply as a magnetoelectric, has a finite $\Delta\alpha_{ij}$ for at least one pair of orientation states. In a magnetoelectric, it is possible to induce a magnetisation (polarisation) with an applied electric (magnetic) field, as can be seen clearly in eq. (1.2) (eq. (1.3)).⁴⁹ This effect is referred to as the *linear* magnetoelectric effect, usually to differentiate it from the looser definition of magnetoelectricity, which can refer to any kind of coupling

⁴⁷MA Carpenter et al. *Am. Mineral.*, **83**: 2–22, 1998.

⁴⁸TL Anderson, RE Newnham, and LE Cross. “Coercive stress for ferrobielastic twinning in quartz” in: *31st Annual Symposium on Frequency Control*. 1977. IEEE 1977. 171–177

*Here, non-conjugate field refers to an external field that would not be the conjugate field of a ferroic property in the case of the corresponding primary ferroic.

⁴⁹M Fiebig. *J. Phys. D Appl. Phys.*, **38**: R123–R152, 2005.

between magnetic and electric order parameters*. Importantly, a magnetoelectric material requires both spatial-inversion to be broken (i.e. the crystal and/or the magnetic structure must be non-centrosymmetric) and time-inversion to be broken (i.e. the material must be magnetically ordered).

The linear magnetoelectric effect, predicted by Dzyaloshinskii in 1959,⁵⁰ was first observed in Cr_2O_3 in 1960,⁵¹ which, due its room-temperature magnetoelectricity, is now one of the most studied magnetoelectric materials. Below its Néel temperature, Cr_2O_3 enters a collinear antiferromagnetic structure lowering its symmetry to the (noncentrosymmetric) magnetic point group $\bar{3}'m'$, satisfying the symmetry requirements for magnetoelectricity. Switching magnetoelectric domains requires the simultaneous application of electric and magnetic fields, originally this was achieved by ‘poling’ the material through the transition,⁵² but since then has been achieved isothermally.⁵³

(Ferro)Magnetoelectricity and (Ferro)Elastoelectricity

It is also possible for materials to display an induced magnetisation or polarisation under an applied mechanical stress or, conversely, an induced strain under an applied magnetic or electric field. Materials that show these properties have a finite ΔQ_{ijk} (ferromagnetoelastics) or Δd_{ijk} (ferroelastoelectrics) in eq. (1.5), respectively, i.e. the elements of the piezomagnetic or piezoelectric tensors differ between domains. In addition to these *linear* effects, there exist higher-order phenomena that couple magnetic and electric orders to mechanical order. Notably, magneto- or electro-strictive materials display an induced strain that varies *quadratically* with the applied magnetic or electric field, respectively.¹⁸

*In these cases, the magnetic and electric order parameters may not simply be the magnetisation or polarisation. For instance, in an antiferromagnet, the magnetic order parameter can be the staggered magnetisation, or, for complex, noncollinear magnetic structures, it may be the magnetic helicity or magnetic polarity.

⁵⁰IE Dzyaloshinskii. *Sov. Phys. JETP*, **10**: 628–629, 1960.

⁵¹DN Astrov. *Sov. Phys. JETP*, **11**: 708–709, 1960.

⁵²S Shtrikman and D Treves. *Phys. Rev.*, **130**: 986, 1963.

⁵³T Ashida et al. *Appl. Phys. Lett.*, **106**: 132407, 2015.

Magnetostriction is of particular interest as it provides a mechanism for coupling the magnetic structure to the crystal structure. It is present in all magnetic materials and although it is of higher-order, it is typically much larger than the piezomagnetic effect.²³ Magnetostrictive effects tend to be small, producing strains on the order of 10^{-6} . One exception to this is the alloy known as Terfenol-D ($\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$, $x \sim 0.3$) whose magnetostrictive strain reaches 0.6 % at saturation,⁵⁴ and is utilised in magnetomechanical sensors, actuators and transducers.⁵⁵

Furthermore, magnetoelastic phenomena can drive the emergence of a ferroelectric polarisation, providing further mechanisms for magnetoelectric coupling. This is observed in some antiferromagnets through *exchange-striction*, an effect analogous to magnetostriction but where the induced strain varies quadratically with the *staggered* magnetisation rather than the applied field (or magnetisation). For instance, in the type-II multiferroics TbMn_2O_5 , GdMn_2O_5 , YMn_2O_5 ^{56–58} the ferroelectric polarisation is driven by movement of the oxygen or metal ions to optimise superexchange energy. These small atomic displacements add coherently throughout the crystal to give rise to a net ferroelectric polarisation.

1.3 Multiferroics

A multiferroic is a ferroic material that can undergo at least two ferroic phase transitions such that multiple forms of ferroic order coexist or a single ferroic phase transition at which multiple forms of ferroic order emerge. More specifically, it is convention that multiferroicity refers to the existence of multiple forms of *primary* ferroic order i.e. ferromagnetism, ferroelectricity and ferroelasticity, along with their ‘antiferro’ and ‘ferri’ counterparts, plus any other forms of ferroic order that would appear as terms linear in their conjugate field in eq. (1.5) (such as those

²³RE Newnham. *Properties of materials: Anisotropy, symmetry, structure*. Oxford University Press, 2005.

⁵⁴D Jiles. *Introduction to magnetism and magnetic materials*. CRC press, 2015.

⁵⁵AG Olabi and A Grunwald. *Mater. Design*, **29**: 469–483, 2008.

⁵⁶LC Chapon et al. *Phys. Rev. Lett.*, **93**: 177402, 2004.

⁵⁷PG Radaelli et al. *Phys. Rev. Lett.*, **101**: 067205, 2008.

⁵⁸N Lee et al. *Phys. Rev. Lett.*, **110**: 137203, 2013.

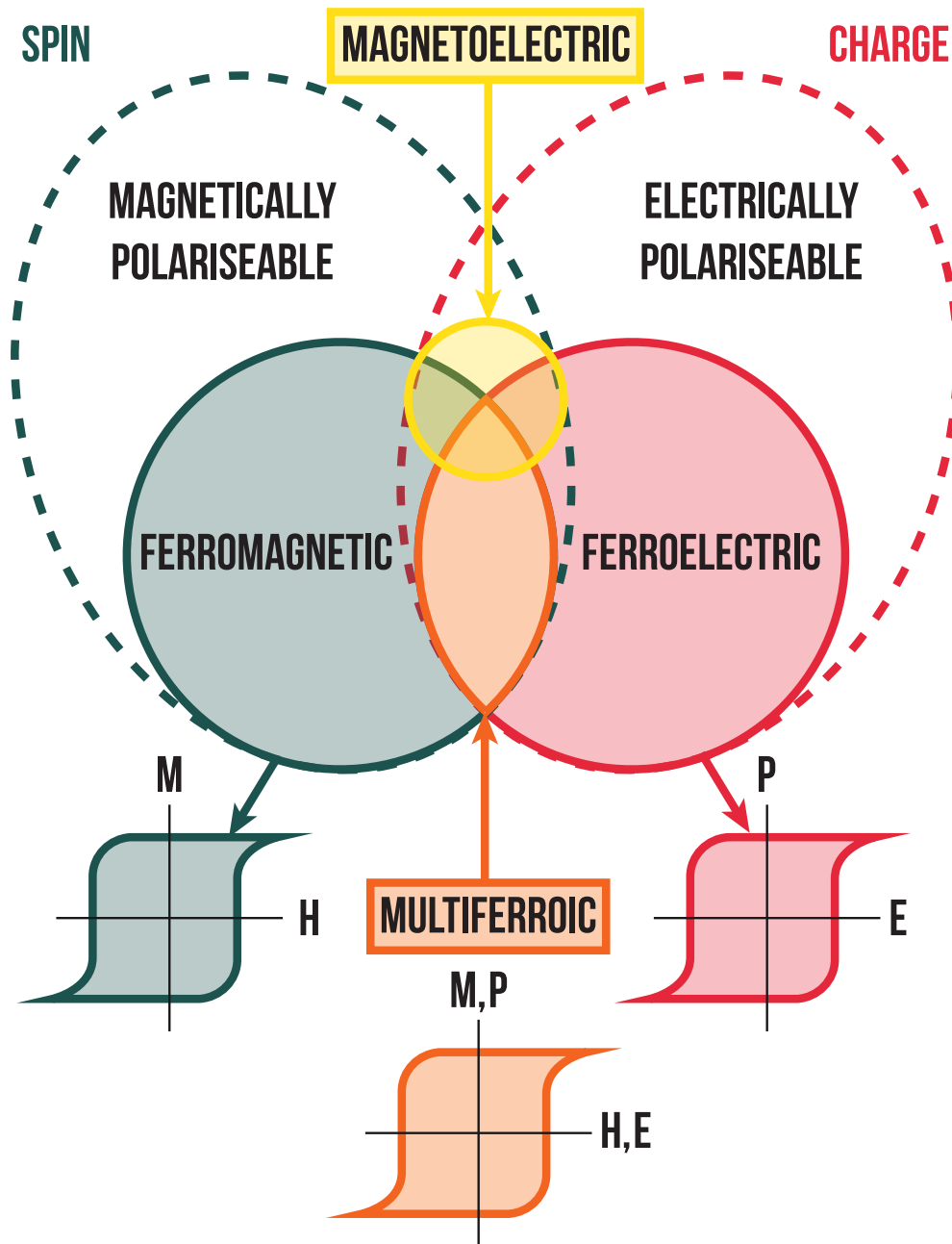


Figure 1.4: **Relationship between multiferroic and magnetoelectric materials.** In the spin domain, ferromagnetic materials form a subset of magnetically polarisable materials and in the charge domain, ferroelectric materials form a subset of electrically polarisable materials. In the ideal scenario, the magnetisation (polarisation) of a magnetoelectric multiferroic material can be switched hysteretically by applied electric (magnetic) field, as shown by the orange hysteresis loop. After Eerenstein *et al.* (2006).⁵⁹

describing rotating magnetic structures). Interest in multiferroics falls principally with those exhibiting both spontaneous magnetic and ferroelectric order, with some coupling between the two (see fig. 1.4), often referred to as ‘magnetoelectric multiferroics’. Although, these materials may indeed exhibit the linear magnetoelectric effect, the term ‘magnetoelectric’ is being used here with its looser definition, referring to some general coupling between magnetic and charge order. I shall adopt this nomenclature for the remainder of the thesis.

A magnetoelectric multiferroic comes with important symmetry restrictions. For a crystal to support both a *polar* polarisation vector and an *axial* magnetisation vector, it must have a point group that leaves these vectors invariant and, hence, necessarily breaks spatial- and time-inversion symmetry. Of the 233 Shubnikov magnetic point groups, only 13 of them: 1, 2, 2', m, m', 3, 3m', 4, 4m'm', m'm2', m'm'2', 6 and 6m'm', satisfy this constraint.⁶⁰ These symmetry restrictions further put constraints on the type of coupling allowed between the magnetic and ferroelectric order.

1.3.1 Classification of multiferroic materials

Multiferroic materials can be classified into type-I and type-II multiferroics, the primary difference being the origin of their ferroelectricity.

Type-I multiferroic materials

In type-I multiferroics, the ferroelectric transition occurs independently of the magnetic transition, at a separate critical temperature, as depicted in fig. 1.5(a). Although the co-existence of the two orders will generally result in some coupling between the polarisation and magnetic structure, the ferroelectric and magnetic order parameters are not directly coupled, often being described as ‘weakly’ coupled.⁶¹ Type-I multiferroics, typically being proper ferroelectrics, have a large ferroelectric polarisation on the order of $100 \mu\text{C}/\text{cm}^2$. They also typically have high

⁶⁰KF Wang, JM Liu, and ZF Ren. *Adv. Phys.*, **58**: 321–448, 2009.

⁶¹D Khomskii. *Physics*, **2**: 20, 2009.

critical temperatures, with the ferroelectric ordering occurring above room temperature, and the magnetic ordering occurring typically in the 50–200 K range. BiFeO₃, the classic example of a type-I multiferroic, ferroelectrically orders at 1100 K⁶² and antiferromagnetically orders at 643 K,⁶³ making it one of the very few room-temperature multiferroics.

Type-II multiferroic materials

In a type-II multiferroic, the ferroelectric polarisation arises simultaneously with the magnetic ordering at a single transition driven by a magnetic order parameter (fig. 1.5). Type-II multiferroics are thus, by definition, improper ferroelectrics in which the polarisation is induced by the magnetic ordering. Their ordering temperatures, in contrast to type-I multiferroics, tend to be rather low (<50 K). This is because the non-centrosymmetric magnetic structures required to drive the system into the ferroelectric state generally arise from magnetic frustration.⁶¹ They also have spontaneous polarisations typically much lower than those of type-I multiferroics, on the order of 0.1 $\mu\text{C}/\text{cm}$. However, given that it is the magnetic ordering itself that causes the ferroelectricity, type-II multiferroics will exhibit, in principle, much stronger magnetoelectric coupling.¹⁵ This class of multiferroics was first discovered in 2003 when Kimura *et al.* observed that the cycloidal magnetic ordering of TbMnO₃ induced a ferroelectric polarisation. They found this polarisation could then be rotated by 90° with an applied magnetic field.⁴⁰ A similar effect was subsequently observed in TbMn₂O₅, in which a magnetic field could completely reverse the ferroelectric polarisation.⁶⁴

1.3.2 Coupling mechanisms

The difference in the transformative properties of the magnetic (time-asymmetric) and electric (space-asymmetric) order parameters imposes symmetry constraints on the possible coupling

⁶²JR Teague, R Gerson, and WJ James. *Solid State Commun.*, **8**: 1073–1074, 1970.

⁶³I Sosnowska, TP Neumaier, and E Steichele. *J. Phys. C: Solid State*, **15**: 4835, 1982.

⁶⁴N Hur *et al.* *Nature*, **429**: 392–395, 2004.

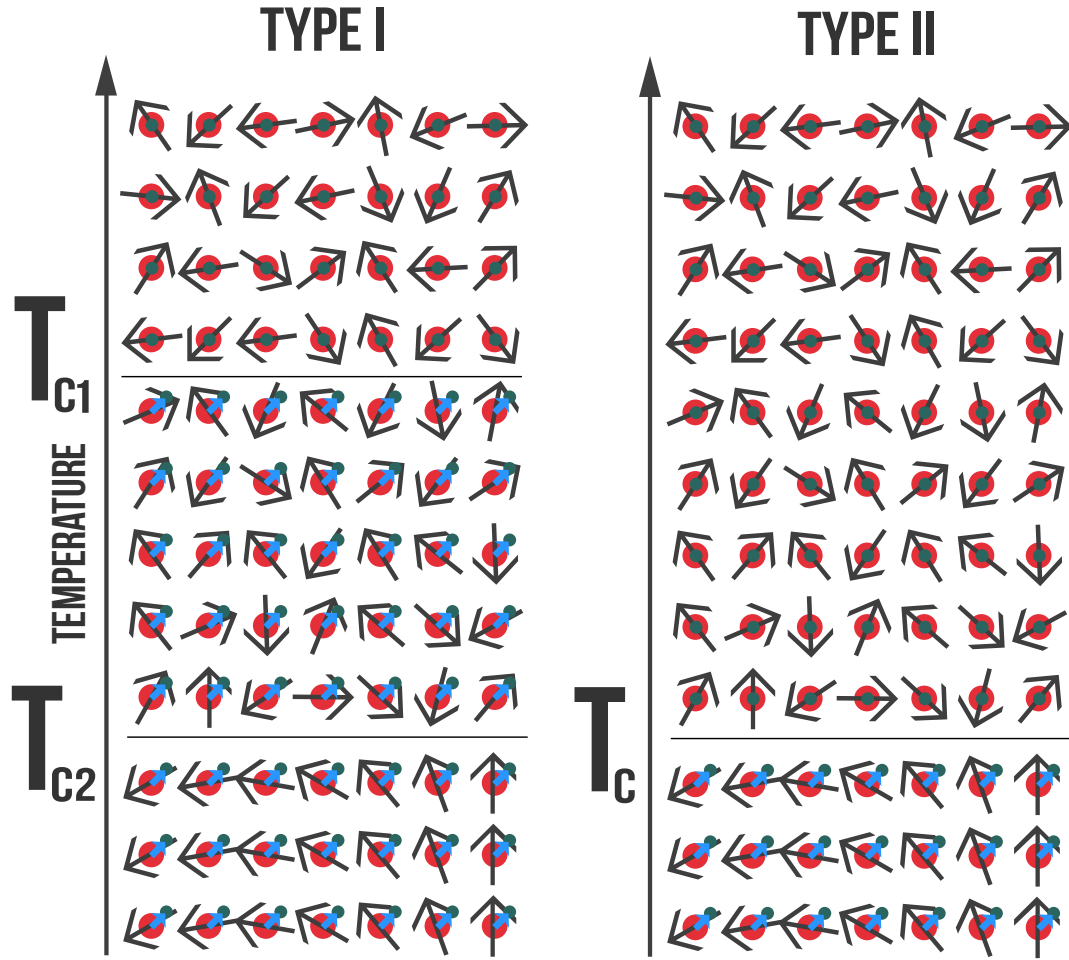


Figure 1.5: **Type-I and type-II multiferroics.** Type-I multiferroics (a,) have independent ferroelectric and magnetic ordering transitions at separate temperatures. Below T_{C1} , a local ionic or charge displacement (blue arrows) gives rise to a macroscopic ferroelectric polarisation, but the system remains magnetically disordered. The system then enters the multiferroic phase at T_{C2} as the spins (black arrows) order in the presence of the pre-existing polarisation. Type-II multiferroics (b,) become magnetically ordered and ferroelectric simultaneously at a single phase transition. The primary magnetic instability driving the transition couples to and induces a ferroelectric polarisation.

between the magnetic and electric order. The linear coupling between $(\mathbf{P}, \mathbf{E})$ and $(\mathbf{M}, \mathbf{H})$ described by Maxwell's equations is not intrinsically achievable within a material as it requires these vectors to vary both spatially *and* temporally. Thus any coupling between the static $\mathbf{P}$ and $\mathbf{M}$ within a multiferroic must be nonlinear in nature, resulting from interactions between charge, spin, orbital and lattice degrees of freedom.¹⁵ For a system with an inhomogeneous magnetisation, a

third-order coupling can lead to a magnetically induced ferroelectric polarisation given by⁶⁵

$$P^i = T^{ijkl} M^j \partial_k M^l, \quad (1.10)$$

where T^{ijkl} is a parity-even materials tensor describing the coupling. Evaluating the coefficients of T^{ijkl} in a cubic system, this simplifies to

$$\mathbf{P} \propto [(\mathbf{M} \cdot \nabla) \mathbf{M} - \mathbf{M}(\nabla \cdot \mathbf{M})]. \quad (1.11)$$

This spatially varying magnetisation is present in all non-collinear magnetic structures, such as the helicoidal spin arrangements shown in fig. 1.3.

Although the above considerations based on Landau theory show that ferroelectric and magnetic order may be coupled to one another, they explain nothing of its microscopic origin. A magnetically induced polarisation may arise from one or more microscopic mechanisms, the main three being the inverse Dzyaloshinskii-Moriya effect, exchange-striction, and d - p hybridisation. We can therefore write the spontaneous polarisation as

$$\mathbf{P} = \overbrace{P_{\text{DM}} \mathbf{r}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)}^{\text{Dzyaloshinskii-Moriya}} + \overbrace{P_{\text{MS}} (\mathbf{S}_i \cdot \mathbf{S}_j) \mathbf{r}_{ij}}^{\text{Exchange-striction}} + \overbrace{P_{\text{O}} [(\mathbf{r}_{ij} \cdot \mathbf{S}_i) \mathbf{S}_i - (\mathbf{r}_{ij} \cdot \mathbf{S}_j) \mathbf{S}_j]}^{d-p \text{ hybridisation}}, \quad (1.12)$$

where $\mathbf{r}_{ij}$ is a vector connecting the positions of the two spins $\mathbf{S}_i$ and $\mathbf{S}_j$.

The first term results from the inverse Dzyaloshinskii-Moriya (DM) interaction,^{66,67} a relativistic correction to the superexchange interaction described by the Hamiltonian $\mathcal{H}_{\text{DM}} = \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j)$, which can explain the ferroelectric polarisation induced by magnetic structures with a cycloidal component. The spin-orbit interaction couples two adjacent non-collinear spins to the lattice and causes a displacement of the ligand perpendicular to the bond (fig. 1.6). If

⁶⁵M Mostovoy. *Phys. Rev. Lett.*, **96**: 067601, 2006.

⁶⁶IE Dzyaloshinskii. *Sov. Phys. JETP*, **19**: 960–971, 1964.

⁶⁷T Moriya. *Phys. Rev.*, **120**: 91, 1960.

all ligands in the structure are displaced in the same direction, this leads to a net polarisation. Alternative proposed mechanisms that give rise to a polarisation of the same form are the spin-current model, in which the spin current induces an electric dipole moment between the pairs of spins (analogous to a charge current generating a magnetic field),⁴¹ and the electric-current cancellation model, a purely electrical model in which electric currents preferentially cancel to give a net polarisation.⁶⁸

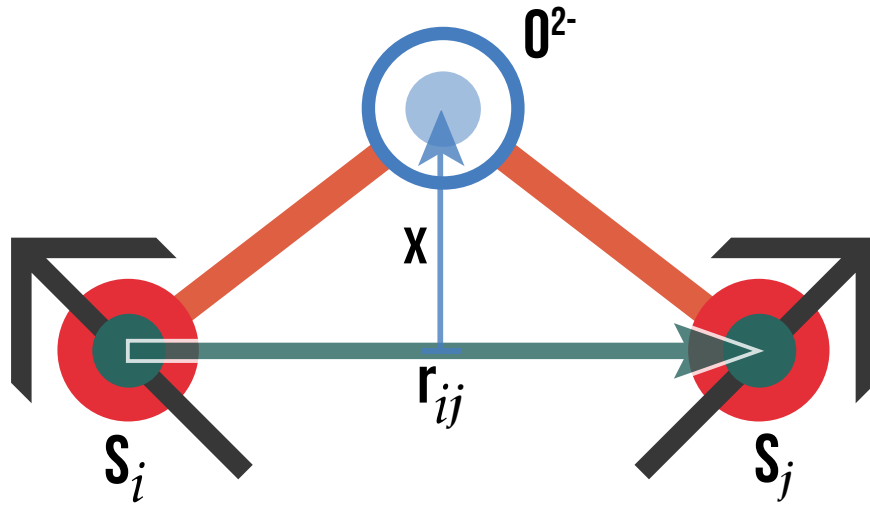


Figure 1.6: **The antisymmetric Dzyaloshinskii-Moriya interaction.** The DM interaction is given by $\mathcal{H}_{\text{DM}} = \mathbf{D}_{ij} \cdot [\mathbf{S}_i \times \mathbf{S}_j]$. The Dzyaloshinskii vector $\mathbf{D}_{ij}$ is proportional to the spin-orbit coupling constant λ and the displacement of the O^{2-} ligand, $\mathbf{D}_{ij} \propto \lambda \mathbf{x} \times \mathbf{r}_{ij}$. After Cheong and Mostovoy (2007).¹⁵

The second term, which has the form of a ferromagnetic exchange interaction, is the so-called exchange-striction term. In a magnetically ordered phase, this will cause the crystal structure to deform, potentially producing a local polarisation. For certain spin arrangements, the magnetic ions may displace uniformly, giving rise to a net polarisation. We note that this term can give rise to ferroelectricity even in a collinear magnetic structure, such as that in the orthomanganites HoMnO_3 ⁶⁹ and TmMnO_3 ,⁷⁰ and does not depend on the spin-orbit interaction

⁶⁸J Hu. *Phys. Rev. Lett.*, **100**: 077202, 2008.

⁶⁹S Picozzi et al. *Phys. Rev. Lett.*, **99**: 227201, 2007.

⁷⁰IA Sergienko, C Şen, and E Dagotto. *Phys. Rev. Lett.*, **97**: 227204, 2006.

The final term results from a spin-orbit-induced variation in the metal–ligand d – p hybridisation and can describe the magnetically induced polarisation resulting from some non-collinear magnetic order in triclinic, monoclinic and trigonal crystal structures.⁷¹ In contrast to the inverse DM interaction, which only gives a polarisation for a cycloidal magnetic structure, the d – p hybridisation term can produce a polarisation for a proper-screw (helical) magnetic structure. This mechanism successfully describes the magnetically induced ferroelectricity in delafossite compounds such as CuFeO_2 ⁷² and CuCrO_2 .⁷³

1.4 Domains

An important consequence of the lowering of point-group symmetry at a ferroic phase transition is that the ferroic phase must have two or more *domains*. At the phase transition, domains are nucleated throughout the material, a process that locally breaks certain symmetry operations of the parent phase. These symmetry operations may be broken in two or more different directions, resulting in homogeneous regions of the material all with the same crystal and/or magnetic structure but different orientations, chiralities and/or locations. These domains, along with the interfaces between them, known as *domain walls*, constitute the domain structure of a material.

The expected number of ferroic domains and how they are related to one another can be determined by considering the symmetry groups of the ferroic and parent, or ‘prototype’, phases. If $\mathbf{G}$ and $\mathbf{H}$ denote the symmetry groups of the prototype and ferroic phases, respectively, then the possible number of ferroic domain types is simply the ratio $|\mathbf{G}|/|\mathbf{H}|^*$. Furthermore, domains can be transformed into one another by the exact symmetry operations of the prototype phase that were broken at the phase transition. For example, consider the cubic-to-tetragonal phase transition in BaTiO_3 , which lowers the point group symmetry from $m\bar{3}m$ to $4mm$. This reduces the number of symmetry operators from 48 to 8, thus $48/8 = 6$ is the number of ferroelectric

⁷¹TH Arima. *J. Phys. Soc. Jpn*, **76**: 073702–073702, 2007.

⁷²T Kimura, JC Lashley, and AP Ramirez. *Phys. Rev. B*, **73**: 220401, 2006.

⁷³S Seki, Y Onose, and Y Tokura. *Phys. Rev. Lett.*, **101**: 067204, 2008.

*Here $|\mathbf{G}|$ denotes the order i.e. the number of symmetry operators, of the symmetry group $\mathbf{G}$.

domains in the tetragonal phase, corresponding to the polarisation lying along the $\pm x$, $\pm y$, and $\pm z$ directions. These can then be transformed into one another with the broken inversion, mirror, and 4-, 3- and 2-fold rotation operations of the cubic phase.

Domain control

Given that all domain variants of a ferroic phase are symmetry equivalent, a ferroic material will generally order with equal populations of all domain variants. This will often lead to a cancelling out effect, causing any ferroic properties to average to zero at the macroscopic level. It is, however, possible to lower the energy of certain domains relative to the others by applying an appropriate external field whilst cooling through the phase transition. This process, known as ‘poling’, biases the growth of certain domains, which can be used, for example, to force a ferroelectric material into a monodomain state by applying an electric field at the phase transition.

Applying external fields *within* the ferroic phase will have a similar effect in energetically biasing certain domains. However, in this case, it is the field-driven motion of domain walls, enlarging some certain domains and shrinking others, that will change the domain population. Thus, switching a ferroic material isothermally typically requires much larger fields than those required to pole the material. The energetics of the domain structure including domain wall dynamics, anisotropy, and the energy cost of any stray fields are the dominant factor in determining the hysteretic behaviour of ferroic materials.

EXPERIMENTAL TECHNIQUES

2.1 Introduction

ALTHOUGH multiferroic materials are in general characterised by the coexistence of magnetic and electric order parameters at the macroscopic level, it is essential to understand the fundamental physics that underpins these phenomena. To fully understand this behaviour requires probing materials on length scales spanning many orders of magnitude: from the macroscopic length scales of a device, all the way down to the electronic and atomic structure of the material.

The interaction of x-ray and neutron radiation with condensed matter systems provides such a probe. Their wavelengths are comparable to the interatomic distances in crystalline materials ($\sim 1 \text{ \AA}$), and thus interference effects can be readily exploited to reveal details of the microscopic structure. Both x-rays and neutrons are particularly appropriate for the study of multiferroics since they are sensitive not only to the structural changes associated with ferroelectric and ferroelastic phase transitions, but also to magnetic ordering via their magnetic component. These details can be probed either locally, or on average, over an entire device, simply by changing the geometry of the experiment. Furthermore, the ability to finely-tune the nature of the radiation-matter interaction by altering the incident energy and polarisation, combined with spectral and polarisation analysis of the scattered radiation, makes these techniques exceptionally versatile.

In this chapter, I will outline the theory and application of the x-ray and neutron techniques used throughout this thesis. These primarily consist of magnetic diffraction and microscopy measurements. After introducing the basic concepts of diffraction, I will discuss the interaction between x-rays and neutrons with matter, and thus how these interactions determine the scattering cross-sections. Finally, x-ray photo-emission electron microscopy is discussed, a complementary technique that allows imaging of both ferromagnetic and antiferromagnetic domains with a resolution on the order of a few tens of nanometres.

2.2 Diffraction fundamentals

When x-ray or neutron radiation scatters from a crystalline material, the interaction with the periodic lattice causes interference effects, which, in certain geometries, give rise to sharp peaks in the scattered radiation. The positions and relative intensities of these peaks can then be used to deduce detailed information on the microscopic structure of the material. Figure 2.1 depicts a generic scattering experiment: x-rays or neutrons with wavevector $\mathbf{k}_i$ and energy $\hbar\omega_i$ are scattered by a crystalline sample into a state with final wavevector $\mathbf{k}_f$ and energy $\hbar\omega_f$. We can characterise this process by the associated change in wavevector, known as the *scattering vector*:*

$$\mathbf{K} = \mathbf{k}_f - \mathbf{k}_i. \quad (2.1)$$

Although in general, both elastic ($\hbar\omega_f - \hbar\omega_i = 0$) and inelastic ($\hbar\omega_f - \hbar\omega_i \neq 0$) scattering processes will occur, the dominant process is elastic, and for the diffraction experiments performed in this thesis, it can be assumed that the intensity due to inelastic scattering is negligible. In the elastic case, we have that $|\mathbf{k}_i| = |\mathbf{k}_f|$, and thus the scattering vector $\mathbf{K}$, is related to the scattering angle 2θ by

$$|\mathbf{K}| = \frac{4\pi \sin \theta}{\lambda}. \quad (2.2)$$

In a diffraction experiment, one measures the scattered intensity $I(\mathbf{K})$ as a function of scattering angle (and hence $\mathbf{K}$). To relate this to the properties of the crystal, it is necessary to consider the interaction potential between the radiation and the material. As shown later in this chapter, the rate of scattering for a given scattering vector (to which the intensity is proportional) is dependent upon the *Fourier transform* of this interaction potential:

$$W \propto \left| \int_{\text{material}} d\mathbf{r} e^{i\mathbf{K} \cdot \mathbf{r}} \mathcal{H}_{\text{int}}(\mathbf{r}) \right|^2 \delta(E_f - E_i), \quad (2.3)$$

*Here we adopt the crystallographers' convention for the sign of the momentum transfer. The momentum transferred to the sample is $\hbar\mathbf{k}_i - \hbar\mathbf{k}_f$.

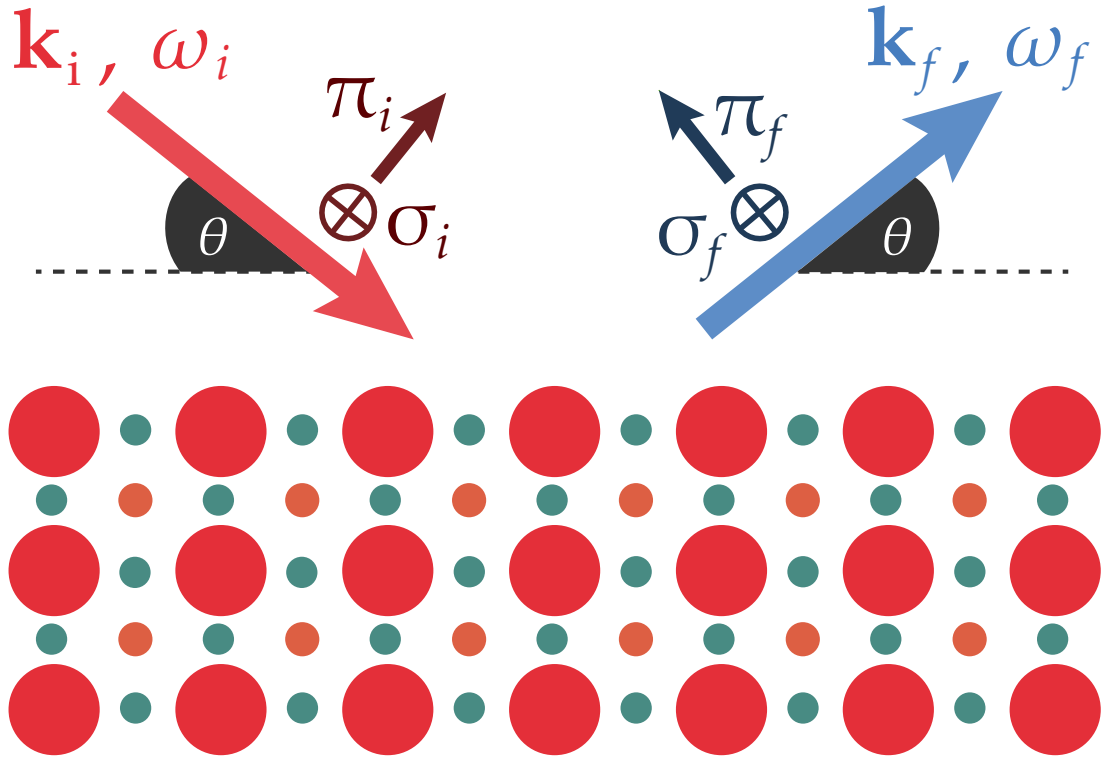


Figure 2.1: **Scattering of radiation from atomic planes in crystalline sample.** The incident (scattered) wavevector and angular frequency are denoted by $\mathbf{k}_i$ and ω_i ($\mathbf{k}_f$ and ω_f), respectively. The dashed lines are parallel to the atomic planes such that θ is half the scattering angle. For x-rays, the directions of the polarisation states σ and π are shown for incident and scattered beams.

where $\mathcal{H}_{\text{int}}$ is the interaction potential and the delta function ensures that energy is conserved. The initial (final) energy of the system is given by $E_i = \hbar\omega_i + E_a$ ($E_f = \hbar\omega_f + E_b$), where E_a (E_b) is the initial (final) energy of the material. Equation (2.3) is valid only in the *first Born approximation*,^{74,75} where the wavefunction calculation of the scattered radiation is expressed as an expansion in the interaction potential, and then only the first term is considered. This is only applicable if the potential can be considered in some sense ‘weak’ and is equivalent to stating that, apart from the change in wavevector, the plane-wave form of the incident radiation wavefunction is unchanged by the scattering process.

⁷⁴LD Landau and EM Lifshitz. *Quantum mechanics: Non-relativistic theory*. Pergamon, 1958.

⁷⁵M Born. *Z. Phys. A*, **38**: 803–827, 1926.

For crystalline materials, it is useful to re-express the general position as $\mathbf{r} = \mathbf{R}_m + \mathbf{x}$, where $\mathbf{R}_m$ is a lattice vector locating the origin of the m^{th} unit cell and $\mathbf{x}$ is a position within the unit cell. Substituting this into eq. (2.3) and using the periodicity of potential with the crystal lattice i.e. $\mathcal{H}_{\text{int}}(\mathbf{R}_m + \mathbf{x}) = \mathcal{H}_{\text{int}}(\mathbf{x})$, we obtain

$$W \propto \left| \overbrace{\left[\sum_m e^{i\mathbf{K} \cdot \mathbf{R}_m} \right]}^{\text{Bragg condition}} \overbrace{\left[\int_{\text{cell}} d\mathbf{x} e^{i\mathbf{K} \cdot \mathbf{x}} \mathcal{H}_{\text{int}}(\mathbf{x}) \right]}^{\text{Structure factor}} \right|^2 \delta(E_f - E_i). \quad (2.4)$$

The first term in square brackets depends only on the crystal lattice and its effect is to impose the diffraction or *Laue condition*. Due to the fact that the points $\mathbf{R}_m$ are evenly distributed in space, this term will in general sum to zero unless the terms add up coherently, thereby limiting the scattering vector to the set of vectors for which constructive interference will occur. The sum is non-zero if and only if

$$\mathbf{K} \cdot \mathbf{R}_m = 2\pi \times \text{integer}. \quad (2.5)$$

This is known as the Laue condition and defines the set of points known as the *reciprocal lattice*.

Consider a three-dimensional crystal whose real-space (direct) lattice is described by the set of vectors $\mathbf{R} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}$, where n_1, n_2 and n_3 are integers, and $\mathbf{a}, \mathbf{b}$ and $\mathbf{c}$ are the basis vectors of the lattice. We may define an associated reciprocal lattice, which consists of the set of vectors that satisfy the Laue condition. These *reciprocal lattice vectors* are given by

$$\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \quad (2.6)$$

where h, k and l are integers (commonly known as *Miller indices*), and $\mathbf{a}^*, \mathbf{b}^*$ and $\mathbf{c}^*$ are the basis vectors of the reciprocal lattice. These basis vectors form the dual basis of the direct lattice and are related to the direct basis as follows:

$$\mathbf{a}^* = \frac{2\pi \mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}, \quad \mathbf{b}^* = \frac{2\pi \mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}, \quad \mathbf{c}^* = \frac{2\pi \mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})}. \quad (2.7)$$

Thus for constructive interference occur, producing an isolated peak in the scattered intensity (known as *Bragg peaks*), we require the scattering vector to be equal to a reciprocal lattice vector i.e.

$$\mathbf{K} = \mathbf{G}. \quad (2.8)$$

This condition relates the points at which these peaks are observed to the real-space crystal lattice and can be shown to be equivalent⁷⁶ to the much celebrated Bragg's law,⁷⁷ given by

$$n\lambda = 2d \sin \theta \quad (2.9)$$

where n is an integer, λ is the wavelength of the incident radiation, and d is the spacing between the family of atomic planes associated with the corresponding diffraction peak. We may then write the first term in eq. (2.4) as a delta function:

$$\left| \sum_m e^{i\mathbf{K} \cdot \mathbf{R}_m} \right|^2 = \frac{(2\pi)^3}{V_{\text{cell}}} N_{\text{cell}} \delta^{(3)}(\mathbf{G} - \mathbf{K}), \quad (2.10)$$

where N_{cell} is the number of unit cells in the portion of the sample contributing to the scattering and the $(2\pi)^3 / V_{\text{cell}}$ prefactor arises from the delta function normalisation.⁷⁶

The second term in square brackets (of eq. (2.4)) is known as the (unit cell) *structure factor*. This depends on the ionic and electronic charge distribution *within* the unit cell and determines the relative intensities of the diffraction peaks. The structure factor $F(\mathbf{K})$ can be simplified by making the substitution $\mathbf{x} = \mathbf{x}_n + \mathbf{x}'$ where $\mathbf{x}_n$ is the position of an atom inside the unit cell and $\mathbf{x}'$ is position relative to this. Substituting this into the expression for the structure factor, we find

$$F(\mathbf{K}) = \sum_n^{\text{cell}} f_n(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{x}_n}, \quad (2.11)$$

⁷⁶J Als-Nielsen and D McMorrow. *Elements of modern X-ray physics*. John Wiley & Sons, 2011.

⁷⁷WH Bragg and WL Bragg. *P. Roy. Soc. A Math. Phys.*, **88**: 428–438, 1913.

where the atomic *form factor* $f_n(\mathbf{K})$ is given by

$$f_n(\mathbf{K}) = \int_{\text{atom}} d\mathbf{x}' e^{i\mathbf{K} \cdot \mathbf{x}'} \mathcal{H}_{\text{int}}(\mathbf{x}_n + \mathbf{x}'). \quad (2.12)$$

The form factors for x-rays and neutrons are very different. This is due to the distinct nature of their interactions with matter. X-rays mostly interact with the electron density and hence x-ray form factors increase with the number of electrons on each atom (or the atomic number). Neutrons on the other hand, interact almost exclusively with nuclei and their form factors depend on the nuclear properties of the atoms present in a material.*

The thermal motion of the atoms can also be taken into account by convolving the atomic positions with a function describing their spread of displacements due to thermal motion.⁷⁸ This will result in an extra multiplicative factor in the Fourier transform of $\mathcal{H}_{\text{int}}(\mathbf{r})$. This extra factor $T_n(\mathbf{K})$ is called the Debye-Waller factor^{79,80} and is given by:

$$T_n(\mathbf{K}) = \exp(\langle i(\mathbf{K} \cdot \mathbf{u}_n) \rangle), \quad (2.13)$$

where $\mathbf{u}_n$ is the displacement of the n^{th} atom. If the motion is isotropic and harmonic, the thermal motion will result in a Gaussian distribution of atomic displacements about the average position with a mean-squared value of $\langle u_n^2 \rangle$ and the Debye-Waller factor is then given by

$$T_n(\mathbf{K}) = \exp(-8\pi^2 \langle u_n^2 \rangle \sin^2 \theta / \lambda^2). \quad (2.14)$$

Including this term in the structure factor gives

$$F(\mathbf{K}) = \sum_n^{\text{cell}} f_n(\mathbf{K}) T_n(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{x}_n}, \quad (2.15)$$

*Though the dependence of neutron form factors on atomic number is much less systematic than for x-rays.

⁷⁸MT Dove. *Structure and dynamics: An atomic view of materials*. vol. 1 Oxford University Press, 2003.

⁷⁹P Debye. *Ann. Phys.*, **348**: 49–92, 1913.

⁸⁰I Waller. *Z. Phys. A*, **17**: 398–408, 1923.

which, along with eq. (2.10), we can finally substitute into eq. (2.4) to give a scattering rate

$$W \propto \frac{(2\pi)^3}{V_{\text{cell}}} N_{\text{cell}} \left| \sum_n^{\text{cell}} f_n(\mathbf{K}) T_n(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{x}_n} \right|^2 \delta^{(3)}(\mathbf{G} - \mathbf{K}) \delta(E_f - E_i). \quad (2.16)$$

In the following two sections we consider the interaction Hamiltonians for x-rays and neutrons with matter and how we can calculate the corresponding atomic form factors (and thus the relative peak intensities), in each case.

2.3 X-ray diffraction

In 1912, shortly after their discovery by Röntgen,⁸¹ von Laue and coworkers demonstrated the utility of x-rays as a probe of the structure of crystalline materials.⁸² The following year saw the development of Bragg's law,⁷⁷ laying the foundations of modern crystallography. Since then, x-ray diffraction has become an invaluable technique for studying the atomic structure of a vast range of compounds, ranging from relatively simple inorganic crystals up to complex proteins.^{83,84} These measurements rely on the leading term in the scattering cross section, that of Thomson scattering, which results from an interaction between the electric field of the x-rays and charge of the electrons. It was later shown, in a measurement of the antiferromagnet NiO by De Bergevin and Brunel in 1970,⁸⁵ that x-rays could also be used to study the *magnetic* structure of solids by exploiting a much weaker interaction between the x-ray magnetic field with electron spin. As is shown later in this section, this interaction gives rise to scattering approximately six orders of magnitude weaker than the charge component. This has been overcome with the advent of so-called third-generation synchrotron x-ray sources, which constitute a $\sim 10^{12}$ factor increase of intensity compared to early lab-based x-ray sources.⁷⁶ Furthermore, synchrotron sources allow

⁸¹WC Röntgen. *Science*, **3**: 227–231, 1896.

⁸²W Friedrich, P Knipping, and M Laue. *Ann. Phys.*, **346**: 971–988, 1913.

⁸³J Als-Nielsen and G Materlik. *Phys. Today*, **48**: 34–41, 1995.

⁸⁴WA Hendrickson. *Phys. Today*, **48**: 42–50, 1995.

⁸⁵F De Bergevin and M Brunel. *Phys. Lett. A*, **39**: 141–142, 1972.

the x-ray energy to be tuned to certain transitions within a compound, resulting in a resonant enhancement of the magnetic signal.^{86,87} These recent advances have brought magnetic x-ray scattering to the forefront as an established technique for studying magnetism in condensed matter systems.

2.3.1 Interaction of light with a collection of electrons

This section comprises an overview of the derivation of the x-ray scattering cross section, of which more rigorous theoretical treatments can be found in many textbooks^{76,88,89} and articles.^{90–93} Following the discussion by Blume,⁹¹ we shall first consider the interaction between electromagnetic radiation and a collection of electrons and then concentrate on the case of a periodic structure. Consider the non-relativistic Hamiltonian for a system of electrons interacting with a vector potential $\mathbf{A}$:

$$\begin{aligned} \mathcal{H} = & \underbrace{\sum_j \frac{1}{2m} \left[\mathbf{p}_j - \frac{e}{c} \mathbf{A}(\mathbf{r}_j) \right]^2}_{\text{Kinetic energy}} + \underbrace{\sum_{i>j} V(|\mathbf{r}_j - \mathbf{r}_i|)}_{\text{Coulomb interaction}} - \underbrace{\frac{e\hbar}{2mc} \sum_j \mathbf{s}_j \cdot [\nabla \times \mathbf{A}(\mathbf{r}_j)]}_{\text{Zeeman interaction}} \\ & - \underbrace{\frac{e\hbar}{2m^2c^2} \sum_j \mathbf{s}_j \cdot \left\{ \mathbf{E}(\mathbf{r}_j) \times \left[\mathbf{p}_j - \frac{e}{c} \mathbf{A}(\mathbf{r}_j) \right] \right\}}_{\text{Spin-orbit interaction}} + \mathcal{H}_{\text{rad}}, \end{aligned} \quad (2.17)$$

where $\sum_j$ sums over all electrons. The first four terms account for both electron–electron and electron–field interactions, and $\mathcal{H}_{\text{rad}}$ is the Hamiltonian describing the electromagnetic radiation

⁸⁶Kazumichi Namikawa et al. *J. Phys. Soc. Jpn*, **54**: 4099–4102, 1985.

⁸⁷Doon Gibbs et al. *Phys. Rev. Lett.*, **61**: 1241, 1988.

⁸⁸Y Waseda, E Matsubara, and K Shinoda. *X-ray diffraction crystallography*. Springer, 2011.

⁸⁹SW Lovesey and SP Collins. *X-ray scattering and absorption by magnetic materials*. OUP, 1996.

⁹⁰F De Bergevin and M Brunel. *Acta Crystallogr. A*, **37**: 314–324, 1981.

⁹¹M Blume. *J. Appl. Phys.*, **57**: 3615–3618, 1985.

⁹²M Blume and D Gibbs. *Phys. Rev. B*, **37**: 1779, 1988.

⁹³JP Hill and DF McMorrow. *Acta Crystallogr. A*, **52**: 236–244, 1996.

field. The first term is the total kinetic energy of the electrons^{*74} and the second term is the repulsive Coulomb interaction between pairs of electrons. The third term is the interaction of the electron's spin with the magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$. The fourth term describes the spin-orbit interaction between the spin of the electron and the magnetic field generated by the orbital motion of the electron due to the electric field.

In the spin-orbit term, we substitute the electric field for $\mathbf{E} = -\nabla\phi - \frac{\dot{\mathbf{A}}}{c}$, where ϕ is the Coulomb potential generated by the electrons. Here it is necessary to note that the vector potential is linear in the photon creation and annihilation operators $\hat{c}_u^\dagger(\mathbf{k})$ and $\hat{c}_u(\mathbf{k})$. Given that a scattering process requires the interaction Hamiltonian to contain terms that annihilate one photon and create another, the terms which are quadratic and linear in $\mathbf{A}$ will contribute as first- and second-order perturbations, respectively. Thus we neglect any spin-orbit terms that are linear in $\mathbf{A}$, as they will give rise to terms of order $(v/c)^4$ in the expression of the transition rate. The resultant Hamiltonian may then be decomposed into electron–electron interactions, $\mathcal{H}_0$, perturbations due to electron–field interactions, $\mathcal{H}'$, and the field-only component, $\mathcal{H}_{\text{rad}}$:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' + \mathcal{H}_{\text{rad}}, \quad (2.18)$$

where the electron–electron interactions (including the electron kinetic energy) are given by

$$\mathcal{H}_0 = \sum_j \frac{1}{2m} \mathbf{p}_j^2 + \sum_{i>j} V(|\mathbf{r}_j - \mathbf{r}_i|) - \frac{e\hbar}{2mc} \sum_j \mathbf{s}_j \cdot [\nabla\phi(\mathbf{r}_j) \times \mathbf{p}_j] \quad (2.19)$$

*It can be shown that replacing the momentum $\mathbf{p}$ with the canonical momentum $\mathbf{p} - \frac{e}{c}\mathbf{A}(\mathbf{r})$ in kinetic energy operator produces the correct equation of motion for an electron in an electromagnetic field.

and the electron–field interactions are given by

$$\mathcal{H}' = \underbrace{\frac{e^2}{2mc^2} \sum_j \mathbf{A}^2(\mathbf{r}_j) - \frac{eh}{2(mc)^2} \frac{e}{c^2} \sum_j \mathbf{s}_j \cdot [\dot{\mathbf{A}}(\mathbf{r}_j) \times \mathbf{A}(\mathbf{r}_j)]}_{\mathcal{H}'_1 \propto \mathbf{A}^2} - \underbrace{\frac{e}{mc} \sum_j \mathbf{p}_j \cdot \mathbf{A}(\mathbf{r}_j) - \frac{e\hbar}{2mc} \sum_j \mathbf{s}_j \cdot [\nabla \times \mathbf{A}(\mathbf{r}_j)]}_{\mathcal{H}'_2 \propto \mathbf{A}}. \quad (2.20)$$

The terms in $\mathcal{H}'$ have been grouped according to their dependence on the vector potential and thus which term in the perturbation expansion they will contribute to.

2.3.2 Calculating the x-ray scattering cross section

To calculate the scattering cross section, we consider the transition rate from an initial state $|a; \mathbf{k}_i, \hat{\mathbf{e}}_i\rangle$, describing the electron-cloud/photon system in which the electrons are in the collective state $|a\rangle$ and the photon has momentum $\hbar\mathbf{k}$ and polarisation $\hat{\mathbf{e}}_i$, to the final state $|b; \mathbf{k}_f, \hat{\mathbf{e}}_f\rangle$, in which the electrons are in the collective state $|b\rangle$ and the photon has momentum $\hbar\mathbf{k}_f$ and polarisation ρ_f . We then make the following two approximations: firstly, the kinematic (or Born) approximation,^{74,75} such that we may treat both the incident and outgoing light as plane waves (of the form $e^{i\mathbf{k}\cdot\mathbf{r}}$), and secondly that the x-rays constitute a *weak* probe of the electrons such that their interaction with them may be treated as a perturbation to the unperturbed states. The transition rate from the initial state $|a; \mathbf{k}_i, \hat{\mathbf{e}}_i\rangle$ to the final state $|b; \mathbf{k}_f, \hat{\mathbf{e}}_f\rangle$ is then given by Fermi's golden rule:

$$W = \frac{2\pi}{\hbar} \left| \langle b; \mathbf{k}_f, \hat{\mathbf{e}}_f | \mathcal{H}'_1 | a; \mathbf{k}_i, \hat{\mathbf{e}}_i \rangle + \sum_n \frac{\langle b; \mathbf{k}_f, \hat{\mathbf{e}}_f | \mathcal{H}'_2 | n \rangle \langle n | \mathcal{H}'_2 | a; \mathbf{k}_i, \hat{\mathbf{e}}_i \rangle}{E_a + \hbar\omega_i - E_n} \right|^2 g(\omega_f) \delta(E_f - E_i), \quad (2.21)$$

where $g(\omega_f)$ is the photon density of (final) states.

From the point of view of magnetic scattering, an important distinction is made between *nonresonant* and *resonant* scattering. In the nonresonant regime, where $\hbar\omega_i \gg E_a - E_n$, both the first-order and second-order terms in eq. (2.21) will give rise to scattered intensity due to interactions with the magnetic state of the electrons. In the resonant regime, the energy of the incident x-rays is tuned to that of an atomic transition such that $\hbar\omega_i \sim E_a - E_n$. This will minimise the denominator of the second-order term, leading to a large resonant enhancement of the magnetic scattering cross section, by up to eight orders of magnitude.⁹⁴

Nonresonant scattering

In nonresonant x-ray diffraction, the energy of the incident x-rays is tuned far from any atomic transitions, usually in energy ranges $\hbar\omega > 5\text{--}10\text{ keV}$. These so called ‘hard’ x-rays allow a large volume of reciprocal space to be accessed (see eq. (2.2)). As mentioned above, it is necessary to consider the contributions from both first- and second-order terms to calculate the nonresonant scattering cross section. Initially, considering just the first-order term in eq. (2.21), we can substitute in $\mathcal{H}'_1$ and evaluate the matrix elements to obtain a transition rate:

$$W^{(1)} = \frac{(2\pi)^3 \hbar c^4}{V^2 \omega^2} \left(\frac{e^2}{mc^2} \right)^2 \times \left[\left| \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} \right|^2 |\hat{\mathbf{e}}_f \cdot \hat{\mathbf{e}}_i|^2 + \left(\frac{\hbar\omega}{mc^2} \right)^2 \left| \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} \mathbf{s}_j \cdot \hat{\mathbf{e}}_f \times \hat{\mathbf{e}}_i \right|^2 \right] g(\omega_f) \delta(E_f - E_i), \quad (2.22)$$

⁹⁴J Fink et al. *Rep. Prog. Phys.*, **76**: 056502, 2013.

Then substituting in the photon density of states $g(\omega_f) = \frac{V}{(2\pi)^3} \frac{\omega_f^2}{\hbar c^3}$ and dividing by the incident flux $I_0 = c/V$, we obtain the (double) differential cross-section*:

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega dE_f} \right)^{(1)} &= \overbrace{r_0^2 \left| \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} \hat{\mathbf{e}}_f \cdot \hat{\mathbf{e}}_i \right|^2}^{\text{Thomson scattering}} \delta(E_f - E_i) \\ &+ \underbrace{r_0^2 \left(\frac{\hbar\omega}{mc^2} \right)^2 \left| \sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} \mathbf{s}_j \cdot \hat{\mathbf{e}}_f^* \times \hat{\mathbf{e}}_i \right|^2}_{\text{Magnetic scattering}} \delta(E_f - E_i) \end{aligned} \quad (2.23)$$

where $r_0 \equiv e^2/(mc^2)$ is the Thomson scattering length.

The first term here corresponds to the interaction of the electric-dipole field of the radiation with the charge of the electrons. Classically, this can be interpreted as an oscillation of the electrons by the electric field of the incident radiation, resulting in electromagnetic dipole radiation of the same wavelength i.e. the scattered beam. The scaling of Thomson scattering with the atomic number Z is contained in the $\sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j}$ term. This can be seen by decomposing this term into a sum over unit cells, atoms and electrons (as in section 2.2), which gives

$$\sum_j e^{i\mathbf{K} \cdot \mathbf{r}_j} \propto \sum_n^{\text{cell}} f_n^0(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{x}_n} \delta^{(3)}(\mathbf{G} - \mathbf{K}) \quad (2.24)$$

where the Thomson form factor is[†] $f_n^0(\mathbf{K}) = \int_{\text{atom}} d\mathbf{x}' e^{i\mathbf{K} \cdot \mathbf{x}'} n(\mathbf{x}') \propto Z_n$.

The *polarisation factor* $\hat{\mathbf{e}}_f^* \cdot \hat{\mathbf{e}}_i$ describes the polarisation of the scattered beam for a given incident polarisation. From the point of view of synchrotron experiments, where the incident x-rays are polarised in a particular direction, it is convenient to represent this factor as a matrix in a basis whose components are perpendicular (σ) and parallel (π) to the diffraction plane (see fig. 2.2) i.e.

*The ratio of the number of particles scattered into direction (θ, ϕ) with final energy E_f per unit solid angle per unit time per unit energy divided by incident flux.

[†]Here we have reexpressed the sum over the electrons around an atom as an integral over the electron density $n(\mathbf{x}')$.aw

$$\begin{bmatrix} \hat{\epsilon}_{\sigma \rightarrow \sigma} & \hat{\epsilon}_{\sigma \rightarrow \pi} \\ \hat{\epsilon}_{\pi \rightarrow \sigma} & \hat{\epsilon}_{\pi \rightarrow \pi} \end{bmatrix} \quad (2.25)$$

where $\hat{\epsilon}_{\sigma \rightarrow \pi}$ means the polarisation state of the incident x-ray photon $\hat{\epsilon}_i$ is σ , and the polarisation state of the scattered photon is $\hat{\epsilon}_f$ is π . Thus we can write the polarisation factor as

$$\hat{\epsilon}_f \cdot \hat{\epsilon}_i = \begin{bmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{bmatrix}. \quad (2.26)$$

It is important to note that this matrix being diagonal means that Thomson scattering cannot give rise to any $\sigma \rightarrow \pi$ or $\pi \rightarrow \sigma$ rotation of the polarisation of the incident beam. Furthermore, the $\cos 2\theta$ dependence the $\hat{\epsilon}_{\pi \rightarrow \pi}$ channel means that, for π -polarised incident x-rays, the intensity at a scattering angle of $2\theta = 90^\circ$ will be zero. As discussed in section 3.3.1, this behaviour can be utilised in polarisation analyser crystals to filter out all but a single linear polarisation channel of the scattered beam.

The second term in eq. (2.23) is the first-order contribution to the magnetic scattering. Here we note that the constant factor $\left(\frac{\hbar\omega}{mc^2}\right)^2$ gives the intensity ratio of nonresonant magnetic scattering to charge scattering. It is also necessary to include the ratio of magnetic (N_m) to nonmagnetic (N) electrons* and the ratio of the magnetic (f_m) and charge (f) form factors†. The intensity ratio is therefore given by⁹¹

$$\frac{I_{\text{Magnetic}}}{I_{\text{Thomson}}} \approx \frac{N_m}{N} \left(\frac{\hbar\omega}{mc^2}\right)^2 \frac{f_m^2}{f^2} \sim 10^{-6}, \quad (2.27)$$

where the 10^{-6} factor has been calculated for Fe with $\hbar\omega = 10 \text{ keV}$, but it is typical of non-resonant magnetic signals in general.⁸⁹ Thus, it is usually only possible to measure antiferromagnetic or rotating (incommensurate) magnetic structures, which give rise to magnetic diffraction

*Only unpaired electrons contribute to the magnetic scattering whereas all electrons contribute to charge scattering.

†The magnetic form factor of an atom falls off faster than the corresponding charge form factor as the magnetisation density is more spatially diffuse than the charge density.

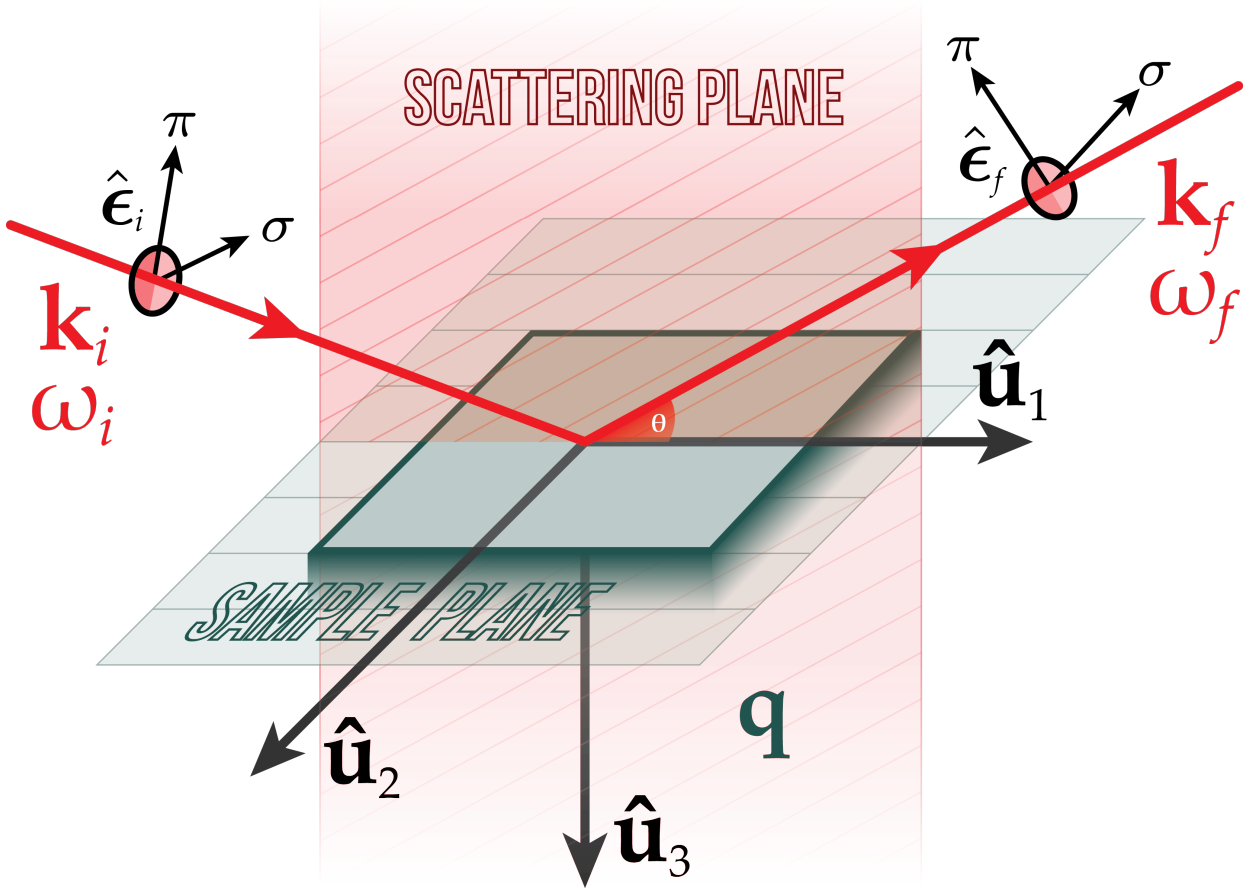


Figure 2.2: **Scattering geometry of an x-ray diffraction experiment.** $\mathbf{k}_i$ and $\mathbf{k}_f$ are the incident and scattered x-ray wavevectors, respectively and θ is half the scattering angle. The incident (final) polarisation state is given by $\hat{\epsilon}_i$ ($\hat{\epsilon}_f$) and the components of the polarisation perpendicular and parallel to the scattering plane are denoted by σ and π , respectively. The vectors $\mathbf{u}_1$, $\mathbf{u}_2$ and $\mathbf{u}_3$ define a useful basis in which magnetic structure factor calculations can be carried out.

peaks at points in reciprocal space where charge scattering is not present. As discussed in the following section, it is also possible to exploit differences in the polarisation of x-rays arising from charge and magnetic scattering processes to separate the two components.

To calculate the full nonresonant magnetic scattering differential cross section, we must also consider the second-order terms in eq. (2.21). Substituting in $\mathcal{H}'_2$ and evaluating the commutators,

it can be shown that the total magnetic differential cross section is given by⁹¹

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{\text{NXMS}} = r_0^2 \left(\frac{\hbar\omega}{mc^2} \right)^2 \overbrace{\left| \sum_j e^{i\mathbf{K}\cdot\mathbf{r}_j} \left[\mathbf{s}_j \cdot \mathbf{P}_S + \frac{i\mathbf{K} \times \mathbf{p}_j}{\hbar k^2} \cdot (\hat{\mathbf{e}}_f^* \times \hat{\mathbf{e}}_i) \right] \right|^2}^{\text{Magnetic structure factor}} \delta(E_f - E_i) \quad (2.28)$$

where $\mathbf{P}_S = \hat{\mathbf{e}}_f^* \times \hat{\mathbf{e}}_i + (\hat{\mathbf{k}}_f \times \hat{\mathbf{e}}_f^*)(\hat{\mathbf{k}}_f \cdot \hat{\mathbf{e}}_i) - (\hat{\mathbf{k}}_i \times \hat{\mathbf{e}}_i)(\hat{\mathbf{k}}_i \cdot \hat{\mathbf{e}}_f^*) - (\hat{\mathbf{k}}_f \times \hat{\mathbf{e}}_f^*)(\hat{\mathbf{k}}_i \times \hat{\mathbf{e}}_i)$. The magnetic structure factor $M(\mathbf{K})$ can then be written explicitly in terms of the Fourier transforms of the electron spin magnetisation $\mathbf{S}(\mathbf{K})$ and the atomic orbital magnetisation $\mathbf{L}(\mathbf{K})$:

$$M(\mathbf{K}) = [\mathbf{S}(\mathbf{K}) \cdot \mathbf{P}_S + \mathbf{L}(\mathbf{K}) \cdot \mathbf{P}_L] \quad (2.29)$$

where $\mathbf{P}_S$ and $\mathbf{P}_L$ are the orbital and spin polarisation factors, respectively. $\mathbf{P}_S$ is given above and $\mathbf{P}_L = -\hat{\mathbf{K}} \times [(\hat{\mathbf{e}}_f^* \times \hat{\mathbf{e}}_i) \times \hat{\mathbf{K}}] 2 \sin^2 \theta$. The Fourier transforms of the spin and orbital magnetisation are defined by:

$$\begin{aligned} \mathbf{S}(\mathbf{K}) &= \int e^{i\mathbf{K}\cdot\mathbf{r}} \mathbf{S}(\mathbf{r}) d\mathbf{r} = \sum_n e^{i\mathbf{K}\cdot\mathbf{r}_n} f_n^S(\mathbf{K}) \mathbf{s}_n \\ \mathbf{L}(\mathbf{K}) &= \int e^{i\mathbf{K}\cdot\mathbf{r}} \mathbf{L}(\mathbf{r}) d\mathbf{r} = \sum_n e^{i\mathbf{K}\cdot\mathbf{r}_n} f_n^L(\mathbf{K}) \mathbf{l}_n \end{aligned} \quad (2.30)$$

where $\mathbf{S}(\mathbf{r})$ is the spin magnetisation, $f_n^{(s)}(\mathbf{K})$ and $\mathbf{s}_n$ are the spin magnetic form factor and spin angular momentum of the n^{th} atom, respectively, and $\mathbf{L}(\mathbf{r})$, $f_n^{(l)}(\mathbf{K})$ and $\mathbf{l}_n$ are the corresponding quantities relating to the orbital magnetisation. Equivalent to the Thomson scattering calculation, the polarisation factors may be conveniently expressed in the σ - π basis:

$$\mathbf{P}_L = \frac{K^2}{2k^2} \begin{bmatrix} 0 & -(\hat{\mathbf{k}} + \hat{\mathbf{k}}') \\ \hat{\mathbf{k}} + \hat{\mathbf{k}}' & 2\hat{\mathbf{k}} \times \hat{\mathbf{k}}' \end{bmatrix}, \quad \mathbf{P}_S = \begin{bmatrix} \hat{\mathbf{k}} \times \hat{\mathbf{k}}' & -\hat{\mathbf{k}}'(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}') \\ -\hat{\mathbf{k}}(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}') & \hat{\mathbf{k}} \times \hat{\mathbf{k}}' \end{bmatrix} \quad (2.31)$$

*Note that these sums $\sum_n$ now sum over all the atoms in the material, rather than the electrons.

The full magnetic structure factor is then given by

$$M(\mathbf{K}) = \begin{bmatrix} \sin(2\theta)S_2 & -2\sin^2(\theta)[\cos(\theta)(L_1 + S_1) - \sin(\theta)S_3] \\ 2\sin^2(\theta)[\cos(\theta)(L_1 + S_1) + \sin(\theta)S_3] & \sin(2\theta)[2\sin^2(\theta)L_2 + S_2] \end{bmatrix} \quad (2.32)$$

where S_i (L_i) are the components of the spin (orbital) structure factor in the $\mathbf{u}_i$ basis (fig. 2.2).

The complex polarisation dependence of the magnetic scattering is an extremely useful property for several reasons. Firstly, we note that, unlike for Thomson scattering, there are off-diagonal elements in this matrix. Thus, measuring intensity in the $\hat{\mathbf{e}}_{\sigma \rightarrow \pi}$ and $\hat{\mathbf{e}}_{\pi \rightarrow \sigma}$ channels is one method that can be used to isolate the magnetic signal from the much brighter charge scattering. Secondly, we note that the diagonal elements of this matrix depend only on the magnetisation oriented perpendicular to the scattering plane, while the off-diagonal elements depend on the magnetisation oriented within the diffraction plane. This directional dependence allows, with the correct experimental geometry, the full magnetic structure of a material to be solved. Finally, the differing polarisation dependencies of the spin and orbital components allows their relative contributions to the magnetisation to be determined.⁹⁵

Resonant x-ray scattering

In resonant x-ray scattering, the incident x-ray energy is deliberately tuned to an atomic transition energy within the material and hence is in the so called ‘soft’ range, $\hbar\omega < 5\text{--}10$ keV. This excites virtual transitions of absorbing electrons, which strongly enhances the intensity of both charge and magnetic scattering. This resonant enhancement comes with another important advantage, of ‘element-specific’ measurements: given that the transition energies are unique to each atomic species in a material, the incident energy may be tuned to isolate the magnetism associated with a single species of atom. One limiting factor of resonant scattering is that, due to the low energies involved (on the order of ~ 100 eV), only a small region of reciprocal space is accessible.

The effect of the resonant enhancement on the differential scattering cross section is made

⁹⁵D Gibbs et al. *Phys. Rev. B*, **43**: 5663, 1991.

most clear when it is written in terms of *scattering amplitudes*. If we denote the total coherent elastic scattering amplitude of the n^{th} ion in a material, then the differential cross section is given by

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{\text{RXMS}} = \left| \sum_n a_n(\mathbf{K}) T_n(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{r}_n} \right|^2 \delta(E_f - E_i) \quad (2.33)$$

We can express the scattering amplitude as a sum of four components:⁹⁶

$$a_n = \underbrace{a_n^0 + a_n^{\text{spin}}}_{\propto W^{(1)}} + \underbrace{a'_n + ia''_n}_{\propto W^{(2)}} \quad (2.34)$$

where the former and latter pairs of terms correspond to processes described by first- and second-order terms in Fermi's golden rule (eq. (2.21)), respectively. $a_n^0 = r_0 f_n^0$ is the Thomson scattering amplitude and a^{spin} is the nonresonant magnetic scattering amplitude (associated with the second term in eq. (2.23)). The scattering amplitudes a' and a'' correspond to the resonant, second-order terms in eq. (2.21), which describe dispersive and absorptive scattering processes. As discussed in the previous section, in the nonresonant regime, scattering associated with these two terms and with a^{spin} results in a total magnetic scattering amplitude of $a_n^{\text{mag}} = ir_0(\hbar\omega/mc^2)M_n(\mathbf{K})$, where M_n is the magnetic structure factor of the n^{th} ion. In the resonant condition however, these terms are resonantly enhanced by electric and magnetic multiple transitions. In fact, it is the *electric* multipole transitions that are the dominant processes and thus resonant x-ray scattering could be considered an 'indirect' probe of the magnetic structure.⁹⁶

The resonant scattering amplitude, calculated for a dipole–dipole transition is given by⁹³

$$f_j^{\text{res}} = (\hat{\mathbf{e}}_f^* \cdot \hat{\mathbf{e}}_i) F^{(0)} - i(\hat{\mathbf{e}}_f^* \times \hat{\mathbf{e}}_i) \cdot \hat{\boldsymbol{\mu}}_j F^{(1)} + (\hat{\mathbf{e}}_f^* \cdot \hat{\boldsymbol{\mu}}_j)(\hat{\mathbf{e}}_i \cdot \hat{\boldsymbol{\mu}}_j) F^{(2)}, \quad (2.35)$$

where $F^{(0)}$, $F^{(1)}$ and $F^{(2)}$ are constants determined by the atomic properties and specific transition(s) excited by the x-ray photon [defined in Hill and McMorro (1996)⁹³]. The first term in

⁹⁶JP Hannon et al. *Phys. Rev. Lett.*, **61**: 1245, 1988.

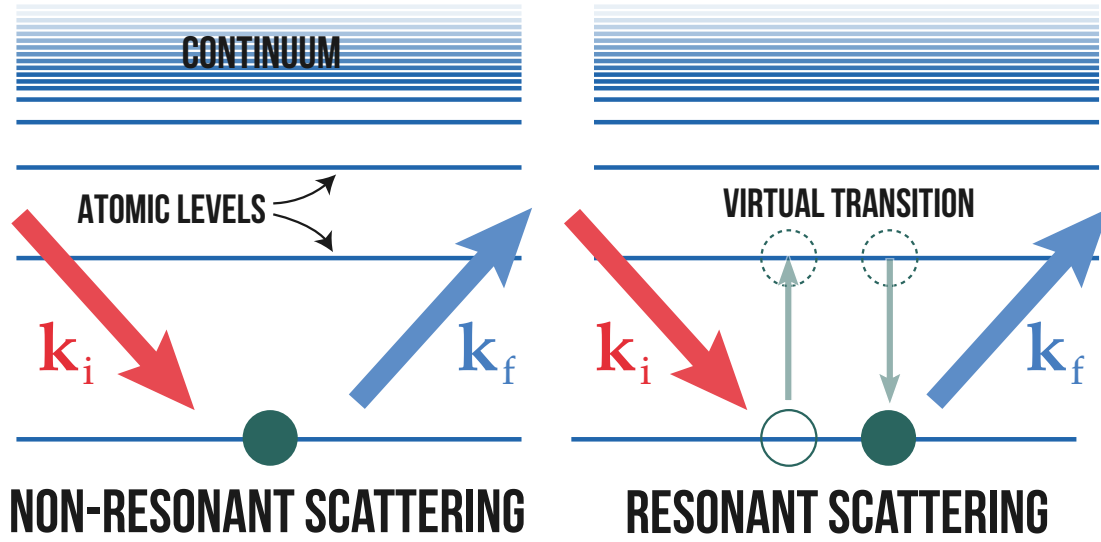


Figure 2.3: **The difference between nonresonant and resonant x-ray scattering.** In nonresonant scattering, the electron oscillates in response to the electric field of the incident x-ray and emits light of the same frequency and polarisation. In resonant scattering however, the electron makes a virtual transition to and from a higher atomic level, radiating an x-ray as it relaxes to the ground state. After Als-Nielsen and McMorro (2011).⁷⁶

eq. (2.35) has no dependence on the magnetic moment and thus contributes only to the charge scattering at the Bragg positions. The second and third terms produce the first and second harmonics of the magnetic satellites, respectively. The full magnetic structure factor is then:

$$M(\mathbf{K}) = \sum_n e^{i\mathbf{K} \cdot \mathbf{r}_n} \left\{ F^{(0)} \begin{bmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{bmatrix} - iF^{(1)} \begin{bmatrix} 0 & z_1 \cos \theta + z_3 \sin \theta \\ z_3 \sin \theta - z_1 \cos \theta & -z_2 \sin 2\theta \end{bmatrix} + F^{(2)} \begin{bmatrix} z_2^2 & -z_2(z_1 \sin \theta - z_3 \cos \theta) \\ z_2(z_1 \sin \theta + z_3 \cos \theta) & -\cos^2(z_1^2 \tan^2 \theta + z_3^2) \end{bmatrix} \right\} \quad (2.36)$$

Given that the second harmonic satellites tend to be significantly weaker,⁹⁷ it is usually only the first two terms of this equation that are of interest. Similar to the nonresonant structure factor (eq. (2.32)), the complex polarisation dependence allows the full magnetic structure to be

⁹⁷G Helgesen et al. *Phys. Rev. B*, 52: 9446, 1995.

reconstructed from a resonant scattering measurement. Although, in this case, it is not possible to extricate the spin and orbital components of the magnetic moment (one of the major advantages of nonresonant over resonant x-ray scattering).

Thus in general, the differential cross section for magnetic scattering can be written

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{\text{Magnetic}} \propto \left| \sum_j^{\text{cell}} a_n^{\text{mag}}(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{x}_n} T_n(\mathbf{K}) \right|^2 |\hat{\epsilon} \cdot \hat{\epsilon}'|^2 \delta^{(3)}(\mathbf{G}_M - \mathbf{K}) \delta(E), \quad (2.37)$$

where a_n^{mag} is the appropriate scattering amplitude (either resonant or nonresonant) and we have decomposed the sum over atoms as in section 2.2 to obtain the Laue condition. $\mathbf{G}_M$ is a reciprocal lattice vector of the magnetic structure, which can be related to the crystal structure reciprocal lattice by $\mathbf{G}_M = \mathbf{G} \pm \boldsymbol{\tau}$, where $\boldsymbol{\tau}$ is the propagation vector of the magnetic structure.*

2.4 Neutron diffraction

Neutrons were discovered in an experiment by Chadwick in 1932⁹⁸ in which he showed they were chargeless particles with a mass approximately equal to that of a proton. Thus, neutrons with energies in the thermal range (~ 25 meV) have a wavelength given by the de Broglie relationship:

$$\lambda_n = \frac{h}{m_n v} \sim 1.8 \text{ \AA}, \quad (2.38)$$

which is comparable to the interatomic spacing in crystalline materials. The potential of neutrons as a diffraction probe was first realised in 1945–1946 by Wollan and Shull⁹⁹ at Oak Ridge National Laboratory. Neutron diffraction has since become an invaluable technique for studying both the

*In the case of a higher harmonic magnetic satellite the reciprocal lattice vector would be $\mathbf{G}_M = \mathbf{G} \pm n\boldsymbol{\tau}$, where n is the degree of harmonic.

⁹⁸J Chadwick. *Nature*, **129**: 312, 1932.

⁹⁹CG Shull. *Rev. Mod. Phys.*, **67**: 753, 1995.

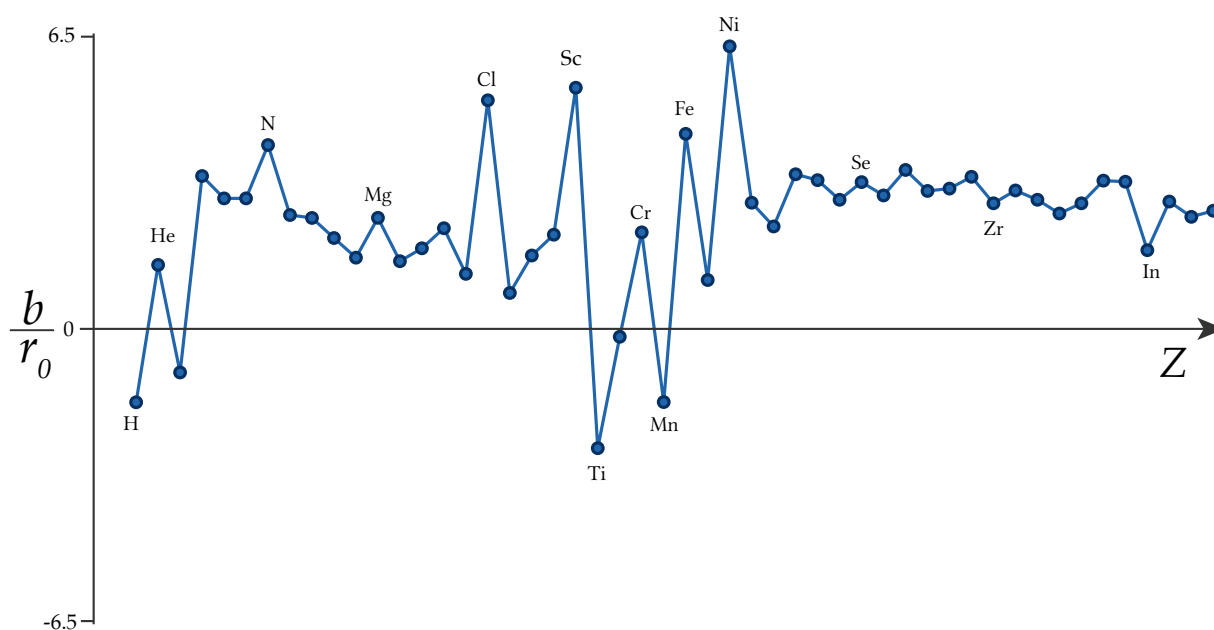


Figure 2.4: **Variation of neutron scattering lengths by element.** The real part of the (bound) coherent scattering lengths of the first 50 elements in the periodic table given in units of the Thomson scattering length. Only the scattering length of the most abundant isotope is plotted. Data taken from Sears (1992).¹⁰¹

crystal and magnetic structure of materials.¹⁰⁰

Although they have some overlap, neutron and x-ray scattering can be seen as complementary techniques, each bringing certain advantages depending on the experimental details. Since x-rays scatter from the electrons in a material, the scattering amplitude is proportional to the atomic number, making light elements very difficult to detect. Neutrons, on the other hand, readily scatter from light elements because (nonmagnetic) scattering of neutrons is due to scattering from *nucleii* via the strong force, the strength of which depends upon the *scattering length*. As shown in fig. 2.4, the scattering length varies rather erratically from element to element (and isotope to isotope) over the periodic table but is generally large enough to allow neutron diffraction measurements of compounds containing almost any element.¹⁰² This variation with element offers a further advantage over x-rays, as it allows neighbouring elements (of similar

¹⁰⁰GE Bacon. *X-ray and neutron diffraction*. Pergamon, 1966.

¹⁰²DS Sivia. *Elementary scattering theory: For X-ray and neutron users*. Oxford University Press, 2011.

atomic number) to be distinguished with a much higher sensitivity. Although the cross-section for charge scattering of x-rays and neutrons are similar (see fig. 2.4), the absorption cross-section for neutrons is much lower*. Therefore another advantage is that neutrons will likely have a penetration depth much larger than the sample dimensions, allowing the entire sample to be measured simultaneously. One major disadvantage of neutron diffraction is the requirement for much larger samples than are needed for x-ray diffraction due there being only relatively low flux available at neutron facilities¹⁰³.

Neutrons can also be used to study the *magnetic* state of a material through interactions between the unpaired electrons in the material with the neutron's intrinsic magnetic moment

$$\mu_n = -\gamma\mu_N\sigma \quad (2.39)$$

where the gyromagnetic ratio $\gamma = 1.913$, the nuclear magneton is given by $\mu_N = e\hbar/2m_p$ and σ is the Pauli spin operator. Importantly, the intensity of this magnetic scattering is of comparable size to that of the nuclear scattering.¹⁰⁴ It is for this reason that neutrons have traditionally been used over x-rays in the study of magnetic materials, although this is becoming less true with continuing advances in modern x-ray techniques. The first successful application of magnetic neutron scattering was achieved by Shull and Smart in 1949,¹⁰⁵ where their measurements of MnO also constituted the first experimental evidence of antiferromagnetism. The use of *polarised* neutrons as an even more sensitive probe of the magnetic structure was later demonstrated, also by Shull and coworkers.¹⁰⁶

* Although the strong force is a very strong interaction, it is very short ranged (acting over $\sim 10^{-14}$ m) and thus the probability of interaction is low.

¹⁰³T Chatterji. *Neutron scattering from magnetic materials*. Gulf Professional Publishing, 2005.

¹⁰⁴GL Squires. *Introduction to the theory of thermal neutron scattering*. Cambridge university press, 2012.

¹⁰⁵CG Shull and JS Smart. *Phys. Rev.*, **76**: 1256, 1949.

¹⁰⁶R Nathans et al. *J. Phy. Chem. Solids*, **10**: 138–146, 1959.

2.4.1 Calculating the neutron scattering cross section

As discussed in the previous section, the interaction of neutrons with a crystalline solid is very different to that of x-rays. In the differential cross sections, these differences are contained mainly in the form factors, but also in the polarisation dependence^{107,108*}.

Nuclear scattering

The strength of the neutron–nuclei interaction results means that, for nuclear scattering of thermal neutrons, the Born approximation is invalid. This can be overcome, however, through a clever ‘trick’ proposed by Fermi,^{109,110} in which the interaction potential is replaced by fictitious one that is suitably weak (such that the Born approximation is valid) but that reproduces correctly the scattered wavefunction calculation to first order. We are then able to use the same formalism as was employed for x-rays in section 2.3.2 and calculate the rate of scattering from Fermi’s golden rule. Given that the neutron–nuclei interactions are extremely short-ranged relative to the long de Broglie wavelength of neutrons, the interaction potential is approximated by a delta function in the Fermi pseudo-potential:¹⁰⁴

$$\mathcal{H}_{\text{Nuclear}}(\mathbf{r}) = \frac{2\pi\hbar^2}{m} \sum_j b_n \delta^{(3)}(\mathbf{r} - \mathbf{r}_n), \quad (2.40)$$

where m is the mass of the neutron and b_n is the scattering length of the n^{th} nucleus. Substituting this into eq. (2.12) gives the simple result

$$f_j = (2\pi\hbar^2/m)b_j, \quad (2.41)$$

¹⁰⁷M Blume. *Phys. Rev.*, **130**: 1670, 1963.

¹⁰⁸F Tasset. *Physica B*, **297**: 1–8, 2001.

*The cross sections for scattering of polarised neutrons and their derivations can be found in Blume (1963)¹⁰⁷ and Tasset (2001)¹⁰⁸ but I will not discuss them further here.

¹⁰⁹Enrico Fermi et al. *Ric. Sci.*, **7**: 13–52, 1936.

¹¹⁰G Breit. *Phys. Rev.*, **71**: 215, 1947.

where we have assumed the incident and final neutron beams can be described as plane waves. The differential cross section for nuclear scattering of neutrons is then given by

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{\text{Nuclear}} = N_{\text{cell}} \frac{(2\pi)^3}{V} \left| \sum_n^{\text{cell}} b_n e^{i\mathbf{K} \cdot \mathbf{x}_n} T_n(\mathbf{K}) \right|^2 \delta^{(3)}(\mathbf{G} - \mathbf{K}) \delta(E_f - E_i), \quad (2.42)$$

where b_n is the scattering length of the n^{th} nucleus in the unit cell.

Magnetic scattering

The magnetic interaction between the magnetic moment of the neutron μ_n and the magnetic field produced by the unpaired electrons in the material $\mathbf{B}(\mathbf{r})$ is given by

$$\mathcal{H}_{\text{Magnetic}}(\mathbf{r}) = -\mu_n \cdot \mathbf{B}(\mathbf{r}). \quad (2.43)$$

If electron has a magnetic moment $\mu_e = -2\mu_B \mathbf{s}$, the magnetic field at a distance $\mathbf{d} = \mathbf{r} - \mathbf{r}_j$ from the j^{th} electron is given by

$$\mathbf{B}(\mathbf{r}) = \overbrace{\frac{\mu_0}{4\pi d^2} \sum_j \left(\nabla \times \mu_{e,j} \times \hat{\mathbf{d}} \right)}^{\mathbf{B}_S(\mathbf{r})} - \overbrace{\frac{\mu_0}{4\pi d^2} \sum_j \left(\frac{2\mu_B}{\hbar} \mathbf{p} \times \hat{\mathbf{d}} \right)}^{\mathbf{B}_L(\mathbf{r})} \quad (2.44)$$

where $\mathbf{B}_S(\mathbf{r})$ and $\mathbf{B}_L(\mathbf{r})$ are the contributions to field resulting from the spin and orbital motion of the electrons, respectively. By substituting eqs. (2.43) and (2.44) into Fermi's golden rule we can calculate the differential cross section:

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{\text{Magnetic}} = \left(\frac{\gamma r_e}{2\mu_B} \right)^2 |\mathbf{M}_{\perp}(\mathbf{Q})|^2 \delta(E_f - E_i), \quad (2.45)$$

where $r_e = \mu_0 e^2 / (4\pi m_m r m e)$ is the classical electron radius and the *magnetic interaction vector* $\mathbf{M}_{\perp}(\mathbf{Q})$ is defined as the component of the magnetic structure factor i.e. the Fourier transform of the magnetisation, perpendicular to the scattering plane, such that $\mathbf{M}_{\perp} = \hat{\mathbf{K}} \times [\mathbf{M}(\mathbf{Q}) \times \hat{\mathbf{K}}]$.

In the dipole approximation this may be written in the familiar form:

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{\text{Magnetic}} = N_{\text{cell}} \frac{(2\pi)^3}{V} \left(\frac{\gamma r_e}{2\mu_B} \right)^2 \left| \sum_n^{\text{cell}} f_n \boldsymbol{\mu}_n e^{i\mathbf{K} \cdot \mathbf{x}_n} T_n(\mathbf{K}) \right|^2 \delta^{(3)}(\mathbf{G} - \mathbf{K}) \delta(E_f - E_i), \quad (2.46)$$

where $\boldsymbol{\mu}_n$ and f_n are the effective magnetic moment and magnetic form factor of the n^{th} atom in the unit cell, respectively.

2.5 X-ray photoemission electron microscopy

Photoemission electron microscopy (PEEM) is a powerful imaging technique employed across a wide range of fields, from materials science to biology. Modern x-ray PEEM allows differences in absorption properties to be imaged over the surface of a material with a resolution on the order of 10 nm. PEEM is an indirect probe of the absorption coefficient as it does not directly measure photoelectrons resulting from the absorption of the x-ray photon, but rather the *Auger* electrons emitted during the relaxation process that follows. As shown in fig. 2.5, when an atom absorbs a resonant x-ray photon, the following relaxation process to fill the core hole may either emit an x-ray photon (fluorescent x-ray emission*) or eject a higher-level electron (Auger electron emission¹¹¹). The ratio between rates of fluorescence and Auger yields varies depends upon the atomic species present in the material, the dominant process being Auger emission for lighter elements ($Z \lesssim 50$) and fluorescence for heavier elements.¹¹² The number of Auger electrons emitted is proportional to the number of x-ray photons absorbed (or alternatively, the absorption coefficient σ_A), and thus can be used to probe the properties of states involved in the x-ray absorption process.¹¹³ This can be used to study the structural, chemical and importantly, magnetic, properties of a material surface at the nanoscale.

*This process is similar to resonant x-ray magnetic scattering (see fig. 2.3), although in that case, the transition is *virtual*.

¹¹¹P Auger. *Sur les rayons [beta] secondaires produits dans un gaz par des rayons x*. Gauthier-Villars, 1925.

¹¹²LC Feldman and JW Mayer. *Fundamentals of surface and thin film analysis*. Elsevier, 1986.

¹¹³JC Vickerman and I Gilmore. *Surface analysis: The principal techniques*. John Wiley & Sons, 2011.

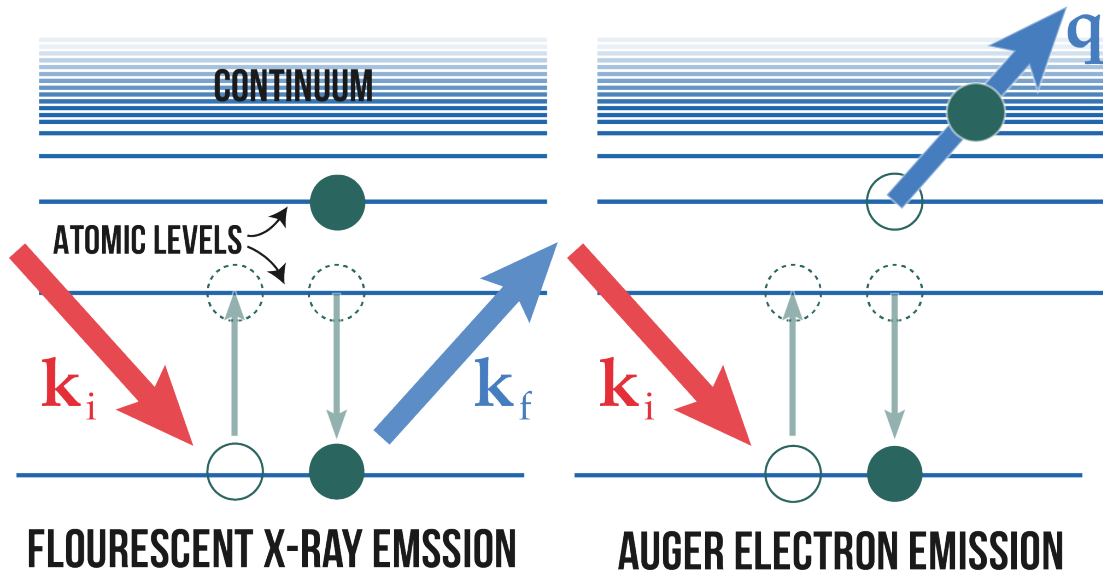


Figure 2.5: **X-ray fluorescence vs Auger electron emission.** There are two possibilities following the x-ray excitation of a core electron: fluorescent x-ray emission or Auger electron emission. In fluorescent emission, an outer-shell electron recombines with the core hole, producing an x-ray photon. *Auger* electron emission is where the energy released by the electron-hole recombination is transferred to another electron. This Auger electron is ejected from the atom with a kinetic energy ($\hbar^2 q^2 / (2m)$) equal to the difference between the energy of the initial relaxation process and the binding energy of the ejected electron. After Als-Nielsen and McMorro (2011).⁷⁶

The first working photoemission electron microscope was built by Brüche in 1932, where he used ultraviolet light to excite the electrons and was able to image the surface of a metal.^{114,115} x-ray PEEM was first demonstrated in 1988¹¹⁶ and shortly afterwards, Stöhr *et al.* observed the first high resolution images of magnetic domains using X-PEEM.¹¹⁷ In the latter experiment, contrast between magnetic domains was achieved by exploiting a phenomenon known as *dichroism*, which results in different absorption properties of magnetic domains for different x-ray polarisations. It is this dependence on the incident x-ray polarisation that allows magnetic domains to be differentiated and mapped over the surface of a magnetic material. Probing magnetic do-

¹¹⁴E Brüche. *Naturwissenschaften*, **20**: 49–49, 1932.

¹¹⁵E Brüche. *Z. Phys. A*, **86**: 448–450, 1933.

¹¹⁶BP Tonner and GR Harp. *Rev. Sci. Instrum.*, **59**: 853–858, 1988.

¹¹⁷J Stöhr *et al.* *Science*, 658–661, 1993.

mains with nanoscale resolution is ideal for studying multiferroic materials, many of which have features on this lengthscale, these being either the intrinsic domain structure or a fabricated device architecture. These measurements provide complementary information to the previously discussed x-ray and neutron techniques, which average over much larger length scales.

The following section comprises an overview of x-ray absorption cross-section calculations in the context of x-ray dichroism experiments, roughly following the treatment by Als-Nielsen and McMorow (2011).⁷⁶ The interested reader is also referred to the in-depth discussions covered in several other textbooks.^{89,118–120}

2.5.1 Calculating the x-ray absorption cross section

The relevant term of the x-ray–electron interaction Hamiltonian $\mathcal{H}$, (see eq. (2.17)) for photoelectric absorption by a single electron is:

$$\mathcal{H}_{\text{Absorption}} = \frac{e}{mc} \mathbf{p} \cdot \mathbf{A}, \quad (2.47)$$

where we have neglected any contributions from magnetic dipole transitions, as these are about 1–2 orders of magnitude smaller for typical x-ray edges.⁹⁶ As depicted in fig. 2.6, we consider an absorption process in which an x-ray photon in the state $|\mathbf{k}, \hat{\mathbf{e}}\rangle_\gamma$ is annihilated and a bound electron, with a binding energy E_b , is ejected into the continuum where it ends in the final state $|\mathbf{q}\rangle_e$ with a momentum $\mathbf{p} = \hbar\mathbf{q}$ and energy $E_f = \hbar^2 q^2 / (2m)$. We can then calculate the x-ray absorption cross section analogously to the calculation for x-ray scattering (see section 2.3.2), with three primary differences. Firstly, given that an absorption process requires the interaction Hamiltonian to contain terms that annihilate the incident photon, and remembering that the

¹¹⁸W Heitler. *The quantum theory of radiation*. Courier Corporation, 1954.

¹¹⁹DC Koningsberger and Roelof Prins. *X-ray absorption: Principles, applications, techniques of EXAFS, SEXAFS, and XANES*. John Wiley and Sons, New York, NY, 1988.

¹²⁰J Feng and A Scholl. “Photoemission electron microscopy (PEEM)” in: *Science of microscopy*. Springer, 2007.

vector potential is linear in the photon annihilation and creation operators, we see that this perturbation will contribute as a first-order perturbation*. Secondly, the process is not elastic as some of the photon energy will be lost to the electron binding energy, requiring an incident energy of $E_i = E_b + E_f$. Finally, the electron may be emitted in any direction and thus it is necessary to integrate the scattering rate over the entire solid angle of 4π steradians. We can

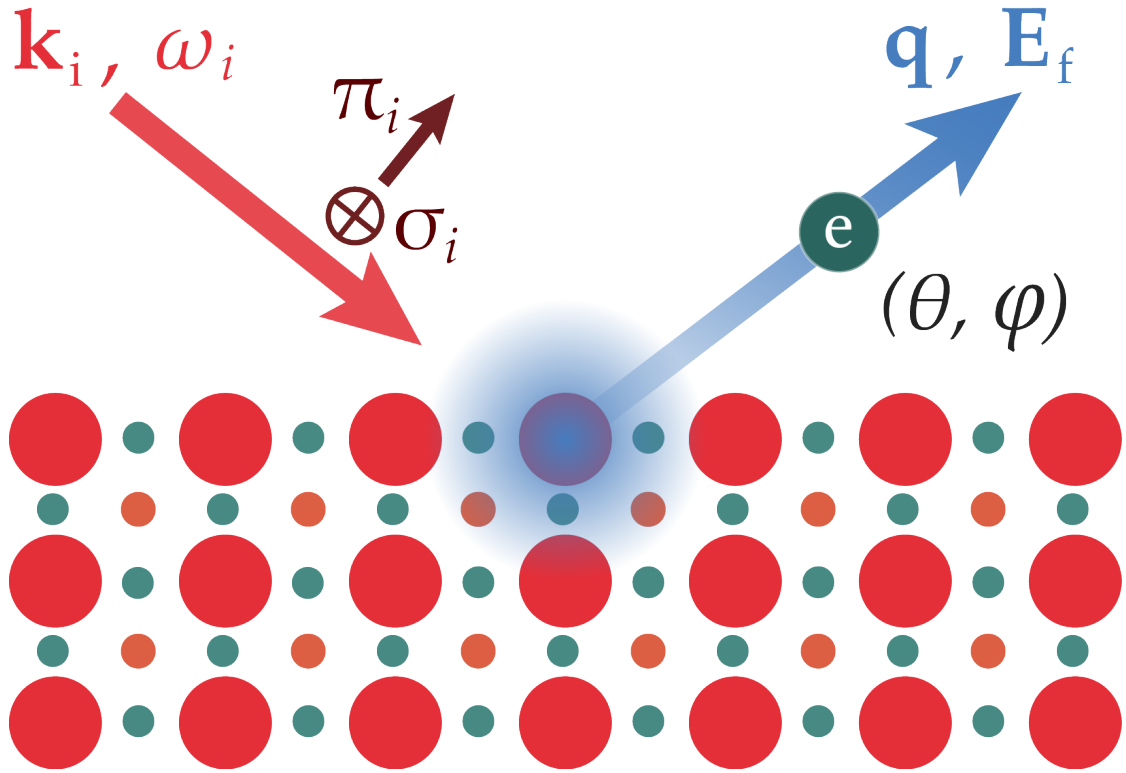


Figure 2.6: **Photoemission of an electron by an x-ray photon.** The incident wavevector and angular frequency of the photon are denoted by $\mathbf{k}_i$ and ω_i , respectively and the directions of the polarisation states σ and π are also indicated. The ejected electron has momentum $\mathbf{p} = \hbar\mathbf{q}$, energy $E_f = \hbar^2 q^2 / (2m)$ and is emitted in the direction (θ, ϕ) . The polar angles (θ, ϕ) are defined in a coordinate system where the z axis and x axis are aligned along the incident wavevector $\mathbf{k}$ and polarisation $\hat{\mathbf{e}}$ directions, respectively. The translucent blue sphere indicates that all directions of $\mathbf{q}$ for the emitted electron have a finite probability.

obtain the differential cross section by substituting eq. (2.47) into Fermi's golden rule, which

*As opposed to in a scattering process, where this interaction term appears as a second-order perturbation since scattering of an x-ray photon requires terms that both annihilate one photon and create another.

gives

$$\left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{\text{Absorption}} = \frac{mqV^2}{2\pi^2\hbar^3} \left| {}_e\langle \mathbf{q} | \frac{e}{mc} \mathbf{p} \cdot \mathbf{A} | \mathbf{k}, \hat{\epsilon} \rangle_{\gamma} \right|^2 \delta(E_e + E_b - \hbar\omega_i) \quad (2.48)$$

where the modulus squared of the matrix element can be shown to be equal to⁷⁶

$$\left| {}_e\langle \mathbf{q} | \frac{e}{mc} \mathbf{p} \cdot \mathbf{A} | \mathbf{k}, \hat{\epsilon} \rangle_{\gamma} \right|^2 = \left(\frac{e\hbar}{m} \right)^2 \frac{2\pi\hbar}{V^2\omega} (q^2 \sin^2 \theta \cos^2 \varphi) \phi^2(\mathbf{K}) \quad (2.49)$$

where $\mathbf{K} = \mathbf{k} - \mathbf{q}$ is the wavevector transfer, the photoelectron is emitted in a direction (θ, ϕ) (see fig. 2.6) and $\phi(\mathbf{K}) = \int \psi_e(\mathbf{r}) e^{i\mathbf{K} \cdot \mathbf{r}} d\mathbf{r}$ is the Fourier transform of the bound-electron wavefunction. Integrating the differential cross section with respect to final energy and angle of emission we obtain the absorption cross section:

$$\sigma_A = \left(\frac{e\hbar}{m} \right)^2 \frac{1}{\pi\omega c} \overbrace{\int \phi^2(\mathbf{K}) q^2 \sin^2 \theta \cos^2 \varphi \delta(E_e + E_b - \hbar\omega_i) d\mathbf{q}}^{\mathcal{I}(\mathbf{K})} \quad (2.50)$$

where the absorption properties are described by integral $\mathcal{I}(\mathbf{K})$. Thus, apart from the $\frac{1}{\omega}$ factor, the dependence of the absorption process on the energy, polarisation and direction of the incident x-ray is entirely determined by the initial electronic state of the ejected electron.

2.5.2 X-ray dichroism

A dependence of the absorption cross section on the incident photon polarisation is called dichroism. Dichroism occurs when there are anisotropies in the system, these can be both due of charge (e.g. molecules aligned along a chain in a Polaroid sheet) and magnetic (e.g. spins aligned along their easy axis in a ferromagnet) origin. For the purposes of imaging magnetic domains, the domains of ferromagnetic and antiferromagnetic materials may be imaged with contrast between x-ray polarisations using x-ray magnetic circular dichroism (XMCD) and x-ray magnetic linear

dichroism (XMLD), respectively.

X-ray circular magnetic dichroism

In an XMCD experiment, the difference in absorption between left-circularly polarised (LCP) and right-circularly polarised (RCP) x-rays can be used to determine the local magnetic moments in a ferromagnetic material. This dichroism results from selection rules governing electronic transitions from core states to higher-energy, spin-split unoccupied states, resulting in preferential absorption of one handedness of light over the other. This splitting of the unoccupied states causes an imbalance in the number of available states with respect to the electrons' angular momenta m_J . Given that LCP and RCP photons carry spin-angular momenta of opposite sign (and thus will produce photoelectrons with opposite angular momenta when absorbed), this imbalance in states causes a proportionate difference in the absorption of each polarisation.

By measuring a ferromagnetic material in an applied magnetic field, it is possible to quantitatively determine both the spin and orbital contributions to the magnetisation using sum rules that combine XMCD measurements over the L_{II} and L_{III} edges.^{121,122} As well as using an applied magnetic field to split the unoccupied states (these being the $3d$ and $4f$ states for the first series of transition metals and rare earths, respectively), this splitting can also occur in the absence of any external fields, simply due to the internal field within a ferromagnetic domain. XMCD-PEEM is now a widely used technique that exploits the contrast between magnetisation directions to image the ferromagnetic domains at the the surface of magnetic materials.¹²³ Unlike diffraction, requiring a coherent assembly of atoms, PEEM could in principle distinguish individual atoms, however, the mean free path of the Auger electrons puts a physical limit on the spatial resolution of ~ 2 nm. Practically, the resolution is limited to a few tens of nanometres by the electron optics although this is now reaching the physical limit with modern aberration

¹²¹BT Thole et al. *Phys. Rev. Lett.*, **68**: 1943, 1992.

¹²²P Carra et al. *Phys. Rev. Lett.*, **70**: 694, 1993.

¹²³CM Schneider and G Schönhense. *Rep. Prog. Phys.*, **65**: 1785, 2002.

correction techniques.^{124,125}

The circular dichroism can be described with a $\cos \theta$ dependence upon the incident circular polarisation $\sigma \hat{\mathbf{k}}_i$ such that

$$\mathcal{I} = (\hat{\mathbf{k}}_i) \propto \sigma(\hat{\mathbf{k}}_i \cdot \boldsymbol{\mu}) = |\boldsymbol{\mu}| \cos \theta \quad (2.51)$$

where $\hat{\sigma}$ is the helicity of the circularly polarised x-ray and θ is the angle between the x-ray helicity and the local moment direction $\hat{\boldsymbol{\mu}}$. By exploiting this interaction, it therefore is possible to measure the projection of the local magnetic moments onto the incident x-ray direction. Thus, by taking two images at 90° to one another, a full vector map of the magnetisation at the surface may be obtained.

X-ray linear magnetic dichroism

In contrast to XMCD, XMLD measures the expectation value of the *square* of the magnetic moment projected along the direction of the x-ray polarisation, and thus can be used to measure antiferromagnetic materials. X-ray dichroism between linear polarisation states was first demonstrated in 1986,^{126,127} and the first images of antiferromagnetic domains recorded using XMLD-PEEM were later obtained in 1999.¹²⁸

As well as from magnetic order, linear dichroism can originate from anisotropies in the charge distribution. Linearly polarised x-rays preferentially excite electrons into states whose spatial distribution has a larger projection along the $\hat{\mathbf{e}}$ vector,¹²⁹ which can give rise to nonmagnetic linear dichroism in materials where the d or f orbitals have some anisotropic character. By symmetry, this effect is limited to crystals with lower than cubic symmetry¹²⁹ and is particularly

¹²⁴T Schmidt et al. *Ultramicroscopy*, **126**: 23–32, 2013.

¹²⁵RM Tromp et al. *Ultramicroscopy*, **110**: 852–861, 2010.

¹²⁶BT Thole, G van der Laan, and GA Sawatzky. *Phys. Rev. Lett.*, **55**: 2086, 1985.

¹²⁷G van der Laan et al. *Phys. Rev. B*, **34**: 6529, 1986.

¹²⁸J Stöhr et al. *Phys. Rev. Lett.*, **83**: 1862, 1999.

¹²⁹J Stöhr. *J. Electron. Spectrosc.*, **75**: 253–272, 1995.

important in the context of multiferroics as there can be contributions to the linear dichroism both from the ferroelectricity as well as from the magnetic order.¹³⁰ It is thus important to design experiments that can distinguish these two components.

The x-ray polarisation dependence of absorption for a (collinear) magnetic material is given by¹³¹

$$\mathcal{I}(\hat{\epsilon}) \propto (3(\hat{\epsilon} \cdot \boldsymbol{\mu})^2 - 1) = |\boldsymbol{\mu}^2|(3 \cos^2 \theta - 1) \quad (2.52)$$

where $\hat{\epsilon}$ is the linear polarisation direction such that θ is the angle between the linear polarisation and the axis along which the local antiferromagnetic spins are aligned. XMLD measurements tend to be more experimentally challenging than XMCD measurements as the magnitude of dichroism is significantly weaker, however, using careful measurements, it is possible to measure the angular dependence of the XMLD and use this information map the antiferromagnetic axis over the surface of a material.^{132,133}

¹³⁰S Polisetty et al. *J. Phys. Condens. Matter*, **24**: 245902, 2012.

¹³¹D Alders et al. *Europhys. Lett.*, **32**: 259, 1995.

¹³²K Arai et al. *J. Phys. Soc. Jpn*, **79**: 013703, 2009.

¹³³K Arai et al. *Phys. Rev. B*, **85**: 104418, 2012.

COHERENT MAGNETOELASTIC DOMAINS IN MULTIFERROIC BiFeO_3 FILMS

The physical properties of epitaxial films can fundamentally differ from those of bulk single crystals, even in films thick enough that size effects become negligible. In this chapter, we use a combination of non-resonant x-ray and neutron diffraction techniques to understand the domain structure of $(111)_{\text{pc}}\text{-BiFeO}_3$ films and find that they comprise a submicron texture of antiferromagnetic domains, which are magnetoelastically coupled to a coherent crystallographic monoclinic twin structure. This unique texture, which is absent in bulk single crystals, should enable control of magnetism in BiFeO_3 film devices via epitaxial strain.

3.1 Introduction

As discussed in section 1.1, electrical manipulation of spins in multiferroic materials is a promising route to a new generation of fast, low consumption electronics.^{14,59,134} Although direct electrical control of ferromagnets is challenging, much progress has been made towards electrical switching of *antiferromagnetic* spins.¹³⁵ Multiferroic BiFeO₃ (BFO) is one of the most promising materials: at room temperature, BFO is both *ferroelectric* and *antiferromagnetic*, and its spins can be rotated by switching the direction of the electrical polarisation.^{136,137} Thus far, a fundamental limitation towards practical BFO devices has been the lack of understanding of the interplay between ferroelectricity, magnetism and lattice distortions (ferroelasticity). The interactions between these ferroic orders in BFO is further complicated by the presence of *domains*, requiring a comprehensive model to account for the numerous ferroelectric, magnetic and ferroelastic domain variants that can coexist within a single material. If properly understood, the coexistence and interplay of these room-temperature multiferroic properties in BFO offers a unique framework to engineer novel and highly-tuneable physical properties in epitaxial films.

The properties of domains in multiferroics have been studied for over 50 years, however, only in the last two decades has the development of atomic resolution microscopy techniques revealed their true complexity. These techniques have lead to discoveries not only regarding the domain morphology but also the behaviour of the *domain walls*. In some cases, novel functionality, not present in the bulk can be found in the wall itself. This phenomena is seen in BFO, where recently it has been shown that 109° and 180° domain walls between ferroelectric domains are

¹⁴F Matsukura, Y Tokura, and H Ohno. *Nat. Nano.*, **10**: 209–220, 2015.

⁵⁹W Eerenstein, ND Mathur, and JF Scott. *Nature*, **442**: 759–765, 2006.

¹³⁴R Ramesh and NA Spaldin. *Nat. Mater.*, **6**: 21–29, 2007.

¹³⁵X He et al. *Nat. Mater.*, **9**: 579–585, 2010.

¹³⁶T Zhao et al. *Nat. Mater.*, **5**: 823–829, 2006.

¹³⁷W Ratcliff II et al. *Phys. Rev. B*, **87**: 140405, 2013.

electrically conductive.^{138–140} Not only is this seen for domain walls in the as-grown state, but for those electrically written into the material.¹⁴¹ Furthermore, it has been shown that the density of domain walls in BFO controls the exchange bias between BFO and ferromagnetic layers in BFO heterostructures.¹⁴²

As a result of recent developments in synchrotron and neutron source technology, cutting edge diffraction techniques can now be applied to thin films to obtain complementary information to scanning probe techniques; these are sensitive to the long-range structural and magnetic ordering within domains and provide a quantitative measurement of the relative populations of domains. In this chapter we employ nonresonant x-ray magnetic scattering (NXMS) and neutron scattering to investigate the multiferroic domain structure of 1 μm -thick BFO films.

3.1.1 Physical properties of BiFeO_3

Being one of the few single-phase materials to exhibit room-temperature magnetoelectric coupling, BFO is the most intensively studied multiferroic to date.¹³⁴ The following sections comprise a brief overview of the structural and magnetic properties of BFO, and how these properties can be altered when grown in thin-film form.

Crystal structure

At a ferroelectric Curie temperature of $T_C = 1103\text{ K}$, BFO undergoes an improper structural phase transition from the orthorhombic β -phase (space group $Pbnm$ ¹⁴³) to the polar α -phase. In the α -phase, it has a rhombohedral distorted perovskite structure (pictured in fig. 3.1) in which the Bi^{3+} and Fe^{3+} cations are displaced away from their centrosymmetric positions along the

¹³⁸J Seidel et al. *Nat. Mater.*, **8**: 229, 2009.

¹³⁹S Farokhipoor and B Noheda. *Phys. Rev. Lett.*, **107**: 127601, 2011.

¹⁴⁰P Maksymovych et al. *Nano Lett.*, **11**: 1906–1912, 2011.

¹⁴¹JC Yang et al. *Annu. Rev. Mater. Res.*, **45**: 249–275, 2015.

¹⁴²LW Martin et al. *Nano Lett.*, **8**: 2050–2055, 2008.

¹⁴³DC Arnold et al. *Phys. Rev. Lett.*, **102**: 027602, 2009.

$[111]_{\text{pc}}$ (indexed in pseudo-cubic (subscript pc) setting of the unit cell) axis.¹⁴⁴ This gives rise to a ferroelectric polarisation of $|\mathbf{P}| \sim 100 \mu\text{C}/\text{cm}^2$, the largest of all known multiferroics. The space group of the α -phase is generally accepted to be the rhombohedral space group $R3c$, with lattice parameters $a_{\text{h}} = b_{\text{h}} = 5.571 \text{ \AA}$ and $c_{\text{h}} = 13.868 \text{ \AA}$ in the hexagonal (subscript h) setting.^{144–146} The pseudo-cubic cell is aligned such that the 3-fold axis $[001]_{\text{h}}$ lies along the pseudo-cubic $[111]_{\text{pc}}$ (see fig. 3.1(d)).

There is, however, some debate on whether the bulk α -phase may have a symmetry *lower* than $R3c$ with a few recent studies suggesting monoclinic and triclinic structures. Sosnowska *et al.* recently proposed a monoclinic Cc ¹⁴⁷ structure from synchrotron powder diffraction measurements and Wang *et al.* suggest a triclinic $P1$ ¹⁴⁸ structure based upon a combined study of synchrotron x-ray diffraction, neutron powder diffraction, and single-crystal electron diffraction. The latter proposed structure was found to be the most stable in a recent density-functional-theory study.¹⁴⁹

Magnetic properties

Figure 3.1d shows the magnetic structure of bulk BFO, which antiferromagnetically orders at a Neél temperature of $T_{\text{N}} \sim 640 \text{ K}$. The structure can be described locally as G-type (i.e. with each spin being almost antiparallel to all its neighbours) as can be seen on the red pseudo-cubic cell. Dzyaloshinskii-Moriya interactions, caused by the ionic displacements associated with the ferroelectric polarisation, produce a local rotation of the Fe magnetic moments, resulting in a long-period ($l \sim 62 \text{ nm}$) cycloidal modulation with moments rotating in a plane containing $\mathbf{P} \parallel [001]_{\text{h}}$ and the magnetic propagation vector $\mathbf{k}$ (indicated by the double-headed green arrow).⁶³

¹⁴⁴JM Moreau *et al.* *J. Phy. Chem. Solids*, **32**: 1315–1320, 1971.

¹⁴⁵C Michel *et al.* *Solid State Commun.*, **7**: 701–704, 1969.

¹⁴⁶A Palewicz *et al.* *Acta Crystallogr. B*, **63**: 537–544, 2007.

¹⁴⁷I Sosnowska *et al.* *J. Phys. Soc. Jpn*, **81**: 044604, 2012.

¹⁴⁸H Wang *et al.* *Inorg. Chem.*, **52**: 2388–2392, 2013.

¹⁴⁹Fayyaz Ahmad *et al.* *J. Korean. Phys. Soc*, **70**: 394–400, 2017.

⁶³I Sosnowska, TP Neumaier, and E Steichele. *J. Phys. C: Solid State*, **15**: 4835, 1982.

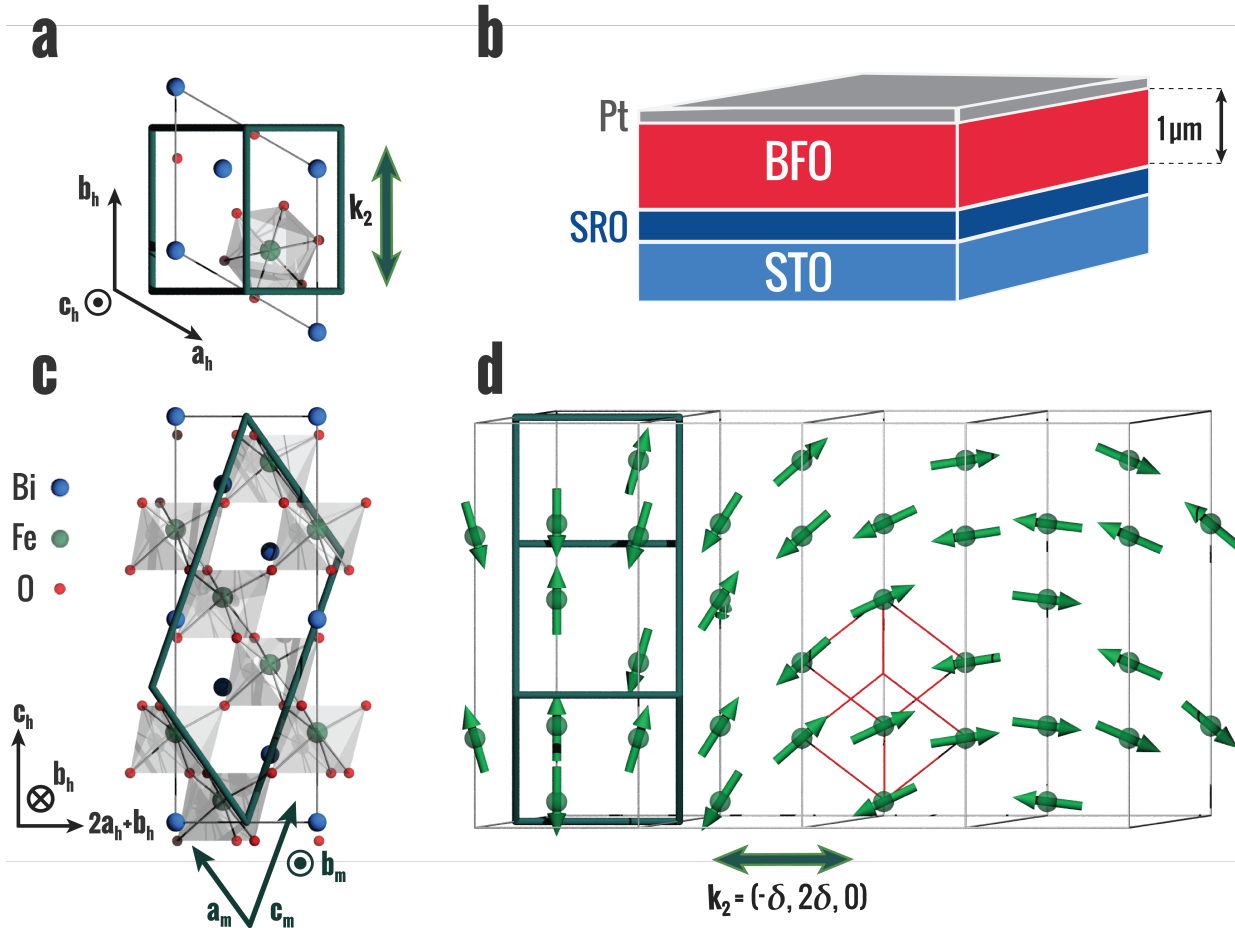


Figure 3.1: **Summary of crystal and magnetic structure.** **a**, Top down (along c axis) projection of BFO crystal structure showing the relationship between the rhombohedral (grey) and monoclinic (green) unit cells. Only the top quarter of the unit cell is draw for clarity. The hexagonal and monoclinic settings are indicated by subscript h and m , respectively. The direction of the magnetic propagation vector k_2 is also shown. **b**, Schematic illustration of the film architecture. **c**, Side on (along b_h axis) projection of BFO crystal structure showing the relationship between the rhombohedral (grey) and monoclinic (green) unit cells and their axes. **d**, Magnetic structure of BFO. The propagation vector has been scaled to accentuate the cycloid. Also shown is the pseudo-cubic cell (red).

Magnetic ordering breaks the symmetry of the three-fold axis, giving rise to three symmetry equivalent $\mathbf{k}$ -domains, with magnetic propagation vectors $\mathbf{k}_1 = (\delta, \delta, 0)_h$, $\mathbf{k}_2 = (\delta, -2\delta, 0)_h$ and $\mathbf{k}_3 = (-2\delta, \delta, 0)_h$ and $\delta = 0.0045$ at 300 K. In high-quality bulk single crystals, antiferromagnetic cycloidal domains were previously imaged by NXMS and found to be of the order of a millimetre in size.¹⁵⁰

3.1.2 BiFeO₃ thin films and devices

The physical properties of BFO films can deviate significantly from their bulk counterparts and these differences are principally determined by the thickness of the film and the strain induced by the film–substrate lattice mismatch.^{151,152} If properly understood, the dependence of the structural, ferroelectric and magnetic properties of BFO films on these parameters can be used to optimise their behaviour for use in devices (for further details see section 4.1). Typical BFO device architectures are based on thin-film heterostructures, and include a ferromagnetic layer, which can be switched via coupling to the BFO spins at the interface, as recently demonstrated for the (001)_{pc} film orientation.^{153,154} However, the lack of a comprehensive understanding of the interplay between ferroelectricity and antiferromagnetism at the BFO interface has thus far represented a fundamental limitation towards engineering high-performance devices. To gain a detailed insight into the multiferroic properties of BFO films, we focus on the (111)_{pc} orientation as it provides, in principle, a model system with minimal extrinsic effects: in this orientation, the out-of-plane polarisation is maximal and importantly, three-fold symmetry is not broken

¹⁵⁰RD Johnson et al. *Phys. Rev. Lett.*, **110**: 217206, 2013.

¹⁵¹DG Schlom et al. *Annu. Rev. Mater. Res.*, **37**: 589–626, 2007.

¹⁵²DG Schlom et al. *MRS Bull.*, **39**: 118–130, 2014.

¹⁵³JT Heron et al. *Nature*, **516**: 370–373, 2014.

¹⁵⁴T Gao et al. *Nano Lett.*, **17**: 2825–2832, 2017.

by the substrate, leaving the crystal structure reportedly rhombohedral.^{155–160} Furthermore, the magnetic modulation is not fixed by symmetry but can occur along three equivalent propagation directions that lie in the plane of the film.

In theory, $(111)_{\text{pc}}$ -oriented films should also be the most attractive for applications but are in practice plagued by electrical breakdown and fatigue problems.¹⁶¹ Consequently, recent research has focussed on the $(100)_{\text{pc}}$ or $(110)_{\text{pc}}$ orientations, which switch deterministically and reliably over 10^6 cycles.¹⁶¹ The poor performance of $(111)_{\text{pc}}$ -oriented films has been linked to a non-deterministic four-stage switching process in which the two intermediate stages have three symmetry-equivalent polarisation directions. Neighbouring regions of the sample randomly follow different switching pathways, and can become pinned due to the formation of charged domain walls.^{161,162} This reduces the switchable polarisation and forms conductive pathways, leading to electrical breakdown. Precise electrical dialling of magnetism in $(111)_{\text{pc}}$ BFO devices would therefore require simultaneous control of the ferroelectric and ferroelastic switching pathways and of the magnetic modulation.

Through the NXMS and neutron diffraction measurements presented in this chapter, we attempt to gain a comprehensive understanding of the fundamental mechanisms, at the level of domains down to the atomic level, which underpin the functionality and limitations of BFO films. A comprehensive understanding of this behaviour opens up routes to manipulate the multiferroic properties of BFO films, potentially allowing the aforementioned problems, especially those associated with the presence of domains, to be eliminated.

¹⁵⁵J Li et al. *Appl. Phys. Lett.*, **84**: 5261–5263, 2004.

¹⁵⁶F Bai et al. *Appl. Phys. Lett.*, **86**: 032511, 2005.

¹⁵⁷D Kan and I Takeuchi. *J. Appl. Phys.*, **108**: 014104, 2010.

¹⁵⁸K Ujimoto et al. *Appl. Phys. Lett.*, **100**: 102901, 2012.

¹⁵⁹F Zavaliche et al. *Phase Transit.*, **79**: 991–1017, 2006.

¹⁶⁰RR Das et al. *Appl. Phys. Lett.*, **88**: 242904, 2006.

¹⁶¹SH Baek et al. *Adv. Mater.*, **23**: 1621–1625, 2011.

¹⁶²X Zou et al. *ACS Nano*, **6**: 8997–9004, 2012.

3.2 Sample preparation

3.2.1 Thin-film growth

1 μm -thick epitaxial films of BFO were grown* in the (111)_{pc} orientation (with the hexagonal c-axis surface normal) using double-gun off-axis sputtering onto a (111)_{pc}-oriented SrTiO₃ (STO) single-crystal substrate.¹⁶⁰ The two sputter guns are offset from the centre of the substrate such that their overlapping flux profiles produce a uniform flux over the substrate. The uniformity is further enhanced by continuously rotating the substrate mount during growth. The films are grown at 1000 K in a 300 mbar atmosphere of Ar:O₂ in a ratio of 3:1. This high pressure atmosphere ensures the correct stoichiometry in the film and minimises ion damage to the film during growth.

Before depositing the BFO layer, a 35 nm-thick SrRuO₃ (SRO) layer was deposited on the STO substrate by 90° off-axis sputtering.¹⁶³ This layer is grown at 820 K in a 250 mbar atmosphere of Ar:O₂ in a ratio of 3:2. The role of this layer is twofold: firstly, it elastically biases the film to grow as a ferroelectric monodomain,^{164,165} and secondly, it acts as a bottom electrode in experiments in which an out-of-plane electric field is applied. After the BFO is grown, a Pt capping layer is deposited by DC on-axis sputtering both to protect the film surface and, if patterned appropriately, to act as a top electrode.

*All BFO films investigated in this thesis were grown by our collaborators Dr. Wittawat Saenrang, Jonathon Schad and Prof. Chang-Beom Eom at the University of Wisconsin-Madison. They also performed all atomic force microscopy and *P-E* loop measurements.

¹⁶³CB Eom et al. *Science*, **258**: 1766, 1992.

¹⁶⁴DD Fong et al. *Phys. Rev. Lett.*, **96**: 127601, 2006.

¹⁶⁵JE Giencke et al. *Curr. Opin. Solid State Mater. Sci.*, **18**: 39–45, 2014.

3.2.2 Characterisation

The crystallinity and epitaxy of the BFO films are measured using a Rigaku SmartLab four-circle laboratory-based x-ray diffractometer fitted with a copper K_α x-ray source. Figure 3.2a shows a rocking curve of the $(006)_h$ reflection, which has a full width at half maximum of 0.12° . This is relatively narrow in comparison to reported values for films grown by sputtering,^{159,160} pulsed laser deposition,^{158,159,166} and molecular beam epitaxy,¹⁶⁷ and thus confirms the high crystalline quality of the films. However, we note this is still four times as broad as for a bulk single crystal, also shown in fig. 3.2(a), indicating the presence of strain, inhomogeneity or mosaic spread in the film.

Figure 3.2c and d show a θ - 2θ scan measured along the specular $(111)_{pc}$ direction and a reciprocal space map around the $(112)_{pc}$ film and substrate peaks. These show that the BFO film was grown epitaxially on the STO substrate with no other structural phases present except for the BFO film, SRO bottom electrode and STO substrate. From the peak position of the BFO film layer, we find that the BFO film is relaxed with pseudocubic lattice parameters $a = 3.96(8) \text{ \AA}$ and $\alpha = 89.5(2)^\circ$. The STO cubic lattice parameter is found to be $a = 3.91(1) \text{ \AA}$, which is within error of the bulk STO value of $a = 3.901 \text{ \AA}$.¹⁶⁸

The ferroelectric properties were measured using a Radiant Technologies Precision multiferroic tester at room temperature. Figure 3.2b shows a representative P-E hysteresis loop measured at 10 kHz on a $150 \mu\text{m}$ diameter circular Pt top electrode. The remanent field of $102 \mu\text{C}/\text{cm}^2$ is comparable to the highest reported literature values for $(111)_{pc}$ -oriented BFO films.^{155,156,160} With this diameter of electrode, the remanent polarisation was found to be stable for $\sim 10^4$ cycles, consistent with previous reports.¹⁶¹ For much larger electrodes, such as $700 \mu\text{m} \times 200 \mu\text{m}$, the number of switching cycles for which the polarisation remained stable was greatly reduced, on

¹⁶⁶YH Chu et al. *Appl. Phys. Lett.*, **90**: 252906, 2007.

¹⁶⁷H Shu-Min et al. *Chinese Phys. B*, **23**: 036801, 2014.

¹⁶⁸Yu A Abramov et al. *Acta Crystallogr. B*, **51**: 942–951, 1995.

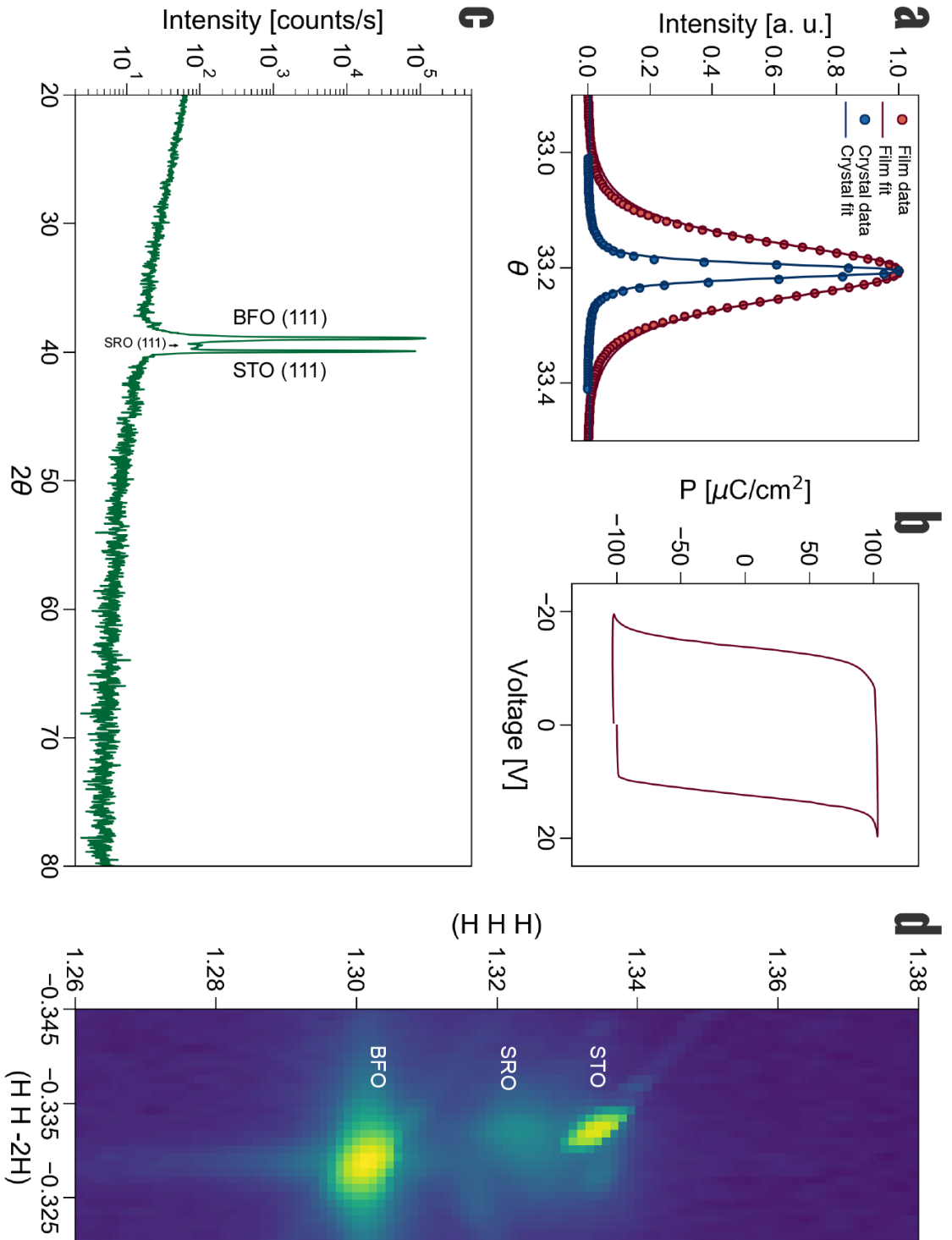


Figure 3.2: **Film characterisation measurements.** **a**, Rocking curve scans of the (006)_h reflection in the film (red) and crystal (blue), respectively. The peak intensities have been normalised to unity. **b**, P-E hysteresis loop measurement. **c**, θ - 2θ scan showing the BFO film and STO substrate (111) peaks. **d**, Reciprocal space map of the (112) peaks of the BFO film and STO substrate.

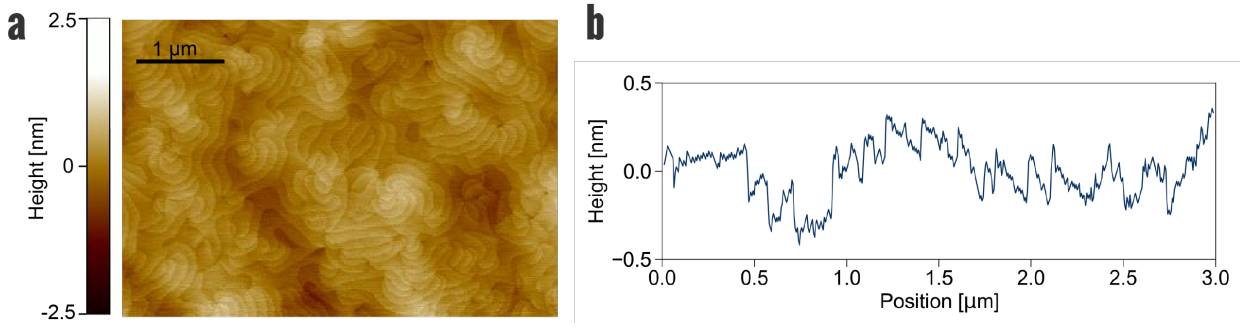


Figure 3.3: **Atomic force microscopy measurements.** Atomic force microscopy **a**, image and **b**, line profile showing the atomically smooth surface of 1 μm -thick $(111)_c$ BiFeO_3 films. AFM data were measured with a Bruker MM-SPM with Nanoscope V.

the order of 1–10 cycles.

The surface topography of the films was characterised using atomic force microscopy (AFM), measured with a Bruker MM-SPM with Nanoscope V. To minimise damage to the surface, the images were measured in ‘tapping mode’ (rather than ‘contact mode’) with the tip oscillating at its mechanical resonant frequency (a few hundred kHz). Figure 3.3a shows an AFM image of a $5\mu\text{m} \times 3\mu\text{m}$ region of the surface and fig. 3.3(b) shows a representative line profile. From these data, it is clear the surface of the films is atomically smooth, with a typical step size on the order of $\sim 1\text{ \AA}$.

3.3 Synchrotron x-ray and neutron diffraction measurements of $\text{BiFeO}_3/\text{SrTiO}_3$ films

To probe the magnetic structure of the film, we measured by NXMS and neutron diffraction the magnetic satellite reflections due to the long-range incommensurate magnetic ordering, which occur near structurally-forbidden Bragg peaks such as the $\mathbf{N} = (0, 0, 3(2n + 1))_h$ peaks*. Although this family of peaks is extinct due to R-centring, the magnetic structure (space group

*Although the satellite peaks are also present about the structurally-allowed Bragg peaks $\mathbf{N} = (0, 0, 6n)_h$, they are not observable as the short propagation vector means they fall within the tails of the much brighter (a factor of $\sim 10^6$ brighter for x-rays) Bragg peaks.

Cc) breaks this symmetry and thus the magnetic peaks are observable at these positions.

3.3.1 Experimental details

Non-resonant x-ray magnetic diffraction on I16

The synchrotron NXMS experiments were performed on beamline I16,¹⁶⁹ Diamond Light Source (UK) using a six-circle kappa diffractometer in the reflection (vertical scattering) geometry, as shown in fig. 3.4. The incident x-ray beam energy was tuned to 4.9 keV, which was selected for several reasons. Firstly, it is off-resonance of all chemical elements present in the sample, such that resonant scattering processes need not be considered. A calculation of the resonant contribution, following that in Walker *et al.* (2013)¹⁷⁰ yields a ratio of non-resonant to resonant contributions to the scattering to be $0.02494 r_0 : 0.00029 r_0$ at this energy, where r_0 is the Thomson scattering length. There are then two important, but competing factors that affect the choice of energy. To minimise absorption by air and the Pt capping layer, a high energy is desired. However, using a higher energy increases the probability of multiple scattering processes (given the larger Ewald sphere), which can overshadow the magnetic signal. The chosen energy of 4.9 keV adequately satisfies both these criteria.

Conversion of the incident x-ray polarisation from σ -polarised x-rays to circularly polarised x-rays was achieved using a 100 μm -thick diamond quarter-wave plate. The scattered x-ray polarisation was determined using a pyrolytic-graphite polarisation-analyser crystal scattering at the (004) reflection, which is built on the detector arm of the diffractometer such that any linear polarisation channel may be selected. The majority of the measurements were taken at an azimuthal angle of $\phi = 90^\circ$ with respect to the $(100)_h$ direction, identified as an experimental geometry in which multiple scattering was minimised. The beam footprint at the sample was set to $50 \mu\text{m} \times 90 \mu\text{m}$ rms.

¹⁶⁹SP Collins et al. , **1234**: 303–306, 2010.

¹⁷⁰HC Walker et al. *Science*, **333**: 1273–1276, 2011.

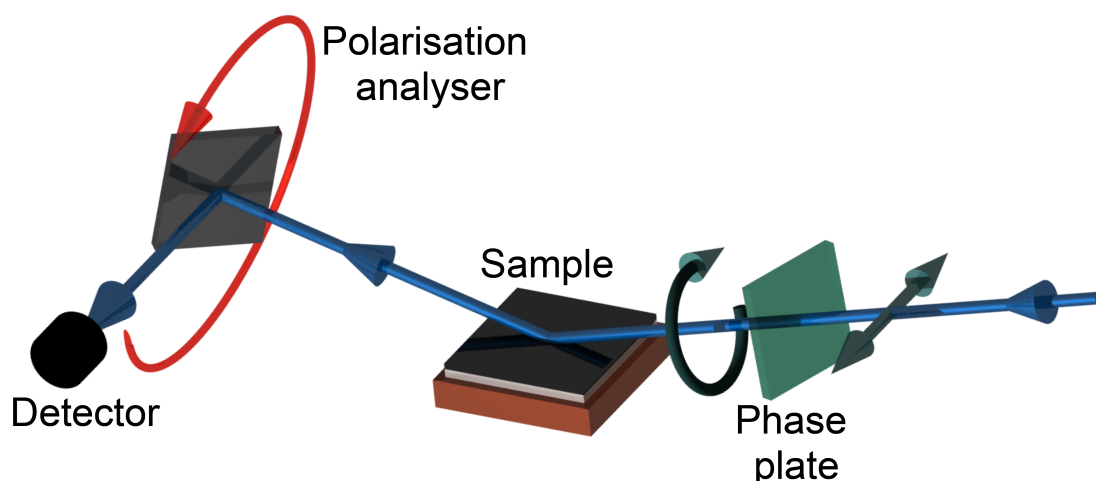


Figure 3.4: **Non-resonant magnetic x-ray scattering experimental setup.** The incident and scattered x-ray beam directions are indicated by the blue arrows. The incident x-rays are linearly polarised with their $\mathbf{E}$ -field vector perpendicular to the scattering plane (σ -polarised). These may be converted to circularly polarised x-rays of either handedness using a diamond phase plate. The polarisation of the scattered x-rays is measured using a graphite analyser crystal, which can be rotated to select any linear polarisation channel.

Single-crystal neutron diffraction on WISH

Single-crystal neutron diffraction measurements were performed on the WISH instrument¹⁷¹ at ISIS, the UK pulsed Neutron and Muon Spallation Source. The sample was oriented with the $(00l)_h$ zone axis in backscattering geometry, which allowed for the highest resolution measurement of magnetic satellites of the $\mathbf{N} = (003)_h$ space-group-forbidden reflection. The neutron beam size at the sample position was 20 mm x 20 mm, fully illuminating the sample. Data taken at room-temperature and 10 K were found to be entirely consistent but with an improved signal-to-background in the 10 K dataset.

3.3.2 Results

The diffraction pattern expected from each of the magnetic $\mathbf{k}$ -domains is a pair of peaks at positions $\mathbf{N} \pm \mathbf{k}_i$, where $\mathbf{k}_i$ is the propagation vector of the corresponding magnetic domain. This

¹⁷¹LC Chapon et al. *Neutron News*, 22: 22–25, 2011.

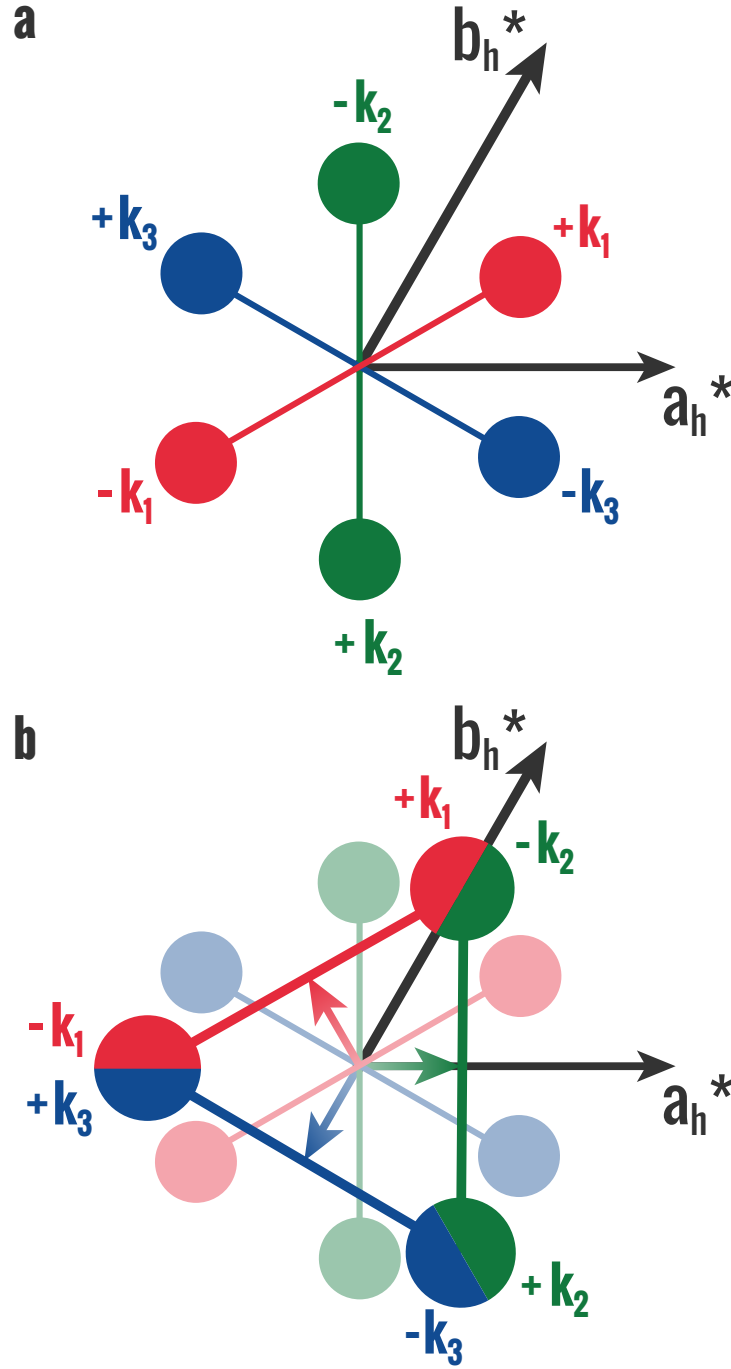


Figure 3.5: **Effect of monoclinic distortion on diffraction pattern.** **a**, Schematic of the expected diffraction pattern about the $\mathbf{N} = (009)_h$ for the undistorted, rhombohedral structure with all three magnetic $\mathbf{k}$ -domains contributing to the diffracted signal. **b**, Schematic showing the effect of the monoclinic distortion model on the diffraction pattern, where the undistorted (translucent) and distorted (opaque) diffraction patterns.

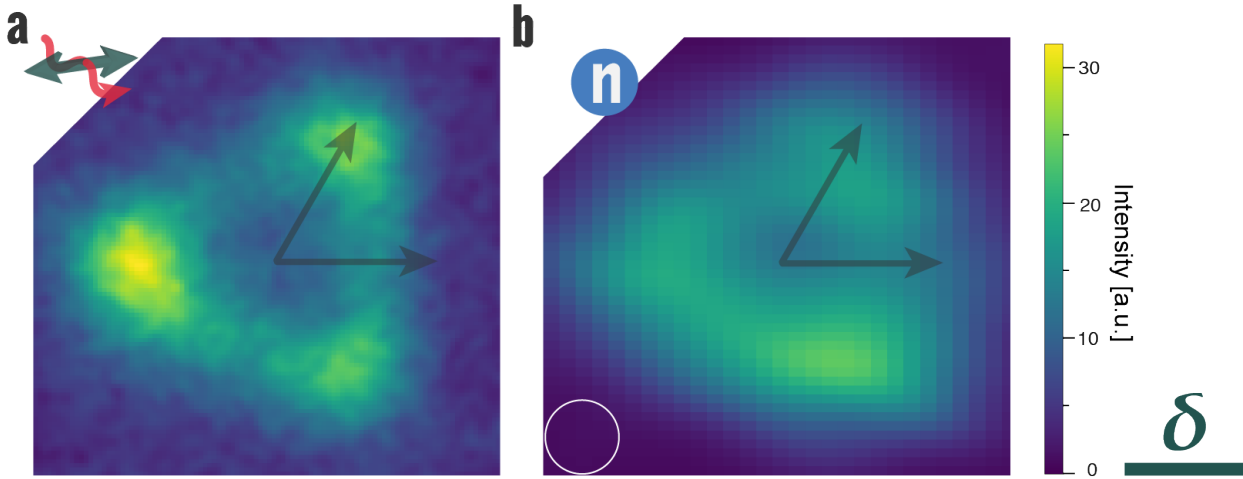


Figure 3.6: **Magnetic x-ray and neutron diffraction reciprocal space maps.** **a**, Reciprocal space map about $(009)_h$ measured at room temperature by NXMS with linear polarised x-rays. **b**, Reciprocal space map about the $(003)_h$ measured at 10 K by neutron diffraction. The white circle in the lower left corner indicates the instrumental resolution. The scale bar in the bottom left shows the magnitude of the propagation vector (both images on the same scale) and the reciprocal lattice directions (in the hexagonal setting) are indicated by the translucent black arrows.

is indeed what has been previously observed from a BFO single crystal by NXMS with a small x-ray beam (such that only a single domain is illuminated).¹⁵⁰ If populations of all three domains are illuminated, one should observe a star of six satellite peaks as depicted in fig. 3.5(a), with the red, green and blue peaks corresponding to propagation vectors $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$, respectively. Figure 3.6a shows the diffraction pattern we observe by NXMS around the $\mathbf{N} = (009)_h$ position, which is in stark contrast with these expectations: within a large scanned volume of reciprocal space about the $\mathbf{N} = (009)_h$, we observe only *three* reflections resembling a triangular shape — a seemingly impossible situation, since for any satellite at $\mathbf{N} + \mathbf{k}$ there *must* be a corresponding satellite at $\mathbf{N} - \mathbf{k}$ as the Fourier decomposition of a real, periodic magnetic structure necessarily contains $+\mathbf{k}$ and $-\mathbf{k}$ components. The only explanation consistent with this diffraction pattern is that each of the peaks in the triangle contains contributions from two domains (thereby preserving a total of six satellites), with the midpoint of each pair of satellites being displaced away from the pseudo-rhombohedral $(009)_h$ position. In fact, the observed diffraction pattern is well modelled by introducing a small monoclinic distortion that translates the six magnetic

satellites in reciprocal space such that pairs of neighbouring reflections lie approximately on top of each other, resulting in three composite peaks $\{+\mathbf{k}_1, -\mathbf{k}_2\}$, $\{+\mathbf{k}_2, -\mathbf{k}_3\}$ and $\{+\mathbf{k}_3, -\mathbf{k}_1\}$ (see fig. 3.5(b)).

At this point, it is worth noting that the intensities of the three peaks in fig. 3.6(a) is consistent with scattering from a region of the sample where all three magnetic (and hence monoclinic) domains are equally populated. This implies that the characteristic domain size must be significantly smaller than the beam profile of $50\text{ }\mu\text{m} \times 90\text{ }\mu\text{m}$, placing an upper limit of the order of $\sim 1\text{ }\mu\text{m}$ on the domain size, in stark contrast to mm-size domains observed in bulk single crystals.¹⁵⁰ To ensure this result was representative of the entire film, we repeated this measurement at multiple ($\gtrsim 15$) positions over the sample and the same relative peak intensities were observed uniformly. Furthermore, the same scattering was also observed in a neutron diffraction measurement of the magnetic satellites about the $\mathbf{N} = (003)_h$ position where the beam illuminated the entire sample, as shown in fig. 3.6(b). This strongly suggests the majority of the film comprises a coherent twin pattern of monoclinic micro-domains, each associated with a particular direction of the propagation vector.

In chapter 6, we probe the near-surface domains of a $(111)_{pc}$ -oriented BFO film using x-ray magnetic linear dichroism photoemission electron microscopy (XMLD-PEEM). We are able to directly image the sub-micron monoclinic/magnetic domain texture, which is found to be fully consistent with the model we use to explain the diffraction results of this chapter and confirms that typical domain size is indeed $\sim 500\text{ nm}$.

As well as the intensity centred at the three composite peak positions, there are lines of diffuse intensity in the intermediate regions, along the ‘sides’ of the triangle. This suggests there is some disorder in the periodicity of the cycloid, potentially due to phase slip defects or confinement of the long-period cycloid caused by the small magnetic domain size. The fact that this intensity is not present in the centre of the triangle, at the pseudo-rhombohedral $(009)_h$ position, provides further evidence for the presence of three structural domains, with their equivalent $(009)_h$ position displaced to be centred between the pairs of composite peaks.

As discussed in section 2.3.2, the polarisation dependence of magnetic x-ray scattering can be used to obtain very detailed information about the magnetic structure of a material. For rotating magnetic structures such as that of BFO, circularly polarised x-rays provide a highly sensitive probe. The scattered intensity of the circularly polarised x-rays depends strongly on the relative directions of the magnetic propagation vector(s) of the illuminated domain(s) and on the wavevectors of the incident and outgoing x-rays. We can therefore use circularly polarised x-rays to deconvolute the intensities that we predict to be scattering into overlapping regions of reciprocal space. Reciprocal space maps about the $(009)_h$ measured with σ , left-handed circular and right-handed circular polarised incident x-rays are shown in fig. 3.7(a–c).

To obtain quantitative information about the magnetic structure and relative domain populations from these diffraction measurements it is necessary to compare the observed peak intensities to theoretical intensities simulated for a multi-magnetic/monoclinic sample. The following section comprises a derivation of the geometrical aspect of the NXMS cross-section for the composite peaks, taking into account the polarisation of the incident x-rays and linear polarisation channel selected by the polarisation analyser. The resulting simulated reciprocal space maps are shown in fig. 3.7(d–f).

3.3.3 Calculating the x-ray magnetic cross-section

This derivation utilises the density matrix formalism for calculating diffraction peak intensities. As shown in section 2.3.2, the magnetic structure factor $M(\mathbf{K})$ may be expressed as a matrix in the σ – π basis. Similarly, we may also write matrices that describe the polarisation of the x-ray beam and polarisation analyser. For a given scattering vector $\mathbf{K}$, Poincaré vector $\mathbf{P}$ and polarisation analyser angle η , the intensity of a magnetic reflection can then be written as

$$I(\mathbf{K}, \mathbf{P}, \eta) \propto \text{tr}[D(\eta) \cdot M(\mathbf{K}) \cdot \rho(\mathbf{P}) \cdot M(\mathbf{K})^\dagger] \quad (3.1)$$

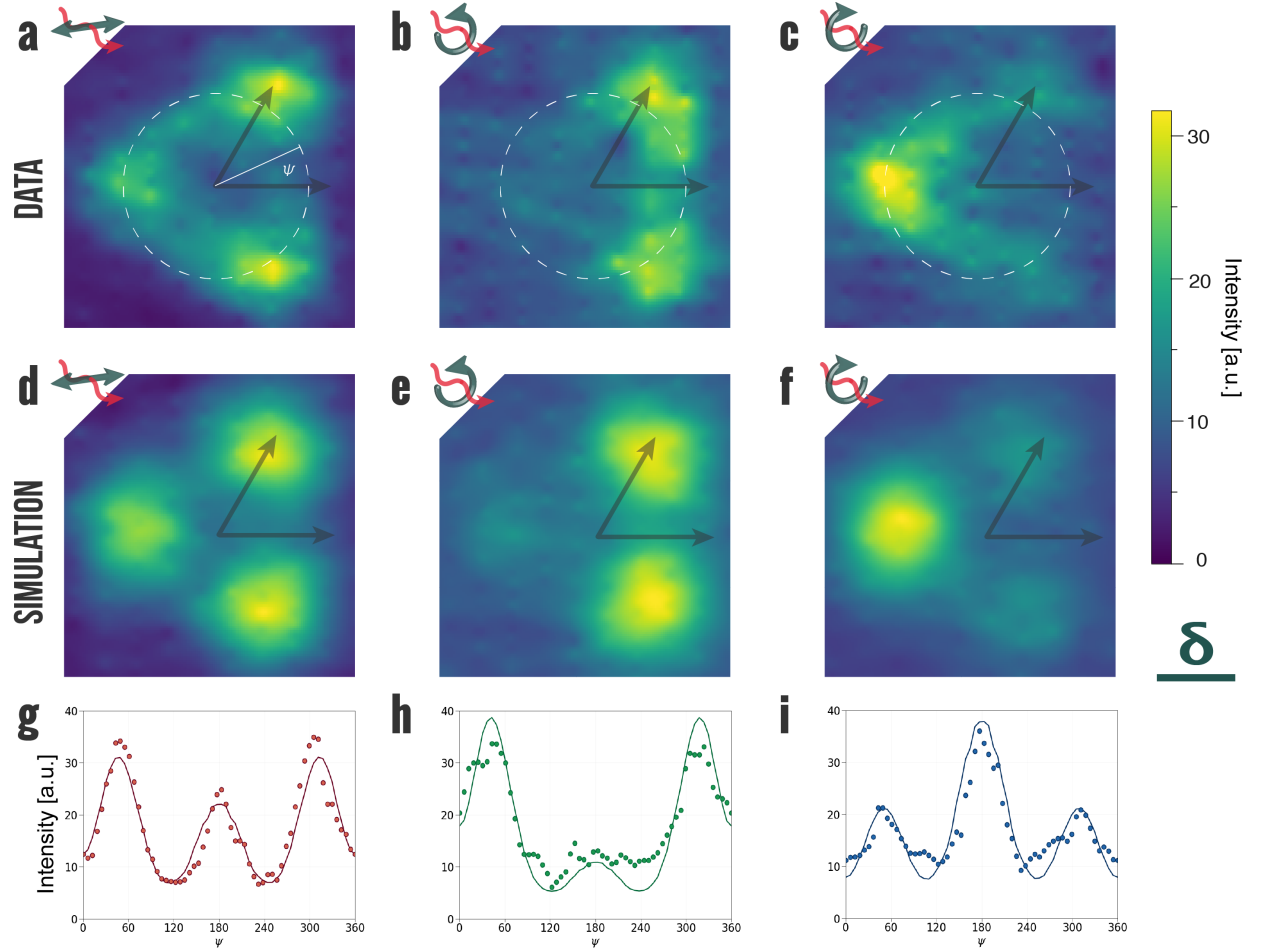


Figure 3.7: **Magnetic x-ray diffraction polarisation dependence.** **a–c**, Reciprocal space maps about $(009)_h$ measured at room temperature by NXMS with σ , left circular and right circular polarised light, respectively. The measured $(009)_h$ position is slightly off centre due to the sphere-of-confusion error of the diffractometer. **d–f**, Simulated NXMS reciprocal space maps about $(009)_h$ with σ , left circular and right circular polarised light, respectively where the added noise has been modelled as Poissonian. **g–i**, Azimuthal line cuts through the measured (circles) and simulated (lines) NXMS reciprocal space maps with σ , left circular and right circular polarised light, respectively. The location of the line cut is shown by the white dotted circles in (a–c). The scale bar in the bottom right shows the magnitude of the propagation vector (all images on the same scale) and the reciprocal lattice directions (in the hexagonal setting) are indicated by the black arrows.

where $D(\eta)$ and $\rho(\mathbf{P})$ are matrices representing the polarisation analyser and incident beam polarisation, respectively.

X-ray polarisation

In the density matrix formalism the beam polarisation may be written as

$$\rho = \frac{1}{2}(\mathbb{I} + \mathbf{P} \cdot \boldsymbol{\sigma}) = \frac{1}{2} \begin{bmatrix} 1 + P_1 & P_2 - iP_3 \\ P_2 + iP_3 & 1 - P_1 \end{bmatrix} \quad (3.2)$$

where $\mathbf{P} = (P_1, P_2, P_3)$ gives the Poincaré-Stokes representation of the polarisation and $\boldsymbol{\sigma} = ((\begin{smallmatrix} 1 & 0 \\ 0 & -1 \end{smallmatrix}), (\begin{smallmatrix} 0 & 1 \\ 1 & 0 \end{smallmatrix}), (\begin{smallmatrix} 0 & -i \\ i & 0 \end{smallmatrix}))$ is a vector of the Pauli matrices*. Light polarised linearly perpendicular ($\hat{\epsilon}_\sigma$) to the scattering plane corresponds to $\mathbf{P} = (1, 0, 0)$, which gives the corresponding polarisation matrix

$$\rho = \begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}. \quad (3.3)$$

According to our convention, in which we define a plane-wave as $\psi = e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)}$, left-handed and right-handed circularly polarised light correspond to $\mathbf{P} = (0, 0, \pm 1)$, respectively. This gives the corresponding polarisation matrices

$$\rho_\gamma = \frac{1}{2} \begin{bmatrix} 1 & -\gamma i \\ \gamma i & 1 \end{bmatrix}, \quad (3.4)$$

where $\gamma = \pm 1$ for left-handed and right-handed circularly polarised light, respectively. According to this definition, the light is left-handed (right-handed) when, from the point of view of an observer looking at the source from a fixed upstream position, the electromagnetic field vectors rotate counterclockwise (clockwise).

*Note that due to how the elements of $\mathbf{P}$ are conventionally ordered, the order of the Pauli matrices here is $\boldsymbol{\sigma} = (\sigma_3, \sigma_1, \sigma_2)$, according to their usual numbering.

Polarisation analyser

The behaviour of the polarisation analyser depends upon the miscut angle θ_M and the angle of the analyser η . Defining $\zeta = \cos^2(2\theta_M)$, the matrix D is written

$$D(\eta) = \begin{bmatrix} \cos^2(\eta) + \sin^2(\eta)\zeta & \sin(\eta) \cos(\eta)(\zeta - 1) \\ \sin(\eta) \cos(\eta)(\zeta - 1) & \sin^2(\eta) + \cos^2(\eta)\zeta \end{bmatrix}. \quad (3.5)$$

The miscut angle depends upon the material used for the analyser crystal and the Bragg reflection it is aligned to scatter from. These are usually chosen such that $2\theta_M \sim 90^\circ$ and thus $\zeta \ll 1$. In the optimal case that $\zeta = 0$, the polarisation analyser transmits a single linear polarisation channel of the scattered light, which may be chosen through the value of η . For instance, choosing a polarisation analyser angle of $\eta = 90$ will give

$$D(\eta) \approx \begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}, \quad (3.6)$$

which will transmit only the π -polarised component of the scattered x-rays. By combining this with σ -polarised incident x-rays, it is possible to isolate the σ - π element of the magnetic scattering. Given that almost all charge-scattering processes do not result in any rotation of the polarisation, we employ this technique to filter out any non-magnetic background. It is, however, still necessary to avoid multiple-scattering processes as these can result in finite intensity in the σ - π channel.

Magnetic polarisation factor

The nonresonant magnetic structure factor $M(\mathbf{K})$ is derived in section 2.3.2 and here we apply this to the case of the cycloidal magnetic structure of BFO. The Fe³⁺ ions in BFO have a ⁶S ground state with a completely quenched orbital momentum.¹⁷² Although a small component of orbital

¹⁷²CY Kuo et al. *Nat. Commun.*, 7: 12712, 2016.

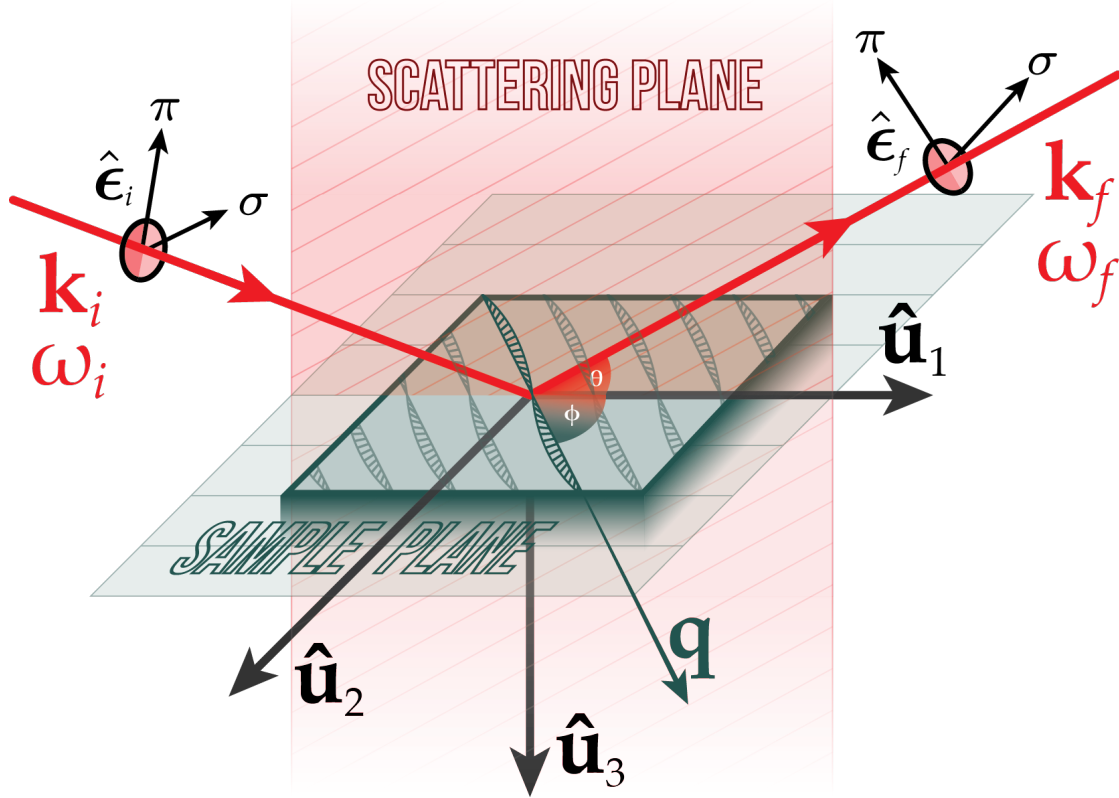


Figure 3.8: **Scattering geometry and conventions used for NXMS calculations.** $\mathbf{k}_i$ and $\mathbf{k}_f$ are the incident and scattered x-ray wavevectors, respectively and θ is half the scattering angle. The incident (final) polarisation state is given by $\hat{\epsilon}_i$ ($\hat{\epsilon}_f$) and the components of the polarisation perpendicular and parallel to the scattering plane are denoted by σ and π , respectively. The vectors $\mathbf{u}_1$, $\mathbf{u}_2$ and $\mathbf{u}_3$ define a the basis in which the magnetic structure is expressed for the purposes of the calculation. The magnetic propagation vector is given by $\mathbf{q}$ and the ϕ is angle between $\mathbf{q}$ and the scattering plane.

angular momentum can be induced through mixing with higher-lying states through spin-orbit coupling and Fe 3d-O 2p hybridisation¹⁷³, this is negligibly small compared to the spin angular momentum, as has been shown in previous NXMS measurements.¹⁵⁰ Thus, we consider only the spin contribution to the magnetic structure factor and we obtain

$$M(\mathbf{K}) = \mathbf{S}(\mathbf{K}) \cdot \mathbf{P}_S = \begin{bmatrix} \sin(2\theta)S_2 & -2\sin^2(\theta)[\cos(\theta)S_1 - \sin(\theta)S_3] \\ 2\sin^2(\theta)[\cos(\theta)S_1 + \sin(\theta)S_3] & \sin(2\theta)S_2 \end{bmatrix}, \quad (3.7)$$

¹⁷³JY Kim, TY Koo, and JH Park. *Phys. Rev. Lett.*, **96**: 047205, 2006.

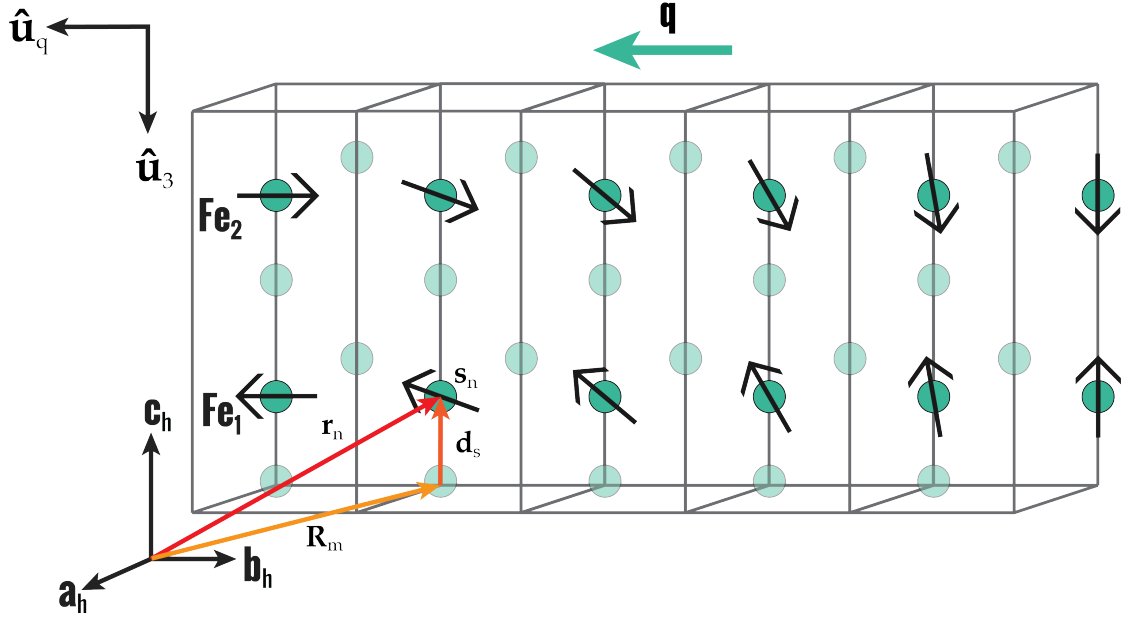


Figure 3.9: **Cycloidal magnetic structure.** Sites related to Fe1 and Fe2 by R-centring are translucent and sites related by lattice translations in the **a** direction have been omitted for clarity. The cycloid shown here has a magnetic polarity (cycloidal sense of rotation) defined by $\beta = -1$.

where the Fourier transform of the magnetic structure $\mathbf{S}(\mathbf{K}) = (S_1\hat{\mathbf{u}}_1 + S_2\hat{\mathbf{u}}_2 + S_2\hat{\mathbf{u}}_3)$ has been expressed in the $\hat{\mathbf{u}}_i$ basis defined in fig. 3.8. From eq. (2.30) we have that

$$\mathbf{S}(\mathbf{K}) = \sum_n e^{-i\mathbf{K} \cdot \mathbf{r}_n} f_n(\mathbf{K}) \mathbf{s}_n \cdot \mathbf{I} \quad (3.8)$$

and therefore, to calculate the components S_i , the first step is to express the magnetic structure in the $\hat{\mathbf{u}}_i$ basis.

The incommensurate cycloidal magnetic structure of BiFeO₃ is depicted in fig. 3.9, where $\mathbf{s}_n$ is the spin angular momentum of the n^{th} ion in the material as position $\mathbf{r}_n$. To calculate $\mathbf{s}_n$, we describe the cycloid by two orthogonal components $s_n\hat{\mathbf{u}}_q$ and $s'_n\hat{\mathbf{u}}_3$ with a phase shift of $\pi/2$ between them. We define $\hat{\mathbf{u}}_q = \cos(\phi)\hat{\mathbf{u}}_1 + \sin(\phi)\hat{\mathbf{u}}_2$ as a unit vector along the cycloid in the $+\mathbf{q}$ propagation direction, where ϕ is the angle between $\hat{\mathbf{u}}_1$ and the propagation vector of the

cycloid $\mathbf{q}$ (see fig. 3.8). We can then write $\mathbf{s}_n$ as

$$\mathbf{s}_n(\mathbf{r}_n) = s_n \cos(\mathbf{q} \cdot \mathbf{r}_n) \hat{\mathbf{u}}_q + s'_n \sin(\mathbf{q} \cdot \mathbf{r}_n) \hat{\mathbf{u}}_3. \quad (3.9)$$

This can be expressed as the sum of a complex vector and its complex conjugate

$$\mathbf{s}_n(\mathbf{r}_n) = \frac{1}{2} e^{i\mathbf{q} \cdot \mathbf{r}_n} [s_n \hat{\mathbf{u}}_q - i s'_n \hat{\mathbf{u}}_3] + \frac{1}{2} e^{-i\mathbf{q} \cdot \mathbf{r}_n} [s_n \hat{\mathbf{u}}_q + i s'_n \hat{\mathbf{u}}_3] \quad (3.10)$$

$$= \frac{1}{2} e^{i\mathbf{q} \cdot \mathbf{r}_n} \mathbf{m}_n^* + \frac{1}{2} e^{-i\mathbf{q} \cdot \mathbf{r}_n} \mathbf{m}_n \quad (3.11)$$

where $\mathbf{m}_n = s_n \hat{\mathbf{u}}_q + i s'_n \hat{\mathbf{u}}_3$. For a circular modulation $s_n = s'_n$, and we have that $\mathbf{m}_n = s_n (\hat{\mathbf{u}}_q - \beta i \hat{\mathbf{u}}_3)$ where $\beta = -1 (+1)$ for a cycloid rotating clockwise (counterclockwise) as it propagates along the $\hat{\mathbf{u}}_q$ direction when viewed with $\hat{\mathbf{u}}_q$ as right axis and $\hat{\mathbf{u}}_3$ is down (see fig. 3.9).

If the n th atom is at position $\mathbf{d}_s$ within the n th unit cell, we can write $\mathbf{r}_n = \mathbf{R}_m + \mathbf{d}_s$, where $\mathbf{R}_m$ is the position of the origin of the m th unit cell (see fig. 3.9). Substituting eq. (3.11) into eq. (3.8), we obtain

$$\mathbf{S}(\mathbf{K}) = \frac{1}{2} \left\{ \sum_m e^{i(-\mathbf{K}+\mathbf{q}) \cdot \mathbf{R}_m} \sum_s e^{i(-\mathbf{K}+\mathbf{q}) \cdot \mathbf{d}_s} f_s \mathbf{m}_s^* + \sum_m e^{i(-\mathbf{K}-\mathbf{q}) \cdot \mathbf{R}_m} \sum_s e^{i(-\mathbf{K}-\mathbf{q}) \cdot \mathbf{d}_s} f_s \mathbf{m}_s \right\}. \quad (3.12)$$

where we note that in a given unit cell, $\mathbf{m}_n = \mathbf{m}_s$ since lattice translations change only the phase factor. This expression will only be non-zero for discrete values of $\mathbf{K} = \mathbf{G} \pm \mathbf{q}$, where $\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ is a reciprocal lattice vector. We hence have that:

$$\mathbf{S}(\mathbf{G} + \mathbf{q}) = \sum_s e^{-i\mathbf{G} \cdot \mathbf{d}_s} f_s \mathbf{m}_s^* \quad (3.13)$$

$$\mathbf{S}(\mathbf{G} - \mathbf{q}) = \sum_s e^{-i\mathbf{G} \cdot \mathbf{d}_s} f_s \mathbf{m}_s. \quad (3.14)$$

As shown in fig. 3.9, there are six magnetic ions in the hexagonal unit cell of BFO. Two sites related by the c-glide: Fe1 at $[0, 0, z]$ and Fe2 $[0, 0, z + \frac{1}{2}]$, plus four related to these by R-centring

$+\left[\frac{1}{3}, \frac{2}{3}, \frac{2}{3}\right]$ and $+\left[\frac{2}{3}, \frac{1}{3}, \frac{1}{3}\right]$. The complex vector $\mathbf{m}_s$ is identical for atoms related by R-centring but since the glide plane contains the spin direction, magnetic moments on the Fe1 and Fe2 sites are antiparallel and hence $\mathbf{m}_{\text{Fe2}} = -\mathbf{m}_{\text{Fe1}}$. Summing over these 6 sites, we then obtain the Fourier transform of the spin magnetisation, calculated for $\mathbf{G} = (0, 0, l)$ reflections:

$$\mathbf{S}(\mathbf{G}_{00l} \pm \mathbf{q}) = 2sf_{\text{Fe}^{3+}}(\hat{\mathbf{u}}_q \pm \beta i \hat{\mathbf{u}}_3)(1 + e^{-i\frac{2\pi l}{3}} + e^{-i\frac{4\pi l}{3}})e^{-2\pi i l z}, \quad (3.15)$$

from which we can then extract the components of S_i to substitute into eq. (3.7).

Satellite peak intensities

We now consider measuring the magnetic satellites arising due to the cycloidal magnetic structure in BFO about the $\mathbf{N} = (0, 0, 9)_h$ reciprocal lattice position (indexed in the hexagonal lattice). Substituting $\mathbf{K} = \mathbf{N} \pm \mathbf{q}$ into eq. (3.15) we obtain the magnetic structure factor of the $\mathbf{N} \pm \mathbf{q}$ reflections

$$\mathbf{S}(\mathbf{N} + \alpha \mathbf{q}) = 6sf_{\text{Fe}^{3+}}(\hat{\mathbf{u}}_q + \alpha \beta i \hat{\mathbf{u}}_3)e^{-18\pi i z} = 6sf_{\text{Fe}^{3+}}e^{-18\pi i z} \begin{pmatrix} \cos(\phi) \\ \sin(\phi) \\ -\alpha \beta i \end{pmatrix} \quad (3.16)$$

which we have parameterised in terms of $\alpha = \pm 1$. Substituting this into eq. (3.7), and a detector angle of $\eta = 90^\circ$ into eq. (3.5), we obtain an expression for the expected intensity with linear σ -polarised light

$$I^\sigma \propto 2 \sin^2(2\theta) \left(\zeta \sin^2(\phi) + \sin^2(\theta) \cos^2(\phi) \right) + 8 \sin^6(\theta) \quad (3.17)$$

which, for a given reflection and detector angle i.e. constant θ and η , depends only on the orientation of the cycloid ϕ . The corresponding expression for circularly polarised light is given

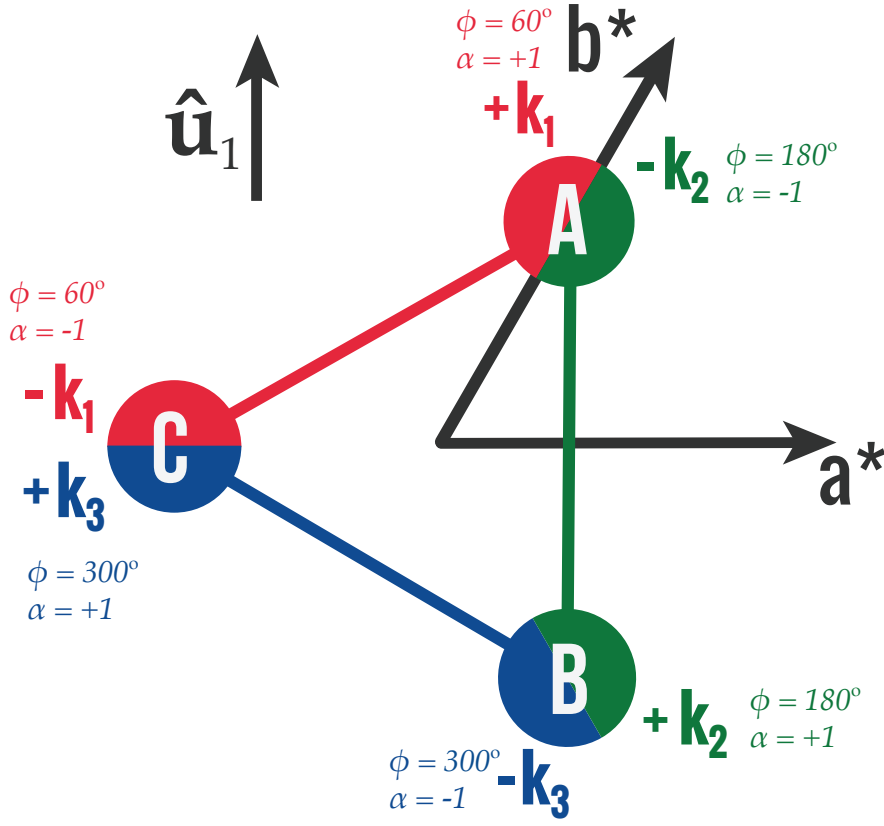


Figure 3.10: **Composite magnetic satellites.** Schematic of the distorted diffraction pattern with values of ϕ and α marked for each composite peak, where ϕ is measured clockwise from $\hat{u}_1$. The direction of $\hat{u}_1$ for the particular azimuth each reciprocal space map in fig. 3.7(a–c) were measured at is indicated.

by

$$I^\gamma \propto (\zeta + 1) \left[\sin^2(2\theta) \left(\sin^2(\phi) + \sin^2(\theta) \cos^2(\phi) \right) + 4 \sin^6(\theta) \right] - 4\alpha\beta\gamma(\zeta - 1) \sin(2\theta) \sin^3(\theta) \sin(\phi) \quad (3.18)$$

which again depends on the orientation of the cycloid (ϕ), but also depends (namely in the sign of the last term) on the magnetic polarity of the cycloid (β), which satellite peak is measured (α) and the handedness of the circularly polarised x-rays (γ).

By summing the appropriate peak intensities, we can calculate the intensities of the composite peaks observed in our (111)_{pc}-BFO films, as shown in fig. 3.10. At an energy of 4.9 keV, we have

that $2\theta = 110.34^\circ$ for each peak and the polarisation analyser miscut is $\theta_M = 49.3^\circ$ giving a value of $\zeta = 0.0224$. For σ -polarised light, we can write the intensity as

$$I^\sigma \propto V_1 + V_2 \sin^2(\phi) + V_3 \cos^2(\phi) \quad (3.19)$$

where we have introduced the constants

$$\begin{aligned} V_1 &= 8 \sin^6(\theta) = 2.45, \\ V_2 &= 2\zeta \sin^2(2\theta) = 0.04, \\ V_3 &= 2 \sin^2(2\theta) \sin^2(\theta) = 1.18. \end{aligned} \quad (3.20)$$

Substituting in the values for ϕ for each peak, we find that peaks A and B have equal intensity given by

$$I_A^\sigma = I_B^\sigma \propto \frac{1}{4} (8V_1 + 3V_2 + 5V_3) \quad (3.21)$$

and peak C has an intensity given by

$$I_C^\sigma \propto \frac{1}{4} (8V_1 + 6V_2 + 2V_3) \quad (3.22)$$

Since V_2 is negligible relative to V_3 , it is clear that peak C will be slightly weaker than A and B. We can express this as a ratio of intensities:

$$\frac{I_C^\sigma}{I_A^\sigma} = 0.866 \approx \frac{\sqrt{3}}{2} \quad (3.23)$$

The reciprocal space map in fig. 3.6 was measured at an azimuthal angle 90° relative to this, and hence the intensities are inverted and the ratio in this case is given by

$$\frac{I_C^\sigma}{I_A^\sigma} = 1.15 \approx \frac{2}{\sqrt{3}}. \quad (3.24)$$

Similarly for circularly polarised light we can write the intensity as

$$I^\gamma \propto W_1 + W_2 \sin^2(\phi) + W_3 \cos^2(\phi) + W_4 \alpha \beta \gamma \sin(\phi) \quad (3.25)$$

where we have introduced the constants

$$\begin{aligned} W_1 &= 4(\zeta + 1) \sin^6(\theta) = 1.25, \\ W_2 &= (\zeta + 1) \sin^2(2\theta) = 0.90, \\ W_3 &= (\zeta + 1) \sin^2(2\theta) \sin^2(\theta) = 0.61, \\ W_4 &= -4(\zeta - 1) \sin(2\theta) \sin^3(\theta) = 2.03. \end{aligned} \quad (3.26)$$

Substituting in the values for ϕ and α for each peak, we find that peaks A and B have equal intensity given by

$$I_A^\gamma = I_B^\gamma \propto \frac{1}{4} \left(8W_1 + 3W_2 + 5W_3 + 2\sqrt{3}\beta\gamma W_4 \right), \quad (3.27)$$

and peak C has an intensity given by

$$I_C^\gamma \propto \frac{1}{4} \left(8W_1 + 6W_2 + 2W_3 - 4\sqrt{3}\beta\gamma W_4 \right). \quad (3.28)$$

It is clear that the W_4 term is dominant in accounting for the difference in intensity between peak A (or B) and peak C. For left-handed circularly polarised light ($\gamma = +1$), peak C is bright and A and B are weak and vice versa for right-handed light ($\gamma = -1$). We can express this as a ratio:

$$\frac{I_C^\gamma}{I_A^\gamma} = \frac{4.15 - 3.51\beta\gamma}{3.93 + 1.76\beta\gamma} \approx \frac{1 - \beta\gamma}{1 + \beta\gamma/2}. \quad (3.29)$$

3.3.4 Discussion

The observed peak intensities shown in fig. 3.7 are found to be in quantitative agreement with above theoretical calculations for a sample containing equal populations of all three cycloidal domains. A simultaneous fit of the model discussed above to the three NXMS reciprocal space maps shown in fig. 3.7, yields $\chi^2_v = 1.418$ (reduced chi squared). The fitting was performed with the propagation vector, monoclinic distortion, peak width, and depolarisation factor as global parameters, but with different scale factors and background parameters for the linearly polarisation and circular polarisation measurements. The depolarisation factor accounts for the imperfect circular polarisation of the beam and any polarisation dependence of the background (for instance due to multiple scattering) and represents the depolarised fraction of the incident beam in the model. The resulting fit parameters are shown in table 3.1 and the corresponding simulations, generated with these parameters, are shown in fig. 3.7. We also note that, although our model does not account for the diffuse scattering in between the pairs of peaks, we see that this intensity also has the expected polarisation dependence.

We find our circular-polarisation data (fig. 3.7(b, c)) are only consistent with a value of $\beta = -1$ i.e. for left-handed circularly polarised light ($\gamma = +1$), peak C is bright and A and B are weak and vice versa for right-handed light ($\gamma = -1$). Noting the ferroelectric polarisation of our film is in the $-\mathbf{c}$ ($\hat{\mathbf{u}}_3$) direction, we find that this agrees with the sign of the coupling between the ferroelectric polarisation and cycloidal magnetic polarity reported in Johnson *et al.*

Table 3.1: Reciprocal space map fit parameters.

Depolarisation factor	0.115(2)
Propagation vector δ	0.004 30(6) Å ⁻¹
Monoclinic distortion	0.030(5)°

(2013)sjcitep[[]johnson2013x for a bulk single crystal sample. The I_C^γ/I_A^γ ratio thus becomes

$$\frac{I_C^\gamma}{I_A^\gamma} = \frac{4.15 + 3.51\gamma}{3.93 - 1.76\gamma} \approx \frac{1 + \gamma}{1 - \gamma/2}. \quad (3.30)$$

Crystallographic details

As be seen from table 3.1, the best fit to the experimental diffraction data is achieved by tilting the c_h^* axis by $0.030^\circ \pm 0.005^\circ$ away from the $[001]_h$ direction and *orthogonal* to $\pm \mathbf{k}_i$. In real space, this corresponds to changing both the monoclinic angle β_m and the c_m/a_m ratio (fig. 3.1(c)), whilst fixing the direction of $[101]_m$ to the surface normal. Our monoclinic structure (fig. 3.1(a, b)) has the same symmetry as the M_A or M_B fully relaxed structures, of $(100)_{pc}$ and $(110)_{pc}$ films of similar thickness.¹⁵⁷ In principle, the monoclinic distortion should also be observable as a splitting of the charge peaks. However, since the width of the charge peaks is an order of magnitude larger than the expected split, we could not observe this effect even at high Miller indices.

The monoclinic distortion breaks threefold symmetry, and the overall crystal symmetry of BFO is lowered from $R3c$ to Cc . In the Cc structure, the electrical polarisation is contained within a plane parallel to the family of c glide planes, whereas the propagation vector is perpendicular to it. The lowering of symmetry gives rise to three equivalent monoclinic domains, related by the three-fold symmetry of the parent rhombohedral structure; we label these $M1$, $M2$ and $M3$ in fig. 3.11. The monoclinic lattice parameters for domain Mi (subscript mi) are related to the rhombohedral lattice parameters (subscript h) by the transformations:

$$\begin{aligned} a_{m1} &= [-1/3, 1/3, 1/3]_h & a_{m2} &= [-2/3, -1/3, 1/3]_h & a_{m3} &= [1/3, 2/3, 1/3]_h \\ b_{m1} &= [1, 1, 0]_h & b_{m2} &= [0, -1, 0]_h & b_{m3} &= [-1, 0, 0]_h \\ c_{m1} &= [1/3, -1/3, 2/3]_h & c_{m2} &= [2/3, 1/3, 1/3]_h & c_{m3} &= [1/2, -2/3, 2/3]_h, \end{aligned}$$

respectively, with $\alpha_m = \gamma_m = 90^\circ$ and $\beta_m = 54.14867^\circ$. This monoclinic cell is the same as

that of the M_A or M_B monoclinic structures^{174*} well known to exist in (100)_{pc} and (110)_{pc} films^{157,175–177}.

Coherent magneto-elastic twinning

It is important to note that our model requires that the magnetic and structural (monoclinic) domains must be *topographically coherent* with each other – in other words, monoclinic domain boundaries are also magnetic domain boundaries such that there is a one-to-one relationship between the structural and magnetic domains. This constraint is naturally imposed by the fact that the symmetry of both the structural and magnetic domains is Cc , which is hence the magneto-structural domain symmetry, a fact that also holds for the large single crystal domains. Furthermore, within each of these magneto-structural domain types $\mathbf{k}_1/\text{M1}$, $\mathbf{k}_2/\text{M2}$ or $\mathbf{k}_3/\text{M3}$ the direction in which the c_h^* axis tilts must always be the same. If this were not the case, the magnetic diffraction would consist of two triangles rotated by 180° around the c -axis, rather than of a single triangle, as observed experimentally. Although less obvious, this also follows naturally from symmetry considerations, since the high-symmetry ($R3c$) parent structure does not possess a 2-fold axis along c_h , and as a consequence the two directions of the c_h^* tilt are not equivalent. Our observations are therefore consistent with the absence of twinning by merohedry over the whole film.

Figure 3.11 illustrates the proposed coherent domain structure of our (111) BFO films. Figure 3.11(a–c) show the three settings of the monoclinic unit cells (M1, M2 and M3) with respect to the rhombohedral cell. The associated magnetic propagation vector, which is always collinear with the b -axis of the monoclinic cell, is also shown. To minimise the energy cost associated with domain wall formation, the twins meet coherently, sharing a specific crystallographic plane,

¹⁷⁴D Vanderbilt and MH Cohen. *Phys. Rev. B*, **63**: 094108, 2001.

*These share the same cell with the polarisation confined to the c -glide plane, lying along $[u, u, v]$ where $u < v$ or $u > v$ for M_A or M_B, respectively.¹⁷⁴

¹⁷⁵G Xu et al. *Appl. Phys. Lett.*, **86**: 182905, 2005.

¹⁷⁶G Xu, J Li, and D Viehland. *Appl. Phys. Lett.*, **89**: 222901, 2006.

¹⁷⁷H Liu et al. *Appl. Phys. Lett.*, **98**: 102902, 2011.

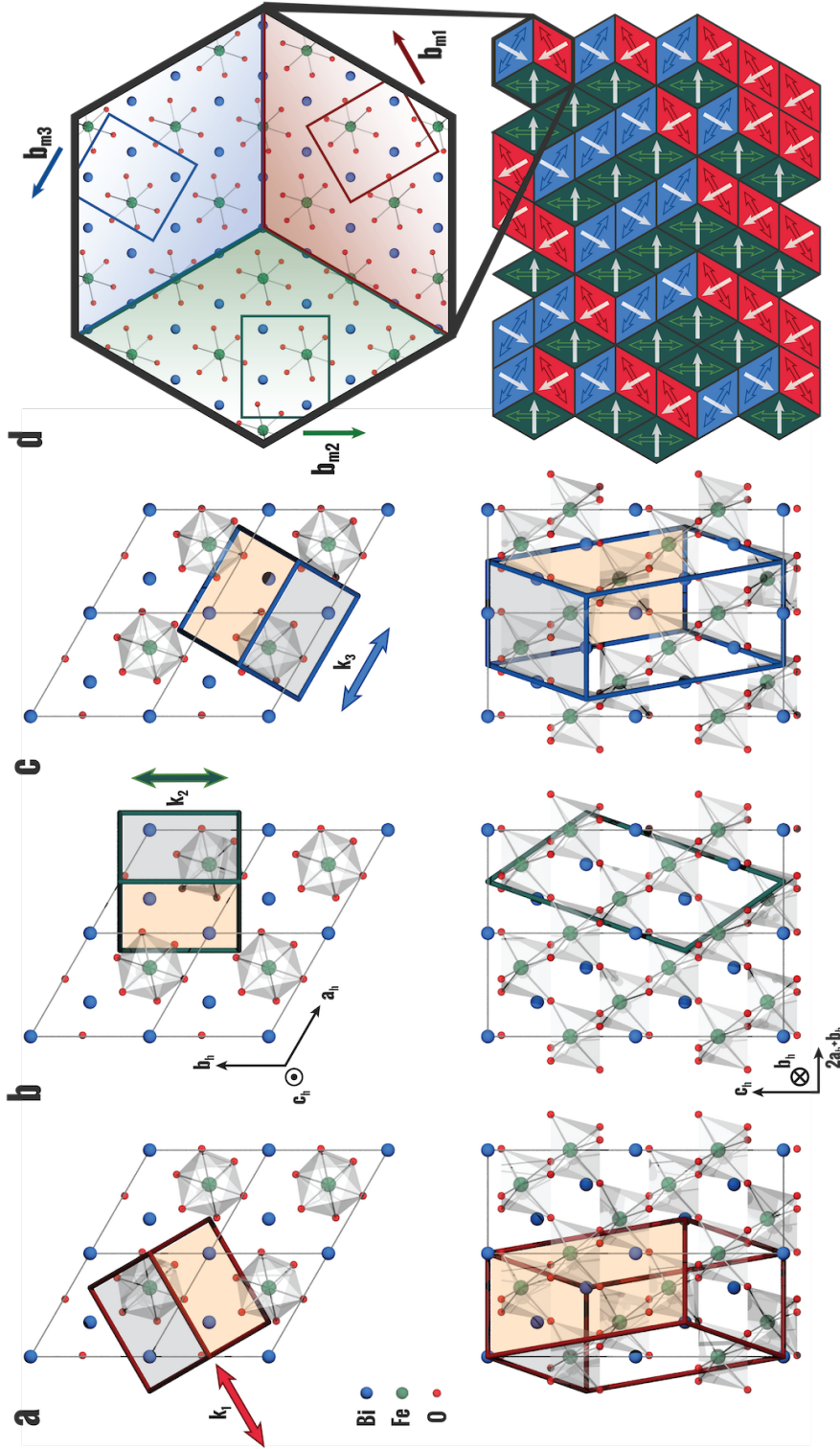


Figure 3.11: **Twinning model for magnetostructural domains.** a–c, Relationship between the unit cells of the rhombohedral (grey) structure and monoclinic twins M1 (red), M2 (green) and M3 (blue). Top down (along $-c_h$ direction) projection and side on (along $+b_h$ direction) projections are shown in upper and lower panels, respectively. For clarity, two faces of the monoclinic cell are shaded and the top down projection shows only the top quarter of the unit cell. d, Proposed coherent twin model. Magnetic/monoclinic $k_1/M1$, $k_2/M2$ and $k_3/M3$ domains are coloured red, green and blue, respectively. The coloured, double-headed arrows represent the direction of the magnetic propagation vectors and the white arrows indicate the direction of the distortion, i.e. the direction in which the c^* axis is tilted.

common to both twins. It follows that walls between neighbouring M1/M2 and M2/M3 domains necessarily share the $(\bar{1}11)_m$ and $(\bar{1}\bar{1}1)_m$ planes, respectively, where the planes are indexed in the M2 lattice. The remaining twin planes can be obtained by cyclically permuting the indices. A possible domain configuration, based on this model, is shown schematically in fig. 3.11(d). It is clear that, according to these constraints, single domains can vary arbitrarily in size but the angles at which different domains meet is fixed. The distortion vectors, indicating the direction of displacement of the c_h^* axis tilt, are also shown as filled white arrows. There are only three (rather than six) such vectors, consistent with the 3-fold parent symmetry and the absence of merohedral twinning. If the vertical topography of the film varies continuously without any steps, a further constraint is that the distortion vectors must meet head-to-head or tail-to-tail, as shown. Although the monoclinic angle β_m and the c_m/a_m ratio are, in general, independent, these parameters are in fact constrained in a coherent twin model, due to the exact lattice matching at the interfaces. The exact relationship between the change in monoclinic angle $\Delta\beta_m$ and the c_m/a_m ratio can be derived as:

$$\frac{c'_m}{a'_m} = \frac{(c_m/a_m) \sin(\beta_m)}{(c_m/a_m) \sin(\Delta\beta_m) + \sin(\beta_m + \Delta\beta_m)}, \quad (3.31)$$

where the primed variables are those of the distorted monoclinic structure.

3.4 Conclusions

In this chapter, we have presented a neutron and x-ray diffraction study of multiferroic domains in 1 μm -thick $(111)_{pc}$ -oriented BFO films. We have found that unstrained BFO films grown on three-fold symmetric STO substrates are in fact not rhombohedral, as is generally believed, but undergo a small, monoclinic distortion away from the bulk rhombohedral structure. This monoclinic distortion is consistent with reported structures of relaxed $(100)_{pc}$ - and $(110)_{pc}$ -oriented films¹⁵⁷ and single crystals.¹⁴⁷ Unlike with the $(100)_{pc}$ - and $(110)_{pc}$ -oriented films, three-fold symmetry is not broken at the BFO–STO interface and the resulting interaction with the substrate stabilises

a sub-micron texture of coherent monoclinic twins. This texture is reminiscent of the dense polydomain states that are thermodynamically stable in ferroelectric perovskites such as PbTiO_3 in the presence of misfit strain.¹⁷⁸

Our observations further demonstrate that the domains in $(111)_{\text{pc}}$ BFO films break three-fold symmetry in *both* magnetic *and* crystal sectors such that the magnetic and monoclinic domain structures are coherent, having matching topography and symmetry elements. These conclusions are further corroborated by the XMLD-PEEM measurements discussed in chapter 6, in which we directly image the magnetostructural domain structure and find it to be consistent with the twinning model proposed here, both in terms of domain size and orientation of the domain walls.

The coupling between the magnetic structure and the monoclinic distortion, results in the magnetic propagation vector being locked to the monoclinic b-axis of the structural domains. The magnetic domain structure of $(111)_{\text{pc}}$ -oriented films should therefore be controllable by strain and substrate miscut as for other BFO orientations. By choosing an appropriate, non-three-fold-symmetric substrate that biases the growth of one monoclinic domain over the other two, one should be able to grow $(111)_{\text{pc}}$ -BFO films as a single multiferroic domain. This may provide an BFO film with maximal ferroic properties, combining the full, surface-normal ferroelectric polarisation with a magnetic structure coherent (up to the level of phase-slip domains) across the entire film.

These results further indicate a possible solution to the polarisation fatigue and electrical breakdown exhibited by $(111)_{\text{pc}}$ -BFO films upon switching. Since the structure is locally monoclinic, it breaks the symmetry that makes the three-switching pathways equivalent and thus it is likely that the switching, rather than being non-deterministic, is pre-biased by the monoclinic distortion. In a monodomain film, it may be possible to achieve deterministic switching via a unique switching pathway. In principle, this could remove any polarisation fatigue/charged domain wall effects that would otherwise prevent the use of $(111)_{\text{pc}}$ -BFO films in practical devices.

As well as the results regarding the domain structure of the BFO films, the NXMS technique

¹⁷⁸VG Koukhar, NA Pertsev, and R Waser. *Phys. Rev. B*, **64**: 214103, 2001.

used to investigate them is also novel. The NXMS measurements presented in this chapter constitute the first application of non-resonant x-ray magnetic scattering to studying magnetism in thin film multiferroics. In this case, our NXMS results enabled us to fully characterise both the magnetic and crystal structure of the films, from the relative cycloidal/monoclinic domain populations, down to the cycloidal plane of rotation and magnetic polarity of the magnetic structure. Many contemporary studies working on multiferroic thin films and devices use bulk transport and magnetisation measurements or surface sensitive techniques such as scanning probe microscopy and X-PEEM measurements to characterise the behaviour of the material.^{134,159,179,180} NXMS provides a unique insight into these materials, probing the magnetic structure on the atomic scale, which, along with ability to readily apply fields *in-situ*, allows device functionality to be understood at a fundamental level. Although the neutron diffraction measurements (also only relatively recently applied to magnetic thin-film systems^{181,182}) provide similar information, the high reciprocal- and real-space resolution offered by NXMS, along with the ability to refine the measurement with polarimetry, make NXMS an ideal tool for investigating multiferroic epitaxial films. This technique could be further applied to many other functional antiferromagnets in device configurations.

¹⁷⁹LW Martin et al. *J. Phys. Condens. Matter*, **20**: 434220, 2008.

¹⁸⁰D Sando, A Barthélémy, and M Bibes. *J. Phys. Condens. Matter*, **26**: 473201, 2014.

¹⁸¹CF Majkrzak. *Physica B*, **221**: 342–356, 1996.

¹⁸²A Schreyer et al. *J. Appl. Phys.*, **87**: 5443–5448, 2000.

SUBSTRATE CONTROL OF MULTIFERROIC DOMAIN POPULATIONS IN BiFeO_3 FILMS

The presence of domains in ferroic materials can diminish their macroscopic ferroic properties and hence their usefulness in device applications. From an experimental perspective, measuring a multidomain sample can complicate the interpretation of material properties and their underlying mechanisms. In the previous chapter, we found that the magnetic and crystallographic domain structures of BFO were intimately coupled, potentially allowing the control of magnetic domains through epitaxial strain. In this chapter, we attempt to grow a $(111)_{\text{pc}}$ -BFO film that is a magneto-structural monodomain through substrate engineering. By using an orthorhombic TbScO_3 substrate, we are able to grow a film that comprises a coherent, $1\text{ }\mu\text{m} \times 10\text{ mm} \times 10\text{ mm}$ crystallographic, magnetic, ferroelectric and ferroelastic monodomain.

4.1 Introduction

IN epitaxially grown BFO films, the effect of lattice mismatch between the film and the substrate can induce strain up to levels of several percent, which can cause the structural, magnetic and electric properties to deviate from their bulk counterparts.^{151,152} Structurally, this can result in the film having a lower symmetry than rhombohedral bulk-like BFO, allowing tetragonal, monoclinic and orthorhombic phases through particular combinations of substrate strain and film orientation.¹⁸⁰ This in turn affects the ferroelectric and magnetic properties of the film allowing them to be ‘strain engineered’. Using the wide range of commercially-available perovskite substrates, it is possible to choose precisely the magnitude and direction of the substrate strain applied. This is principally determined by the composition and orientation of the substrate, but can be further tuned by applying a miscut to the surface of the substrate. Substrate-induced changes can be used to rotate the polarisation vector,¹⁸³ alter the Curie temperature,¹⁸⁴ and tune the propagation vector and plane of rotation of the magnetic moments.¹⁸⁵ By growing films below a certain critical thickness of ~100 nm, it is even possible to remove the cycloidal rotation entirely.¹⁵⁴

The domain structure, both in terms of domain size and morphology can also be tailored via substrate engineering.^{186,187} Growing BFO films that are ferroelectric and ferroelastic monodomains can be reliably achieved through a combination of a conducting buffer layer between

¹⁵¹DG Schlom et al. *Annu. Rev. Mater. Res.*, **37**: 589–626, 2007.

¹⁵²DG Schlom et al. *MRS Bull.*, **39**: 118–130, 2014.

¹⁸⁰D Sando, A Barthélémy, and M Bibes. *J. Phys. Condens. Matter*, **26**: 473201, 2014.

¹⁸³HW Jang et al. *Phys. Rev. Lett.*, **101**: 107602, 2008.

¹⁸⁴IC Infante et al. *Phys. Rev. Lett.*, **105**: 057601, 2010.

¹⁸⁵D Sando et al. *Nat. Mater.*, **12**: 641–646, 2013.

¹⁵⁴T Gao et al. *Nano Lett.*, **17**: 2825–2832, 2017.

¹⁸⁶YH Chu et al. *Adv. Mater.*, **18**: 2307–2311, 2006.

¹⁸⁷CJM Daumont et al. *Phys. Rev. B*, **81**: 144115, 2010.

the substrate and BFO film to bias the growth of a single ferroelectric domain,^{164,165,188} and, depending on the orientation of the film, an appropriate substrate miscut to bias the growth of a single ferroelastic domain.¹⁸⁹ However, reliably engineering a BFO film comprising a single cycloidal magnetic domain has not previously been achieved. Although single-magnetic-domain films of BFO have been previously reported, this has only been achieved in ultrathin, (100)_{pc}-oriented films.¹⁷² By growing a 4 nm film on a NdGaO₃ substrate, which imposes a large in-plane anisotropic strain on the BFO layer, Kuo *et al.* were able to engineer a BFO film comprising a G-type antiferromagnetic monodomain, however, films above this thickness grown on the same substrate were seen to revert to a multidomain state.

The magnetoelastic coupling we have observed in the BFO/STO films opens up the possibility to strain engineer the magnetic domain structure of BFO. By engineering the BFO in a such way as to bias the growth of a single monoclinic domain, the one-to-one coupling between magnetic and structural domains will ensure that the entire film would also comprise a single *magnetic k*-domain. In an attempt to grow a 1 μm -thick (111)_{pc}-BFO film comprising a single monoclinic and magnetic domain, we have adopted two different approaches. Firstly, we try to break the three-fold symmetry of a (111)_{pc}-STO substrate by introducing a miscut along a particular direction. Secondly, we use a substrate of lower symmetry, which provides a mechanism to break three-fold symmetry even in the absence of a miscut.

To determine the relative magnetic *k*-domain populations of the substrate-engineered BFO films, we measure by NXMS and neutron diffraction the magnetic satellite peaks arising from the cycloidal magnetic structure. The experimental setup and method are identical to those described in the previous chapter (see section 3.3).

¹⁶⁴DD Fong et al. *Phys. Rev. Lett.*, **96**: 127601, 2006.

¹⁶⁵JE Giencke et al. *Curr. Opin. Solid State Mater. Sci.*, **18**: 39–45, 2014.

¹⁸⁸YH Chu et al. *Adv. Mater.*, **19**: 2662–2666, 2007.

¹⁸⁹SH Baek et al. *Nat. Mater.*, **9**: 309–314, 2010.

¹⁷²CY Kuo et al. *Nat. Commun.*, **7**: 12712, 2016.

4.2 Substrate miscut - 4° miscut SrTiO₃ substrate

A 1 μm -thick (111)_{pc}-BFO film was grown on a STO substrate that had been miscut at an angle of 4° along a direction parallel to the $[010]_h$ direction in the BFO layer. This direction is parallel to $\mathbf{k}$ and orthogonal to the distortion direction (tilting direction of $\mathbf{c}^*$) of the $\mathbf{k}_2/\text{M2}$ magnetostructural domain we observed in the (111)_{pc} film grown on a non-miscut STO substrate (see section 3.3.4). This miscut breaks three-fold symmetry between the monoclinic domains with the distortion directions of the M1, M2 and M3 domains pointing (approximately) down the slope, perpendicular to the slope, and (approximately) up the slope of the miscut, respectively. The growth procedure was otherwise identical to that described in section 3.2.1, including the SRO buffer layer to bias a single ferroelectric domain.

4.2.1 Nonresonant magnetic x-ray and neutron diffraction reciprocal space mapping

Figure 4.1a shows a reciprocal space map measured by NXMS about the $\mathbf{N} = (009)_h$ position and the corresponding neutron diffraction pattern, measured about the $\mathbf{N} = (003)_h$ position, is shown in fig. 4.1(b). The theoretical intensities calculated from the model discussed in section 3.3.3 fit the data well ($\chi^2_v = 2.2$) with a propagation vector of $\delta = 0.0042(1) \text{ \AA}^{-1}$, consistent with the result obtained on the non-miscut BFO/STO film. By allowing the magnetic domain populations to freely refine during the regression, we find that the $\mathbf{k}$ -domains are equally populated and the neutron data indicate that this result is representative of the entire film. We therefore find that, applying a 4° miscut to a STO substrate along the $[010]_h$ BFO direction appears to have no observable effect on either the magnetic domain populations or domain size.

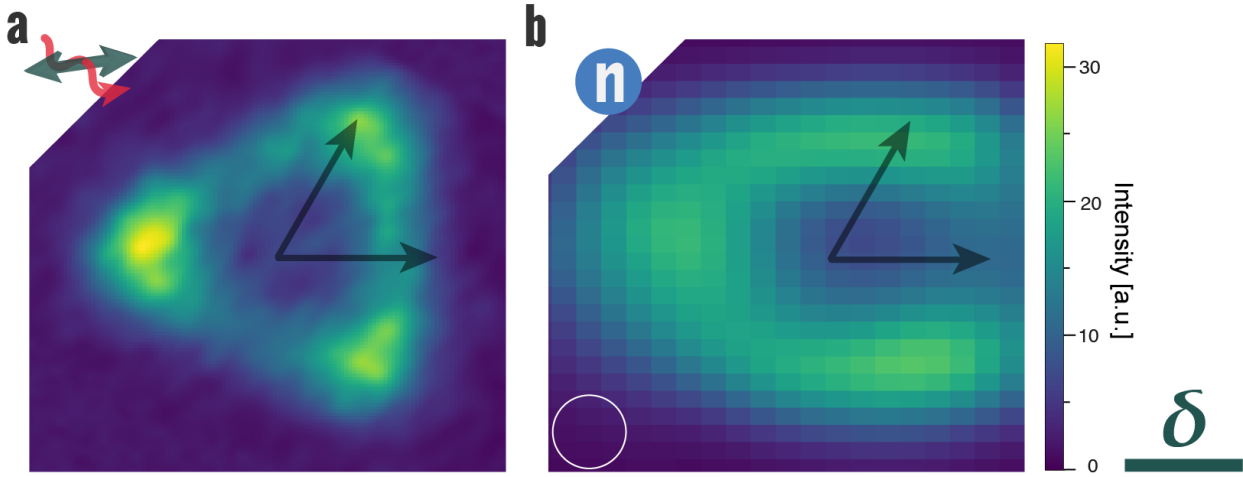


Figure 4.1: **Magnetic x-ray and neutron diffraction reciprocal space maps of BFO/STO (4° miscut).** **a**, Reciprocal space map about $(009)_h$ measured at room temperature by NXMS with linear polarised x-rays. **b**, Reciprocal space map about the $(003)_h$ measured at room temperature by neutron diffraction. The white circle in the lower left corner indicates the instrumental resolution. The scale bar in the bottom left shows the magnitude of the propagation vector (both images on the same scale) and the reciprocal lattice directions (in the hexagonal setting) are indicated by the translucent black arrows.

4.3 Substrate symmetry - Orthorhombic TbScO₃ substrate

A 1 μm -thick $(111)_{pc}$ -BFO film was grown on an orthorhombic TbScO₃ (TSO) substrate oriented such that the specular direction is $[011]_o$, indexed in the orthorhombic (subscript o) TSO unit cell. The BFO layer is oriented such that the $\mathbf{b}_h$ axis of the BFO lines up with the $\mathbf{a}_o$ axis of the TSO substrate. The growth procedure was otherwise identical to that described in section 3.2.1, including the SRO buffer layer to bias a single ferroelectric domain.

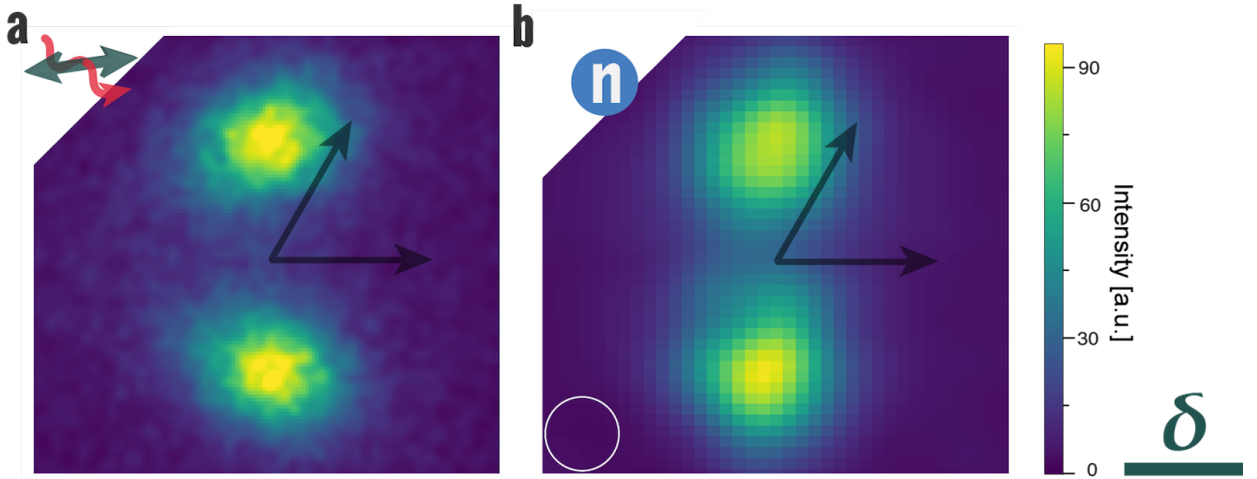


Figure 4.2: **Magnetic x-ray and neutron diffraction reciprocal space maps of BFO/TSO.** **a**, Reciprocal space map about $(009)_h$ measured at room temperature by NXMS with linear polarised x-rays. **b**, Reciprocal space map about the $(003)_h$ measured at room temperature by neutron diffraction. The white circle in the lower left corner indicates the instrumental resolution. The scale bar in the bottom left shows the magnitude of the propagation vector (both images on the same scale) and the reciprocal lattice directions (in the hexagonal setting) are indicated by the translucent black arrows.

4.3.1 Nonresonant magnetic x-ray and neutron diffraction reciprocal space mapping

Figure 4.2 shows a reciprocal space map measured by NXMS about the $\mathbf{N} = (009)_h$ position. Instead of the ‘triangular’ diffraction pattern we have observed in our $(111)_{pc}$ -oriented films thus far, we observe only a single pair of satellite peaks positions at $\pm \mathbf{k}_2$ relative to the $\mathbf{N} = (009)_h$. This demonstrates that the region of the film illuminated by the x-ray spot is within a single cycloidal domain. The theoretical intensity calculation fits the data well ($\chi^2_v = 1.618$) and yields a propagation vector of $\delta = 0.0042(1) \text{ \AA}^{-1}$. We note that the increase in the peak intensity relative to the previous measurements of the multidomain BFO/STO films is consistent with scattering being condensed into just two satellite peaks. To test whether this result was representative of the entire film, we repeated this measurement at several other positions over the sample and obtained an identical result at each position.

The corresponding neutron diffraction pattern, measured about the $\mathbf{N} = (003)_h$ position, is shown in fig. 4.1(b). Given that the neutron beam illuminates the entire sample, this verifies that the entire film comprises a magnetic monodomain. The propagation vector of the cycloidal domain is $\mathbf{k}_2$, which is along the $[010]_h$ direction of the BFO and the $[100]_o$ direction of the TSO substrate. We also note the absence of the diffuse tails of intensity between the two peaks, which indicates the magnetic structure is largely coherent throughout the film. This would be consistent with the hypothesis that the small domain size in the multidomain BFO/STO films is an important factor in causing the disorder resulting in the diffuse scattering observed in those films.

4.3.2 Nonresonant magnetic x-ray polarimetry

To further characterise the magnetic structure of the BFO/TSO monodomain film, we performed polarisation analyser scans of the magnetic peak intensity using linear and circular polarised x-rays. These measurements can be used to extract information on the fine details of the cycloidal magnetic structure and are especially sensitive to the plane of rotation of the cycloid. Figure 4.3a and b show polarisation analyser scans of the $(009)_h + \mathbf{k}_2$ and the $(009)_h - \mathbf{k}_2$ peaks, respectively. To account for the sphere-of-confusion error of the polarisation analyser, at each value of η , a rocking curve of the polarisation analyser crystal is recorded and the integrated area of the rocking-curve scan is used as a measure of the scattered intensity. Although the polarisation dependence of the data is reminiscent of what one would expect, i.e. identical behaviour on both peaks for σ -polarised x-rays and the interchanged behaviour for circular-left and circular-right polarised x-rays between peaks, the η -dependence for all polarisations does not have the expected shape. Importantly, η -dependences for left- and right-handed x-ray polarisations must be mirror images of one another (i.e. related by a reflection about their midpoint in intensity) for a cycloidal magnetic structure, regardless of the plane of rotation. This suggests the unexpected η -dependences may be due to an extra polarisation dependence originating from the background.

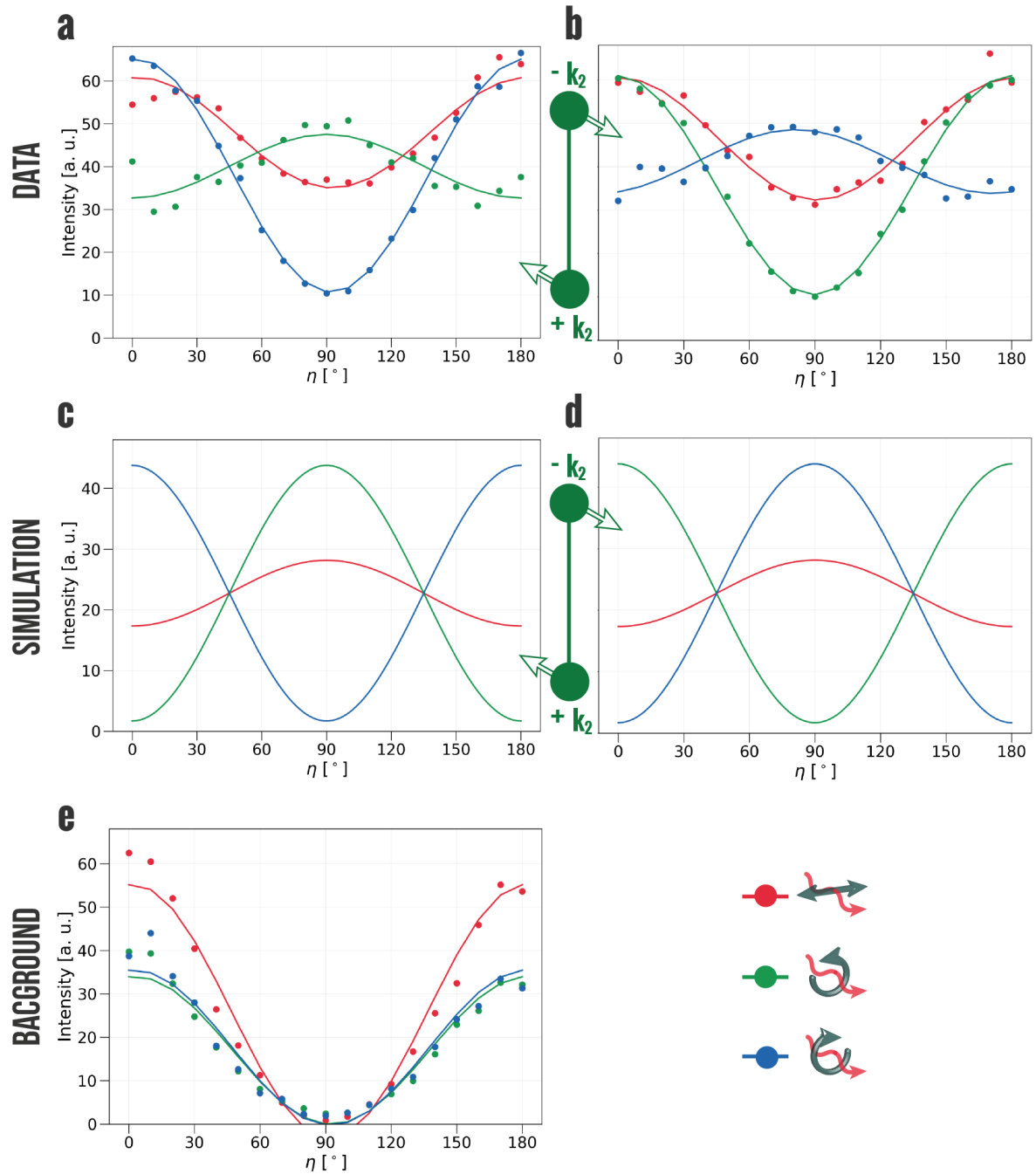


Figure 4.3: **Polarisation analyser scans of magnetic satellite peaks of BFO/TSO.** Polarisation analyser scans of the $(009)_h + \mathbf{k}_2$ (a,) $(009)_h - \mathbf{k}_2$ (b,) peak, measured with incident linear horizontal (red), circular left (green) and circular right (blue) polarised x-rays. The circles show the experimentally measured intensities and the solid lines show the results of a least-squares refinement of a sin-squared function as a guide to the eye. Simulated polarisation analyser scans of the $(009)_h + \mathbf{k}_2$ (c,) and $(009)_h - \mathbf{k}_2$ peaks (d,) for the a single cycloidal magnetic domain. (e,) Polarisation analyser scans of the background measured with incident linear horizontal (red), circular left (green) and circular right (blue) polarised x-rays. All measurements were taken at room temperature.

Figure 4.3c and d show the theoretical η -dependences of the scattered intensity expected for a single cycloidal domain measured on the $(009)_h + \mathbf{k}_2$ and the $(009)_h - \mathbf{k}_2$ peaks, respectively. Comparing these to the corresponding measurements in fig. 4.3(a) and (b), it appears the discrepancy is somewhat systematic. A polarisation scan of background, shown in fig. 4.3(e), reveals the strong polarisation dependence of the background to be the source of the discrepancy. This polarisation dependence arises due the fact that the scattering processes contributing to the background predominantly scatter into the σ - σ channel. Although in many experiments this background dependence is small relative to the magnetic signal and thus may often be neglected, it is crucial to account for it in thin-film diffraction experiments because the scattering volume is so low.

To obtain the polarisation dependence of the pure magnetic signal without the additional background component, we perform the following background subtraction: for each value of η we perform a rocking-curve scan of the polarisation analyser crystal both on the magnetic peak and on the background. We then subtract the rocking curve of the background from the that of the magnetic peak and integrate the background-subtracted rocking-curve scan. The resulting background-corrected polarisation analyser scans of the $(009)_h + \mathbf{k}_2$ and the $(009)_h - \mathbf{k}_2$ peaks are shown in fig. 4.4(a) and (b), respectively. These now appear to have the expected η -dependence and we can fit the intensities predicted by the model described in section 3.3.3 to the data.

The solid lines in fig. 4.4(a) and (b) show fits of the theoretical η -dependences of the scattered intensity to the data and it is clear that they describe the data very well. These were performed by simultaneously refining the theoretical scattered intensity of all three polarisations calculated for a single cycloidal domain parameterised only by a global scale, constant background, and depolarisation factor. This factor accounts for the imperfect circular polarisation achieved by the phase plate. For both circular polarisations, the beam was found to be 93 % polarised where the remainder of the beam was modelled as being totally unpolarised, which is consistent with

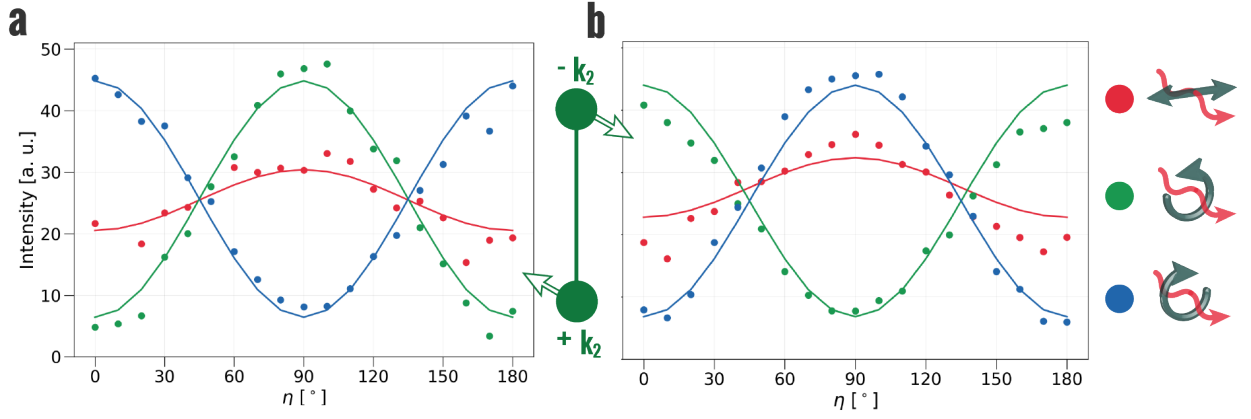


Figure 4.4: **Background-corrected polarisation analyser scans of magnetic satellite peaks of BFO/TSO.** Polarisation analyser scans of the $(009)_h + \mathbf{k}_2$ (a,) and $(009)_h - \mathbf{k}_2$ peaks (b,) measured with incident linear horizontal (red), circular left (green) and circular right (blue) polarised x-rays. The circles show the experimentally measured intensities and the solid lines show the results of a least-squares refinement of the theoretical scattered intensity for a single cycloidal domain. All measurements were taken at room temperature.

previous reports using an identical experimental setup.¹⁵⁰ We therefore conclude that the data is only consistent with a cycloidal magnetic structure with spins rotating in a plane containing the $[001]_h$ (out-of-plane) direction and the $\mathbf{k}_2$ (in-plane) propagation vector direction. These scans also indicate the sample is a monodomain in the magnetic polarity (the ‘sense of rotation’) of the cycloidal magnetic structure, as the opposite magnetic polarity domain would have opposite circular polarisation dependence (i.e. the blue and green data points would be interchanged). We can infer that this measurement of magnetic polarity is representative of the entire film: given that the magnetic polarity is coupled directly to the ferroelectric polarisation, and the film is a ferroelectric monodomain (with the polarisation pointing along the $[00\bar{1}]_h$ direction), we would expect the magnetic polarity to be homogeneous.

4.4 Conclusions

In summary, we have successfully engineered a $(111)_{pc}$ -BFO film that is a single ferroelectric, structural and magnetic domain. Using NXMS and neutron diffraction, we determined the mag-

¹⁵⁰RD Johnson et al. *Phys. Rev. Lett.*, **110**: 217206, 2013.

netic structure and relative domain populations of $(111)_{\text{pc}}$ -BFO films grown on a miscut STO substrate and an orthorhombic TSO substrate. Despite the three-fold symmetry of the STO being broken by the 4° miscut, this did not have any observable effect on the relative domain populations or size of the domains when compared to an equivalent film grown on non-miscut STO. However, using the bias from a TSO substrate, we found that we were able to eliminate the magnetic/monoclinic $\mathbf{k}_1/\text{M1}$ - and $\mathbf{k}_3/\text{M3}$ -domain populations entirely, such that the entire film comprised a $\mathbf{k}_3/\text{M3}$ monodomain, increasing the domain size by five orders of magnitude. Using x-ray polarimetry we were able to confirm that not only is the sample a single domain in the propagation vector but also in the magnetic polarity of the cycloidal magnetic structure.

Growing a truly monodomain $(111)_{\text{pc}}$ -BFO film, coherent (up to the level of any mosaicity) across the entire $10\text{ mm} \times 10\text{ mm}$ film, represents a crucial step towards realising a BFO-based logic device. Not only does a monodomain film provide a model system to study both bulk and surface effects in BFO, but the elimination of extrinsic domain effects means that the full functionality of BFO may be realised. Furthermore, using a monodomain film in a heterostructure device has clear advantages as, depending on the termination layer of BFO, it could provide an entirely uniform interaction at the interface.

ELECTRICAL SWITCHING OF MAGNETIC POLARITY IN A MULTIFERROIC DEVICE

Despite the many encouraging results in multiferroic device research in recent years, there has been relatively little progress in relating macroscopic device switching to microscopic changes in the magnetic structure at the atomic level. In particular, electrical reversal of a magnetic order parameter in a Type-I multiferroic has yet to be observed. In this chapter, we measure by NXMS the effect of electrical switching on the magnetic polarity of a $(111)_{\text{pc}}\text{-BiFeO}_3$ film device, a direct test of the fundamental coupling between magnetism and ferroelectricity. We find that the magnetic polarity switches reversibly upon switching the ferroelectric polarisation and are able to map this over the device, distinguishing between regions of the sample electrically addressed into the two magnetic states with a resolution of a few tens of microns.

5.1 Introduction

ONE of the most interesting and technologically useful properties of multiferroics is their magnetic response to an applied electric field. This coupling between ferroelectricity and magnetism is manifest in the Landau free energy expansion for the multiferroic phase, which will contain a term that is the product of ferroic order parameters representing the magnetic and ferroelectric order. Typically, this consists of an antiferromagnetic order parameter that is *quadratic* in the magnetic moments* and is *linearly* coupled to the ferroelectric polarisation.

The various coupling mechanisms discussed in section 1.3.2 differ in the nature of this magnetic order parameter: for the most common cycloidal multiferroics,⁶⁵ this parameter is represented by a *magnetic polarity*, and is commonly referred to as “cycloidal rotation direction” or “magnetic chirality”[†]. For the other two known varieties — ferroaxial¹⁹⁰ (including p-d hybridised⁷¹) multiferroics and exchange-striction multiferroics⁵⁶ — this order parameter is represented by a magnetic helicity or a staggered exchange scalar field, respectively.

In the case of BFO, a cycloidal multiferroic, the quadratic order parameter is the magnetic polarity λ . This is a vector quantity that describes not only the plane of rotation of the cycloid, but also its ‘sense of rotation’ i.e. the handedness of rotation from one spin to the next along the propagation vector $\mathbf{k}$, when the spins are viewed from a given direction. The magnetic polarity is defined as $\lambda \equiv \mathbf{k} \times \mathbf{S}_i \times \mathbf{S}_j$, where $\mathbf{S}_i$ and $\mathbf{S}_j$ are spins on adjacent sites that are sequential along the direction of $\mathbf{k}$. This is depicted in fig. 5.1, which shows two cycloidal spin arrangement of opposite magnetic polarity.

*For the magnetic order to exist in the absence of any external magnetic fields, time reversal symmetry requires that this order parameter an even power of the angular momentum operators.

⁶⁵M Mostovoy. *Phys. Rev. Lett.*, **96**: 067601, 2006.

[†]This latter term is a misuse of chirality, as a cycloid, a two dimensional object, is decidedly *not* chiral (or helical).

¹⁹⁰RD Johnson et al. *Phys. Rev. Lett.*, **107**: 137205, 2011.

⁷¹TH Arima. *J. Phys. Soc. Jpn*, **76**: 073702–073702, 2007.

⁵⁶LC Chapon et al. *Phys. Rev. Lett.*, **93**: 177402, 2004.

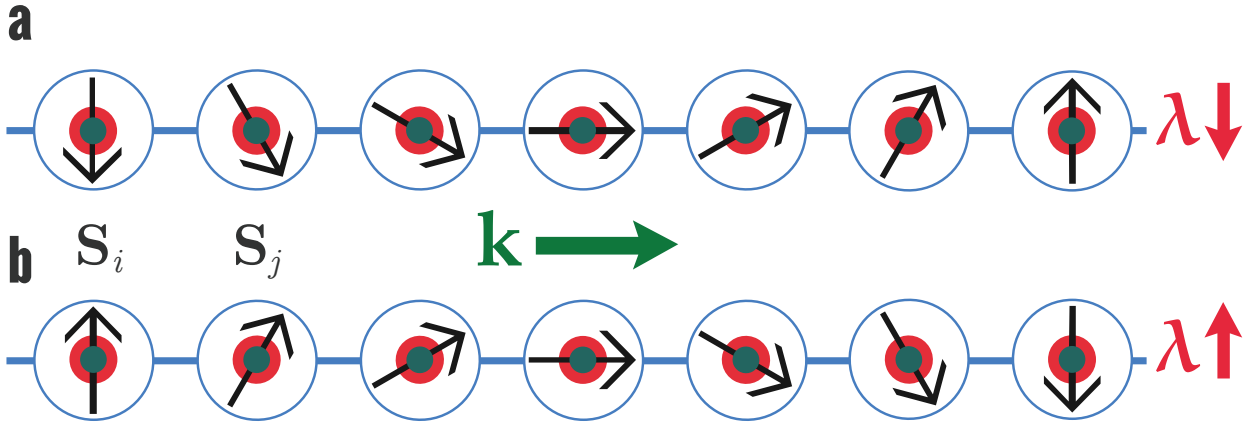


Figure 5.1: **Definition of magnetic polarity.** a,b, Magnetic spin cycloids of opposite magnetic polarity.

The term in the free energy describing the linear coupling of λ to the polarisation is given by

$$F_{\text{MF}} = \nu \lambda \cdot \mathbf{P}, \quad (5.1)$$

where ν is the coupling constant. Therefore, in the absence of any other magnetic anisotropies, the magnetic polarity should remain parallel or antiparallel (determined by the sign of ν) to the polarisation.

5.1.1 Electrical control of magnetism in multiferroics

A clear consequence of the linear coupling to $\mathbf{P}$ in eq. (5.1) is that if the polarisation were to change direction, the magnetic polarity should change accordingly. This behaviour is mirrored for any linear coupling of magnetism to ferroelectricity, thus enabling control of the magnetic structure with an electric field. Electrical control of magnetic domains at low temperature has indeed been demonstrated on bulk single crystals of several Type-II multiferroics by neutron

polarimetry^{57,191–193} and magnetic x-ray scattering.¹⁹⁴ In the latter study, Fabrizio et al. were able to exploit the small x-ray beam size to image the gradual switching of magnetic cycloidal domains. The use of this microdiffraction technique to image magnetic domains has since been expanded to other (non-switching) studies of both Type-I¹⁵⁰ and helical Type-II¹⁹⁵ multiferroics.

Electrical control of the magnetic order parameter in a Type-I multiferroic has yet to be unambiguously demonstrated. As discussed in section 1.3.1, the coupling between ferroelectricity and magnetism in Type-I multiferroics is often described as ‘weak’⁶¹ due to the independent origins of their ferroelectric and magnetic order. A direct observation of the coupling between magnetic and ferroelectric order parameters in a Type-I multiferroic would therefore shed light on the nature of this interaction and is a missing milestone in the quest for practical applications of these materials.

Switching magnetic polarity in BiFeO₃

Given its room-temperature multiferroicity and large ferroelectric polarisation, BFO is the ideal system in which to demonstrate this coupling. Although electrical manipulation of spins in BFO has been demonstrated in numerous studies (see below), the exact mechanism is obscured by the simultaneous changes in the ferroelastic state of the material upon switching the polarisation.

As discussed in section 3.1.1, the spontaneous electric polarisation $\mathbf{P}$ is directed along one of the $[111]_{pc}$ axes of the BFO pseudo-cubic cell and is associated with a ferroelastic distortion along the same direction, resulting in the rhombohedrally distorted perovskite structure discussed in section 3.1.1. The polarisation can be switched by 71° , 109° , or 180° between the 8 possible $[111]_{pc}$

⁵⁷PG Radaelli et al. *Phys. Rev. Lett.*, **101**: 067205, 2008.

¹⁹¹Y Yamasaki et al. *Phys. Rev. Lett.*, **98**: 147204, 2007.

¹⁹²I Cabrera et al. *Phys. Rev. Lett.*, **103**: 087201, 2009.

¹⁹³AJ Hearmon et al. *Phys. Rev. Lett.*, **108**: 237201, 2012.

¹⁹⁴F Fabrizio et al. *Phys. Rev. B*, **82**: 024434, 2010.

¹⁵⁰RD Johnson et al. *Phys. Rev. Lett.*, **110**: 217206, 2013.

¹⁹⁵Y Hiraoka et al. *Phys. Rev. B*, **84**: 064418, 2011.

⁶¹D Khomskii. *Physics*, **2**: 20, 2009.

directions, where switching by 71° , 109° is also accompanied by a switching of the ferroelastic state.¹⁵⁹ It has been shown that when switching between 71° ferroelastic domains in single crystals of BFO, that both direction of the cycloidal propagation vector and the spin rotation plane can be manipulated,^{196–198} where the spin rotation plane rotates as would be expected due to the coupling to the ferroelastic domain via magneto-elastic strain.¹⁸⁵ Similar experiments have been performed on $(100)_{\text{pc}}$ -oriented thin films of BFO, where the changes to magnetic structure were observed with XMLD-PEEM^{136,199} and neutron diffraction.^{137,199} These experiments similarly demonstrated a rotation of the cycloid plane upon 71° switching, although the cycloid plane was seen to deviate from its expected orientation, instead lying closer to the plane of the film.

In spite of these encouraging results, there has been relatively little progress in understanding macroscopic device switching in terms of the microscopic multiferroic mechanism coupling the magnetic structure to the polarisation, at the atomic level. Since the rhombohedral axis is unchanged when the polarisation is switched by 180° , the ferroelastic domain also remains unchanged and thus observing the response of the magnetic polarity under 180° electrical switching would constitute an unambiguous measurement of coupling between ferroelectricity and magnetism in BFO. Obtaining such information in an epitaxial film device requires a polarimetric scattering technique with both high sensitivity and high spatial resolution — a combination that had not been achieved so far.

Having understood the complex domain structure of $(111)_{\text{pc}}$ -oriented BFO films in chapters 3 and 4, here we present the results of a NXMS study in which we measure changes in the magnetic polarity induced by ferroelectric switching of a BFO epitaxial-film device. Unlike previous studies,

¹⁵⁹F Zavaliche et al. *Phase Transit.*, **79**: 991–1017, 2006.

¹⁹⁶D Lebeugle et al. *Phys. Rev. Lett.*, **100**: 227602, 2008.

¹⁹⁷S Lee et al. *Phys. Rev. B*, **78**: 100101, 2008.

¹⁹⁸S Lee et al. *Appl. Phys. Lett.*, **92**: 192906, 2008.

¹⁸⁵D Sando et al. *Nat. Mater.*, **12**: 641–646, 2013.

¹³⁶T Zhao et al. *Nat. Mater.*, **5**: 823–829, 2006.

¹⁹⁹W Saenrang et al. *Nat. Commun.*, **8**: 1583, 2017.

¹³⁷W Ratcliff II et al. *Phys. Rev. B*, **87**: 140405, 2013.

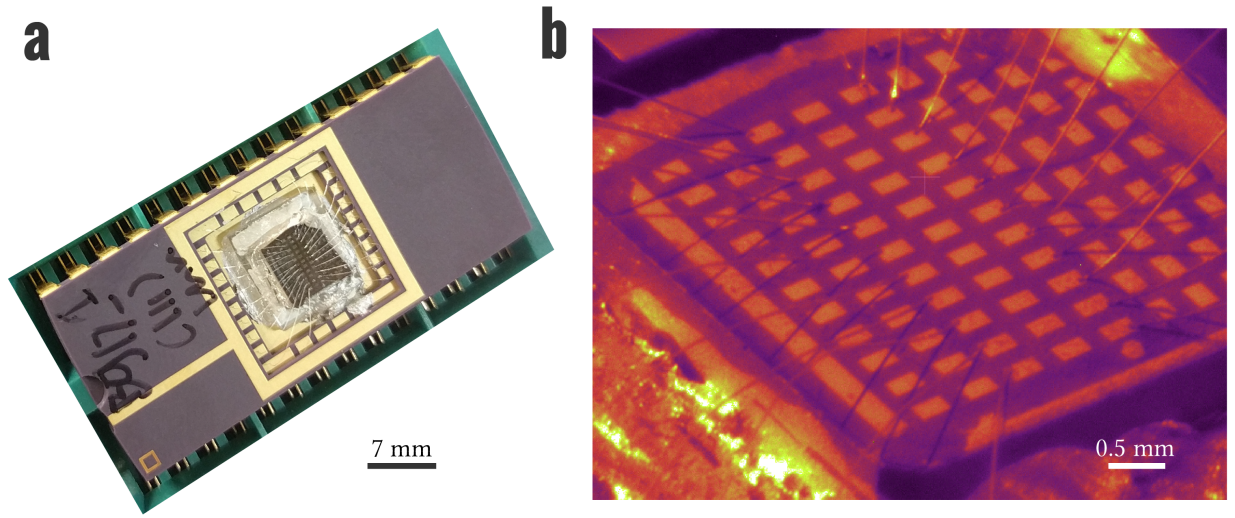


Figure 5.2: **Optical images of the BFO-film device.** Camera **a**, and microscope **b**, optical photographs of the $(111)_{\text{pc}}$ -BFO film device. The electrodes are wire bonded to a chip carrier and the SRO layer is contacted via conductive silver paste.

our $(111)_{\text{pc}}$ -oriented device architecture has the full component of the electric polarisation aligned parallel to the applied (surface-normal) electric field, such that 180° switching of both electric polarisation and magnetic polarity may be achieved. We further use microdiffraction to map the magnetic polarity over the device with a $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ resolution.

5.2 Experimental details

5.2.1 Film preparation and characterisation

$1\text{ }\mu\text{m}$ -thick epitaxial films of $(111)_{\text{pc}}$ -oriented BFO were grown on $(111)_{\text{pc}}$ -oriented STO substrates using an identical procedure to that described in section 3.2.1. In this study, the SRO buffer layer, as well as biasing the film to grow as a ferroelectric monodomain, also fulfils the role of bottom electrode for switching the polarisation and for polarisation hysteresis loop measurements. $300\text{ }\mu\text{m} \times 200\text{ }\mu\text{m} \times 25\text{ nm}$ Pt top electrodes were patterned on the surface of the film using photolithography, as can be seen in fig. 5.2. The electrodes were then wirebonded to a chip carrier and the SRO layer was contacted to the chip carrier using conductive silver paste, as

can be seen in fig. 5.2. This setup allows electric fields to be applied along the $[111]_{\text{pc}}$ direction, perpendicular to the surface of the film.

The structural, ferroelectric and AFM characterisation of the film yielded results consistent with the previous batch, for which the characterisation measurements are discussed in section 3.2.2.

5.2.2 Preparing the ferroelectric state of the device

We label the ferroelectric domain with polarisation directions along $[111]_{\text{pc}}$ (surface normal, pointing out of the film) and $[\bar{1}\bar{1}\bar{1}]_{\text{pc}}$ (surface normal, pointing into the film) as $\text{FE} \uparrow$ and $\text{FE} \downarrow$, respectively. The as-grown state of the film is a $\text{FE} \downarrow$ monodomain, as tested by P-E loop measurements on electrodes on this sample and piezoresponse force microscopy on other representative samples. Regions of the sample were switched into the $\text{FE} \uparrow$ polarisation state prior to the experiment by applying a number of successive triangular waves at 5 kHz, with a maximum voltage of 22 V. To test the reversibility of this process, we switched some of these regions back into the $\text{FE} \downarrow$ polarisation state, using an inverted signal. The electric field profiles used to prepare the ferroelectric state of the BFO film are shown in fig. 5.3(a) and (b) and the corresponding responses of the polarisation are shown in fig. 5.3(c) and (d).

5.2.3 Nonresonant magnetic x-ray scattering experimental details

As shown in section 3.3.3, the magnetic polarity of the cycloidal magnetic structure in BFO may be determined by NXMS. Using circularly-polarised incident x-rays, in conjunction with a post-scatter linear polarisation analyser, produces a scattered intensity that is highly sensitive to the magnetic polarity of the illuminated magnetic domains. In this study, all NXMS measurements were made on beamline I16, Diamond Light Source, and use an almost identical method and experimental setup to that described in section 3.3.1. One important difference is that it was necessary to use the primary beam (upstream) exit slits to reduce the x-ray beam cross section

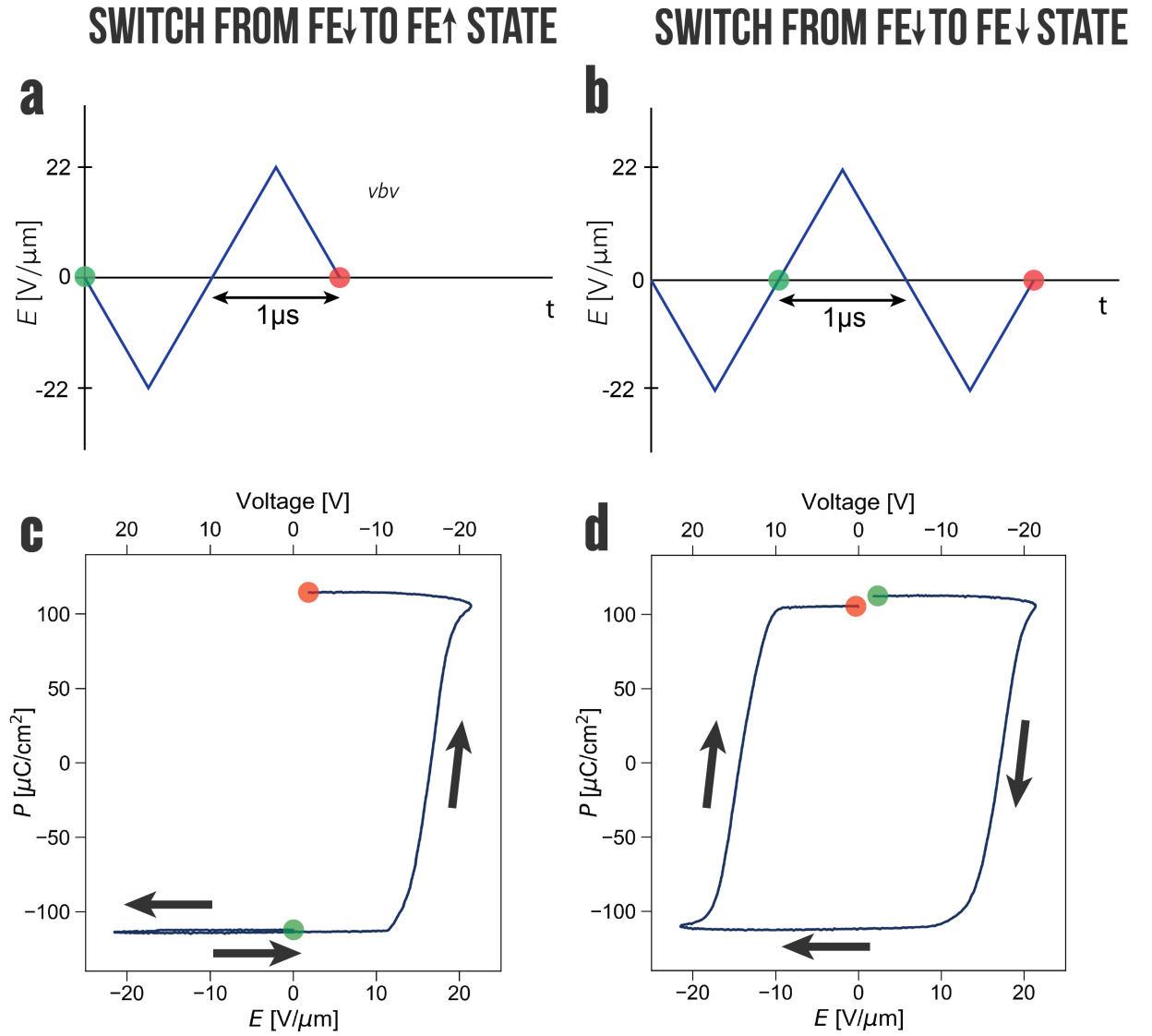


Figure 5.3: **Preparation of the ferroelectric state.** Electric field profiles applied to prepare the **a**, $FE\uparrow$ and **b**, $FE\downarrow$ states of the BFO film. The response of the ferroelectric polarisation to the field profiles preparing the **c**, $FE\uparrow$ and **d**, $FE\downarrow$ states. The corresponding start and end points on the field profiles and polarisation measurements are shown by the green and red circles, respectively. The black arrows indicate the electric-field sweep direction.

to $\approx 50 \mu\text{m} \times 50 \mu\text{m}$. This was to ensure that, when measuring a region of the sample under one of the electrodes, that only the switched region was illuminated by the beam and any intensity coming from the surrounding, switched region was minimal. The experiment was performed with an incident x-ray beam energy of 4.8 keV and an azimuthal angle of $\phi = 94^\circ$ with respect to the $(100)_h$ direction, which was identified as an experimental geometry in which multiple scattering was minimised.

5.3 Results and discussion

5.3.1 Nonresonant magnetic x-ray reciprocal space mapping

To determine cycloidal magnetic polarity of the $\text{FE} \uparrow$ and $\text{FE} \downarrow$ states, we measured by NXMS the magnetic satellite reflections that occur near the structurally-forbidden $\mathbf{N} = (009)_h$ Bragg peak using circularly polarised x-rays. This measurement was performed both on a ‘virgin’, unswitched region of the film (in the $\text{FE} \downarrow$ state), and on an electrode which had been switched into the $\text{FE} \uparrow$ state. Given that the film is grown on STO, we expect the same multidomain texture that was observed in chapter 3 with a typical domain size on the order of ~ 100 nm. We therefore expect approximately equal populations of all three $\mathbf{k}$ /monoclinic-domains to fall under the x-ray spot and hence to see the characteristic triangular diffraction pattern. For more details, see section 3.3.2.

Figure 5.4a and b show, for a region of the sample in the ‘virgin’ $\text{FE} \downarrow$ state, reciprocal space maps of the magnetic satellites about the $\mathbf{N} = (009)_h$ position for left-circular and right-circular polarised light, respectively. Figure 5.4e and f show the equivalent measurement on a region of the sample that has been switched into the $\text{FE} \uparrow$ state. We note that, as the diffraction intensity is centred at the same point in reciprocal space for the $\text{FE} \downarrow$ and $\text{FE} \uparrow$ states, both states are in the same pseudo-rhombohedral ferroelastic domain. The data agrees well with the corresponding simulations, shown in fig. 5.4(c, d) and (g, h), respectively, and with previous measurements

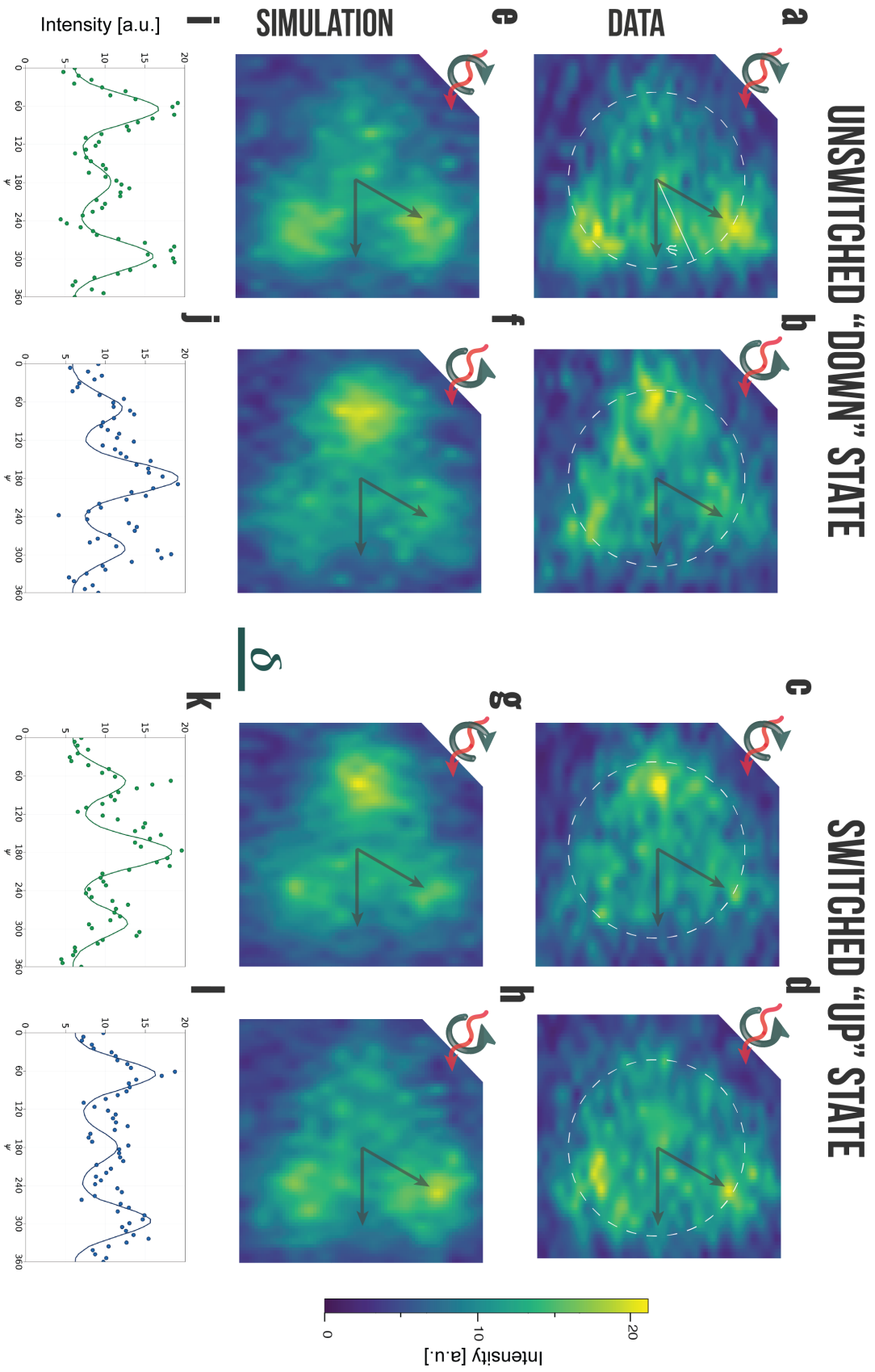


Figure 5.4: **Magnetic diffraction reciprocal space maps.** NXMS Reciprocal space maps about $(009)_h$ with left-circular and right-circular polarised light, respectively in the virgin FE $\downarrow$ state (**a,b**) and the (nominally) FE $\uparrow$ state (**c,d**). Fitted NXMS reciprocal space maps about $(009)_h$ with left circular and right circular polarised light, respectively in the virgin FE $\downarrow$ state (**e,f**) and the (nominally) FE $\uparrow$ state (**g,h**). Azimuthal line cuts through the measured (circles) and fitted (lines) NXMS reciprocal space maps with left circular and right circular polarised light, respectively in the virgin FE $\downarrow$ state (**i,j**) and the (nominally) FE $\uparrow$ state (**k,l**). The location of the line cuts are shown by the white dotted circles in (a–d). The scale bar in shows the magnitude of the propagation vector (all reciprocal space maps on the same scale) and the reciprocal lattice directions (in the hexagonal setting) are indicated by the translucent black arrows on the reciprocal space maps. The noise added to the fitted maps has been modelled as Poissonian.

taken with higher statistics (see section 3.3.2). The simulations shown here are generated with the parameters obtained by simultaneously fitting all reciprocal space maps (see section 5.3.2). Although these data were measured with increased counting times relative to those shown in section 3.3.2 on equivalent BFO/STO films, the signal-to-noise ratio is significantly worse. This is due to the smaller beam size, which results in reduction in incident flux by a factor of ~ 6 .

The theoretical intensity calculation for the composite magnetic peaks shown in fig. 5.4 yields

$$\frac{I_C}{I_{A,B}} \approx \frac{1 + \beta\gamma}{1 - \beta\gamma/2} \quad (5.2)$$

where the subscript denotes the individual peaks, labelled as A, B, and C (using the same labelling scheme as in chapter 3, see fig. 3.5) and where $\gamma = +1$ or -1 for left circular and right circular polarised light, respectively. The direction of the magnetic polarity is parametrised by $\beta = -\frac{\lambda \cdot \hat{n}}{|\lambda|}$, where $\hat{n}$ is the film surface normal. It is clear the sign of the second term in both the numerator and denominator of this ratio will invert if either of γ or β are changed, which is indeed what we observe when switching x-ray circular polarisation (fig. 5.4(a) vs (b)) and switching magnetic polarity (fig. 5.4(a) vs (e)). We find that magnetic polarity of a given domain is aligned antiparallel to the FE polarisation, hence $\beta = +1$ or -1 for the fully-polarised FE $\uparrow$ state and FE $\downarrow$ state, respectively, and $\nu = -1$ in eq. (5.1). This is in agreement both with our (better statistics) data on another BFO/STO film (section 3.3.2) and with a previous study on a bulk single crystal sample.¹⁵⁰

5.3.2 Magnetic polarity domain fractions

To quantitatively determine the domain populations of the $\beta = \pm 1$ magnetic polarity states for the FE $\uparrow$ state and FE $\downarrow$ states, the reciprocal space map data were fit using an identical model to that described in section 3.3.3. The switched percentage of magnetic polarity was obtained from a simultaneous fit of all four reciprocal space maps, measured with both circular left and circular right polarised light on both a virgin, FE $\downarrow$ region of the sample and a switched, FE $\uparrow$ region (data

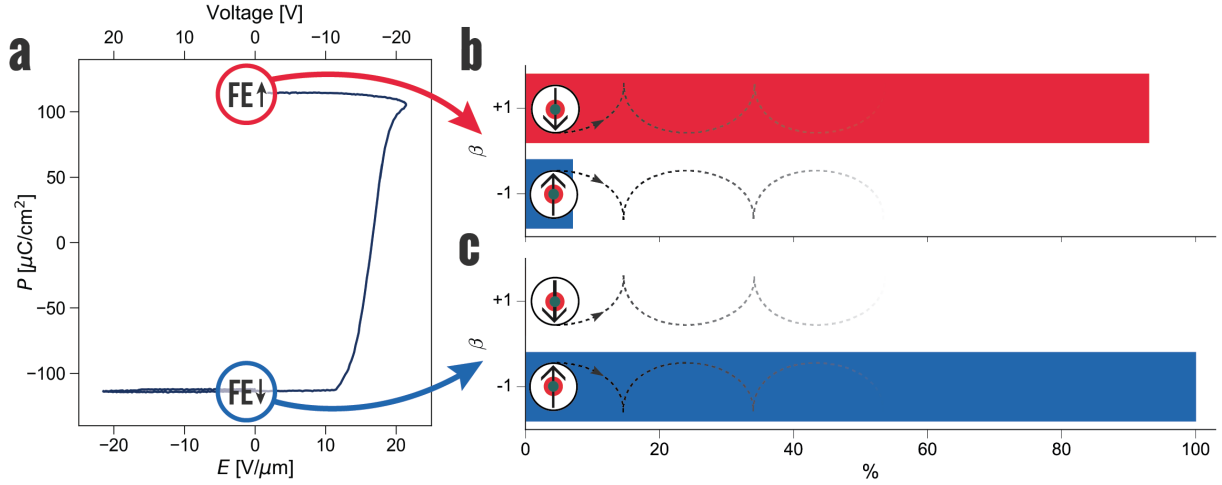


Figure 5.5: **Magnetic polarity domain fractions.** **a**, Ferroelectric polarisation of the sample measured while switching from the virgin $\text{FE} \downarrow$ state into the $\text{FE} \uparrow$ state. The black arrow indicates the electric-field sweep direction. **b,c**, The fitted percentage fraction of both the $\beta = +1$ and $\beta = -1$ magnetic polarity domains of the measured regions for the $\text{FE} \uparrow$ and $\text{FE} \downarrow$ states, respectively, as indicated by the coloured arrows.

shown in fig. 5.4(a, b) and fig. 5.4(e, f)). Four parameters describing the $\beta = \pm 1$ magnetic polarity state populations for both the $\text{FE} \uparrow$ and $\text{FE} \downarrow$ measurements were refined along with the three $\mathbf{k}$ -domain fractions, global parameters for the propagation vector and monoclinic distortion, and peak shape and background parameters. A global depolarisation factor was also included to account for the contribution from a weak multiple scattering peak centred on the $\mathbf{N} = (009)_h$ position and the imperfect efficiency of the x-ray phase plate. Previous measurements with better statistics and no contributions from multiple scattering showed that the virgin $\text{FE} \downarrow$ polarisation state has 100 % population of the $\beta = -1$ magnetic polarity state. The depolarisation factor was calculated by comparing this value to the value obtained from the fit to the data shown in fig. 5.4.

The model was found to fit the data well, with the simultaneous fit yielding $\chi^2_v = 1.484$. As shown in fig. 5.5(b, c), we found that there was a 93.0(6) % switch of magnetic polarity from the virgin $\text{FE} \downarrow$ state to the $\text{FE} \uparrow$ state. We further find, consistent with the results in section 3.3.4, that the three $\mathbf{k}$ -domains are equally populated in both the unswitched and switched states, within error. The unswitched 7 % could be explained by a fraction of the film being pinned in the

FE $\downarrow$ state, likely due to the bias at the BFO/SRO interface that stabilises a FE $\downarrow$ monodomain in the as-grown BFO film.^{164,165} A small pinned fraction would not be detected in the ferroelectric polarisation measurement in fig. 5.5(a) since this measurement is relative i.e. there is an arbitrary offset in the magnitude of $\mathbf{P}$. Furthermore, although the majority of the beam intensity was focussed into an $\approx 50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ footprint, low intensity tails of the beam may extend slightly beyond this so it is possible that a small region of the surrounding film in the FE $\downarrow$ state was illuminated. The depolarisation factor was found to be 0.194(4), which is significantly larger than the 0.07 depolarisation factor obtained in section 4.3.2. This is likely due to the multiple scattering peak centred on the $(009)_h$ position, which was not present in those measurements and whose polarisation dependence will be convoluted with that of the magnetic peaks.

5.3.3 Mapping magnetic polarity over the device

The response of the magnetic structure to electrical switching was further investigated by mapping in real space the magnetic polarity over an extended region of the device. Figure 5.6a and b show real space maps of an area of the sample containing regions that have been switched up and an area containing a region that has been switched up and then down again, respectively. These images were collected by rastering a $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ beam over the sample surface and recording the intensity of peak C (fig. 3.5) at each point. The intensity was measured with both left-handed (+) and right-handed (-) circular polarisation at every position. The maps were constructed by plotting the dichroic asymmetry, $(I_C^+ - I_C^-)/(I_C^+ + I_C^-)$; this quantity should be negative for the FE $\downarrow$ state (fig. 5.4(a, b)) and positive for the FE $\uparrow$ state (fig. 5.4(e, f)). In fig. 5.6(a) it is clear that, for the majority of the sample region that has been switched into the FE $\uparrow$ state, the magnetic polarity has also switched relative to the unswitched film in the FE $\downarrow$ state. This is further made clear by overlaying the real space measurements onto an optical image of the device, shown in fig. 5.7.

¹⁶⁴DD Fong et al. *Phys. Rev. Lett.*, **96**: 127601, 2006.

¹⁶⁵JE Giencke et al. *Curr. Opin. Solid State Mater. Sci.*, **18**: 39–45, 2014.

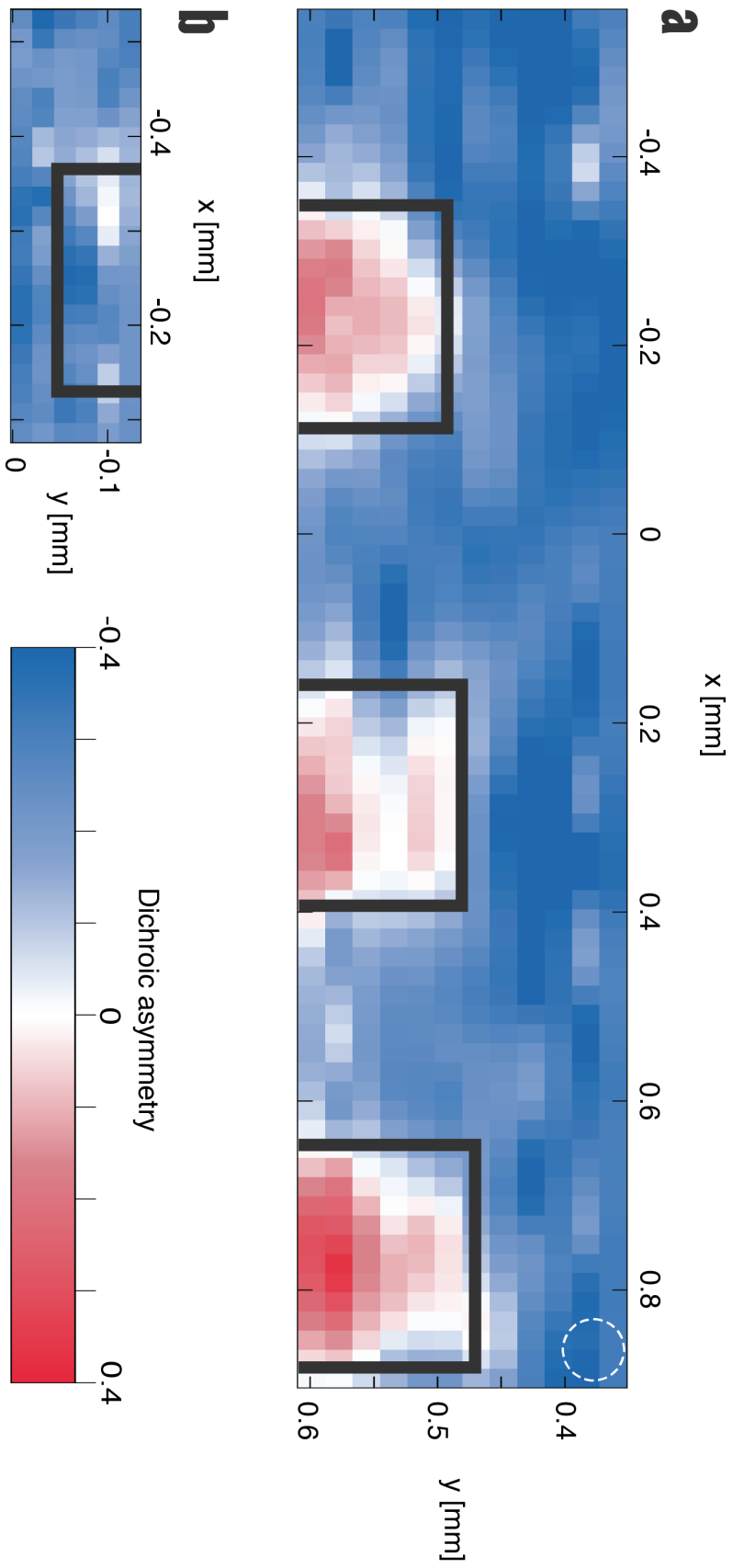


Figure 5.6: **Real space maps of magnetic polarity.** **a**, Magnetic polarity real space map of an area of the sample containing regions that have been switched into the $\text{FE} \uparrow$ state. The white dotted circle in the lower left corner indicates the spatial resolution of the measurement. **b**, Magnetic polarity real space map of an area of the sample containing regions that have been switched into the $\text{FE} \uparrow$ state and then switched back into the $\text{FE} \downarrow$ state. The regions underlying the Pt electrodes are outlined by the grey solid lines and the surrounding regions are in the virgin $\text{FE} \downarrow$ state. x and y are two orthogonal directions that describe the lateral sample translation. These maps have been overlaid on an image of the sample in fig. 5.7(c).

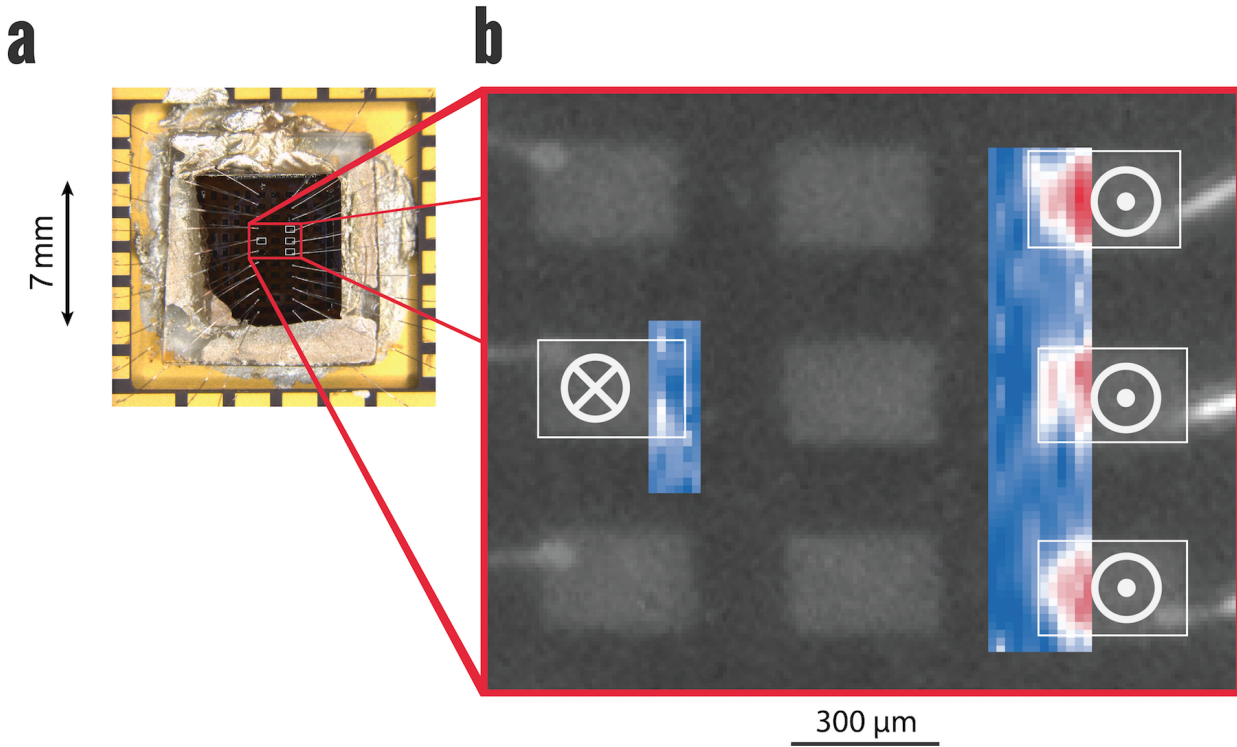


Figure 5.7: **Mapping magnetic polarity over a device.** **a**, Photo of the (111)_{pc}-BFO film. **b**, Optical image of the (111)_{pc}-BFO film surface. Maps of the magnetic polarity (see fig. 5.6) are overlaid showing regions of the sample switched into the FE↓ and FE↑ state and the direction of the FE polarisation is shown by the white symbols.

The areas where the magnetic polarity appears not to have switched are concentrated around the edges of the switched electrodes. This can largely be explained by the resolution limitation of the measurement (indicated by the white dotted circle in fig. 5.6(a)), but it is also possible that electric-field edge effects resulted in incomplete FE switching at the outside of the pads. By contrast, the sample region below the electrical pad that has been switched into the FE↑ state and then *back* into the FE↓ state, has unchanged magnetic polarity relative to the surrounding region of unswitched BFO, indicating that the magnetic state is recovered entirely. This also rules out the possibility that the change in contrast is due to an effect related to the sample having been switched at all, independent of the direction of polarisation.

5.4 Conclusions

In summary, we have demonstrated electrical switching of magnetic polarity in a BFO device at room-temperature, a direct measurement of the multiferroic coupling between antiferromagnetic and ferroelectric order parameters. By combining circularly polarised x-rays and post-scatter polarisation analysis, we determined absolutely the magnetic polarity of the cycloidal magnetic structure for two FE polarisation states. We further use this to map the magnetic polarity over the device with a $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ resolution, demonstrating that the magnetic polarity of micron scale regions of the sample may be addressed by an electric field. The observed reversal of the magnetic polarity of the cycloid represents a major rearrangement of the magnetic structure, with magnetic moments rotating on average by 90° upon switching. Furthermore, since these samples consist of equal populations of submicron **k**-domains, we have been able to show that this effect occurs equally in all three species of magnetic domain.

The observed response of the magnetic structure to electrical switching is in contrast to the general belief that the coupling between magnetism and ferroelectricity is rather weak in Type-I multiferroics,⁶¹ and the form of the is in full agreement with theoretical predictions.²⁰⁰ The experimental demonstration of polarity switching in a BFO device represents a crucial step towards developing full control of the interfacial exchange interactions in BFO-based composite multiferroic devices.

Furthermore, the ability to map the magnetic order parameter directly over a device structure illustrates the utility of NXMS as a technique for studying the microscopic mechanisms behind the macroscopic behaviour of multiferroic devices, on a tens-of-micron lengthscale. In principle, the resolution of this technique could be further increased down to submicron lengthscales by using Kirkpatrick-Baez mirrors to focus the incident x-ray beam.

²⁰⁰AM Kadomtseva et al. *JETP Lett.*, **79**: 571, 2004.

PEEM INVESTIGATION OF A MULTIFERROIC HETEROSTRUCTURE

The conclusions we have reached so far about the multiferroic domain structure of (111)_{pc}-BiFeO₃ films have been inferred from diffraction measurements, which average over the thousands of domains that fall within the x-ray or neutron beam profile. In this chapter, we use vector-mapped x-ray magnetic linear dichroism photoemission electron microscopy (XMLD-PEEM) to directly image the sub-micron scale cycloidal domain structure. Adopting the twinning model of chapter 3, we are able to construct a full vector map of the magnetostructural domains in unprecedented detail. Using circular dichroism in conjunction with XMLD-PEEM we then go on to examine the correlations between this domain structure and the ferromagnetic domains in a ferromagnetic overlayer. We find that there is a one-to-one correspondence between multiferroic and ferromagnetic domains, opening up a route for future exchange-bias multiferroic devices.

6.1 Introduction

THE phenomenon of exchange bias can be used to stabilise ferromagnetic (FM) spins along a certain direction in a magnetic heterostructure.^{201,202} This effect is widely employed in modern magnetic-storage technology, such as in spin-valves used in magnetic read heads, where the magnetic moments in the hard FM reference layer are pinned by the interfacial exchange-bias interaction with an antiferromagnetic (AFM) underlayer.^{203,204} The consequences of the interaction between the FM and AFM layers are, firstly, that the AFM axis imposes *uniaxial* anisotropy in the FM layer and secondly, depending on the terminating layer of AFM spins, there may further be a *unidirectional* anisotropy for the FM spins, signified by a characteristic shift of the FM hysteresis loop along the magnetic field axis.^{205,206}

Microscopically, it is generally accepted that the key component of the exchange-bias mechanism is the pinned layer of spins in the ferromagnet and the terminating layer of spins in the antiferromagnet to which they are coupled.²⁰⁷ This can be well understood in terms of interfacial exchange between the spins in the FM layer and an *uncompensated* i.e. having finite magnetisation, termination layer of spins in the antiferromagnet. However, exchange bias effects have also been observed in bilayers with *compensated* spins in the AFM termination layer.^{201,208,209} The microscopic theory in these cases is not fully understood, especially in case of complex, non-collinear antiferromagnets such as BFO.^{201,202,210} This picture has then yet another level of

²⁰¹J Nogués and IK Schuller. *J. Magn. Magn. Mater.*, **192**: 203–232, 1999.

²⁰²L Duò, M Finazzi, and F Ciccacci. *Magnetic Properties of Antiferromagnetic Oxide Materials: Surfaces, Interfaces, and Thin Films*. John Wiley & Sons, 2010.

²⁰³B Dieny et al. *Phys. Rev. B*, **43**: 1297, 1991.

²⁰⁴JC Mallinson. *Magneto-resistive and spin valve heads: fundamentals and applications*. Academic Press, 2001.

²⁰⁵WH Meiklejohn and CP Bean. *Phys. Rev.*, **102**: 1413, 1956.

²⁰⁶WH Meiklejohn. *J. Appl. Phys.*, **33**: 1328–1335, 1962.

²⁰⁷AE Berkowitz and K Takano. *J. Magn. Magn. Mater.*, **200**: 552–570, 1999.

²⁰⁸JX Shen and MT Kief. *J. Appl. Phys.*, **79**: 5008–5010, 1996.

²⁰⁹PJ van der Zaag et al. *J. Magn. Magn. Mater.*, **148**: 346–348, 1995.

²¹⁰NC Koon. *Phys. Rev. Lett.*, **78**: 4865, 1997.

complexity if there are AFM domains that differ in the direction of their AFM axis.

As well as having applications in traditional magnetic storage media, exchange bias could also be used in a multiferroic memory device, to couple the AFM structure of the multiferroic to a FM overlayer.^{13,134} By exploiting the magnetoelectric coupling in the multiferroic layer to electrically switch the magnetic structure, and thus the AFM spins at the interface, it is proposed that the magnetisation of the FM layer could be controlled with an *electric* field. Some success has been achieved in this regard: measurements on prototypical devices, involving a thin FM layer grown on top of BFO, have shown a reorientation of the FM moments upon switching the ferroelectric polarisation of BFO.^{154,180,211–214} This has also been demonstrated in using other systems such as the multiferroic YMnO₃²¹⁵ and the magnetoelectric Cr₂O₃.^{53,216} In BFO-based heterostructures, it has been shown that the overlayer magnetisation can be completely reversed upon switching between 71° ferroelastic domains^{153,217} — an effect, which was believed to be forbidden by simple symmetry considerations.

Despite these promising results, the exact nature of the coupling between BFO and the FM layer is not fully understood, especially in the presence of multiple ferroelectric, ferroelastic and/or AFM domains. For progress to be made towards a functional ferromagnet/BFO heterostructure device, it is critical to develop a detailed understanding of the AFM domain structure of BFO. Although we have already learned much about the domain structure through the diffraction

¹³M Bibes and A Barthélémy. *Nat. Mater.*, **7**: 425–426, 2008.

¹³⁴R Ramesh and NA Spaldin. *Nat. Mater.*, **6**: 21–29, 2007.

¹⁵⁴T Gao et al. *Nano Lett.*, **17**: 2825–2832, 2017.

¹⁸⁰D Sando, A Barthélémy, and M Bibes. *J. Phys. Condens. Matter*, **26**: 473201, 2014.

²¹¹YH Chu et al. *Nat. Mater.*, **7**: 478–482, 2008.

²¹²H Béa et al. *Phys. Rev. Lett.*, **100**: 017204, 2008.

²¹³D Lebeugle et al. *Phys. Rev. B*, **81**: 134411, 2010.

²¹⁴SM Wu et al. *Phys. Rev. Lett.*, **110**: 067202, 2013.

²¹⁵V Laukhin et al. *Phys. Rev. Lett.*, **97**: 227201, 2006.

⁵³T Ashida et al. *Appl. Phys. Lett.*, **106**: 132407, 2015.

²¹⁶P Borisov et al. *Phys. Rev. Lett.*, **94**: 117203, 2005.

¹⁵³JT Heron et al. *Nature*, **516**: 370–373, 2014.

²¹⁷JT Heron et al. *Phys. Rev. Lett.*, **107**: 217202, 2011.

measurements of chapters 3 to 5, these measurements average over the thousands of domains that fall within the x-ray or neutron beam profile. In this chapter, we use vector-mapped XMLD-PEEM to directly image the sub-micron scale AFM domain structure of epitaxial $(111)_{\text{pc}}$ -BiFeO₃ films. We then repeat this experiment on a Co/BFO heterostructure to study domain correlations between the AFM BFO domains with the FM Co domains in the overlayer. By imaging the FM-Co and AFM-BFO domains using, respectively, XMCD-PEEM and XMLD-PEEM at the same spot on the sample surface, we are able to directly image the domain overlap between the two layers.

6.2 Experimental details

6.2.1 Film preparation and characterisation

For the initial investigation to observe the multiferroic domains in BFO, we use the same film as was measured in chapter 3; a 1 μm -thick epitaxial films of $(111)_{\text{pc}}$ -oriented BFO grown on a $(111)_{\text{pc}}$ -oriented STO substrate. In order to investigate the interfacial correlations between multiferroic and ferromagnetic domains, a further batch of films was grown with a layer of Co deposited directly on top of the BFO as well as an Al capping layer, both by on-axis DC sputtering at room temperature.

For a PEEM experiment, the Pt or Al metal capping layer fulfils an additional role: as well as protecting the sample surface from mechanical damage, moisture damage and oxidation of the Co layer, it also acts as a source of electrons that can replace those ejected by the x-ray absorption processes. This prevents the sample surface gaining a net charge, which would otherwise perturb the local electrostatic field and lead to image distortions and anomalous features in the data. Given that the maximum depth from which Auger electrons can escape the sample is ~ 5 nm, it is necessary keep the thickness of the capping layer to $\lesssim 2$ nm. For the Co/BFO films, both the Co and Al layers were grown with a thickness of 1 nm as the electrons coming from the BFO layer have to exit through both layers.

The structural, ferroelectric and AFM characterisation of the film yielded results consistent with the previous batch, for which the characterisation measurements are discussed in section 3.2.2. The ferromagnetic properties of the Co layer on the bilayer films were also characterised prior to the PEEM experiment by magneto-optical Kerr effect (MOKE) measurements. It was found that the Co layer exhibited a characteristic hysteresis loop with a coercive field of 8 mT.

6.2.2 X-ray photoemission electron microscopy

Measurements were carried out on beamline I06,²¹⁸ Diamond light Source (UK) using an Elmitec SPELEMM-III microscope, which can routinely achieve a spatial resolution of 50 nm. The microscope was operated with an accelerating potential of 20 kV between the sample and objective lens. The sample manipulator has a motorised stage that allows in-plane translations of the sample and rotations of the sample in the range $-30^\circ < \phi < 150^\circ$ about the surface normal direction. The incident x-ray energy and polarisation is set by tuning the undulator gaps and row phase. The insertion device on I06 allows incident x-ray energies between ~ 100 eV and 1500 eV and both circular and linear (at arbitrary angle) polarisation. The x-rays illuminate the sample at a grazing incidence angle of 16° .

To image the AFM domains in BFO, we record images with x-rays that are linearly polarised in the plane of the film (σ) at two energies E_1 and E_2 close to the Fe L_{III} absorption edge. These two energies were identified prior to the PEEM measurements using the XMCD/XMLD x-ray dichroism endstation on I06. Absorption spectra with both incident in-plane (σ -) and out-of-plane (π -) polarised x-rays were measured, where the x-ray absorption was measured by a drain current from the sample. When subtracted, two extrema with opposite sign in the XMLD spectrum at energies E_1 and E_2 were observed.

We record images with σ -polarised x-rays only, to reduce the measurement time, rather than

²¹⁸SS Dhesi et al. , **1234**: 311–314, 2010.

taking images using both σ - and π - polarised x-rays*. From this we can calculate the XMLD asymmetry:

$$I_{LD} = \frac{I_{E_1}^\sigma - I_{E_2}^\sigma}{I_{E_1}^\sigma + I_{E_2}^\sigma}, \quad (6.1)$$

where the energies $E_1 = 708.2$ eV and $E_2 = 708.9$ eV and correspond to -0.2 eV and 0.4 eV from the Fe L_{III} absorption edge, respectively. Although this does not constitute a true dichroism measurement in which images measured with orthogonal linear polarisations are subtracted from one another, I_{LD} does give equivalent information. However, it will also reveal any other features that have a *non-dichroic* energy dependence, which would otherwise be removed by the subtraction of images at orthogonal polarisations. In this case our films had no non-dichroic resonant features and thus using the expression in eq. (6.1) sufficed.

Due to weakness of the XMLD signal from BFO, reasonable signal to noise could only be achieved by averaging $\gtrsim 200$ asymmetry images, each composed of average of 20 images (10 each at E_1 and E_2) each with a 1 s exposure time. Thus, the cumulative measurement time for a complete measurement at a given azimuth is ~ 2 h.

To image the ferromagnetic domains in the Co overlayer, we record images with left- and right-handed circularly-polarised incident x-rays at both on- and off-resonance energies. The XMCD asymmetry is then given by

$$I_{CD} = \frac{I^+ - I^-}{I^+ + I^-}, \quad (6.2)$$

where $I_\pm = I_{E_1}^\pm / I_{E_2}^\pm - 1$ are the normalised resonant intensities for left and right circular polarised x-rays. Here E_1 (777 eV) and E_2 (770 eV) are, respectively, the on-resonance and pre-edge off-resonance energies taken at the Co L_{III} absorption edge. The division by the off-resonance energy accounts for any difference in incident flux between the two circular polarisations and any inhomogeneous illumination of the field of view.

*Although the scattering plane is not well defined for an absorption process, for convenience we have adopted the polarisation notation from x-ray diffraction. We define ‘scattering plane’ for X-PEEM to be the plane containing the incident x-ray wave vector and sample surface normal direction.

6.3 Imaging magnetostructural domains in a BiFeO₃ film

As discussed in section 2.5.2, the x-ray absorption cross section of linearly polarised x-rays depends upon the projection of the x-ray polarisation onto the magnetic moments. This dependence results in a contrast, observable by XMLD-PEEM, between AFM domains with different orientations of their AFM axis oriented differently with respect to the x-ray polarisation direction. In the case of (111)_{pc}-BFO, the contrast between cycloidal **k**-domains is slightly more complex due to the rotating magnetic structure. As shown in section 3.3.3, a spin cycloid may be decomposed into two orthogonal spin-density waves, aligned along in-plane and out-of-plane directions, which are dephased by $\pi/2$. Although the out-of-plane components of the three **k**-domains are identical, the propagation direction of the in-plane components differ by 120° and thus should be observable in their XMLD contrast. Figure 6.1 shows XMLD-PEEM images of a $\sim 8\text{ }\mu\text{m}$ -diameter circular region of the surface of the film measured with σ -polarised x-rays over a range of azimuthal angles. Contrast features with length scales on the order of $< 1\text{ }\mu\text{m}$ are clearly visible in all images collected. This is consistent with the maximum domain size inferred from the x-ray and neutron diffraction data discussed in chapter 3.

To confirm the in-plane nature of the contrast between different **k**-domains, we recorded an XMLD image with π -polarised x-rays. This was found to show identical features to the image recorded with σ -polarised light at a sample azimuth 90° away but with significantly weaker contrast, consistent with the small contrast expected due to the $\sim 16^\circ$ grazing incidence angle of the x-rays. The magnetic origin of the PEEM contrast is further corroborated by its temperature dependence (60 % reduction at 475 K), which was found to be quantitatively consistent with the temperature dependence of the ordered moment,²¹⁹ and was reversed upon cooling. These data confirm the cycloidal magnetic ordering at the surface of our (111)_{pc} film, with in-plane

²¹⁹M Ramazanoglu et al. *Phys. Rev. B*, **83**: 174434, 2011.

propagation vectors and planes of rotation orthogonal to the film plane, identical to the bulk magnetic structure we measured with NXMS (see section 3.3.4). We note that any ferroelastic contribution to the PEEM contrast¹³⁶ can be ruled out as our $(111)_{\text{pc}}$ film is a ferroelectric *monodomain*.

To extract the full domain structure of the film, it is necessary to observe the angular dependence of the XMLD signal. The intensity of the XMLD signal for a cycloidal magnetic structure, is obtained by a spatial average of the collinear AFM case discussed in section 2.5.2. Therefore the polarisation dependence of the XMLD signal on the x-ray linear polarisation for a single cycloidal domain is given by

$$I_{\text{LD}} \propto \mathbf{M}^2 \left[\frac{3}{2}(\hat{\mathbf{k}} \cdot \hat{\mathbf{E}})^2 + \frac{3}{2}(\hat{\mathbf{z}} \cdot \hat{\mathbf{E}})^2 - 1 \right], \quad (6.3)$$

where $\mathbf{M}^2$ is the square of the local magnetic moment, while $\hat{\mathbf{k}}$ and $\hat{\mathbf{z}}$ are the directions of the propagation vector and of the surface normal, respectively, and $\hat{\mathbf{E}}$ is the polarisation vector of the light. The first term generates the XMLD contrast between $\mathbf{k}$ -domains as, regardless of the polarisation direction, the 2nd term gives the same for all three domains. The signal is maximum ($\propto +\mathbf{M}^2/2$) for $\hat{\mathbf{E}}$ along the propagation vector, in which case the signal from the other two domains is $\propto -5\mathbf{M}^2/8$. With π -polarised x-rays, $\hat{\mathbf{E}}$ is aligned 16° to surface normal and the XMLD signal is almost equal for all three domains ($\propto +\mathbf{M}^2/2$), consistent with our observations of weak contrast.

The XMLD images in fig. 6.1 are arranged such that images in the same column were taken at azimuthal angles 90° apart. From eq. (6.3), we would expect these images to be inverses of one another. Although, there are some optical distortions due to the change in orientation of the sample with respect to the optical axes of the microscope, it is clear that light and dark regions are interchanged between these images.

¹³⁶T Zhao et al. *Nat. Mater.*, 5: 823–829, 2006.

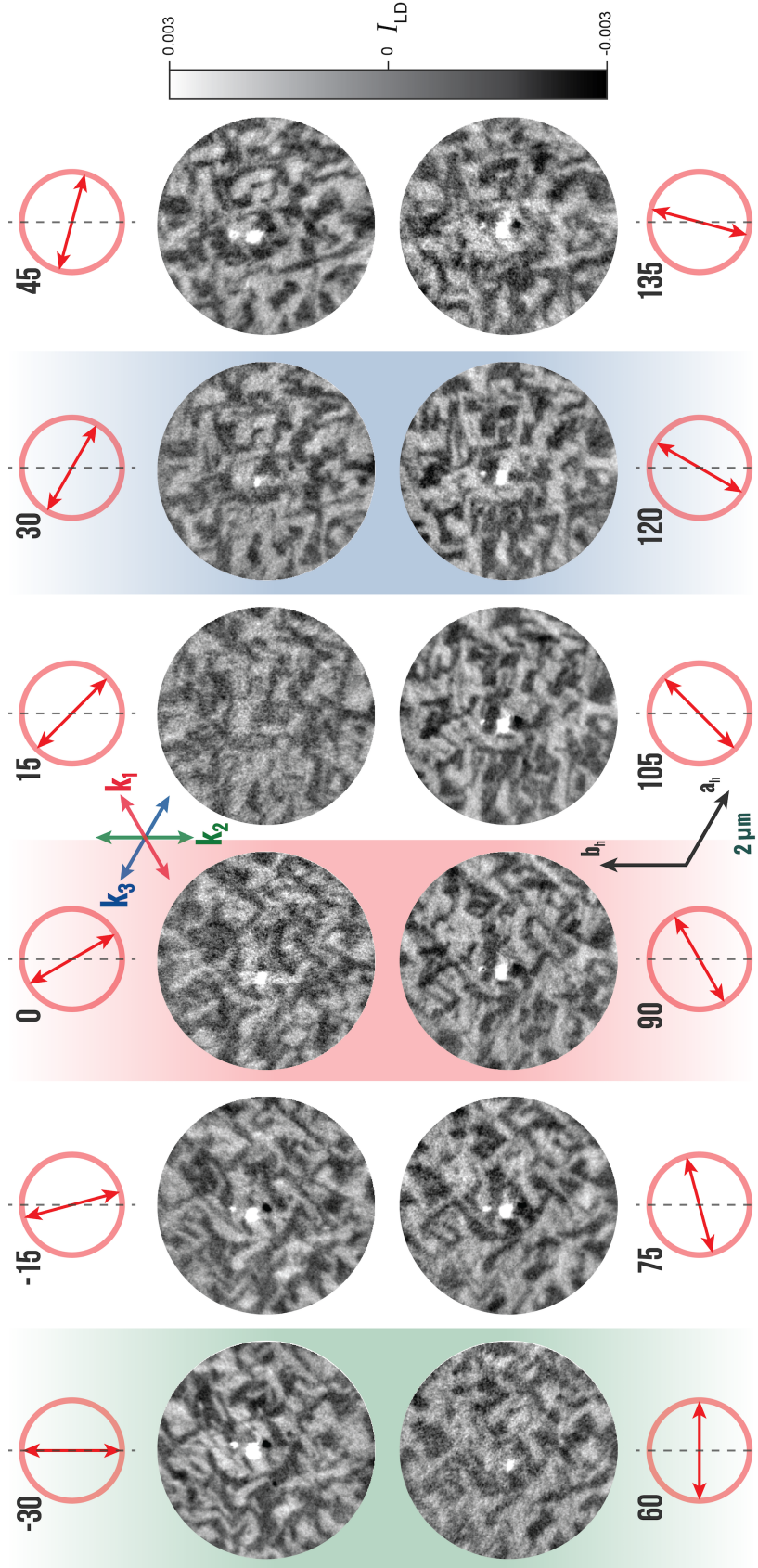


Figure 6.1: XMLD-PEEM angular dependence of multiferroic domains. XMLD-PEEM images taken at different sample rotations (azimuthal angles) every 15° in the range $\phi = -30^\circ$ – 150° . The red arrow inside the circle indicates the orientation of the in-plane x-ray polarisation. The highlighted images are where the incident x-ray polarisation is either parallel or perpendicular to one of the cycloidal propagation vectors. The black axes show the in-plane BFO crystallographic directions and the colour arrows show the directions of the magnetic propagation vectors of the three $\mathbf{k}$ -domains. The scale bar refers to all images.

6.3.1 X-ray magnetic linear dichroism image processing

During an XMLD measurement, it is necessary to regularly correct for both beam and sample drift, typically resetting both every 10–20 min. Given that each image in fig. 6.1 is the average of ~ 200 asymmetry images, the sample drift requires each asymmetry image to be drift corrected (although this is usually done using the sum $I_{E1}^\sigma + I_{E2}^\sigma$ image as a reference), before they are averaged. Beam drift results in a slight variation of the beam profile between asymmetry images, and thus when they are averaged, the final image ends up with an highly nonlinear background. To account for this, the outer $\sim 2\mu\text{m}$ region of the image is cropped as this effect is accentuated at the edges and then a polynomial background is subtracted to flatten the image.

Due to the fact we are comparing images taken at different sample rotations, the astigmatism corrections induce optical distortions of the image that vary with sample azimuth. As the sample is rotated, the relative orientation of the sample and optical axes changes and thus any elliptical distortion of the image is applied along a different direction in the image. This effect can clearly be seen between the two images taken at $\phi = 15^\circ$ and 105° : the light feature in the upper centre of the 15° image is elongated in the vertical direction relative to the corresponding dark feature in the 105° image. To correct for these optical distortions, we apply an affine transformation (linear scale and skew along two orthogonal directions) to map features on each rotated image to match those on the image taken at 0° .

6.3.2 Angular reconstruction

To construct a full vector map of the cycloidal $\mathbf{k}$ -domains at the surface of the film, we combine XMLD-PEEM images taken at appropriate angles that maximise the contrast of a single magnetic domain. Maximal contrast between one domain and the other two is achieved by aligning the polarisation vector of the incident x-rays such that they are either parallel (one domain light/two

*The images shown in fig. 6.1 have been cropped and flattened, but they have not been drift or distortion corrected.

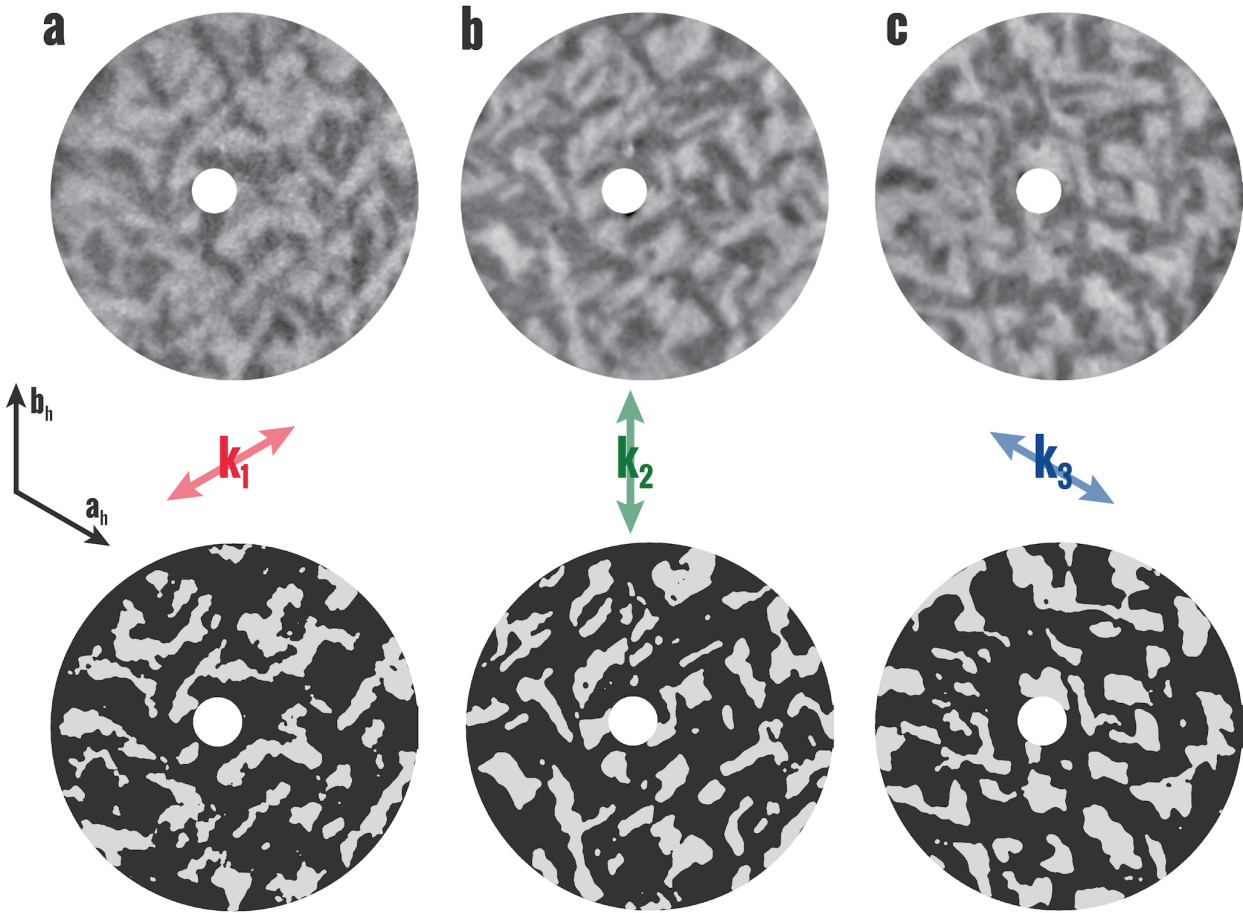


Figure 6.2: **Binarisation of PEEM images to extract single domains.** Three PEEM images where the light regions indicate the (a,) k_1 -, (b,) k_2 -, and (c,) k_3 -domain regions. The upper row of images are the combined processed data taken an azimuthal angles with the polarisation vector of the light both perpendicular and parallel to the propagation vector. The lower row of images have been binarised using the threshold method described in the main text.

domains dark) or perpendicular (one domain dark/two domains light) to the $\mathbf{k}$ -vector of the domain. We therefore use three pairs of images highlighted in fig. 6.1, where those highlighted red, green and blue correspond to maximal contrast for $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ domains, respectively. We combine the pairs of images for the i th domain by inverting the image taken with the polarisation perpendicular to $\mathbf{k}_i$ and adding it to the image with the polarisation parallel to $\mathbf{k}_i$. The final three images in which the light areas correspond to the $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ domains are shown in fig. 6.2(a), (b) and (c), respectively.

These images are then converted to binary maps using a threshold value centred between the light and dark regions. Additionally, a small-width intensity band centred on this threshold value is subtracted, assuming this region to be the domain walls. Finally, the images are smoothed using a median filter to reduce the level of high-frequency noise and any defects are masked (as shown by the white circle in fig. 6.2). The binarised images showing the locations of the $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ domains are shown in fig. 6.2(a), (b) and (c), respectively. These appear to be along the lines of what we would expect: roughly one third of each image consists of light regions and the domain walls show a clear hint of some orientational dependence.

To generate a full vector map of the cycloidal domains, we assign each of the binary images to red, green and blue, respectively (see fig. 6.3(a–c)), and then combine the three images to generate fig. 6.3(d). We find that the majority of the image corresponds to the three magnetic domains we expect, consistent with the x-ray and neutron diffraction results in section 3.3.2. However, there are some regions where the binary maps overlap, resulting in areas that are cyan/purple/yellow. These may be explained by a combination of effects. Due to the weak finite XMLD contrast, there is a small inherent uncertainty in the exact value of the threshold that should be used to discretise the images. This is exacerbated by the polynomial background subtraction that does not fully account for the nonlinear background, resulting in a threshold that is not uniform over the whole image. Furthermore, the linear distortion correction does not entirely compensate for the optical distortions, which will also result in some overlapping regions. Finally, the escape probability of the electrons falls off with depth and hence PEEM preferentially probes the domains at the

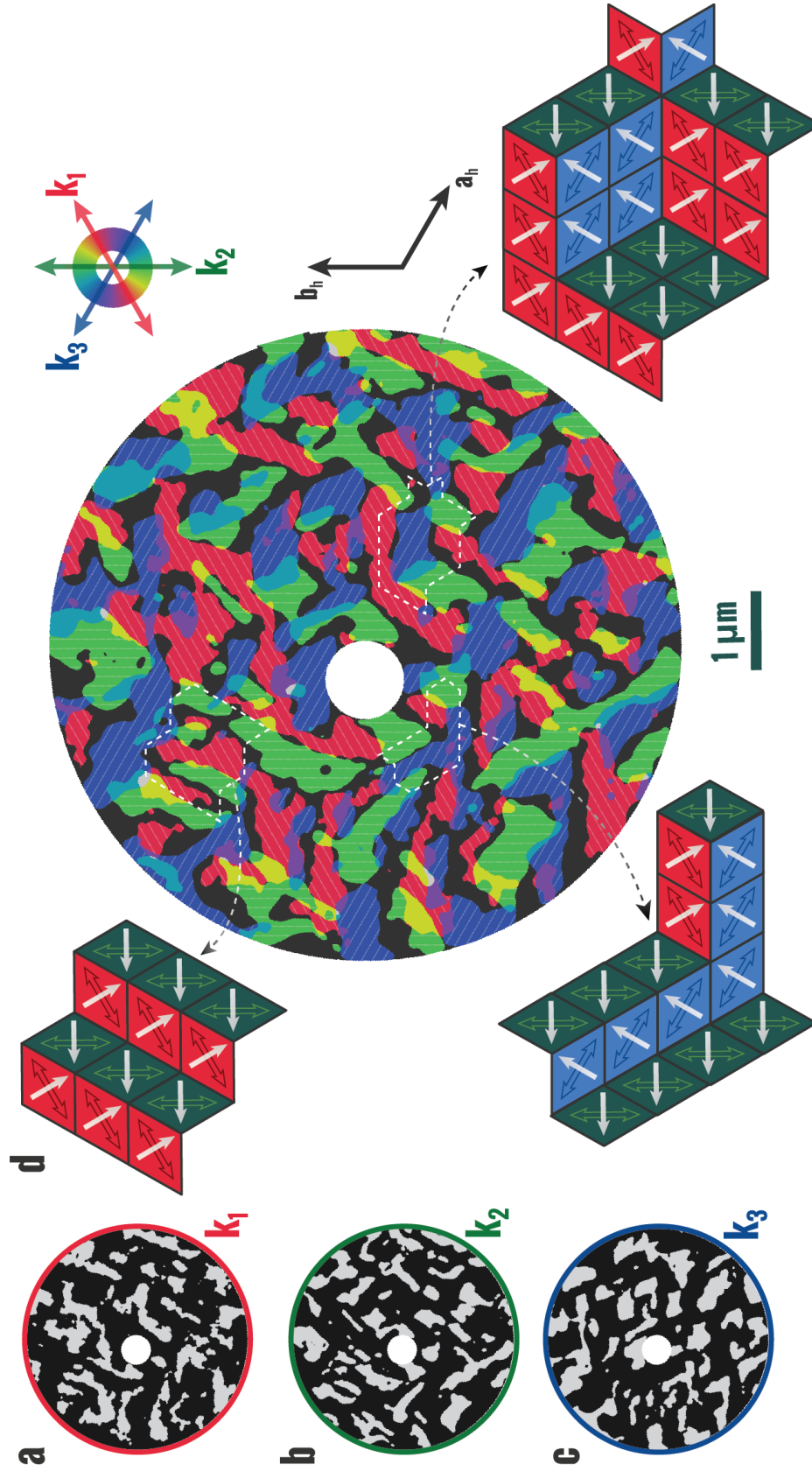


Figure 6.3: **RGB reconstruction of monoclinic/k-domains.** **a–c**, Binarised PEEM images obtained using x-ray linear dichroism (XMLD) with the light areas corresponding to domains of k_1 , k_2 and k_3 propagation vectors, respectively. **d**, Discrete vector map of the k -domains from **a–c**, where the direction of the propagation vector is indicated by the white stripes and coloured arrows. Schematic depictions of the magnetostructural domains are shown next to corresponding regions of the vector map, outlined with white dotted lines. The scale bar refers to **d**.

very surface. However, if the domain topography changes with depth in the top ~ 5 nm, then these underlying domains may be apparent and overlap with other domains at the surface. The black areas correspond to regions being below the threshold for all three images and could be considered to be ‘domain walls’, although, due the issues discussed above, these areas will likely also contain edges of domains that were not fully resolved.

Thus the contrast in fig. 6.3 is consistent with approximately equal populations of the three $\mathbf{k}$ -domains (see fig. 6.4(c)) present at the sample surface. Given that these domains are in fact *magnetostructural*, then by imaging the magnetic domain structure, we have simultaneously imaged the *monoclinic* domain structure, since their topography is identical (see section 3.3.4). Comparing the observed domain structure to the schematic domain structure predicted from diffraction measurements, shown in fig. 3.11, we see there are many similarities. Three regions that particularly seem to agree with the model are indicated by white dotted areas, with the corresponding schematic domain pattern depicted adjacent to them. Importantly, orientations of the domain boundaries primarily correspond to those predicted by the twinning model: we see that the red/green, green/blue and blue/red domain boundaries are parallel to the $(110)_h$, $(\bar{1}20)_h$ and $(\bar{2}10)_h$ planes, respectively.

6.3.3 X-ray magnetic linear dichroism sign convention

There is an assumption in the sign of the dichroism, namely that when the incident x-ray polarisation is aligned parallel to a particular $\mathbf{k}$ -direction, the corresponding domains show up as light areas and the other two domains, whose $\mathbf{k}$ -vectors are not aligned with the polarisation, appear as dark regions. Depending on the sign of the dichroism, these light and dark regions could be interchanged, which would drastically change both the binary maps and resulting vector map in fig. 6.3.

From the x-ray and neutron diffraction data discussed in section 3.3.2, we know that the majority of the domains must have propagation vectors along the three principal $\mathbf{k}_i$ directions i.e.

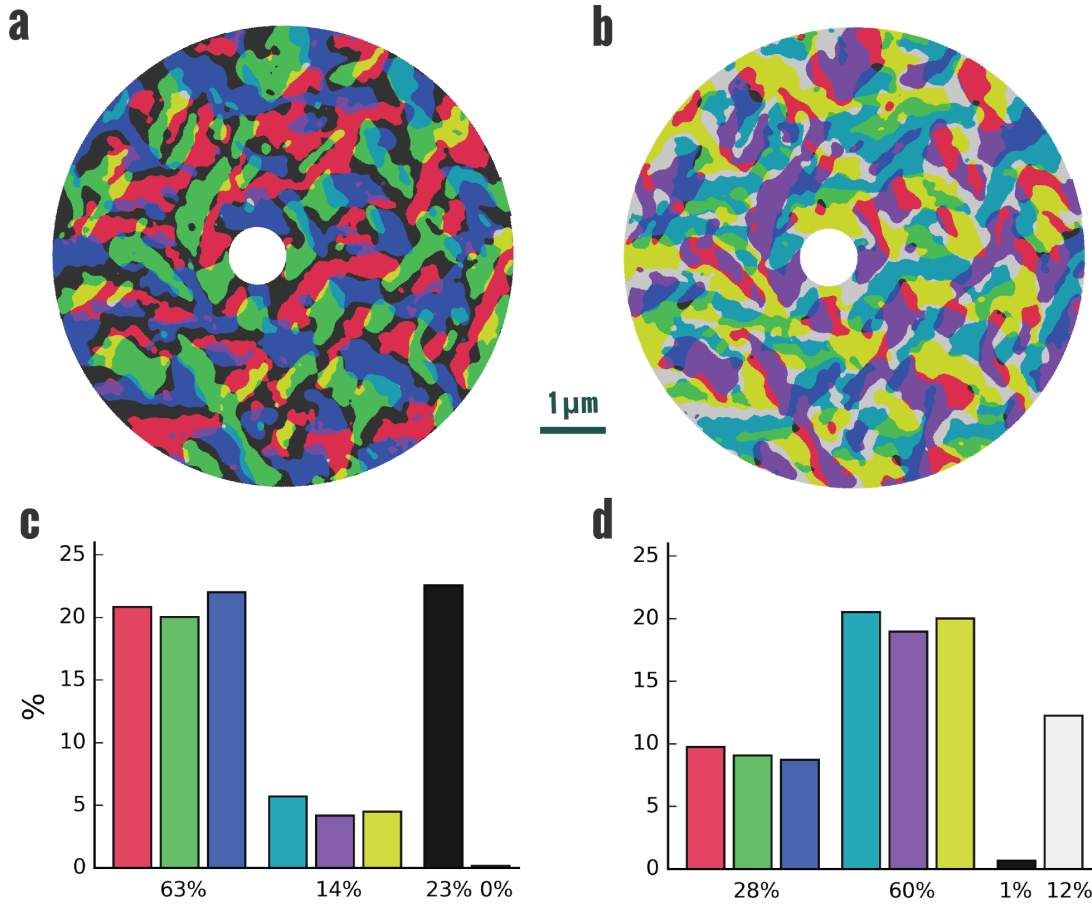


Figure 6.4: **XMLD sign convention for magnetic k-domains.** Discrete XMLD-PEEM vector maps constructed using the original convention (a,) and the opposite convention (b,) Histograms showing the percentage of different coloured regions in the maps generated using the original convention (c,) and the opposite convention (d,). The scale bar refers to a and b.

there must be a majority of red/green/blue domains. Thus, in principle, this ambiguity could be resolved from a single XMLD image with the polarisation either parallel or perpendicular to the propagation vector. Assuming that there are equal populations of all three domains, there should be one domain, consisting of approximately 1/3 of the image, that is distinct from the other two. The sign of the dichroism should then be evident from the colour of this domain. Given that the light/dark proportions of the image are sensitive to the threshold used to binarise the images, we adopt a more robust approach involving all three XMLD images and compare the vector maps generated from both sign conventions.

We therefore need to repeat the image binarisation process using the opposite convention, i.e. starting with the images where the x-ray polarisation is aligned perpendicular to each $\mathbf{k}$ -domain and choosing a binarisation threshold centred between new (inverted) the light and dark contrasts. The discrete vector maps generated from both the original convention (i.e. the convention used to generate fig. 6.3) and the opposite convention are shown in fig. 6.4(a) and (b), respectively. The histograms shown in fig. 6.4(c) and (d) show the proportions of red/green/blue, cyan/purple/yellow and black/white regions in each vector map. Clearly, the opposite convention results in a much higher percentage of cyan/purple/yellow than red/green/blue regions and thus can be discounted.

6.4 Ferromagnetic/multiferroic domain correlations in a Co/BiFeO₃ heterostructure

Having directly imaged the near-surface multiferroic domain structure of a (111)_{pc}-BFO film, and found it to be consistent with our domain model inferred from diffraction measurements, we now turn our attention to the effect these domains may have on an adjacent FM layer. To study the FM/AFM correlations, we measure a Co (1 nm)/BFO (1 μm) heterostructure using a combination of XMCD- (to image FM domains) and XMLD-PEEM (to image AFM domains). By tuning the incident x-ray energy to the Fe and Co L_{III} edges, we are able to isolate the dichroism signal from each layer, and thus image the overlapping FM/AFM domains at the Co/BFO interface.

6.4.1 Vector mapping cycloidal domains in BiFeO₃ layer

A map of the cycloidal $\mathbf{k}$ -domains of the BFO layer, obtained using an identical method to that described in section 6.3.2, is shown in fig. 6.5(a). However, due to time constraints, we were only able to measure XMLD-PEEM images with a sufficient signal-to-noise ratio at sample rotations of $\phi = 0^\circ$ and 60° . These two images allow us to isolate the $\mathbf{k}_1$ and $\mathbf{k}_2$ domains; the $\mathbf{k}_3$ domains

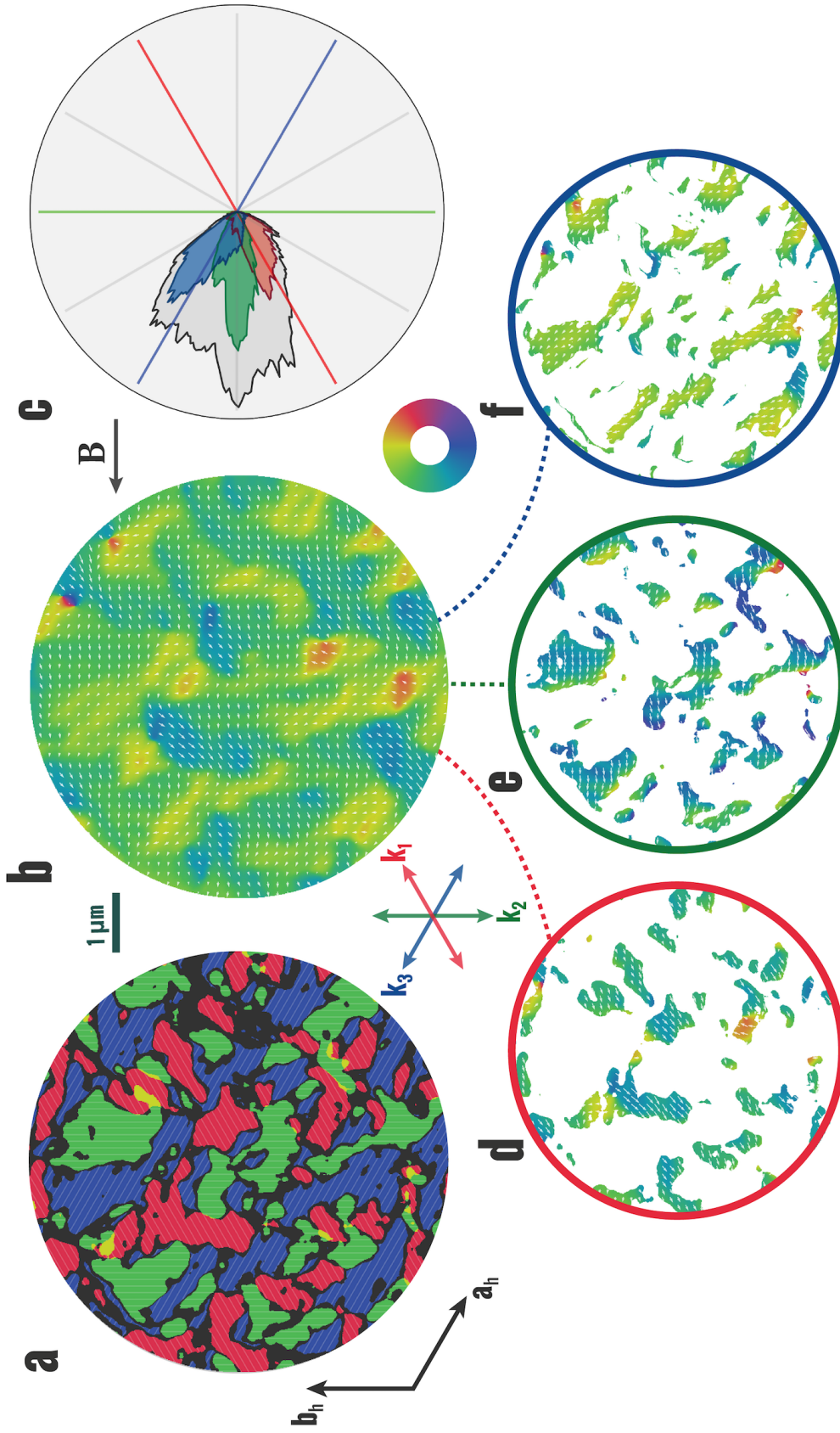


Figure 6.5: FM-AFM domain correlations in a Co/BFO heterostructure. **a**, Discrete vector map of the $\mathbf{k}$ -domains in BFO layer, where the direction of the propagation vector is indicated by the white stripes. **b**, Vector map of in-plane magnetisation of the Co layer. White arrows indicate the magnitude and direction of the local magnetisation and the colour wheel indicates direction only. **c**, Polar histogram of the Co-magnetisation. The grey line is a histogram of the whole Co vector map minus the domain walls. The red, green and blue lines are histograms of the subsections of the Co vector map located directly above the $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ BFO domains, respectively. The red, green and blue lines indicate the $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ directions, respectively. **d-f**, Subsections of the Co vector map, masked by the $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ domains of the BFO layer, respectively. The scale bar refers only to a and b.

were assumed to be the negative space left over after binarising these two images. We find that the magnetic domain structure of BFO at the BFO/Co interface is largely consistent with the domain structure previously observed with XMLD-PEEM (fig. 6.3), both in terms of typical domain size and domain boundary orientations.

6.4.2 Vector mapping ferromagnetic domains in Co layer

We next image the FM domains in the corresponding region of the Co overlayer using XMCD-PEEM. Given that an XMCD measurement images the projection of the local Co magnetisation along the incident x-ray directions (see eq. (2.51)), we can construct a vector map by combining two images, one at 0° and one at 90° . Figure 6.5b shows a vector map of the in-plane magnetisation of the Co overlayer in the heterostructure. We note that it was not possible to image the Co layer in its ‘as-grown’ state because the sample was characterised prior to this measurement by MOKE. Thus, to leave the Co magnetised in a known direction prior to imaging both the BFO and Co layers, we applied a magnetic field of 275 mT along the $[\bar{2}\bar{1}0]_h$ direction. As expected, the net magnetisation appears to be along the direction the field was applied, shown by the black arrow labelled **B**. This can be seen more clearly in the polar histogram of the Co moment directions (grey) shown in fig. 6.5(c), which is centred on the $[\bar{2}\bar{1}0]_h$ direction.

6.4.3 Domain correlations

Comparing the BFO and Co domain structures, there seems to be a correlation between the two, with $\mathbf{k}_1$ domains (red) matching the turquoise areas, $\mathbf{k}_2$ domains (green) matching the green/blue areas, and $\mathbf{k}_3$ domains (blue) matching the yellow/green areas. To examine this effect in more detail, we use the three binary maps of the BFO domains as masks on the Co image. This process generates a subimage containing only the regions of Co image that lie directly above the corresponding $\mathbf{k}_i$ domain of the BFO. The three subimages corresponding to the Co domains on top of the $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ domains are shown in fig. 6.5(e), (f) and (g), respectively. We then take

polar histograms of each of these images, which are shown in red, green and blue in fig. 6.5(c), respectively.

If there were no correlation between the BFO and Co domains, we would expect the red, green and blue polar histograms to be identical, with the only anisotropy imposed by the field applied before imaging. Given that there are three distinct lobes corresponding to Co regions overlapping the $\mathbf{k}_1$, $\mathbf{k}_2$ and $\mathbf{k}_3$ domains, we see that the BFO domains have had a dramatic effect on the Co domains. It appears that each BFO domain has imposed a different uniaxial anisotropy in the Co layer. For the $\mathbf{k}_1$ and $\mathbf{k}_2$ domains, this axis is parallel to the cycloidal propagation vector, whereas for the $\mathbf{k}_3$ domain, it is perpendicular to propagation vector.

The microscopic mechanism that produces this coupling remains a matter of speculation. Given that the net moment of a cycloid averages to zero over a single period, the interaction must be fundamentally different to the exchange coupling that causes exchange-bias for an uncompensated layer of AFM spins. Perpendicular coupling between FM domains and simple collinear AFM domains has previously been observed in Co/NiO heterostructures for both compensated and uncompensated NiO termination layers.²²⁰ In this study, van der Laan *et al.* attribute the coupling to strain-induced changes in the magnetocrystalline anisotropy at the CoNiO interface. Recalling that the BFO domains are also structural in nature, it could be that strain also plays a role in the coupling we observe. One could speculate that for a given FM domain, there are two minima in the energy landscape, corresponding to aligning perpendicular or parallel to the cycloidal propagation vector, and that competition between this anisotropy and ferromagnetic interactions between Co domains could stabilise domains along either direction.

6.5 Conclusions

In summary, we have directly imaged the cycloidal magnetic domain structure of (111)_{pc}-oriented-BFO films using vector-mapped XMLD-PEEM and, in doing so, we have simultaneously

²²⁰G van der Laan et al. *Phys. Rev. B*, **83**: 064409, 2011.

imaged the monoclinic domain structure to which the magnetic structure is coupled. We find that the magnetostructural domains are fully consistent with previous NXMS and neutron diffraction measurements (section 3.3.2) both in terms of their size and morphology. Although simple 90° AFM domains had been imaged prior to this study,¹²⁸ measuring a full vector map of AFM domains with ~50 nm resolution is, to our knowledge, unprecedented. Given its high spatial resolution, this technique is applicable to many other AFM systems in device configurations; it has since been applied to the orthoferrite LaFeO₃ to image the six-fold magnetostructural domains.²²¹

By combining this technique with XMCD-PEEM we were able to image the AFM–FM domain correlations in a Co/BFO heterostructure. We found that the cycloidal domains in BFO imposed an easy-axis anisotropy in the Co layer such that there is an almost one-to-one coupling between the BFO cycloidal domains and FM domains in the Co. It seems the direction of the anisotropy axis imposed in the Co can be either parallel or perpendicular to the propagation vector of the corresponding BFO domain. This coupling is rather surprising since naively one might think that for a rotating magnetic structure, any interaction should average to zero. However, its presence motivates further work to fully understand the mechanism and has significant implications for future multiferroic devices that exploit coupling to a ferromagnetic layer. For instance, if one were able to switch between different cycloidal domains, one would, in principle, be able to switch the direction of the Co layer.

¹²⁸J Stöhr et al. *Phys. Rev. Lett.*, **83**: 1862, 1999.

²²¹I Hallsteinsen et al. *APL Mater.*, **5**: 086107, 2017.

CONCLUSIONS

7.1 Summary

BiFeO_3 is a material whose impressive room-temperature functionality and rich multiferroic properties have led to it being the most intensively studied multiferroic to date. Despite this attention, a BFO-based device demonstrating robust and reversible control of ferromagnetic domains that is well-understood in terms of its microscopic mechanisms is yet to be demonstrated. Progress has been hindered in many cases by the multiple ferroelastic, ferroelectric and magnetic domains typically present in BFO films. These domains not only lessen the macroscopic multiferroic properties of BFO, but also obfuscate the roles of spin, charge and strain in the switching process. In this thesis we have endeavoured, through the use of state-of-the-art diffraction and microscopy techniques, to gain a detailed and comprehensive understanding of the multiferroic domain structure of thin-film BFO.

In chapter 3 we used nonresonant x-ray magnetic scattering and neutron diffraction to probe the domain structure of $1\text{ }\mu\text{m}$ -thick $(111)_{\text{pc}}$ -oriented BFO films. We chose this orientation to minimise extrinsic effects as it preserves the high-symmetry axis of the crystal structure, and thus results in films that are, in principle, as close to a model bulk-like system as possible. Contrary to the general belief that $(111)_{\text{pc}}$ -BFO films grow as of a rhombohedral monodomain, we found that they in fact comprise a sub-micron texture of monoclinic twins. We further found that the magnetic and monoclinic structures, which share the same group-subgroup relationship to the parent phase, are intimately coupled such that magnetic propagation vector is locked to the monoclinic b -axis.

With this coupling in mind, in chapter 4 we attempted to bias the growth of a single magnetostructural domain. Firstly, we attempted to break the three-fold symmetry of the $(111)_{\text{pc}}$ -STO interface by applying a 4° miscut to the substrate. However, this appeared to have no effect on the domain structure of the BFO film, giving results consistent with films grown on non-miscut STO. Secondly, we grew films on $[011]_{\text{o}}$ -oriented TbScO_3 , an orthorhombic substrate that intrin-

sically breaks three-fold symmetry. In this case, the effect on the domain structure was dramatic, resulting in the entire $10\text{ mm} \times 10\text{ mm}$ film comprising a ferroelastic, ferroelectric and magnetic monodomain.

In chapter 5, we investigated the effect of electrical switching on the magnetic structure of thin-film BFO. Despite the vast amount of research on electrical control of magnetism in BFO, electrical switching of the magnetic order parameter in BFO, or indeed any type-I multiferroic, had not been unambiguously demonstrated. Using NXMS, a technique that uniquely combines sensitivity to the magnetic structure on the atomic scale, with high real space resolution, we were able to measure and map the magnetic polarity over a BFO device. Contrary to the general belief that the coupling between magnetism and ferroelectricity in type-I multiferroics is weak, our results demonstrated that, upon 180° switching of the ferroelectric polarisation, the magnetic polarity is correspondingly switched.

Finally, we investigated the interfacial coupling and domain correlations between thin-film BFO and a ferromagnetic Co overlayer. In an experiment demonstrating unprecedented detail in antiferromagnetic imaging, we used vector-mapped XMLD-PEEM to image the near-surface cycloidal magnetic domain structure of BFO. The domain structure was found to be entirely consistent with previous diffraction results. We then used a combination of XMLD- and XMCD-PEEM to image the magnetic domain structures of both the BFO and Co layers at the same spot. We found that there was a one-to-one coupling between the domains in each layer, where the BFO domains had imprinted an easy-axis anisotropy into the Co layer.

7.2 Outlook

The work presented in this thesis constitutes a significant step towards realising a functional multiferroic device. The detailed understanding we have gained of $(111)_{\text{pc}}$ -oriented BFO films provides a foundation for subsequent work on BFO-based devices. In particular, the observation of monoclinicity and domain texture, and the explicit demonstration of coupling between mag-

netic and ferroelectric order parameters will inform future switching and device studies, allowing their results to be understood in greater depth.

Furthermore, we have demonstrated certain phenomena that may provide new functionality in future BFO-based devices. The observed coupling between magnetic and structural domains opens up a new route to strain engineer the domain structure of BFO films. By exploiting this effect, we successfully engineered a monodomain film, thus creating a truly model system, void of any extrinsic domain effects, and highly attractive from both an experimental and technological perspective. This magnetoelastic coupling has many other potential applications that it would be valuable to investigate, such as using patterned substrate strain to ‘write’ magnetic domains or biasing a ferroelectric switching pathway to resolve issues of polarisation fatigue.

Given that a likely architecture for a multiferroic device involves coupling to a ferromagnetic layer, the correlations between cycloidal and ferromagnetic domains we observed in the Co/BFO heterostructure are clearly of technological significance. In order to better understand the nature of the coupling mechanism, it would be useful to observe the behaviour of the domains as a function of applied magnetic and electric fields, and then to repeat the measurements with the BFO layer replaced with a monodomain film. These results should elucidate somewhat how the interfacial coupling may be exploited to control the ferromagnetic layer.

Finally, we have developed several cutting-edge techniques for studying magnetism in thin films. We have reported the first application of both NXMS polarimetry and vector-mapped XMLD-PEEM to studying magnetism in these systems and, more broadly, the combination of NXMS, neutron diffraction, and vector-mapped XMLD-PEEM allowed us to gain a detailed picture of the interplay between magnetism and lattice from 1 cm to less than 100 nm—an approach applicable to many other functional antiferromagnets in device configurations.

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