

Magnetic and Electronic Phenomena in Oxide Interfaces, Thin Films and Heterostructures



Stephen Barry Porter

School of Physics and CRANN

Trinity College Dublin

Magnetism and Spin-Electronics Group

A thesis submitted to the University of Dublin, Trinity College
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

June 29, 2018

Declaration

I have read and I understand the plagiarism provisions in the General Regulations of the University Calendar for the current year, found at <http://www.tcd.ie/calendar>.

I have also completed the Online Tutorial on avoiding plagiarism 'Ready Steady Write', located at <http://tcd-ie.libguides.com/plagiarism/ready-steady-write>.

Signature

Date

Summary

The miniaturisation of integrated circuit technology and the rapidly increasing demand for fast, reliable, low power non-volatile memory solutions, as well as novel sensor applications is driving the demand for new materials in device design. With the focus on tailored materials with a wide range of tunable properties, nanoscale oxide heterostructures represent an exciting frontier in electronics and magnetism. The electronic properties of complex transition metal and rare earth magnetic oxides are widely tunable by control of stoichiometry or by exploiting their high sensitivity to strain, allowing for the adaptable influence of substrate strain in thin film heterostructures.

This work addresses a number of different material properties for technologically relevant oxides, from the point of view of addressing the issues preventing them from being adapted and applied in thin film-based devices. The work includes the electrical characterisation of a device designed to combine the ferromagnetic and ferroelectric properties of the constituent materials in an artificial multiferroic tunnel junction.

In the first chapter, the basic concepts of magnetism which apply to the materials characterised in the work, as well as an overview of the applications of magnetism in devices and the forms of multiferroicity are presented. A comprehensive overview of the experimental techniques and their associated principles is given in the second chapter with particular attention to the techniques of reciprocal space mapping and synchrotron X-ray techniques including resonant inelastic scattering experiments.

The first of the three experimental results chapters is concerned with the question of magnetic dead layers in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, a historically-important conductive ferromagnetic oxide which is highly spin polarised. The dead layer thickness is first determined by extrapolating from magnetometry measurements of films of different thickness, then the nature of the dead layers is discussed in terms of the results of X-ray dichroism experiments and put in the context of experiments and theory which may be found in the

literature. The direct contribution of the substrate to the magnetism of LSMO is discussed. The second of the experimental chapters is concerned with oxide thin films that exhibit insulating and ferrimagnetic order. Results of studies on NiFe_2O_4 and CoFe_2O_4 , two prime candidates for spin filtering tunnel barriers, are also shown in in this chapter, where the growth of NiFe_2O_4 is achieved on the conductive oxide SrRuO_3 and the effects of substrate strain and deposition conditions on magnetisation and anisotropy of highly magnetostrictive CoFe_2O_4 are shown. The fourth chapter deals with NiO , an oxide exhibiting antiferromagnetism and a candidate for exchange-biasing magnetic oxide films. It is examined in thin film form by inelastic X-ray scattering, and the spin-wave dispersion is shown for the first time in thin films, allowing for the extraction of the exchange constants responsible for antiferromagnetism. The final chapter examines BaTiO_3 , a ferroelectric oxide with potential applications in ferroelectric memory, leveraging the stable polarisation states of the material for the storage of bits, analogous to with the ferromagnetic bits of modern hard disk drives, but with lower energy costs associated with lower write-currents than those required to create Ørsted fields in magnetic memory. The chapter also presents the experiments in ferroelectric tunnelling electroresistance performed on artificially multiferroic tunnel junctions.

To Mum, Dad, Tim and Fin.

“Ar gcáit a céile a máireann na daoine”

-Seanfhocal, anaithnid

Keywords and Abbreviations

Keywords

Magnetism, thin films, multiferroics, tunnelling magnetoresistance, tunnelling electroresistance, pulsed laser deposition, oxide interfaces

Abbreviations

AMR	Anisotropic magnetoresistance	LSMO	$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$
GMR	Giant magnetoresistance	XRD	X-ray diffractometry
TMR	Tunnelling magnetoresistance	XRR	X-ray reflectometry
TER	Tunnelling electroresistance	TEM	Tunnelling electron microscopy
SQUID	Superconducting quantum interference device	SEM	Scanning electron microscopy
VSM	Vibrating sample magnetometry	AFM	Atomic force microscopy
FTJ	Ferroelectric tunnel junction	EFM	Electrostatic force microscopy
MTJ	Magnetic tunnel junction	MFM	Magnetic force microscopy
RSM	Reciprocal space map	DPFM	Direct piezo force microscopy
LSAT	$\text{La}_{0.26}\text{Sr}_{0.76}\text{Al}_{0.61}\text{Ta}_{0.37}\text{O}_3$	XAS	X-ray absorption spectroscopy
PLD	Pulsed laser deposition	XMCD/XMLD	X-ray magnetic circular/linear dichroism
RHEED	Reflection high energy electron diffraction	RIXS	Resonant inelastic X-ray scattering
DMI	Dzyaloshinski-Moriya interaction	FET	Field effect transistor
UV	Ultraviolet	STTRAM	Spin-transfer torque random access memory
FMI	Ferromagnetic insulator	RAM	Random access memory
MBE	Molecular beam epitaxy	MRAM	Magnetic random access memory
RF	Radio-frequency	YBCO	$\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_x$
PPMS	Physical property measurement system	MPMS	Magnetic property measurement system
CCD	Charge-coupled device	DMI	Dzyaloshinski-Moriya interaction

Nomenclature

$\mathbf{B}$	Magnetic field
$\mathbf{M}$	Saturation magnetisation
$\mathbf{H}$	Magnetic field strength (magnetising force)
$\mathbf{m}$	Magnetic moment
$\mathbf{E}$	Electric field
$\mathbf{P}$	Electric polarisation
$\mathbf{p}$	Electric dipole
$\mathcal{N}$	Demagnetising tensor
m_e	Electron mass (9.11×10^{-31} Kg)
$\hbar = \frac{h}{2\pi}$	(Reduced) Plank's constant (1.054×10^{-34} J s)
χ_M	Magnetic susceptibility
χ_E	Dielectric susceptibility
μ	Magnetic permeability
ϵ	Dielectric permittivity
μ_B	Bohr magneton (9.274×10^{-24} Am ²)
R	Resistance
G	Conductance
V	Voltage
C	Capacitance
I	Current
MR	Magnetoresistance
ϕ	Magnetic flux
E, ε	Energy
$\mathbf{k}$	Wave-vector
f	Frequency
λ	Wavelength

c	Speed of light ($3 \times 10^8 \text{ m s}^{-1}$)
λ_{TF}	Thomas-Fermi length
L/S/J	Orbital/Spin/Total angular momentum quantum number
γ	Surface free energy
ϕ	Potential energy
e	Euler's number
α	Magnetoelectric coupling constant
σ	Conductivity
ρ	Resistivity
T	Temperature

Acknowledgments

After four years of PhD study and the proceeding four years of undergraduate study, it is clear to me now, at the end of this chapter of my life, that no matter what I do from here on in, where I go or who I eventually become, my time spent at Trinity College will have indelibly influenced the path that lies ahead in so many ways. It has armed me with the tools for the challenges, successes and failures of that future by the experiences that I have had here, and by the relationships forged. These things have already served me well along the way, and seen me through my darkest hours and the brightest moments of joy, for it is an education not just in the physical sciences that I have received here but in the living of life itself, through the people that I have come to know and love, and in the wisdom shared by them. I will name here only those who have helped me through the last four years of PhD study directly, as the list of those important people who made the whole experience of university what it is is surely far too long to be written here.

The first of those I wish to thank are my supervisors, Profs. Michael Coey and Plamen Stamenov. It is through their constant guidance and advice that I was given the drive and confidence to see this PhD through to its conclusion. I have learned so much from both of them. I have never met, and perhaps will never meet, two more intelligent people who have retained their capacity for understanding human frailty and they have accommodated me in my weakest moments of either motivation or emotion, though their methods are significantly different. To Plamen I owe a particular debt of gratitude in this regard, whose support at a particularly critical juncture has meant more than he could know.

The postdoctoral researchers in Group D are a crack team of excellent scientists with a serious passion for their work, but nonetheless have found an amazing amount of time for my basic questions about physics and engineering problems. I would like to thank Venky for his practical assistance in all of the machines in the SNIAM lab, as

well as helping me to prepare for group meetings in some way every Tuesday morning when I come to him at the last minute and his general advice about life in the outside world. I would also like to thank Karsten for giving me much of my insight into the techniques of PLD, XRD, XRR, interpreting synchrotron data and for having faith in my abilities where I may have doubted myself, and providing me with many great opportunities for recreational libation along with Gwenael, Zsolt and the Friday afternoon crew. Gwenael himself has been a great fount of wisdom and a continuous help with practical experimental problems who is always ready to help. Zsolt, for being a steady encouragement and giving me advice on both physics and life.

I also wish to thank my fellow PhD students and those with whom I share the coolest office in CRANN. Akshara, who has been a great friend since the start of my PhD, like a sister I never had and my spiritual guide. The newest additions to our group, Kat and Ajay who have an exciting journey ahead of them, and made the last year of my PhD good fun. The office 4.22 gang members not in the research group, in order of appearance, Chuan, Matthias, Gaurav, Robbie, Joao and Sonia, who made the worst days of the PhD liveable and the best days even better (in spite of the constant threat of mutual nerf annihilation). Also a shoutout to the PCAMs and honorary PCAMs of 2013 for all of the deplorable and unspeakably good times.

A heartfelt thanks must also go out to the former members of the group (including the project students), Hongjun, Amir, Alex, Rens, Fateme, Alice, Ciaran, Zhu, Peter, Karl and especially the DnD team; Davide, for an extraordinary amount of help conducting, interpreting and publishing synchrotron results, Kiril, for the hours and hours of work that we did together (that I'm confident will eventually be publishable, but for now... нямам резултати!), and for being a true Slav-superstar friend, Yong Chang for being a fantastic scientist and helping me out whenever I asked, seriously, he is a genius and a gentleman.

Last and quite the opposite of least, Jane, without the support of whom I cannot imagine finishing this PhD. She has been with me every step of the way, there in

support when I stumble, and celebrating with me every little victory. Jane has been a continuous source of inspiration for the last five years, and I look forward to being inspired by her for many years to come.

I mo tuisiam, nuair a rmaoiníom riam uirtú, is ias na mblianta a chait me i gColáirte na Tríonóire na blianta ba tadhactaí i rít mo fáil. Ón céad lá ra coláirte reo, an céad léadct agus an céad turgnamh ra faotarlann fírice go dtí reo, tá fáil agus foghlaim tar éir teadct oim gac lá. Dáinneoin rin, ní móir dom cuimhniú ar an áit agus an tríd ina tógad mé, na treoirphionabail a bfuair mé ó na tuisiamteoirí, múinteoirí agus áiríoe oíir, Eoin, Caoimhín, Olan, Oirín agus Séamus ina measc, agus an éireadct a faib acú oim. Cuimhín ar na daoine a tug cabhair dom, nac bfuil linn a tuile, dóib atá an obair reo tiomnaite com mac, agus maireann rias go deo ran éireadct atá acú ar an obair a déanam amac anreo.

Contents

Summary	ii
Keywords and Abbreviations	vi
Nomenclature	vii
List of Figures	xv
List of Tables	xxi
1 Introduction	1
1.1 Basic Concepts of Magnetism	1
1.1.1 Exchange Interactions	4
1.1.2 Spin-Orbit Coupling	6
1.1.3 Anisotropy	7
1.1.3.1 Shape Anisotropy	8
1.1.3.2 Magnetocrystalline Anisotropy	8
1.1.3.3 Induced Anisotropy	9
1.2 Basic Magnetic Phenomena in Devices	10
1.2.1 Magnetoresistance	10
1.2.1.1 AMR & GMR	11
1.2.1.2 TMR	13
1.2.1.3 Spin Filtering	15
1.3 Oxide Electronics and Multiferroics	16
1.3.0.1 Group Symmetry: Crystallographic and Magnetic Point Groups	17
1.3.0.2 Antisymmetric Exchange	20
1.3.0.3 Inversion Symmetry Breaking at interfaces	22
1.3.1 Intrinsic Multiferroic Materials	22
1.3.2 Artificial Multiferroic Materials	24
1.4 Scope of Thesis	25
2 Experimental Methods	27
2.1 Pulsed Laser deposition	27
2.1.1 Target preparation	28
2.1.2 Substrate Preparation	29
2.1.3 Thin Film Complex Oxides	30
2.1.3.1 Growth of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$	31
2.1.3.2 Growth of SrRuO_3 and BaTiO_3	32
2.1.3.3 Growth of NiO , NiFe_2O_4 and CoFe_2O_4	33
2.2 Analysis of Crystal Structure	35
2.2.1 X-Ray Diffraction	35
2.2.1.1 Symmetric $\theta - 2\theta$ scans	37
2.2.1.2 Reciprocal Space Mapping	38

2.2.2	X-Ray Reflectometry	42
2.2.3	Reflection High Energy Electron Diffraction	43
2.3	Magnetic Characterisation	46
2.3.1	Vibrating Sample Magnetometry	46
2.3.2	SQUID magnetometry	47
2.3.3	Synchrotron X-Ray Techniques	49
2.3.3.1	X-Ray Magnetic Circular Dichroism	49
2.3.3.2	X-Ray Magnetic Linear Dichroism	51
2.3.3.3	Resonant Inelastic X-Ray Scattering	54
2.4	Transport Measurements	56
2.4.1	Resistivity	56
2.4.2	Tunnelling Electroresistance	57
2.5	Scanning Probe Microscopy	58
2.5.1	Atomic Force Microscopy	58
2.5.2	Electrostatic Force Microscopy	60
2.5.3	Direct-Piezoelectric Force Microscopy	61
3	La_{0.7}Sr_{0.3}MnO₃: Towards a Highly Spin-polarised Oxide Electrode	64
3.1	Introduction and Literature Review	64
3.1.1	The Mixed-valence Manganites	64
3.1.2	Thin Film Manganites	69
3.1.3	LSMO in Modern Research and Future Applications	70
3.1.4	Motivation	72
3.2	Experimental Results	73
3.2.1	Structure and Morphology of LSMO films	73
3.2.2	Magnetism in LSMO films	75
3.2.3	Magnetic Dead Layer Thickness Determination	81
3.2.4	Electronic Dead Layer Thickness Determination	82
3.2.5	Nature of the Dead Layers	83
3.3	Discussion and Conclusion	88
4	CoFe₂O₄ & NiFe₂O₄: Insulating and Magnetostrictive Spinel Ferrites	92
4.1	Introduction and Literature Review	92
4.1.1	Ferrimagnetism in NiFe ₂ O ₄ and CoFe ₂ O ₄	92
4.1.2	Motivation	95
4.2	Experimental Results	96
4.2.1	Structure and Morphology	96
4.2.1.1	CoFe ₂ O ₄	96
4.2.1.2	EDX of CoFe ₂ O ₄ Thin Films and Target	97
4.2.1.3	NiFe ₂ O ₄	99
4.2.2	Magnetism	102
4.2.2.1	CoFe ₂ O ₄	102
4.2.2.2	NiFe ₂ O ₄	107
4.3	Discussion	108

4.4	Conclusions	111
5	NiO: An Antiferromagnetic Oxide as a Test Case for RIXS in Thin Films	113
5.0.1	Antiferromagnetism in NiO	113
5.0.2	Motivation	114
5.1	Experimental Results	115
5.1.1	Structure and Morphology	115
5.1.1.1	NiO	115
5.1.2	Magnon Disrpsions in NiO Thin Films by RIXS	117
5.2	Discussion and Conclusions	121
6	BaTiO₃: Artificial Multiferroicity and Ferroelectric Thin Films	122
6.1	Introduction and Literature Review	122
6.1.1	Ferroelectricity and Multiferroics	122
6.1.2	BaTiO ₃ in Device Structures	125
6.1.3	Motivation	127
6.2	Experimental Results	128
6.2.1	Structure and Morphology of Films	128
6.2.1.1	SrRuO ₃ /BaTiO ₃ Bilayers	128
6.2.1.2	SrRuO ₃ /BaTiO ₃ /LSMO Trilayers	129
6.2.1.3	SrRuO ₃ /NiFe ₂ O ₄ /BaTiO ₃ /LSMO Stacks	131
6.2.2	Electrostatic Force Microscopy of SrRuO ₃ /BaTiO ₃ Bilayers . . .	132
6.2.3	Direct Piezo Force Microscopy of BaTiO ₃ Films	133
6.2.4	Transport in Patterned Devices	133
6.3	Discussion and Conclusions	136
7	Conclusions and Outlook	142
7.1	Conclusions	142
7.2	Outlook	144
	Bibliography	146
	Presentations and Publications	168

List of Figures

1.1	Vector model illustrating the total spin angular momentum of an electron, and its possible projections along Oz	4
1.2	A basic GMR structure in a) parallel and b) antiparallel states. A higher resistance is associated with the antiparallel arrangement due to the majority spins from one FM layer being scattered upon entering the second FM layer.	12
1.3	Schematic of the spin density of states in the conduction bands of two ferromagnets for a) antiparallel and b) parallel alignment.	14
1.4	Potential energy diagram of a spin filtering junction under bias showing thermal electron and lower energy electron energies.	15
1.5	The unit cell of α -Fe ₂ O ₃ showing the antiferromagnetic spin structure and the (111) plane bisecting the unit cell.	21
1.6	Schematic of polarisation in BiFeO ₃ , along the [111] direction.	24
2.1	Diagrams of the three main growth modes in thin film deposition. . . .	30
2.2	Schematic of the magnetic annealing furnace used during the fabrication of single domain NiO thin films.	34
2.3	Diagram of Bragg diffraction from planes.	36
2.4	Illustration of path difference between rays scattered between two points separated by displacement vector $\mathbf{d}$	36
2.5	Reitveld fitting of the powder diffraction pattern of a corundum target using Mo K_α radiation.	38
2.6	Schematic of X-ray diffraction geometries for (a) symmetric and (b) asymmetric scans.	39
2.7	Schematic representation of the region of reciprocal space that can be probed by X-Rays of wavelength λ . Adapted from [72].	40
2.8	Reciprocal lattices of two different single crystals of similar unit cell dimensions which may be epitaxially compatible.	41
2.9	The effect on points in reciprocal space corresponding to Bragg reflections of a thin film which is (a) relaxed, (b) fully strained and (c) of different composition with respect to those of a reference single crystal substrate and the bulk reflections.	42
2.10	Diffraction patterns corresponding to (a) highly ordered smooth, (b) terraced and (c) rough (bulk like) surfaces.	44
2.11	Relationship between (a) domain size and (b) glancing angle θ and RHEED diffraction spot shape. Adapted from [76].	44
2.12	Schematic of RHEED diffraction geometry.	45
2.13	RHEED intensity during the deposition of 56 unit cells of LSMO under a relatively low oxygen pressure of 0.2 mbar. Sudden changes in intensity are due to the adjustment of the filament current to keep the data within the detector range.	46
2.14	Illustration of the orientation of a sample during synchrotron X-ray absorption measurements, with the beam at 70° to the normal.	50

2.15	Operations performed on the Mn XAS spectra in the application of the sum rules for spin and orbital moment. (a) isotropic XAS spectrum of equation 2.15 and the two-step background to be subtracted, (b) integration of the L_2 and L_3 peaks of the isotropic XAS, and (c) integration of the dichroic signal.	52
2.16	Distortion of the charge anisotropy in a cubic potential under the influence of spin orbit coupling in NiO.	54
2.17	Schematic of the detector side of the RIXS configuration, adapted from Ghiringhelli <i>et al.</i> [92]	56
2.18	Illustration of the configuration of contacts for resistivity measurements by the van der Pauw method.	57
2.19	Plot of the correction factor for the van der Pauw formula (equation 2.21) against the ratio of measured resistances.	58
2.20	Schematic of an AFM apparatus.	59
2.21	Lennard-Jones potential describing tip-sample interaction energy, and regions corresponding to contact and tapping mode AFM.	60
2.22	Electrostatic force microscopy of an (a) unpolarised and (b) polarised BaTiO ₃ thin film.	62
2.23	Schematic of a DPFM apparatus. Adapted from T. Mori <i>et al.</i> [96] . . .	63
3.1	The ideal cubic perovskite structure of SrTiO ₃	68
3.2	Diagram of the crystal structure of La _{0.7} Sr _{0.3} MnO ₃ showing a) La/Sr, Mn and O positions and b) the corner-sharing oxygen octahedra about the Mn-sites.	69
3.3	Simplified schematic of a solid fuel cell showing air and fuel (hydrogen) entering at the cathode and anode respectively, and the transfer of two electrons to each oxygen, which then travel through the electrolyte to combine with two reduced hydrogen ions at the anode to produce water.	71
3.4	X-ray diffraction pattern of 20 - 30 nm thick films of LSMO on (001)-oriented LSAT, STO and LAO substrates. There is a well defined peak in the case of LSAT and STO, but there is strong shouldering in the case of LAO, indicating that the film is not entirely defect free and continuous.	74
3.5	Reciprocal space maps about the (113) reflex of (a) STO, (b) LAO and (c) LSAT substrates showing the LSMO (113) _{pc} peak.	76
3.6	Optical images of blank LaAlO ₃ , SrTiO ₃ , and LSAT substrates used for the growth of LSMO thin films. The substrates have been treated under deposition conditions (700 °C) for one hour prior to imaging. Note the multiple twins in LaAlO ₃	77
3.7	RHEED intensity during the initial deposition of 8.9 nm of LSMO on LSAT, 40 nm on LAO and 5 nm on STO.	78
3.8	4 K magnetisation curves (a) of LSMO on different (001)-oriented substrates, where the moments are of order 2×10^{-7} A m ² and (b) of substrates exposed to the deposition conditions of LSMO of 700 °C, 0.3 mbar of oxygen for one hour.	79

3.9	Temperature scans of the moment in (a) thin LSMO films on LaAlO_3 (b) SrTiO_3 and (c) LSAT in an applied field of 100 mT. The moment of the 1.9 nm thick film on LaAlO_3 indicates that at this thickness the LSMO film is entirely “dead”, and that the full negative moment is attributable to the diamagnetism of the substrate. An appreciable positive temperature independent moment is seen to persist above the Curie temperature in all three films on SrTiO_3 , which is attributed to the anomalous substrate magnetism mentioned in section 3.2.2. In the case of LSAT it is clear that the 1 nm thick film is below the dead layer thickness, which must be 3 unit cells or more.	80
3.10	The Curie temperature of thin LSMO films plotted against thickness for different substrates and a simple $1/n$ model showing the approach to the bulk value of 370 K. A model correcting for a dead layer of 4 unit cells is also plotted. The inset shows a plot of $1/n$ against T_C for both models.	82
3.11	Plot to determine the dead layer thicknesses in LSMO on different substrates. A linear fit of the slope of each dataset gave dead layer thicknesses of 0.8, 1.5 and 3.0 nm for LSMO grown on LSAT, STO and LAO substrates respectively.	83
3.12	Plot to determine the electronic dead layer thicknesses in LSMO on different substrates.	84
3.13	XMCD of (a) STO (2 nm) capped 3.9 nm and (b) 2.9 nm thick films of LSMO on STO in the demagnetised state, and under fields of 1 T and 9 T and at remanence.	85
3.14	XMLD of (a) 24.3 nm and 1.9 nm and (b) 2.9 nm and STO (2 nm) capped 3.9 nm thick LSMO films.	87
3.15	Illustration of the preferential occupation of d_{z^2} and $d_{x^2-y^2}$ under different conditions of strain and deformation of the oxygen octahedra in LSMO.	90
3.16	Schematic of the configuration of spins in the dead layer which is likely the case that gives rise to the XMLD results.	91
4.1	The structure of the cubic spinel ferrites showing (a) the atomic positions of the ions and (b) the octahedral and tetrahedral sites in the structure.	93
4.2	Reciprocal space maps about the (113) reflex of MgO under deposition conditions of 600 °C and a partial oxygen pressure of (a) 100 μbar , (b) 0.2 μbar and (c) vacuum showing the CoFe_2O_4 (226) peak.	98
4.3	Reciprocal space maps about (a) the (226) reflex of MgAl_2O_4 and (b) the (113) reflex of LSAT under deposition conditions of 600 °C at vacuum showing the CoFe_2O_4 (226) peak.	99
4.4	XRD pattern of a SRO/NFO bilayer structure on STO (black line). The thickness of the NiFe_2O_4 layer is about 6 nm, which gives a very broad, low intensity peak. The red line is the XRD pattern of a single 100 nm thick SRO layer on STO for comparison.	100

4.5	The surface of NiFe_2O_4 is shown here in AFM height contrast. The image was captured in contact mode, so as to obtain good resolution in height. (a) and (b) show the height-maps at different lateral scales and (c) shows the line profile indicated in (a).	101
4.6	Room temperature magnetisation loops of CoFe_2O_4 thin films deposited on $\text{MgO}(001)$ at temperatures of 500°C and 600°C	102
4.7	Room temperature magnetisation curves of CoFe_2O_4 thin films grown in vacuum and at $P_{\text{O}_2} = 20\text{ }\mu\text{bar}$, with the applied field both in the plane of the film and out, on MgO substrates.	103
4.8	Room temperature magnetisation for CoFe_2O_4 films deposited on $\text{MgO}(001)$ at 600 K for a six different oxygen pressures with a constant laser fluence of 2.1 J cm^{-2}	104
4.9	Magnetisation as a function of substrate temperature T_S for CoFe_2O_4 films deposited on $\text{MgO}(001)$ in vacuum and at $20\text{ }\mu\text{bar}$ measured at room temperature. The laser fluence used was 2.1 J cm^{-2} , except for the triangle (2.7 J cm^{-2}).	104
4.10	Magnetisation loops for CoFe_2O_4 grown at a substrate temperature of 600°C in vacuum using a laser fluence of 2.7 J cm^{-2}	105
4.11	Magnetisation curves of CoFe_2O_4 thin films, with the applied field both in the plane of the film and out, on (a) MAO, (b) LSAT and (c) LAO substrates.	106
4.12	Room temperature SQUID M - H loop for thin NiFe_2O_4 grown on a SrRuO_3 layer on (001) -oriented SrTiO_3 . Opening of the hysteresis loop is likely due in part to the formation of magnetic structures at the $\text{NiFe}_2\text{O}_4/\text{SrRuO}_3$ interface.	108
4.13	Temperature scan of the $\text{SrRuO}_3/\text{NiFe}_2\text{O}_4$ structure. Bulk T_C of SrRuO_3 is indicated.	109
5.1	The structure of NiO showing (a) the octahedral O coordination of the Ni site, (b) the spin structure consisting of alternating anti-parallel $\langle 11\bar{2} \rangle$ oriented spins along the (111) direction and (c) the exchange between Ni ions in the (100) plane.	114
5.2	X-ray diffraction patterns from thin films of NiO grown to different thicknesses on on MgO substrates. Kiessig fringes and a small linewidth in the thicker film indicates that there is ideal single crystal epitaxy in the films. The slight deviation from the bulk NiO peak position indicates that there is some strain in the film.	116
5.3	Rietveld fitting of the powder diffraction pattern of the NiO target used in the growth of thin films. The presence of peaks at low angles ($< 15^\circ$) corresponding to a spacing of 280 pm could be attributed to a small secondary phase of NiO_2 (space group $C12/m1$, $d_{(010)} = 281\text{ pm}$) [183].	116
5.4	Evolution of $a_{\parallel}$ in NiO thin films during growth deduced from RHEED spot separation.	117

5.5	Experimental and simulated (a) absorption spectra and (b) RIXS at $Q = 8.3 \text{ nm}^{-1}$ along the [101] direction for NiO thin films. The arrow indicates the energy at which the RIXS experiment was performed. The transitions have been convoluted with Gaussians to match the peak shapes.	118
5.6	RIXS spectra using horizontally polarised X-rays (in the film plane) for a range of Q parallel to [111]. The extended relative photon energy is shown in panel (a) and the low energy part of the spectra are shown in (b). Blue spectra correspond to Q vectors at the zone boundary. The Gaussian curves used to find the peak positions are shown in green. . .	119
5.7	Single magnon dispersion along the [111] direction for NiO/MgO. The fit to the curve is obtained by linear spin wave theory, in the form of equation 5.7 [186].	120
6.1	Schematic of capacitor structure for ferroelectric polarisation characterisation. The ferroelectric (yellow) is polarised between the two electrodes (amber)	123
6.2	Microscopic distortions of the structure of BaTiO ₃ and the associated energy diagram [188, 189]	124
6.3	Illustration of the cross section of a multiferroic tunnel junction stack .	127
6.4	XRD pattern of a SrRuO ₃ /BaTiO ₃ bilayer structure on SrTiO ₃ (black line). The thickness of the BaTiO ₃ layer is about 9 nm, which gives a very broad, low intensity (002) peak. The red line is the XRD pattern of a single 18 nm thick BaTiO ₃ layer on SrTiO ₃ for comparison.	129
6.5	XRD pattern of a SrRuO ₃ /BaTiO ₃ /LSMO trilayer structure on SrTiO ₃ .	130
6.6	SEM images of the surface of a representative set of trilayer samples after ion milling to make it possible to address the bottom SrRuO ₃ layer. The horizontal line in (a) and (b) is due to charging from the electron beam during a linescan to adjust contrast and brightness.	131
6.7	Cross sectional TEM images of the full stack and the interface of SrRuO ₃ with the substrate.	132
6.8	Electrostatic force microscopy images of the unpolarised (a) and polarised (b) BaTiO ₃ surface.	134
6.9	Direct piezo force microscopy images of the polarised BaTiO ₃ surface for a SrRuO ₃ /BaTiO ₃ bilayer on SrTiO ₃ . The images show the polarised region with (a,b,c) and without (d,e,f) PID feedback gain. The height-maps (a,d), deflection of the tip as detected by the AFM diode (b,e) and the piezo-response of the film (c,f) are shown.	135
6.10	I - V characteristic of one of the patterned device stacks with a SrTiO ₃ bottom electrode, NiFe ₂ O ₄ /BaTiO ₃ barrier, and a LSMO top electrode on SrTiO ₃ showing the evolution of resistance with repeated cycling. . .	136
6.11	I - V characteristic of a patterned junction below the fields required for switching behaviour. There is a large switching voltage pulse ((a) 2 V, (b) 6 V) applied before measuring each curve. The resistance of the two states after the 2 V pulses is shown in panel (c).	137

6.12	Potential profiles of the two possible polarisation states within the symmetric FTJ barrier of thickness t where x is the axis of electron propagation. Adapted from [206].	139
6.13	Potential profiles of the two possible polarisation states within the shorted asymmetric FTJ barrier with one electrode perfectly screening the depolarisation charge. Adapted from [206].	140

List of Tables

1.1	The crystallographic point groups in different crystal systems and their order.	18
1.2	The crystallographic point groups and related magnetic point groups. Ferromagnetic group symbols are given in bold.	20
2.1	Wavelengths associated with emissions from various excimer laser active media and the dissociation energies of common metal oxide bonds. . . .	28
2.2	Optimised deposition conditions of LSMO using the PLD system described in section 2.1	32
2.3	Optimised deposition conditions of SrRuO_3 and BaTiO_3 by PLD. . . .	32
2.4	Optimised deposition conditions of NiO , NiFe_2O_4 and CoFe_2O_4 by PLD. . . .	33
3.1	Mn-site spin moments from sum rule calculations on XMCD spectra for thin LSMO films grown on SrTiO_3 substrates.	86
4.1	Deposition conditions and magnetisations reported for CoFe_2O_4 in previous literature.	95
4.2	EDX analysis of Fe:Co ratios in CoFe_2O_4 samples. Ratios shown are the average of 5 separate scans for each sample.	100
4.3	Anisotropy of CoFe_2O_4 films deposited at 600°C in vacuum on different (100)-oriented substrates. The line separates the parameters that are greater than or less than that of CoFe_2O_4 , 839 pm	107

Chapter 1

Introduction

1.1 Basic Concepts of Magnetism

The study of *magnetism* is that of *magnetic fields* and *magnetic materials*, including effects arising from changing electric fields and the angular momentum and associated magnetic moment of electrons especially their intrinsic angular momentum as elementary particles, called *spin*. Magnetic fields, denoted by the vector quantity $\mathbf{B}$ (in units of tesla), can be represented by continuous closed lines of force that act on moving charged particles and on elementary magnetic moments m . The fields are produced by the magnetic ‘dipole’ moments or ensembles thereof, and also by moving electric charges. A magnetic dipole moment may be produced by a current loop in a wire, an electron in an atomic orbital or an elementary particle with spin, especially the electron.

One property of magnetic fields is that they are non-divergent, $\nabla \cdot \mathbf{B} = 0$, as implied by the closed lines of continuous force there are no magnetic charges that act as sources and sinks of $\mathbf{B}$. Materials which can produce magnetic fields in the absence of an external magnetic field are called *ferromagnets*; they possess a spontaneous magnetisation. These materials consist of an ensemble of atomic scale magnetic moments which sum to give the magnetisation. The magnetisation is a vector quantity defined as the net sum of magnetic moments per unit volume $\mathbf{M} = \frac{\mathbf{m}}{V}$. Strictly speaking, ferromagnets are magnetic materials in which all the magnetic moments from the electron spins are aligned parallel. Materials where there is a net moment, but there are two oppositely aligned atomic moment populations, are termed *ferrimagnets*. In the case where there is no net moment, but two equivalent oppositely directed ensembles of atomic moments, we have an *antiferromagnet*.

The magnetic field strength, $\mathbf{H}$ (in units of A m^{-1}), is a vector quantity which in free space describes the local magnetic field, just as $\mathbf{B}$ does, and is related by $\mathbf{B} = \mu_0 \mathbf{H}$, where μ_0 is the magnetic permeability of free space, $4\pi \times 10^{-7} \text{ T m A}^{-1}$. The distinction between $\mathbf{B}$ and $\mathbf{H}$ arises within magnetic materials, where the magnetisation of an object reflects the local value of $\mathbf{H}$. The magnetic field within a magnetic material is given by

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}). \quad (1.1)$$

Outside of a magnet, there is little distinction between $\mathbf{B}$ and $\mathbf{H}$ aside from the proportionality constant μ_0 , whereas within the magnet the case is described by equation 1.1. By definition $\nabla \cdot \mathbf{B} = 0$ is always true, so equation 1.1 can be rewritten as

$$\nabla \cdot \mathbf{M} = -\nabla \cdot \mathbf{H} \quad (1.2)$$

giving $\mathbf{H}$ the opposite sign to $\mathbf{B}$ inside a magnetic material. It is termed a demagnetising field H_d in this case, and can be thought of as similar to an electric field emanating from the top and bottom surfaces of the magnet as if there existed a density of positive and negative magnetic charges on the opposite faces, which correspond to the ‘North’ and ‘South’ poles of the magnet. The demagnetising field is uniform in an ellipsoid and it is related to the magnetisation by the three dimensional 3×3 demagnetising tensor, $\mathcal{N}_{ij}$ in the form

$$\mathbf{H}_{di} = -\mathcal{N}_{ij} \mathbf{M}_j \quad \dots i, j = x, y, z \quad (1.3)$$

The principal components of $\mathcal{N}$, $\mathcal{N}_x, \mathcal{N}_y$ and $\mathcal{N}_z$ or diagonal components of the symmetric matrix, are known as the demagnetising factors and have the relationship

$$\mathcal{N}_x + \mathcal{N}_y + \mathcal{N}_z = 1 \quad (1.4)$$

The demagnetising factors deduced from symmetry for thin films are 0 and 1 for magnetisations parallel to the plane and perpendicular to the plane, respectively, which leads to the strong tendency for films to have easy axis in the plane of the film.

It is the quantity $\mathbf{M}$ which is generally of interest in materials science, as well as the mechanisms coupling the individual spin and orbital moments of the electron that constitute the atomic moments of a material. These are predominantly *exchange interactions* and the *spin-orbit interaction*. The former interaction comes in many forms depending on the material, be it metallic, semiconducting or insulating, or strongly correlated like many oxides and nitrides. The latter interaction is the interaction of the spin moment of the electron with its orbital moment. Since 1930 magnetism has been formulated at the microscopic level in terms of quantum mechanics. The electrons, which can be described by a complex wave function $\psi(r)$, has a probability of being found within an infinitesimal volume δ^3r given by $\delta P = \psi^*(r)\psi(r)\delta^3r$ where $\psi^*(r)$ is the complex conjugate of $\psi(r)$. $\psi(r)$ must fulfil the normalisation condition

$$\iiint_V \psi^*(r)\psi(r)d^3r = N \quad (1.5)$$

where V is the volume of the system that contains N electrons. Electrons are elementary particles with mass $m_e \approx 9.109 \times 10^{-31}$ kg, charge $e = -1.602 \times 10^{-19}$ C and intrinsic spin angular momentum is $\frac{1}{2}\hbar = 0.5273 \times 10^{-34}$ Js, denoted by the spin quantum number, $s = 1/2$. Two electrons cannot occupy the same quantum state. This condition is called the Pauli exclusion principle, and combined with the Coulomb repulsion of two nearby electrons, is the origin of exchange interactions. In the following sections the phenomena of exchange interactions and spin orbit coupling will be described, broadly following the formulations given in J.M.D. Coey's book [1]. The quantum state of an electron is represented by the quantum number $s = \frac{1}{2}$ and another quantum number $m_s = \pm\frac{1}{2}$ which denotes its components of spin angular momentum $\hbar m_s = \pm 0.5273 \times 10^{-34}$ Js along the quantisation axis (z-axis) as depicted in figure 1.1.

The magnetic moments associated with the two spin states are $\pm \frac{e\hbar}{2m_e}$ where $\frac{e\hbar}{2m_e}$ is the Bohr magneton. Since e is negative, the magnetic moment of the electron is oppositely

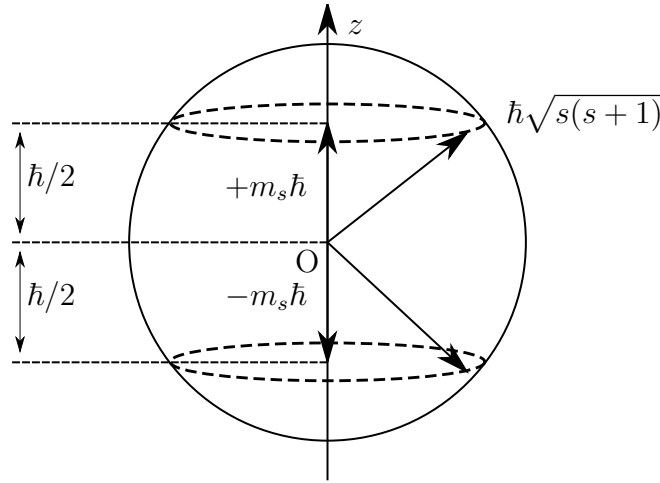


Figure 1.1: Vector model illustrating the total spin angular momentum of an electron, and its possible projections along Oz .

directed to its quantised angular momentum, represented by $\uparrow$ for $m_s = \frac{1}{2}$ and $\downarrow$ for $m_s = -\frac{1}{2}$.

1.1.1 Exchange Interactions

Two configurations of the spin states of electrons on neighbouring atoms i, j are $\uparrow_i \uparrow_j$ and $\uparrow_i \downarrow_j$, for which there is an energy difference between the two states. This is usually much weaker than the exchange between electrons on the same atom. As electrons are identical, the exchange of two electrons should not change the probability density of finding electrons in a given system implying that the wavefunction for a two electron system is antisymmetric, $\Psi(1, 2) = -\Psi(2, 1)$. The total wavefunction is the product of spatial and spin functions, $\phi(r_1, r_2)$ and $\chi(s_1, s_2)$. The simplest example of exchange is that of the hydrogen molecule, with two hydrogen atoms, each with a single electron in the $1s$ -orbital. Schrödinger's equation gives the energy ε of the system

$$\mathcal{H}(r_1, r_2)\Psi(r_1, r_2) = -\frac{\hbar^2}{2m_e} [\nabla^2 + V] \Psi(r_1, r_2) = \varepsilon\Psi(r_1, r_2). \quad (1.6)$$

Combination of the two atomic orbitals of spatially separated hydrogen atoms into the H_2 molecule creates two molecular orbitals, a symmetric bonding and antisymmetric

antibonding orbital. In the former case the distribution of electrons across the molecule is symmetric, with the electron density adding between the atoms. In the case of antibonding, there is a node in the electron density between the atoms. Their respective spatial wave functions are given in terms of the atomic orbitals as

$$\phi_s = \frac{\psi_1 + \psi_2}{\sqrt{2}} \quad \phi_a = \frac{\psi_1 - \psi_2}{\sqrt{2}}. \quad (1.7)$$

The total spin quantum number of system is $S = s_1 + s_2$ and the corresponding spin projection quantum number is M_S . S can take values of 1 and 0, and M_S can take values of 1,0,-1. This corresponds to spin triplet $S = 1$ and singlet $S = 0$ states. We can represent the symmetric (singlet) and antisymmetric (triplet) spin function in terms of S and M_S as

$$\begin{aligned} S = 1, \quad M_S = 1, 0, -1; \\ \chi_s = \begin{cases} |\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}} [|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle] \\ |\downarrow\downarrow\rangle \end{cases} \\ S = 0, \quad M_S = 0; \\ \chi_a = \frac{1}{\sqrt{2}} [|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle] \end{aligned} \quad (1.8)$$

Combining with symmetric and antisymmetric spatial wavefunctions gives total antisymmetric wavefunctions of

$$\Psi_I = \phi_s(1, 2)\chi_a(1, 2), \quad \Psi_{II} = \phi_a(1, 2)\chi_s(1, 2). \quad (1.9)$$

The using the Hamiltonian of equation 1.6, the energy of the states can be obtained, giving ε_I and ε_{II} where $\varepsilon_I < \varepsilon_{II}$. In other words: the energy of the spatially symmetric

bonding/antisymmetric spin singlet configuration lies below the antibonding triplet configuration in this case. The exchange integral is $J = (\varepsilon_I - \varepsilon_{II})/2$. Following Heisenberg, the energy of the two electron system can be written as

$$\varepsilon = -2(J/\hbar^2)\mathbf{s}_1 \cdot \mathbf{s}_2 \quad (1.10)$$

where $\mathbf{s}_1 \cdot \mathbf{s}_2$ is evaluated from $\mathbf{s}_1 \cdot \mathbf{s}_2 = \frac{1}{2}[(s_1 + s_2)^2 - s_1^2 - s_2^2]$. The energy levels for $\mathbf{s}_1 + \mathbf{s}_2 = 0$ and $\mathbf{s}_1 + \mathbf{s}_2 = 1$ are $\frac{3}{4}\hbar^2$ and $\frac{1}{4}\hbar^2$. This was generalised to many-electron atomic spins $\hat{\mathbf{S}}_1$ and $\hat{\mathbf{S}}_2$ in Heisenberg's Hamiltonian:

$$\mathcal{H} = -2\mathcal{J}\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \quad (1.11)$$

where $\mathcal{J} = J/\hbar^2$. In magnetic materials with many electron atoms, ferromagnetic interactions are indicated by $\mathcal{J} > 0$ and antiferromagnetic by $\mathcal{J} < 0$.

The specific exchange mechanisms of magnetic materials studied as part of this work are discussed in the relevant chapters, and are broadly concerned by the exchange mechanisms of transition metal oxide magnetism, namely *double exchange* and *superexchange*.

1.1.2 Spin-Orbit Coupling

An atomic orbital in the Bohr model consists of an electron orbiting a nucleus in a loop of area A which constitutes an electric current I . This creates a magnetic moment $\mu_1 = IA$ (A m²) which, in terms of the orbital angular momentum of the electron $\mathbf{l}$ is

$$\boldsymbol{\mu}_1 = -\frac{e}{2m_e}\mathbf{l} = \gamma\mathbf{l} \quad (1.12)$$

where γ is the gyromagnetic ratio. One consequence of the confinement of electrons into orbits is that the energy of the states of the electron, and hence their angular momentum, is quantised. It is quantised in units of $\hbar$ and its component along the z -axis for $\mathbf{l} = l\hbar$ can be $m_l\hbar$, where m_l can take one of $2l + 1$ possible values ($l, l -$

$1, \dots, -|l-1|, -l$). Equation 1.12 can be expressed in the fundamental unit of atomic magnetism, the Bohr magneton $\mu_B = \frac{e\hbar}{2m_e}$ and the orbital g-factor g_L as

$$\boldsymbol{\mu}_l = -g_L \mu_B \mathbf{l} / \hbar \quad (1.13)$$

where combining equations 1.12 and 1.13 gives $g_L = 1$. In analogy to this, we can express the intrinsic magnetic moment of the electron spin $\boldsymbol{\mu}_s$ in terms of a spin g-factor g_S as

$$\boldsymbol{\mu}_s = -g_S \mu_B \mathbf{s} / \hbar \quad (1.14)$$

where $g_S \approx 2.0023$. Coupling of the orbital and spin angular momenta gives the total angular momentum $\mathbf{j} = \mathbf{l} + \mathbf{s}$ and the associated moment is given by

$$\boldsymbol{\mu}_j = -g_J \mu_B \mathbf{j} / \hbar. \quad (1.15)$$

The quantity g_J is the Landé g-factor.

So far we have dealt with $\mathbf{j}, \mathbf{l}$ and $\mathbf{s}$, which is the conventional notation for isolated electrons in [1]. In many electron systems the notation $\mathbf{J}, \mathbf{L}$ and $\mathbf{S}$ is used, as mentioned in section 1.1.1. In the ‘Russel-Saunders’ or $\mathbf{L} - \mathbf{S}$ coupling scheme, $\mathbf{L} = \sum \mathbf{l}$, $\mathbf{S} = \sum \mathbf{s}$ and $\mathbf{J} = \mathbf{L} \pm \mathbf{S}$. In other words, the individual $\mathbf{l}$ and $\mathbf{s}$ are summed individually before calculating $\mathbf{J}$ which is a good approximation where there is small spin-orbit coupling, as in light transition metals. The coupling is expressed as

$$E_{SO} = \lambda \mathbf{L} \cdot \mathbf{S}. \quad (1.16)$$

1.1.3 Anisotropy

One of the requirements for stable magnetisation in ferro- and ferrimagnets is that there be a particular axis along which is a minimum energy axis for the magnetisation. The magnetisation can lie in either direction along this *easy axis*, due to time reversal

symmetry. This is represented by the *anisotropy energy* $E_a(\text{J m}^{-2})$, of which the leading term takes the form

$$E_a = K_1 \sin^2 \theta \quad (1.17)$$

where θ is the angle between the magnetic easy axis and the magnetisation and K_1 is the anisotropy constant. In bulk ferromagnets and ferrimagnets there are three main contributions to the anisotropy; *shape anisotropy*, which is a consequence of the demagnetising field H_d , *magnetocrystalline anisotropy*, which is intrinsic and related to the crystal symmetry of the material, and *induced anisotropy* which is extrinsic and caused by stress or heat treatments of the material.

1.1.3.1 Shape Anisotropy

The shape anisotropy can be calculated for a given single ferromagnetic domain of a simple shape that may be approximated an ellipsoid with demagnetising factors of $\mathcal{N}$ and $\mathcal{N}' = \frac{1}{2}(1 - \mathcal{N})$ along the easy and hard directions, respectively. Given the magnetostatic energy of a magnetised domain of volume V

$$\varepsilon_m = \frac{1}{2} \mu_0 V \mathcal{N} M_s^2, \quad (1.18)$$

the shape anisotropy constant, K_s , is merely the energy difference per unit volume between the domain uniformly magnetised along the easy and hard directions;

$$K_s = \frac{1}{4} \mu_0 M_s^2 (1 - 3\mathcal{N}). \quad (1.19)$$

It is notably zero for a sphere where $\mathcal{N} = 1/3$. The sphere has no preferred easy direction.

1.1.3.2 Magnetocrystalline Anisotropy

There are two main sources of magnetocrystalline anisotropy, single-ion and two-ion anisotropy. Single ion anisotropy is a major source of anisotropy in ferromagnets,

the spin orbit interaction stabilises a particular magnetic moment direction relative to the crystal symmetry directions. The interaction of the crystal field with ions stabilises particular orbitals, which tend to determine the spin moment direction via the spin orbit interaction. Two-ion anisotropy reflects the anisotropy of the dipole-dipole interaction, where head-to-tail configurations are favoured over side-to-side configurations. The sum of dipolar interactions over the entire lattice depends on the symmetry of the lattice, and disappears in cubic lattices.

The magnetocrystalline anisotropy constant in a uniaxial crystal can be expressed in terms of the anisotropy field H_a , which is defined as the applied field required to fully magnetise a film along the hard axis, from the equation for the energy

$$E = K_u \sin^2 \theta - \mu_0 M_s H \cos(\pi/2 - \theta) \quad (1.20)$$

where θ is the angle between the applied field H and the easy axis. The minimisation of the energy with respect to θ and setting $\theta = \pi/2$ gives,

$$H_a = 2K_u / \mu_0 M_s. \quad (1.21)$$

1.1.3.3 Induced Anisotropy

Two main methods are used to induce anisotropy in ferromagnets. The first is magnetic annealing, where at high temperatures, atomic diffusion in the presence of a magnetic field allows magnetic atoms in alloys to align as head to tail pairs, which are aligned by the external magnetic field. The second is strain induced magnetic anisotropy, which can be induced by substrates in thin films of ferromagnetic materials, where there exists magnetostrictive effects. In this case the anisotropy constant is $K_{u\sigma} = \frac{3}{2}\sigma\lambda_s$ where σ is the uniaxial stress and λ_s is the saturation magnetostriction. This effect is related to both single ion and two-ion anisotropies.

1.2 Basic Magnetic Phenomena in Devices

Devices based on magnetic effects generally leverage the stable states of ferromagnetism defined by the remnant magnetisation remaining after an external field has eliminated the domain structure and saturated the spontaneous magnetisation. The remanence can be understood as the aggregate magnetic moment, per unit volume that remains polarised along some particular energetically favourable direction. Antiferromagnets have no net magnetisation as the interaction between adjacent spins favours an antiparallel arrangement and there are two antiparallel magnetic sublattices. Antiferromagnets can be used in thin film form to stabilise one orientation of magnetisation of an adjacent ferromagnetic layer. This is known as exchange bias, which is an effect of exchange coupling between the two materials leading to a unidirectional anisotropy, not a uniaxial anisotropy. Exchange bias is used to pin the magnetisation of one of the ferromagnetic layers in spin valves, which are discussed in 1.2.1.1. It is primarily s -like bands which contribute to conduction in ferromagnetic metals. The magnetism of these bands is aligned with the magnetisation of the host material by coupling via $s-d$ or $s-f$ intra-atomic interactions with the core spins of magnetic elements, which lie in the d or f bands. Electrons which enter a medium which does not have available states to accommodate their spins are scattered or reflected. This effect is the basis for many magnetic thin film devices.

1.2.1 Magnetoresistance

The phenomenon of spin selective transport through junctions and the applications of this effect in technology are of great importance in the modern information age. The ability to rapidly sense the magnetic moments of discrete microscopic elements and relate them to the ones and zeroes of Boolean logic enabled a huge increase in mass data storage capacity and complexity of computational systems over the last 60 years. This is due to the development of magnetic sensors which have changing resistance

that is characteristic of the orientation of the stray magnetic field produced by the microscale structure of the magnetic recording medium.

1.2.1.1 AMR & GMR

The discovery in 1856 that the resistance of bulk iron or nickel subjected to a magnetic field depends on the orientation of the field is attributed to the 1st Lord Kelvin, William Thompson[2]. He noticed that when magnetic field lines lie perpendicular to the direction of current flow in the magnetic metals, the resistance is lower than when they are parallel. It would be about a century until this effect was eventually used to create sensors, and only implemented as read heads in hard drive disks by IBM in 1990. T.R. McGuire and R.I. Potter describe the effect in detail in their review[3]. In this article the effect is referred to as anisotropic magnetoresistance (AMR) and the associated figure of merit is the anisotropic magnetoresistance ratio given below.

$$\frac{\Delta\rho}{\rho_{\text{av}}} = \frac{\rho_{\parallel} - \rho_{\perp}}{\frac{1}{3}\rho_{\parallel} + \frac{2}{3}\rho_{\perp}} \quad (1.22)$$

The terms $\rho_{\parallel}$ and $\rho_{\perp}$ refer to the resistivities measured with current parallel and perpendicular to the magnetic moment of a domain. $\Delta\rho$ is the difference $\rho_{\parallel} - \rho_{\perp}$ and ρ_{av} is the average resistivity of a demagnetised ferromagnetic metal given by $\frac{1}{3}\rho_{\parallel} + \frac{2}{3}\rho_{\perp}$.

The effect is small at room temperature, and an AMR ratio of at most a few percent can be expected in materials like $\text{Ni}_{0.70}\text{Co}_{0.30}$ for which the ratio at 4 K is about 27%. The AMR ratio places a limit on the sensitivity of magnetic detection, and hence the density of magnetic storage and the speed with which the media can be addressed. The limits were improved by the introduction of sensors based on giant magnetoresistance and tunnelling magnetoresistance.

Giant magnetoresistance (GMR) was discovered independently in 1988 by Albert Fert and Peter Grünberg and is described for the first time in the paper by M.N. Baibich, J. Broto, A. Fert *et al.* [4]. The effect is based on the scattering of electrons impinging on

a ferromagnetic metal due to the misalignment of their spins with the magnetisation of the host material. Devices based on GMR generally consist of two ferromagnetic (FM) layers separated by a non-magnetic (NM) metallic spacer to prevent magnetic coupling of the two FM layers. A basic visualisation of a GMR device is shown in Figure 1.2. In this example the bottom FM layer, known as the free layer, is switched between having its magnetization (a) parallel and (b) antiparallel relative to the top FM fixed layer. Both current-in-plane (CIP) and current-perpendicular-to-plane (CPP) arrangements are shown, along with representative electron paths.

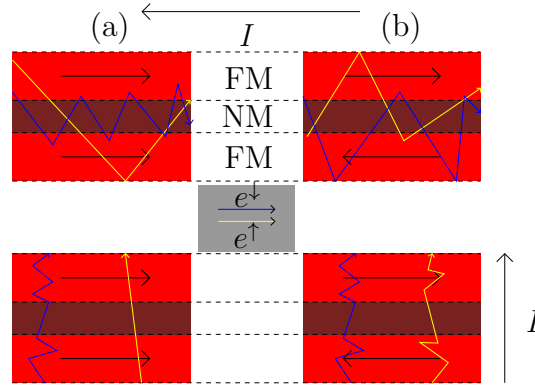


Figure 1.2: A basic GMR structure in a) parallel and b) antiparallel states. A higher resistance is associated with the antiparallel arrangement due to the majority spins from one FM layer being scattered upon entering the second FM layer.

The magnitude of the GMR effect is usually around ten percent, and is given by the ratio $\Delta R/R$ where ΔR is the resistance change in the field and R is the resistance of the device in zero field. The expression which describes this is

$$\frac{\Delta R}{R} = \frac{R_{ap} - R_p}{R_{ap}} \quad (1.23)$$

where R_{ap} is the resistance of the antiparallel configuration and R_p is that of the parallel configuration. Pinning one of the magnetic layers to an antiferromagnet by exchange bias allows the creation of a spin valve, where the free magnetic layer can be switched relative to the fixed exchange-biased layer [5].

1.2.1.2 TMR

Tunneling magnetoresistance is the effect seen in magnetic tunnel junctions (MTJ) which are thin film trilayer structures which contain a 1–2nm barrier of some insulating material. The effect is described in [1] as follows. The probability T of an electron tunnelling across a potential barrier of height ϕ above the Fermi level and width w from one electrode to an identical electrode on the other side of the barrier is

$$T = ae^{-bw\phi^{1/2}} \quad (1.24)$$

where a and b are constants. Applying a bias to the junction makes the barrier asymmetric and the tunnelling probability increases. In the case of ferromagnetic electrodes, the transmission probabilities of electrons of majority and minority spins are dependent on the spin density of states $N_{maj/min}$ in each electrode at the Fermi level. The number of states available for incident tunnelling electrons will depend on the magnetic alignment of both metals. This is shown schematically in figure 1.3 for the simplest case, where only spin conserving tunnelling processes are considered. The above explanation is valid in the absence of spin filtering (described in 1.2.1.3), and assumes that the transmission probability is proportional to the net spin density of states. If G is the conductance, it follows from this assumption that, for two ferromagnetic metals separated by an insulator

$$G_{ap} \propto N_{1,maj}N_{2,min} + N_{1,min}N_{2,maj} \quad (1.25)$$

$$G_p \propto N_{1,maj}N_{2,maj} + N_{1,min}N_{2,min}. \quad (1.26)$$

If we take the maximum magnetoresistance MR_{max} to be

$$MR_{max} = \frac{\Delta G}{G} = \frac{G_p - G_{ap}}{G_{ap}} \quad (1.27)$$

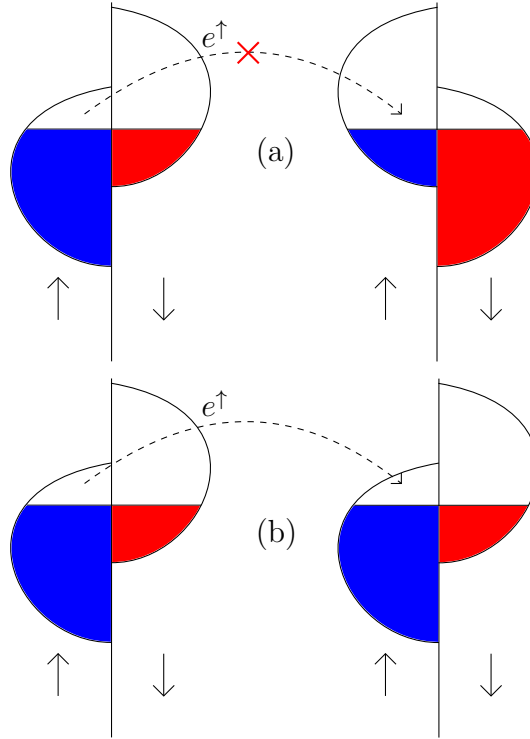


Figure 1.3: Schematic of the spin density of states in the conduction bands of two ferromagnets for a) antiparallel and b) parallel alignment.

which, if we take the case of two identical metals, can be written in terms of spin densities for spin up $\uparrow$ and down $\downarrow$ as

$$MR_{max} = \frac{N_{\uparrow}^2 + N_{\downarrow}^2 - 2N_{\uparrow}N_{\downarrow}}{2N_{\uparrow}N_{\downarrow}} = \frac{(N_{\uparrow} - N_{\downarrow})^2}{2N_{\uparrow}N_{\downarrow}} \quad (1.28)$$

then we can express MR_{max} in terms of the spin polarisation $P = (N_{\uparrow} - N_{\downarrow})/(N_{\uparrow} + N_{\downarrow})$ of the ferromagnets

$$MR_{max} = \frac{2P^2}{1 - P^2}. \quad (1.29)$$

This expression is referred to as Jullière's formula and can be extended to systems with two metals of different polarisations, P_1 and P_2 as

$$MR_{max} = \frac{2P_1P_2}{1 - P_1P_2}. \quad (1.30)$$

1.2.1.3 Spin Filtering

A spin filtering structure of the kind utilised in this project also consists of a ferromagnetic insulator (FMI) between two non-magnetic metals (M). In this case the potential barrier heights for spin up and spin down electrons can differ by a few hundred meV. Tunnelling currents are therefore spin polarised as there is a different transmission probability for electrons of different spin. The effect was first observed at low temperature in EuS [6] and has since been seen at low temperature in the inverse spinel oxides NiFe_2O_4 [7, 8] and CoFe_2O_4 [9] and at room temperature in CoFe_2O_4 [10, 11]. The energy diagram of a spin filter is shown in figure 1.4 where E is energy, V is applied potential, Φ is the average barrier height, ΔU is the difference in barrier height for different spins, w is the barrier width and E_F is the Fermi level. Spin filtering is generally measured by superconducting spin analysers using the Meservey-Tedrow technique [8, 9, 12]. Another efficient form of spin filtering is achieved in Fe/MgO/Fe. In this case the overlap of the electron wavefunction of Fe with that of MgO ensures a much higher transmission probability for the highly spin polarised Δ_1 band, whereas the wavefunctions of electrons in other bands which contain minority spins decay much faster in the barrier [13].

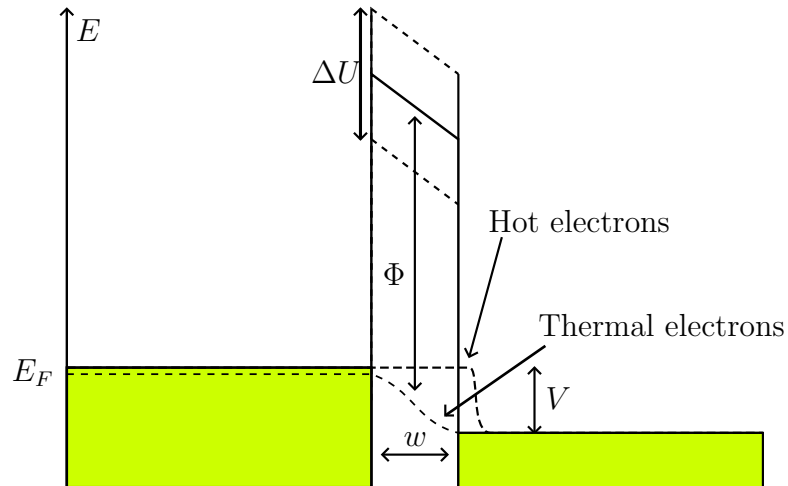


Figure 1.4: Potential energy diagram of a spin filtering junction under bias showing thermal electron and lower energy electron energies.

1.3 Oxide Electronics and Muliferroics

The field of nanoscale oxide electronics is one that has only recently been opened up by the development of various thin film deposition techniques such as pulsed laser deposition, magnetron sputtering and molecular beam epitaxy. These techniques allow the fabrication of thin films and heterostructures based on complex oxides which display a broad range of optical, electronic, structural and magnetic behavior, with some of the most interesting properties arising from the interface [14]. A disadvantage of oxides is that very few of them are conductive and those that are have high effective electron masses usually related polaron formation in the ionic lattice. The diversity in the properties of complex oxides is largely due to the fact that they are highly electronically correlated systems and often consist of various cations of different valences. Here we provide a brief introduction to the multiferroic effects that are associated with oxides in the context of oxide electronics.

The phenomenological coupling of magnetic and electric properties are described in [15] and the perturbative thermodynamic expression for the associated free energy per volume F is

$$F = F_0 - \mathbf{P}_s \cdot \mathbf{E} - \mu_0 \mathbf{M}_s \cdot \mathbf{H} - \frac{1}{2} \epsilon_0 \chi_E \mathbf{E}^2 - \frac{1}{2} \mu_0 \chi_M \mathbf{H}^2 - \alpha \mathbf{E} \cdot \mathbf{H} \quad (1.31)$$

with the last term, containing the magnetoelectric coupling constant α in units of s m^{-1} is the linear magnetoelectric contribution to the reduction in free energy. In single phase magnetoelectric compounds α can be as large as 36.7 ps m^{-1} in TbPO_4 [16] and even much larger in composite materials such as $\text{BaTiO}_3/\text{CoFe}_2\text{O}_4$ where it reaches $\approx 720 \text{ ps m}^{-1}$ in dynamic measurements [17]. Here $\mathbf{H}$ is the applied magnetic field, $\mathbf{E}$ is the applied electric field, $\epsilon_0, \mu_0, \chi_M$ and χ_E are the vacuum permittivity, permeability, magnetic and electric susceptibilities and P_s and M_s are the spontaneous polarisation and magnetisation, respectively. Before discussing some of the specific

phenomena which couple magnetic and electric order, it is instructive to consider the symmetry of crystal systems which can accommodate these orders.

1.3.0.1 Group Symmetry: Crystallographic and Magnetic Point Groups

The magnetic properties of materials are inextricably linked to the symmetry of the crystals which possess them, and hence can be understood in terms of group theory, specifically to crystallographic group theory. Point groups are sets of symmetry operations under which an object or set of objects is mapped onto identical objects, leaving one point fixed. The operations, in Hermann-Mauguin notation, the symbols of which consists of n -rotation axes, $\bar{n}$ -rotoinversion (rotation and inversion about a point on the axis of rotation), mirror planes m (equivalent to rotoinversion $\bar{2}$), and $\frac{n}{m}$ for mirror planes perpendicular to n -rotational axes which can be written as n/m in a ‘short symbol’ if all other rotation axes can be obtained by the symmetry elements present in the symbol, for example $\frac{4}{m} \frac{2}{m} \frac{2}{m}$ can be written as $4/mmm$. Supplementing these operations with two more operators, the identity operator E and the inversion operator i , we can describe the operations in terms of a set of operators $\{E, n, m, i\}$, where there can be multiple n and m .

Crystallographic point groups are those point groups which also have translational symmetry. Table 1.1 lists the Hermann-Mauguin (HM) symbols for the 32 crystallographic point groups, their classes and the order of the group which is the number of unique operations defining the group.

The crystallographic point groups apply to lattices of points, and do not necessarily apply to vectors. Two types of vector, polar and axial, correspond to those with a direction and those with both a direction and a sense of rotation. These can be understood as lattice sites with electric polarisation and magnetic moment, respectively. As we define a magnetic moment in terms of a circulating current I loop of arbitrary area A by $|\mathbf{m}| = IA$ with the direction of the moment given by the current direction, the effect of a mirror plane depends on the relative orientation of the moment. If

Table 1.1: The crystallographic point groups in different crystal systems and their order.

Crystal System	HM (Long)	HM (Short)	Order
Triclinic	1	1	1
	$\bar{1}$	$\bar{1}$	2
Monoclinic	2	2	2
	m	m	2
	$\frac{2}{m}$	$2/m$	4
Orthorhombic	222	222	4
	$mm2$	$mm2$	4
	$\frac{2}{m} \frac{2}{m} \frac{2}{m}$	mmm	8
Tetragonal	4	4	4
	$\bar{4}$	$\bar{4}$	4
	$\frac{4}{m}$	$4/m$	8
	422	422	8
	$4mm$	$4mm$	8
	$\bar{4}2m$	$\bar{4}2m$	8
	$\frac{4}{m} \frac{2}{m} \frac{2}{m}$	$4/mmm$	16
Trigonal	3	3	3
	$\bar{3}$	$\bar{3}$	6
	32	32	6
	$3m$	$3m$	6
	$\bar{3} \frac{2}{m}$	$\bar{3}m$	12
Hexagonal	6	6	6
	$\bar{6}$	$\bar{6}$	6
	$\frac{6}{m}$	$6/m$	12
	622	622	12
	$6mm$	$6mm$	12
	$\bar{6}m2$	$\bar{6}m2$	12
	$\frac{6}{m} \frac{2}{m} \frac{2}{m}$	$6/mmm$	24
Isometric	23	23	12
	$\frac{2}{m} \bar{3}$	$m\bar{3}$	24
	432	432	24
	$\bar{4}3m$	$\bar{4}3m$	24
	$\frac{4}{m} \bar{3} \frac{2}{m}$	$m\bar{3}m$	48

we now consider this effect on a moment perpendicular to a mirror plane, we find that the result is a moment with the same direction. If the moment is parallel to the mirror plane, the moment is reversed under the mirror operation. Applying the same logic to electric dipoles, which are described by polar vectors, we can see that a mirror operation on a polar vector perpendicular to the mirror plane reverses the direction of the polarisation, and does not effect the direction of one parallel to the

plane. There are 12 of the 32 crystallographic point groups which are ferromagnetic when the magnetisation has a component along the rotation axis or perpendicular to the mirror plane, which are $1, 2, m, 2/m, 3, \bar{3}, 4, \bar{4}, 4/m, 6, \bar{6}$ and $6/m$. Of these, magnetic subgroups can be generated by combining the elements of a given group with R , the time reversal operator, where for any operator O the ‘anti-symmetry’ operator O' is generated by

$$RO = OR = O'. \quad (1.32)$$

For the set of basic operators of point group symmetry $\{E, n, m, i\}$ there is a set of anti-symmetry operators $\{R, n', m', i'\}$ giving a full set of $\{E, n, m, i, R, n', m', i', \}$. Magnetic point groups are made by identifying elements of halving subgroups (subgroups of index 2) of crystallographic point groups, subtracting the elements, operating on the remaining elements with R and combining subtracted elements with the derived elements, repeating for all remaining elements of the halving subgroup. Table 1.2 lists the crystallographic point groups and the 58 corresponding magnetic point groups, where the symbols of the 31 groups that allow for a ferromagnetic state are given in bold font.

This in general follows the rule that for ferromagnetic crystals, the magnetisation vectors must lie along the highest 2,3,4,6-fold axis and be perpendicular to the mirror planes. It must also be perpendicular to the twofold anti-symmetric rotation axes ($2'$) and parallel to anti-symmetric mirror planes m' . Somewhat contrarily for ferroelectric crystals, the polarisation must lie along the highest 2,3,4,6-fold axis, be perpendicular to the anti-symmetric mirror planes and twofold anti-symmetric axes and parallel to mirror planes [18].

Table 1.2: The crystallographic point groups and related magnetic point groups. Ferro-magnetic group symbols are given in bold.

Point Group	Magnetic Point Group				
1					
$\bar{1}$	$\bar{1}'$				
2	2'				
m	m'				
2/m	2'/m'	2/m'	2'/m'		
222	2'2'2				
mm2	m'm'2	2'm'm			
mmm	mm'm'	m'm'm'	mmm'		
4	4'				
$\bar{4}$	$\bar{4}'$				
4/m	4'/m	4/m'	4'/m'		
422	4'22'	42'2'			
4mm	4'mm'	4m'm'			
$\bar{4}2m$	$\bar{4}'2m'$	$\bar{4}'m2'$	$\bar{4}2'm'$		
4/mmm	4'/mmm'	4/mm'm'	4/m'm'm'	4/m'mm	4'/m'm'm
3					
$\bar{3}$	$\bar{3}'$				
32	32'				
3m	3m'				
$\bar{3}m'$	$\bar{3}m$	$\bar{3}'m'$	$\bar{3}'m$		
6	6'				
$\bar{6}$	$\bar{6}'$				
6/m	6'/m'	6/m'	6'/m		
622	6'22'	6m'm'			
6mm	6'mm'	6m'm'			
$\bar{6}m2$	$\bar{6}'2m'$	$\bar{6}'m2'$	$\bar{6}m'2'$		
6/mmm	6'/m'mm'	6/mm'm'	6/m'm'm'	6/m'mm	6'/mmm'
23					
$m\bar{3}$	$m'\bar{3}'$				
423	4'32'				
$\bar{4}3m$	$\bar{4}'3m'$				
$m\bar{3}m$	$m\bar{3}m'$	$m'\bar{3}'m'$	$m'\bar{3}'m$		

1.3.0.2 Antisymmetric Exchange

One of the effects which is important in the pursuit of functional multiferroics is that of antisymmetric exchange. It's associated energy takes the general form

$$\mathcal{H} = -\mathcal{D} \cdot [\mathbf{S}_1 \times \mathbf{S}_2] \quad (1.33)$$

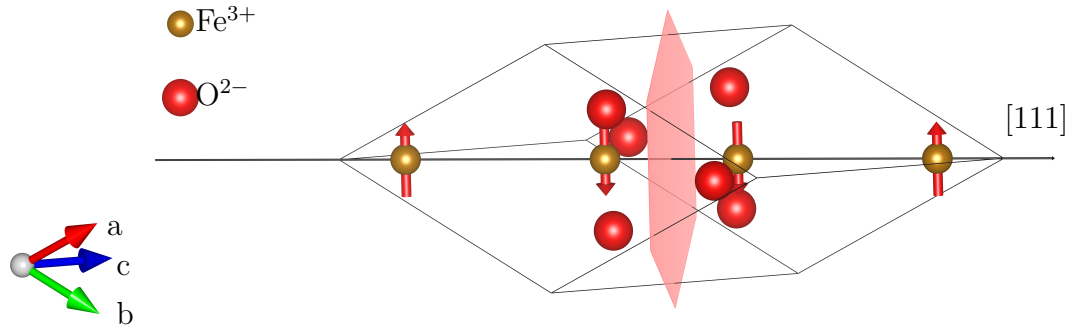


Figure 1.5: The unit cell of $\alpha\text{-Fe}_2\text{O}_3$ showing the antiferromagnetic spin structure and the (111) plane bisecting the unit cell.

where $\mathcal{D}$ is a constant vector. This term in the Hamiltonian is needed to account for the fact that anti-symmetric coupling is possible between two ions with oppositely directed moments in a crystal as a direct consequence of the time reversal symmetry of magnetic moments under certain conditions of symmetry. Consider the example of $\alpha\text{-Fe}_2\text{O}_3$ introduced by I. Dzyaloshinski [19], the structure of which is shown in 1.5. The spin only antiferromagnetic configuration of the four Fe^{3+} ions in the unit cell along the trigonal axis is $\mathbf{s}_1 = -\mathbf{s}_2 = -\mathbf{s}_3 = \mathbf{s}_4$ with the spins lying parallel to the symmetry plane bisecting the trigonal axis along the [111] direction. In order to explain why weak ferromagnetism is observed in $\alpha\text{-Fe}_2\text{O}_3$, Dzyaloshinski determined that the magnetic symmetry of the antiferromagnetic state and one with all spins rotating away from the symmetry plane were identical by constructing the magnetic space group from the crystallographic space group of $\alpha\text{-Fe}_2\text{O}_3$ ($R\bar{3}c$ in the Hermann-Mauguin short notation, D_{3d}^6 in Schoenflies notation) by combinations of R (the time reversal symmetry operator of section 1.3.0.1) with the allowed symmetry operations of the crystallographic space group. He found that the two states were equivalent by symmetry. T. Moriya then showed that while equation 1.33 describes the energy of the interaction phenomenologically, it was necessary to invoke spin-orbit coupling to describe the microscopic origins of the effect [20] and explicitly calculate $\mathcal{D}$. Antisymmetric exchange is therefore also called the Dzyaloshinski-Moriya interaction (DMI).

One of the driving causes of antisymmetric exchange in superexchange-coupled oxide antiferromagnets is the distortion of the oxygen sublattice relative to that of the cations,

as it is through the oxygen lattice the magnetic cations have superexchange interactions. This coupling of magnetism and structure is one of the mechanisms by which multiferroicity is realised, as relative displacements of cations and anions caused by ferroelectric polarisation can influence the bond angles defining the superexchange.

1.3.0.3 Inversion Symmetry Breaking at interfaces

The corresponding symmetry effect for artificial multiferroics is the Rashba-Dresselhaus spin-orbit coupling. G. Dresselhaus first described how the bulk spin-orbit coupling leads to band splitting in zinc-blende structures [21] and E. I. Rashba [22, 23] (Russian and English). The effect in both cases is due to the effect of the crystal field gradient in crystals on moving electrons. Consider that an electron moving in a magnetic field with momentum $m_e \mathbf{v}$, experiences a force $\mathbf{F} = -e\mathbf{v} \times \mathbf{B}$ and has Zeeman energy of $E_Z = \mathbf{m} \cdot \mathbf{B}$. In analogous terms, the electron moving in an electric field experiences an effective magnetic field $\mathbf{B}_{eff} \approx \mathbf{E} \times \mathbf{v} / c^2$ where c is the speed of light. The corresponding Zeeman energy is the spin orbit coupling $E_{SO} \approx (\mathbf{E} \times \mathbf{v}) \cdot \mathbf{m} / c^2$ [24]. In centrosymmetric crystal systems this is averaged out, but in systems which lack spatial inversion symmetry and have significant spin-orbit coupling, this effect becomes significant and can lead to the creation of spin currents. In artificial (not-single phase) systems like interfaces and graded compounds, the symmetry is also broken. This provides a means to influence the effective spin-orbit field by ferroelectric layers due to surface charges induced by the polarisation.

1.3.1 Intrinsic Multiferroic Materials

Non-volatile magnetic random access memory (MRAM) technologies have reached the limit of Ørsted field writing capabilities and much research effort is being made to find new data storage media. One method employed to achieve this without the use of external magnetic fields is spin-transfer torque (STTRAM) technology, which uses an injected spin current from one ferromagnet to switch the magnetisation of a free

layer by transfer of carrier spin angular momentum to the free layer magnetisation. This method, however, may suffer from Joule heating problems because of the high current density required and dielectric breakdown in the magnetisation reversal mechanism. Another new mechanism by which the magnetic properties of a material can be addressed by electric field control is that of intrinsic magnetoelectric multiferroicity which is defined as simultaneous existence of multiple ferroic orders in a given material, such as magnetic and ferroelectric orders [25, 26]. The field of multiferroics has had a relatively recent surge in interest. The first discoveries leading to an understanding of magnetoelectric coupling were Röntgen's discovery that a moving dielectric became magnetised when placed in an electric field in 1888 [27] and the subsequent discovery 17 years later of electric polarisation in a dielectric rotating in a magnetic field [28]. In 1894, P. Curie recognised that symmetry could drive magnetoelectric coupling in stationary crystals [29], but it was decades later before it was realised that the effect requires time asymmetry. This was first considered by Landau and Lifshitz [30] and shown explicitly Dzyaloshinski [31]. Interest in the magnetoelectric effect declined for about 20 years from 1970s until the 1990s, due in part to the small scale of the effects observed and the small number of compounds which displayed the behaviour, of which many had Curie or Néel temperatures below room temperature. With the new experimental techniques available in the 1990s, the field was revived.

A famous example of multiferroic order in a material is that of BiFeO_3 , a rhombohedral ferroelectric antiferromagnetic oxide with a ferroelectric Curie temperature of ≈ 1095 K, and polarisation along the pseudocubic [111] direction [32]. The magnetic structure of bulk BiFeO_3 is antiferromagnetic along the pseudocubic [111] axis, and ferromagnetic within in the (111) planes. It has a Néel temperature of 643 K. The ferroelectricity resides in the lone pair of s^2 orbital electrons on bismuth, which are displaced relative to the atomic nucleus in an applied electric field to produce a net dipole moment centred on the A-site of the ABO_3 perovskite. The magnetism of BiFeO_3 comes from the B-site Fe^{3+} cation, which is surrounded by six antiparallel spins on the nearest Fe neighbours. The spins are not perfectly antiparallel due to DMI (section 1.3.0.2) and have a net

magnetic moment perpendicular to the trigonal axis (the pseudocubic $[111]$ direction in this case). In BiFeO_3 it is related to the rotational distortion of oxygen octahedra along the $[111]$ axis. Superimposed on the weak ferromagnetism is a cycloidal rotation of the moments along the $[110]$ directions [33].

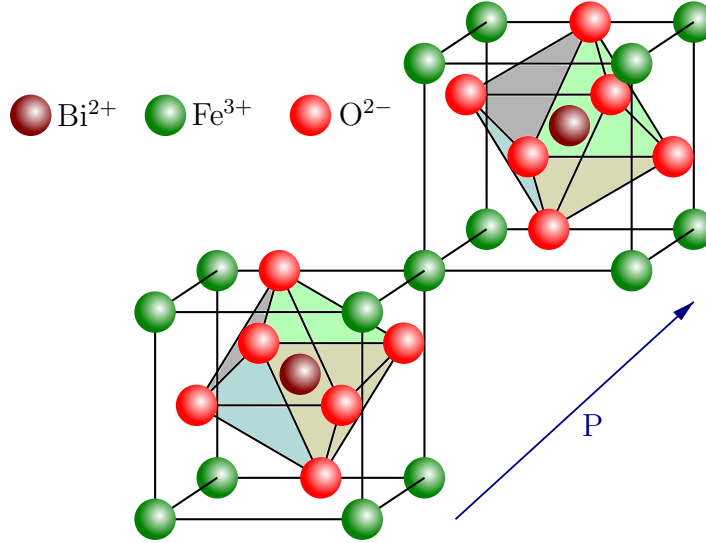


Figure 1.6: Schematic of polarisation in BiFeO_3 , along the $[111]$ direction.

The effect of polarising the material is to distort the structure rhombohedrally as shown in figure 1.6 which influences the rotations of the oxygen octahedra.

1.3.2 Artificial Multiferroic Materials

The ferroic properties such as ferroelectricity, antiferroelectricity, ferromagnetism, antiferromagnetism, and ferroelasticity, can couple in a number of different ways in materials [34–38]. Here we are concerned with the magneto-electric coupling α between two thin films. One interesting mechanism by which this can happen is analogous to the standard field effect transistor (FET) gating effect. Polarised ferroelectric thin films have an effective surface charge at each surface. Polarisation of a ferroelectric layer in contact with a metal layer leads therefore to a compensating mirror charge effect in the metal. This screening charge is efficient over the Thomas-Fermi length $\lambda_{TF} = (e^2\rho/\epsilon_0)^{-1/2}$, where ρ is the density of states, e is the electron charge and

ϵ_0 is the vacuum permittivity [39]. The effect is particularly pronounced in carrier-mediated magnetic materials such as mixed valence manganites like $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, where $\lambda_{TF} \approx -0.2 \text{ nm}$ [40]. λ_{TF} can be spin dependent, and hold separate values for different spin densities of states [41] and hence modify the magnetism.

1.4 Scope of Thesis

In this thesis, a number of different material systems are investigated with their potential technological applications in mind. The overarching goal of the work is to create a functional all-oxide device which utilises both ferroelectricity and ferromagnetism to achieve low energy voltage controlled tunnelling magnetoresistance via an artificially multiferroic tunnel junction. The design of such a device is that of a spin filtering tunnel junction, where the spin filtering effect is provided by NiFe_2O_4 or CoFe_2O_4 tunnel barriers, utilising $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ as a ferromagnetic spin analyser layer. SrRuO_3 , a conductive paramagnetic oxide at room temperature, serves as the other electrode in this design. The multiferroicity of the device comes from the combination of the spin filtering layer with a ferroelectric BaTiO_3 layer to create an artificially multiferroic tunnel barrier which utilises the stable polarisation states of the ferroelectric in combination with the spin filtering of the NiFe_2O_4 or CoFe_2O_4 layer.

Before this can be achieved, however, it is necessary to look at the components of this device in isolation, and address issues associated with each layer. Chapter 3 deals with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, the ferromagnetic layer, which is affected by the presence of a magnetic and electronic dead layer, a region of insulating and non-magnetic film existing at either the free surface or interface of the films with the substrate on which they are grown. Chapter 4 then deals with the spin filtering layers, and obtaining suitable conditions for the growth of tunnel barrier layers, while still retaining the desired properties of NiFe_2O_4 and CoFe_2O_4 . Chapter 5 explores the antiferromagnet NiO , a potential exchange bias layer in oxide spintronic devices, although in this work it is not incorporated into the final device structure, but examined by a novel method of determining

the antiferromagnetic exchange constants, resonant inelastic X-ray scattering (RIXS). The final experimental chapter, chapter 6, examines BaTiO₃ thin films and their ferroelectricity, and deals with the electrical characterisation of the fully integrated artificial multiferroic stack mentioned above.

Chapter 2

Experimental Methods

In this section, I will discuss the various experimental techniques used during the course of my PhD. The majority of thin films are grown by pulsed laser deposition in a chamber supplied by SURFACE technology (GmbH). The targets used as source material for the pulsed laser deposited films are synthesised by solid state chemical reactions and formed into pellets by pressing and sintering. Devices are primarily fabricated by UV lithographic techniques, in combination with Ar plasma milling and hydrofluoric acid based wet chemical etching processes. Microstructural properties and thickness of thin films are characterised by X-Ray diffraction (XRD) and X-Ray reflectometry (XRR) respectively. Reciprocal space mapping (RSM) is also performed to determine the strain and volume conservation of films. Magnetic characterisation is carried out by vibrating sample magnetometry (VSM) in a physical property measurement system (PPMS) with a 14 T superconducting magnet, as well as superconducting quantum interference device (SQUID) magnetometry and synchrotron X-Ray magnetic circular and linear dichroism (XMCD and XMLD).

2.1 Pulsed Laser deposition

The technique of pulsed laser deposition (PLD) is a method for the growth of thin films which utilises high energy laser pulses to ablate a target material and transfer it to a substrate. It was first applied experimentally by Smith and Turner using a Q-switched ruby laser to deposit a number of different materials by ablation of powders in vacuum [42]. Among the various physical vapour deposition techniques used in thin film fabrication, it is perhaps PLD which has been most extensively used to deposit films of complex oxides over the last 30 years. The prevalence of PLD began after a surge in popularity with its successful application by Dijkkamp in the growth of high quality

Medium	Wavelength	Energy	Bond	Diss. Energy [44]
ArF	193 nm	6.4 eV	Mn - O	4.21 eV
KrF	248 nm	5.0 eV	Sr - O	4.17 eV
XeF	351 nm	3.5 eV	Mn - Mn	0.9 eV

Table 2.1: Wavelengths associated with emissions from various excimer laser active media and the dissociation energies of common metal oxide bonds.

superconducting YBCO films using an excimer laser [43]. PLD is often the method of choice for the deposition of complex metal oxides over other thin film deposition techniques such as sputtering, molecular beam epitaxy (MBE) and evaporation. This is due to the readily achievable stoichiometric transfer of species from the target to the substrate by control of the laser energy and the wide range of chamber pressures and substrate temperatures in which a controllable growth rate can be achieved. This pressure and temperature control allows for the crystallisation and oxidation of films as they grow, and can be fine tuned to achieve control over the growth mode and morphology of films. The limitation of PLD is in both the complexity of the interaction of the laser pulse with the matter of the target material and the difficulty in scaling up the process for large area deposition.

The photon energies of excimer lasers lie in the range 3.5 - 6.4 eV and are comparable to the dissociation energies of many bonds in ceramic materials and metals, such as those shown in table 2.1. Rapid heating of the target material for the pulse duration (25 ns) causes the vaporisation of the surface layers. The vaporised material is ionised by interaction with the laser photons.

2.1.1 Target preparation

The basic process for creating targets for pulsed laser deposition is a solid state reaction involving the oxides of the various cations that constitute the required compound. A stoichiometric mixture of the cations (disregarding the oxygen stoichiometry) is ground manually in a mortar and pestle until the mixture is visibly homogeneous and fine. It is important to note that some oxides (e.g. La_2O_3) are hygroscopic, and need to

be dried at around 200 °C for about 5 hours prior to weighing. The powder is then calcined at an appropriate temperature (e.g. 1000 °C is an appropriate temperature for the formation of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$) in oxygen or atmosphere for up to 20 hours. After calcination the powder is reground and pressed to form a 19 mm pellet under a static pressure of 150 bar for 10 minutes in air. The pellet is then sintered in atmosphere at high temperature for a further 12 – 15 hours before it is ready to be used. X-ray diffraction, discussed in section 2.2.1, should be used at this point to assess the quality of the pellet. Another method for the fabricating targets such as $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ which have hygroscopic source materials is to dissolve the nitrates of the cations in water, again with the desired cation ratio, for more effective mixing. The water must be evaporated and the precipitate calcined at high temperature in oxygen or atmosphere. It is important to note that the calcination should be performed in a well ventilated room, ideally in a fume hood, to avoid the inhalation of nitrogen based gases released during the process. The calcined powder can then be processed as above into targets by pressing and sintering.

2.1.2 Substrate Preparation

For many of the films grown on SrTiO_3 substrates during the work presented in this thesis, a HF acid treatment is performed on the (100)-oriented SrTiO_3 to achieve a TiO_2 termination, as introduced by Kawasaki *et al.* in [45]. The motivation for this is to be able to reliably reproduce the initial growth mode of SrRuO_3 and obtain an atomically regulated epitaxial growth during pulsed laser deposition.

Substrates are initially soaked in de-ionised water for 10 minutes to form a Sr-OH complex, so as to increase the etch selectivity of the NH_4F buffered hydrofluoric [7 : 1] acid solution towards regions of SrO termination, as in [46].

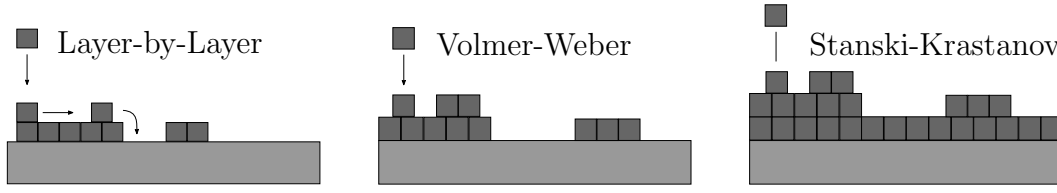


Figure 2.1: Diagrams of the three main growth modes in thin film deposition.

2.1.3 Thin Film Complex Oxides

Most of the samples fabricated for this work consist of PLD-grown oxide thin films. Stable growth of oxide crystals requires a precise control of the sample temperature, atmospheric pressure and composition, energy of the additive species and material flux. Under specific stable conditions for a given oxide, high-quality epitaxial films of precise stoichiometry can be grown. As mentioned in section 2.1, the pedigree of PLD is testament to its applicability to the growth of such films, and hence is the method chosen for this work. The growth of epitaxial thin films in general can be characterised by the different growth modes by which a film is formed. These consist primarily of the Frank-van der Merwe (hereafter referred to as layer-by-layer growth), Volmer-Weber (3D island growth and coalescence), Stranski-Krastanov (layer-by-layer transitioning to Volmer-Weber) [47] and in the case of SrRuO_3 , step-flow growth [48]. The growth mode of each material is determined *in-situ* by reflection high energy electron diffraction (RHEED), as explained in section 2.2.3. The mode of film formation can be viewed from a basic thermodynamic standpoint, where one considers the energies of the free surfaces γ_A, γ_B and interfaces γ^* in the growth system.

$$\gamma_A + \gamma^* \leq \gamma_B \quad (2.1)$$

$$\gamma_A + \gamma^* \geq \gamma_B \quad (2.2)$$

The Volmer-Weber growth mode, where island growth and coalescence are observed, is described by the first case. In this mode, the species arriving at the surface are strongly bound to each other, and the free energy is reduced to a greater degree by

forming clusters or islands than by bonding to the substrate. Layer-by-layer growth is more appropriately described by the second case. Here atoms or molecules arriving at the substrate surface are more strongly bound to the substrate than to each other, so condensing species form a complete monolayer. The second layer is slightly less tightly bound than the first, and there is a monotonically decreasing surface binding energy with each layer. As long as the binding energy decreases monotonically, the layer-by-layer growth can continue. Stranski-Krastanov growth is something of an intermediate case, where some factor interrupts the monotonic decrease in binding energy, and islands are formed on the initial interfacial layer. In step flow growth, the deposited species find energy minima at the step edges of a terraced surface, where there are the highest number of dangling bonds.

2.1.3.1 Growth of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

There exists a wealth of literature too broad to catalogue here on the growth of thin film manganites, and the preponderance of those are concerned with the growth, by PLD, of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) [49–54]. There are also many papers on the growth of high quality LSMO by DC and RF magnetron sputtering [55–58], and it is assumed for the purpose of this work that these films are of comparable quality to those grown by PLD. Optimised conditions for the growth of LSMO on SrTiO_3 , $\text{La}_{0.26}\text{Sr}_{0.76}\text{Al}_{0.61}\text{Ta}_{0.37}\text{O}_3$ (LSAT) and LaAlO_3 substrates determined during this work are summarised in Table 2.2. The parameter space is thoroughly explored by varying the substrate temperature T from 650 - 900 °C, the laser repetition rate f_{laser} from 1 - 5 Hz, the laser fluence from 0.6 - 1.6 J/cm², and the oxygen pressure P_{O_2} from 0.07 - 0.35 mbar. The growth mode of LSMO is found to be layer-by-layer under the most ideal conditions, leading to reasonably low roughness and fully strained films on SrTiO_3 and LSAT substrates, while the recrystallisation of LaAlO_3 substrates makes it difficult to determine whether the high roughness could be attributed to the substrate or the film itself.

Table 2.2: Optimised deposition conditions of LSMO using the PLD system described in section 2.1

T (°C)	P_{O_2} (mbar)	Fluence (J/cm ²)	f_{laser} (Hz)	$\frac{\Delta d}{\Delta t}$ (nm/min)
700	0.3	1.3	3	1.3

2.1.3.2 Growth of SrRuO₃ and BaTiO₃

SrRuO₃ is an orthorhombic perovskite with $a = 557.3$ pm, $b = 785.6$ pm and $c = 553.8$ pm, with four formula units per cell. It can be reduced to a pseudocubic unit cell with one formula unit, and $a_{pc} = 392.8$ pm, which matches the lattice parameter of SrTiO₃ of 390.5 pm reasonably well. Under the conditions shown in table 2.3, the films are found to grow by the step-flow growth mode after an initial three to four layers growing layer-by-layer, and at higher fluence, the coalescence of steps causes the formation of steps many unit cells high. SrRuO₃ is found to have more of a dependency on the substrate preparation conditions than other oxides grown during this work, where films grown on the mixed termination SrTiO₃ (001) surface tend to have a higher roughness than those which have been HF treated (section 2.1.2). This is likely due to a difference in diffusivity of the species arriving at the surface during deposition.

Table 2.3: Optimised deposition conditions of SrRuO₃ and BaTiO₃ by PLD.

Film	T (°C)	P_{O_2} (mbar)	Fluence (J/cm ²)	f_{laser} (Hz)	$\frac{\Delta d}{\Delta t}$ (nm/min)
SrRuO ₃	700	0.1	1.5	5	2
BaTiO ₃	600	0.01	1.2	1	1.8

BaTiO₃ is found to grow in the layer-by-layer growth mode under the conditions shown in table 2.3. It is highly sensitive to the oxygen pressure and laser fluence used during deposition. At low oxygen pressure, defects formed during deposition could lead to conductivity [59] and low laser fluence causes changes in the surface crystal structure, observed by RHEED. The structural changes may be due to changes in the stoichiometry which have been shown to occur at low fluence [60]. At high pressures and fluence, the films become rough as a result of increased collisions with gas causing coalescence and droplet forming effects, respectively.

2.1.3.3 Growth of NiO, NiFe₂O₄ and CoFe₂O₄

The growth of NiO thin films for this work is achieved by PLD on MgO substrates of (100) and (110) orientation. Optimised growth conditions are given in table 2.4 and are determined from starting conditions based on previous reports as the growth of NiO is well established by PLD. Although many reports describe the deposition at room temperature [61–63], the decision reported here are deposited at elevated temperatures to ensure the the films were smooth and highly crystallised, in the hopes of minimising the number of grain boundaries and defects which could serve as nucleation sites for magnetic domains. Nonetheless it is important to optimise the laser fluence used, as there is often considerable disagreement in the values of fluence used for a given material growth process across the literature.

Table 2.4: Optimised deposition conditions of NiO, NiFe₂O₄ and CoFe₂O₄ by PLD.

Film	T (°C)	P_{O_2} (mbar)	Fluence (J/cm ²)	f_{laser} (Hz)	$\frac{\Delta d}{\Delta t}$ (nm/min)
NiO	600	0.01	1.2	5	1.8
NiFe ₂ O ₄	400	0.045	1.0	5	0.2
CoFe ₂ O ₄	600	$\leq 1 \times 10^{-6}$	2.0	10	1.8

After deposition, the films are annealed at 600 K under an applied magnetic field of 500 mT at one atmosphere of ambient pressure for one hour. The sample is oriented so that the applied field is along the [110] direction in each case, so that the Ni spins were oriented along the axis perpendicular to one of the $\langle 11\bar{2} \rangle$ easy axes in the magnetic structure of NiO (see section 5.0.1). The annealing temperature is set above the Néel temperature so that the film is in a paramagnetic state, and hence it is possible to orient them. The apparatus is shown in figure 2.2.

Upon cooling in field, the spins should orient evenly along a single easy axis perpendicular to the applied field direction. The purpose of the magnetic annealing step is to limit the number of antiferromagnetic domains to as few as possible.

Table 2.4 also shows optimised deposition conditions for NiFe₂O₄ and CoFe₂O₄. NiFe₂O₄ grows at a particularly low deposition rate, and is optimised for growth only on SrRuO₃

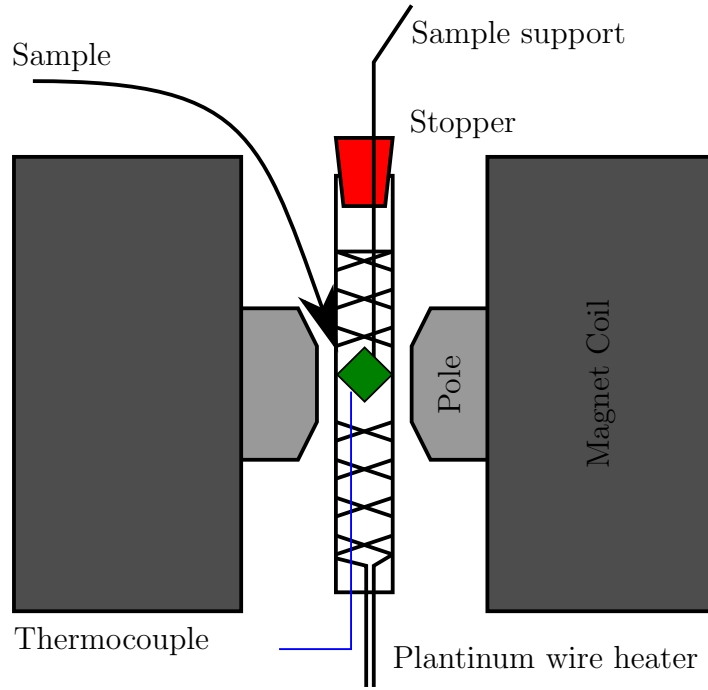


Figure 2.2: Schematic of the magnetic annealing furnace used during the fabrication of single domain NiO thin films.

buffer layers. There is a limited amount of literature on epitaxial PLD-grown NiFe_2O_4 [64–66], which necessitates the optimisation of the growth parameters from a basic standpoint. First, the ablation threshold of the target material is found using a Langmuir probe to sense the onset of plasma flux due to laser ablation, and the parameter space is explored by variation of temperature and oxygen pressure, using long deposition times in case of low deposition rates.

CoFe_2O_4 has been optimised in collaboration with a fellow PhD researcher, F. Eskandri. An extensive parameter space has been explored, due to the effect of oxygen pressure on the magnetisation which is discussed in chapter 4. CoFe_2O_4 is grown on MgO , LaAlO_3 , MgAl_2O_4 , LSAT and SrTiO_3 substrates under a range of different conditions. Those quoted in table 2.4 give the best magnetic and structural properties, where the effects of substrate strain are observed, as well as the highest magnetisations.

2.2 Analysis of Crystal Structure

In this section, the various methods used to determine the microstructural properties of samples prepared during this work are described. Initially, a general description of X-ray diffraction is given with descriptions of the two formulations of diffraction, namely the Bragg and von Laue formulations. Then symmetric X-ray diffraction and reciprocal space mapping measurements are described, followed by a brief description of X-ray reflectometry. Finally, an overview of reflection high energy electron diffraction is given.

2.2.1 X-Ray Diffraction

The theory of X-ray diffraction can be described based on the Bragg formulation, named after William Henry Bragg and his son William Lawrence Bragg who proposed the model in 1913 [67]. In this formulation, the crystal which is to be analysed is considered to be made up of semi-transparent atomic sheets (hence it is referred to as specular reflection from planes). The geometrical model presented in figure 2.3 is mathematically represented as

$$n\lambda = 2d\sin(\theta) \quad (2.3)$$

where λ is the wavelength of the X-ray light used, d is the distance between neighbouring planes and θ is the angle of incidence. By this formulation the reflections for every family of planes within a crystal can be indexed and every value of θ can have a corresponding lattice constant associated with it.

The von Laue formulation, proposed by Max von Laue at around the same time, does not require the division of a crystal into planes or an assumption of specular reflection [39]. The model of the crystal used for the formulation is that of an array of discrete identical objects placed at sites $\mathbf{R}$ of a Bravais lattice. These objects serve to scatter the incident radiation in all directions. Peaks are observed when the direction of X-rays of a given wavelength are scattered from all lattice points and interfere constructively.

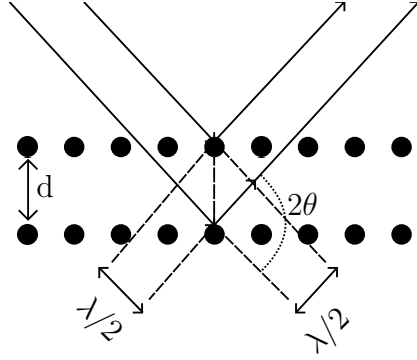


Figure 2.3: Diagram of Bragg diffraction from planes.

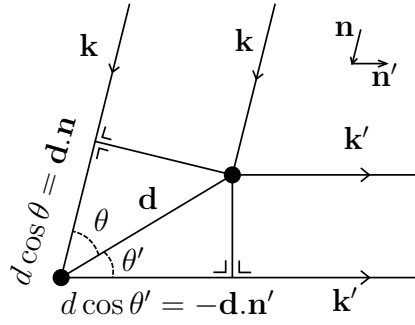


Figure 2.4: Illustration of path difference between rays scattered between two points separated by displacement vector $\mathbf{d}$.

Considering at first just two scatterers separated by a displacement vector $\mathbf{d}$, an incident X-ray along the direction $\mathbf{n}$ with wavelength λ and wavevector $\mathbf{k} = 2\pi\mathbf{n}/\lambda$ will produce a scattered ray in the direction $\mathbf{n}'$ with wavelength λ and wavevector $\mathbf{k}' = 2\pi\mathbf{n}'/\lambda$ if the path difference between the scattered rays from the two scatterers is an integral number of wavelengths. Given the geometrical consideration of figure 2.4 the path difference is

$$d \cdot \cos(\theta) + d \cdot \cos(\theta') = \mathbf{d} \cdot (\mathbf{n} - \mathbf{n}'). \quad (2.4)$$

Taking into account the condition for interference

$$\mathbf{d} \cdot (\mathbf{n} - \mathbf{n}') = m\lambda; \quad m \in \mathbb{Z} \quad (2.5)$$

and multiplying both sides by $2\pi/\lambda$

$$\mathbf{d} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m; \quad m \in \mathbb{Z} \quad (2.6)$$

we get an expression in terms of the wavevectors. Now we extend the two point lattice to an array of scatterers, with the origin at one point on the lattice. The Bravais lattice vectors $\mathbf{R}$ define the spacings between lattice points so the condition 2.6 holds for all values of $\mathbf{R}$. Therefore

$$\mathbf{R} \cdot (\mathbf{k} - \mathbf{k}') = 2\pi m; \quad m \in \mathbb{Z} \quad (2.7)$$

or equivalently

$$e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}} = 1 \quad (2.8)$$

is the condition for constructive interference in the von Laue formulation. Given the definition of a reciprocal lattice vector $\mathbf{K}$, $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$, $(\mathbf{k} - \mathbf{k}')$ is a reciprocal lattice vector.

2.2.1.1 Symmetric $\theta - 2\theta$ scans

Symmetric X-ray diffraction scans shown in this work are performed on three four-circle goniometers, a Phillips Panalytical X'Pert Pro, a Bruker D8 Advance powder diffraction and a Bruker D8 High Resolution XRD system. All three of these diffractometers utilise multi-strip detectors, which allow for the integration of each point along 2θ over the detector array for quick acquisition. The Phillips and Bruker High Resolution systems use Cu-tube K_α ($\lambda_{Cu,K_\alpha} = 154.05$ pm) radiation as the primary probing X-ray wavelength, although in the latter case, a Gobel mirror is used in conjunction with a monochromator to provide parallel X-rays as opposed to the point source of the Philips machine. The Bruker Powder diffractometer uses a point source Mo-Tube for a wavelength of $\lambda_{Mo,K_\alpha} = 70.929$ pm.

In the case of oriented thin films on single crystal substrates, the scans are symmetric about the direction normal to the primary crystalline plane of the polished face of the substrate. In this way, as the angle 2θ is varied by symmetrically varying the angular positions of the detector and source, only reflections belonging to the primary family of planes will be detected, as well as reflections from planes within the crystalline thin film with periodicity in the direction normal to those planes.

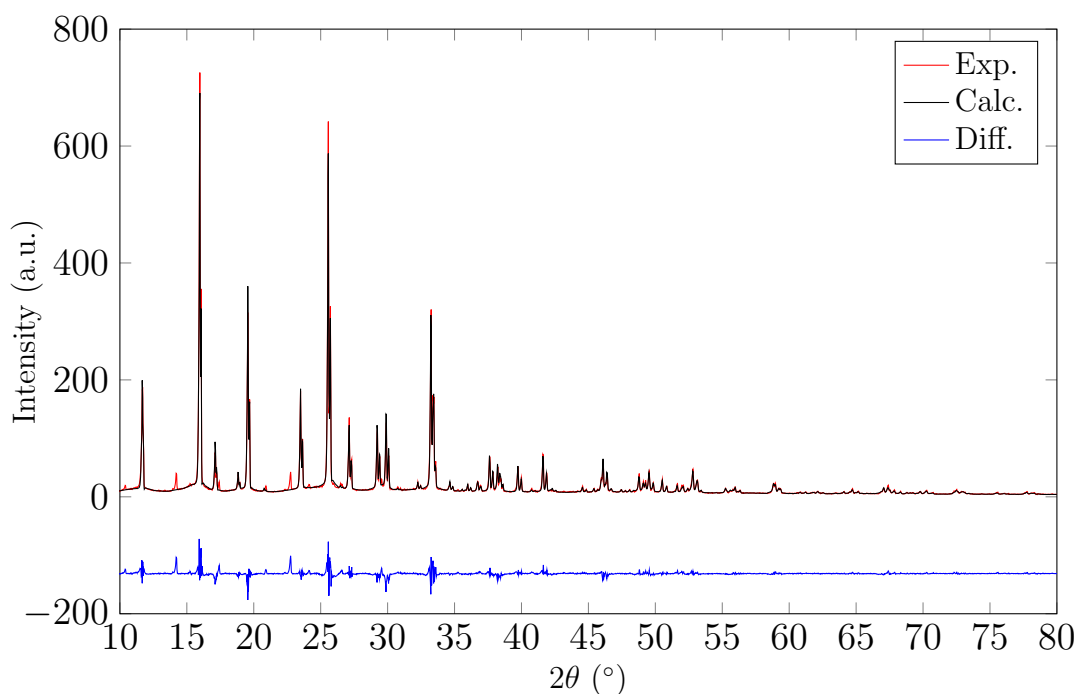


Figure 2.5: Reitveld fitting of the powder diffraction pattern of a corundum target using Mo K_{α} radiation.

The diffraction patterns of powders in symmetric XRD scans are collected by scans symmetric about the direction normal to some flat surface of the powder such as the flat face of a pressed pellet or a carefully levelled loose powder. Because of the statistically large number of randomly oriented crystallites that exist in a sufficiently large sample of micro- or nano-powder, there will be particles which show periodicity in the normal direction defined above for any given family of planes. This is aided by the use of divergent X-ray sources, which probes a small distribution of periodicities for a given 2θ angle, allowing for slight misalignment or crystallites to the normal direction. Figure 2.5 shows a powder diffraction pattern of a corundum (Al_2O_3) reference target fit using the Rietveld method [68–71].

2.2.1.2 Reciprocal Space Mapping

Reciprocal or diffraction space mapping involves making a 2-dimensional map of the diffraction pattern about a particular reflection by asymmetrical scans (from atomic planes which are not in the plane of the film), where the two dimensions that are

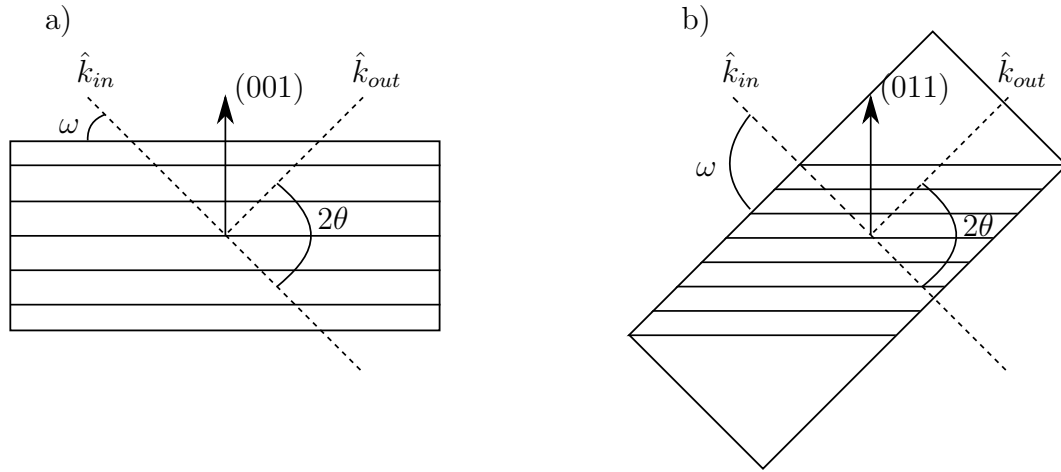


Figure 2.6: Schematic of X-ray diffraction geometries for (a) symmetric and (b) asymmetric scans.

recorded are ω (rocking curves) and 2θ (detector scans) or $\omega - 2\theta$ (coupled scans). The ω and 2θ angles are shown schematically in figure 2.6 for symmetric and asymmetric scans for a (001)-oriented single crystal.

The strain imposed on epitaxial thin films by the substrate is biaxial in the plane of the film, so a symmetric scan of $\theta - 2\theta$ will give information on the perpendicular lattice parameters (the separation atomic planes parallel to the film plane, or perpendicular to the growth direction) but contains no information on the in-plane lattice parameters. Normally, these can be inferred by assuming the conservation of the volume of the unit cell, but this makes assumptions about the homogeneity of the films in terms of strain and composition that are not necessarily borne out in reality. To map the diffraction pattern of planes which have components of their reciprocal lattice vectors in the plane of the film however, it is necessary not only to perform asymmetric scans about the corresponding planes of the substrate, but also to vary the angle ω , as the planes are no longer constrained to be parallel to those of the substrate as in the case of symmetric scans.

To understand how a map of the reciprocal space (RSM) can be made about a point in the reciprocal lattice of a single crystal, consider the region of reciprocal space which can be probed by an incoming X-ray of wavelength λ (wavevector $\hat{k}_{in}$) shown in the

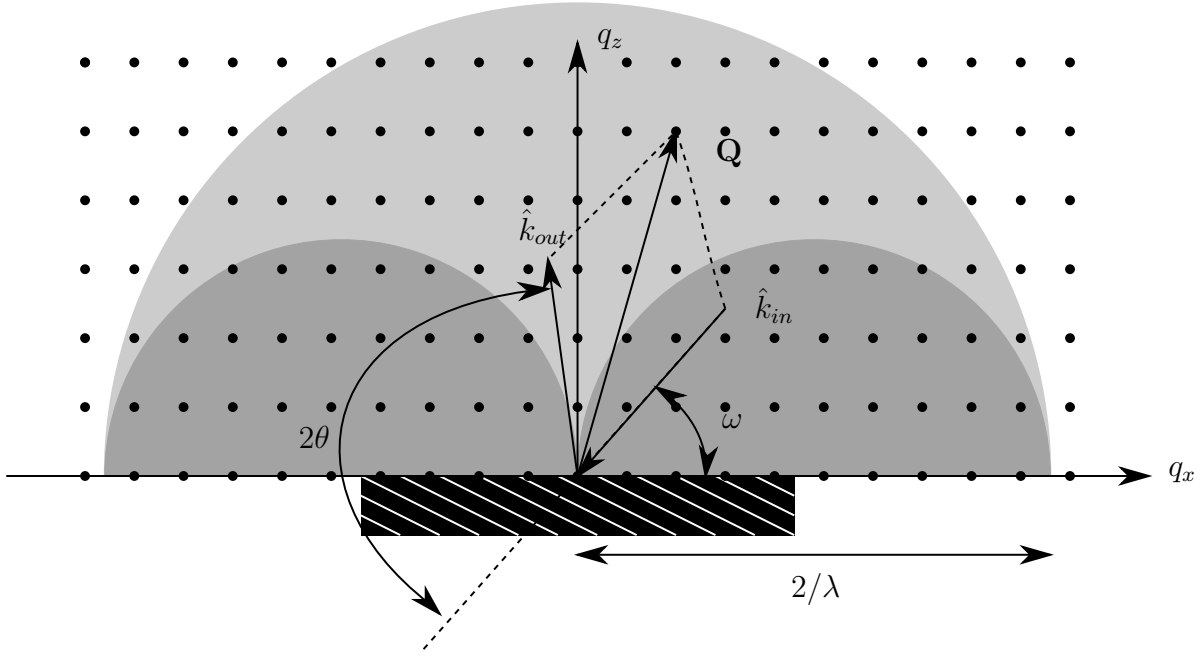


Figure 2.7: Schematic representation of the region of reciprocal space that can be probed by X-Rays of wavelength λ . Adapted from [72].

light grey region of figure 2.7. The array of points represent conditions for the fulfilment of the Bragg condition, equation 2.3, for a given reflex in plane of the reflection. The vector $\mathbf{Q} = \hat{k}_{in} - \hat{k}_{out}$ is the probe of reciprocal space when performing the RSM experiment. The dark grey regions of the figure are inaccessible due to the geometry of Bragg scattering, where the beam must enter and exit the sample via the top surface, giving the boundary condition $0 < \omega < 2\theta$, where the scattering angle 2θ corresponds to an arbitrary position of the detector with respect to the incoming beam. The map can be drawn by rastering the following degrees of freedom: varying ω (rocking curve) traces an arc centered on the origin, varying the detector position, 2θ traces an arc along the Ewald sphere circumference and a coupled $\omega - 2\theta$ scan traces a straight line away from the origin.

To map the angular coordinates $(\omega, 2\theta)$ of a scan to q-space coordinates, the following geometric relationship is used

$$(q_x, q_y) = \frac{2\pi}{\lambda} ([\sin(2\theta - \omega) + \sin(\omega)], [\cos(\omega) - \cos(2\theta - \omega)]). \quad (2.9)$$

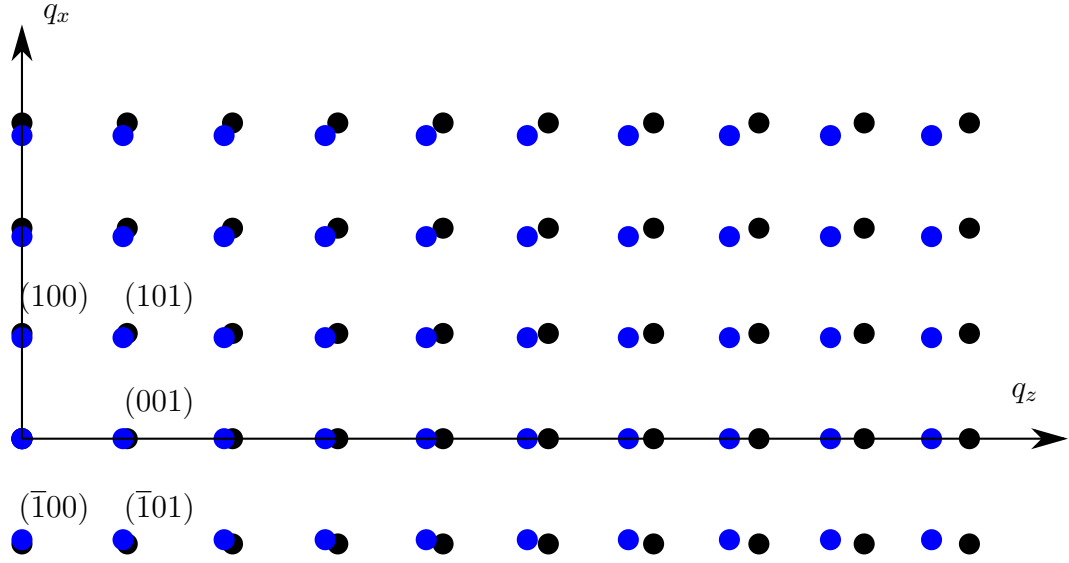


Figure 2.8: Reciprocal lattices of two different single crystals of similar unit cell dimensions which may be epitaxially compatible.

A thin film and substrate typically have slightly different lattice parameters where epitaxy is concerned, and as a result have different reciprocal lattices. A depiction of two different reciprocal lattices is shown in figure 2.8.

In the case of perfect epitaxy of materials with cubic crystal symmetry, the substrate constrains the periodicity of the film in the plane of the film, thereby matching the positions of the reciprocal lattice points in the plane. There is a corresponding displacement of out-of-plane points from their equilibrium positions by conservation of the unit cell volume, giving a tetragonal distortion. When the film is relaxed, and there is no epitaxial constraint, a symmetric scan and an asymmetric coupled scan of $2\theta - \omega$ will each give two peaks along the scan axis, as all of the corresponding families of planes are parallel and at different periodicity. A film which does not conserve unit cell volume or symmetry, for example a compound film which is off stoichiometry, may show a similar symmetric scan to a fully strained film. The three cases are shown in figure 2.9.

From the discussion above, it can be concluded that the nature of defects in a thin film can also be deduced based on the shape of the film peak in RSM. For example, a compositional gradient is indicated by broadening of the peak along the $2\theta - \omega$ axis,

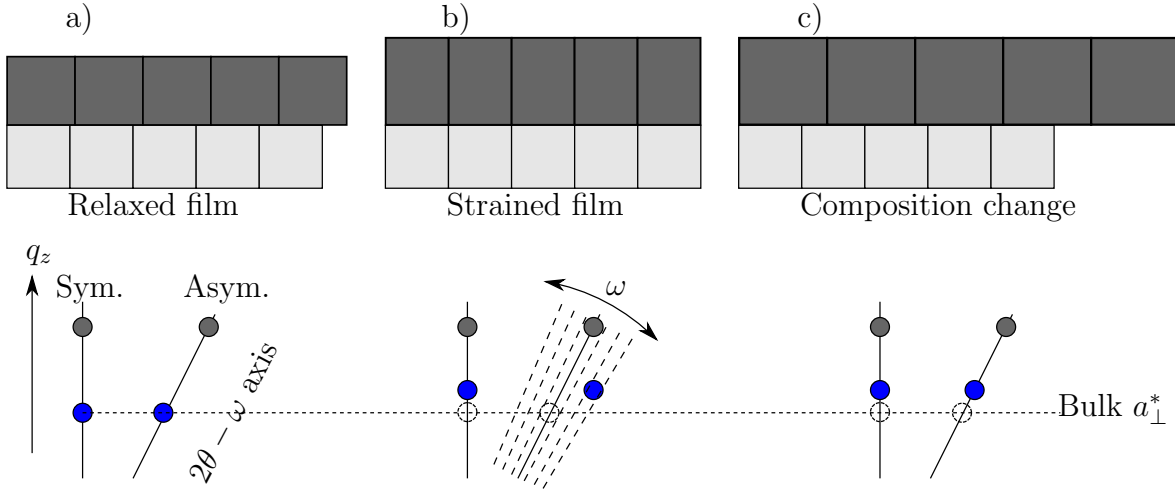


Figure 2.9: The effect on points in reciprocal space corresponding to Bragg reflections of a thin film which is (a) relaxed, (b) fully strained and (c) of different composition with respect to those of a reference single crystal substrate and the bulk reflections.

and a strain gradient gives a peak which is skewed towards the position of that of a relaxed, bulk like film.

2.2.2 X-Ray Reflectometry

The use of glancing angle X-ray reflectometry to study material properties was initially proposed by Lyman G. Parratt [73]. The angular dependence of the intensity of an incident X-ray beam near the critical angle θ_c was derived from consideration of the reflections and refractions of X-rays at different interfaces and in differing media. The behaviour of X-rays in a given medium is essentially dependent on the electron density within the media, so a different curve of intensity versus incident angle θ could be expected for two different thin films of the same thickness. The ratio of reflected to incident intensity for a given media is given by

$$\frac{I_R}{I_0} = \left| \frac{E_1^R}{E_1} \right|^2 = \frac{h - \left(\frac{\theta}{\theta_c}\right)\sqrt{2}(h-1)^{\frac{1}{2}}}{h + \left(\frac{\theta}{\theta_c}\right)\sqrt{2}(h-1)^{\frac{1}{2}}} \quad (2.10)$$

where

$$h = \left(\frac{\theta}{\theta_c}\right)^2 + \left\{ \left[\left(\frac{\theta}{\theta_c}\right)^2 - 1 \right]^2 + \left(\frac{\beta}{\delta}\right)^2 \right\}^{\frac{1}{2}}.$$

Here E_1^R and E_1 are the electric field vectors of the reflected and incident beams, and the refractive index of the material is given by

$$r = 1 - \delta - i\beta.$$

The thickness of films investigated by this technique could be estimated by a combination of this Fresnel-type model and calculating the interference pattern between reflected X-rays at the top surface and those which have been refracted through the layer and reflected at the interface with the substrate. The oscillations in intensity of X-rays observed as a function of angle produced in this manner are referred to as Kiessing fringes, as they were first observed by H. Kiessing [74]. An effective model for estimating the effect of roughness is offered in [75].

2.2.3 Reflection High Energy Electron Diffraction

High energy electron diffraction experiments were first conducted in low angle reflection geometry by Nishikawa and Kikuchi in 1928 [76] during which time Seishi Kikuchi was conducting a number of experiments on electron beam diffraction of single crystals of mica and calcite [77–81] in the earliest days of X-ray and electron diffraction from single crystals.

The interaction of a grazing-incidence high energy electron beam with the surface of a crystalline material produces a diffraction pattern which strongly depends on the orientation and surface morphology of the material. This effect can be used to qualitatively characterise the surface roughness and can also be used to monitor the growth rate during deposition. Monitoring of the growth rate is achieved by observing the periodic variations in intensity of the diffraction spots as a function of time. The effect is caused by the formation of monolayers due to the arrival of ablated material at the surface of the substrate, which occurs over many ablation events. The formation of an incomplete layer corresponds to a minimum in intensity as the surface is highly disordered. As a layer is completed, the intensity reaches a maximum. A surface with high

roughness (but maintaining surface feature size of the order of electron transparency length scales) can appear to have a bulk-like diffraction pattern. Figure 2.10 shows the diffracted pattern from the surfaces of varying roughness, with the pattern corresponding to SrTiO_3 showing Kikuchi lines due to diffuse electron channelling through the bulk of the sample due to the high crystallinity. The typical energy of electrons incident on the sample surface is of order 25 keV.

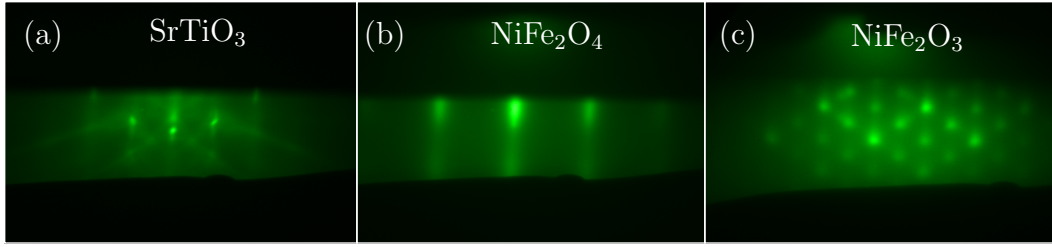


Figure 2.10: Diffraction patterns corresponding to (a) highly ordered smooth, (b) terraced and (c) rough (bulk like) surfaces.

The appearance of streaks in the RHEED patterns of crystalline surfaces were explained by Kirchner and Raether in 1932 [76]. They arise from small domains on the surface, where for a square array of lattice points of dimensions L_1 and L_2 , perpendicular and parallel to the electron direction of propagation respectively, the broadening of the diffraction spots is inversely proportional to these lengths and depends on the angle of incidence, θ , in a manner as shown in figure 2.11.

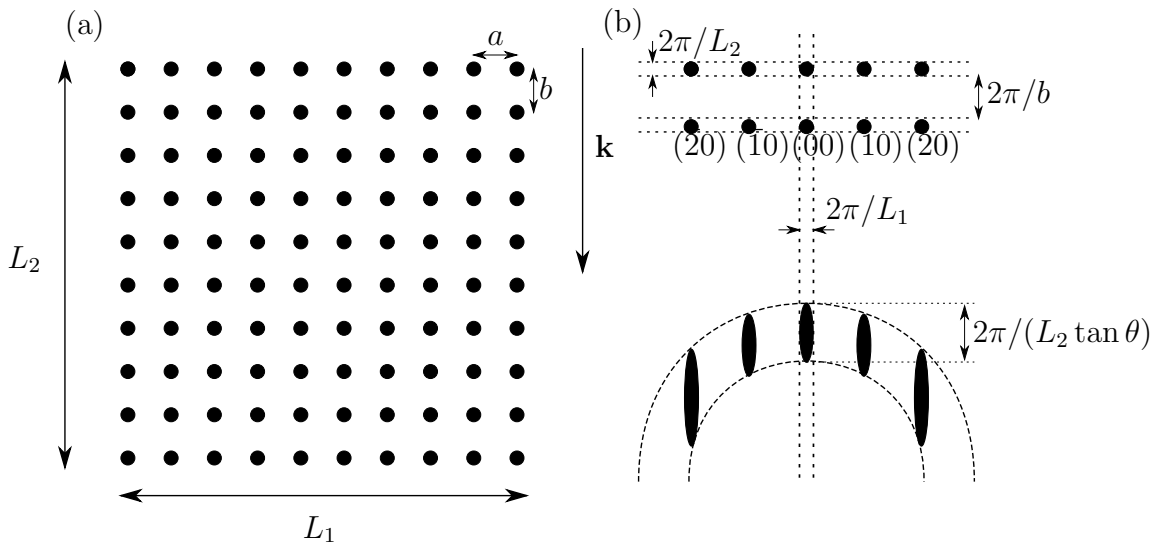


Figure 2.11: Relationship between (a) domain size and (b) glancing angle θ and RHEED diffraction spot shape. Adapted from [76].

The experimental set up consists of an electron column which is differentially pumped by two turbomolecular pumps to allow for a high pressure in the deposition chamber while preventing the electronics in the column from arcing due to ionisation. The electron beam is directed towards the sample at a low angle of incidence, and the diffracted electron pattern is imaged on a fluorescent screen. The arrangement is shown schematically in figure 2.12.

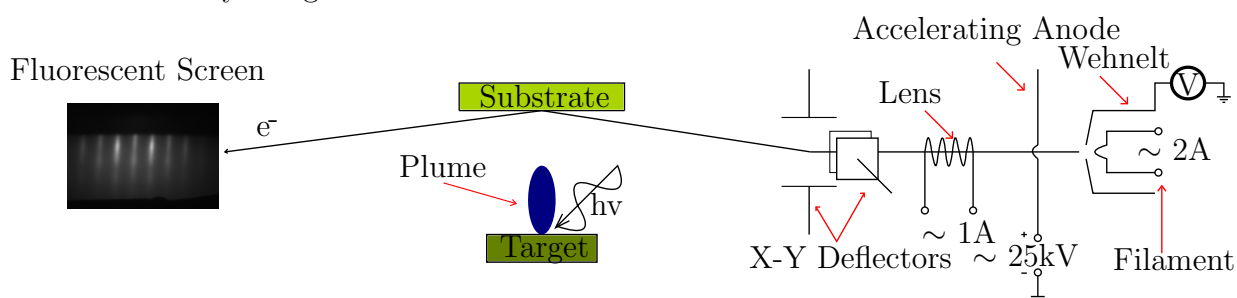


Figure 2.12: Schematic of RHEED diffraction geometry.

The principle of operation is similar to that of a scanning electron microscope column with a tungsten filament thermionic emission source. The column is kept at high vacuum to prevent the formation of gas ion filaments between the thermionic source and the casing, and also to provide a long mean-free-path for the electrons. Electrons are extracted from the vicinity of the tungsten filament by an accelerating potential of order 25 kV towards an anode. The distribution of energies is limited and the beam converged by a negative “Wehnelt” potential applied to a shield which is in close proximity to the filament. Accelerated electrons are then focussed magnetically using a lensing coil, so that a spot is formed on the surface of the sample. Diffracted electrons then form an image on a fluorescent screen, which is then digitised using a charge coupled device (CCD) camera. The beam can also be deflected electrostatically using the X-Y plate deflectors by applying a static potential between them. Figure 2.13 shows an example of a plot of RHEED spot intensity during the deposition of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. The oscillations of intensity correspond to the formation of individual monolayers.

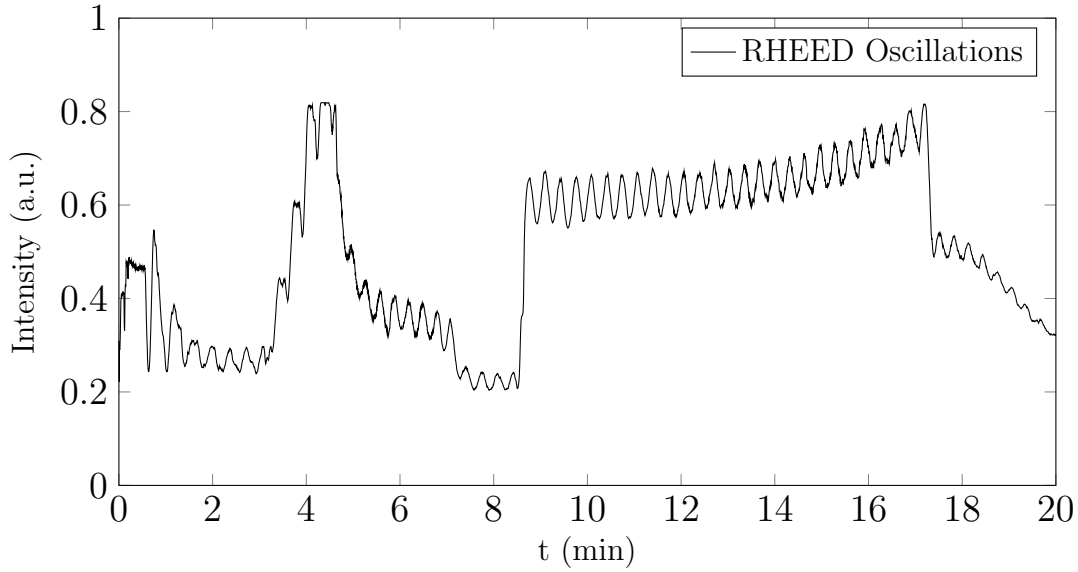


Figure 2.13: RHEED intensity during the deposition of 56 unit cells of LSMO under a relatively low oxygen pressure of 0.2mbar. Sudden changes in intensity are due to the adjustment of the filament current to keep the data within the detector range.

2.3 Magnetic Characterisation

The magnetic characterisation of samples is carried out by two main techniques. The first of these is vibrating sample magnetometry, which allows for the measurement of magnetic moments in fields of up to 14 T in-plane and out-of-plane for thin film samples. The second method is SQUID magnetometry, which allows for high sensitivity measurements in samples with low moment. Three different synchrotron X-ray measurements with magnetic sensitivity, namely X-ray magnetic circular dichroism, X-ray magnetic linear dichroism and resonant inelastic X-ray scattering, are also described.

2.3.1 Vibrating Sample Magnetometry

Vibrating sample magnetometry (VSM) is a popular, inexpensive method of measuring the magnetisation of materials which was invented in the 1950's by S. Foner [82] after the similar concept of a vibrating coil magnetometer was developed by D. O. Smith [83]. The basic principle upon which VSM is based is that the change in flux threading a coil of conductive wire will give a corresponding change in voltage measured across

the coil. The sample to be measured is first placed within a sensing coil, located inside the coils creating the applied field. The sample is then linearly oscillated in and out of the sensing coil. The flux threading a sensing coil of cross section A , while the sample is within the coil is

$$\phi_{m1} = \mu_0(H + M)A \quad (2.11)$$

and when the sample is removed the flux is

$$\phi_{m2} = \mu_0 H A. \quad (2.12)$$

For a sensing coil of N turns, the voltage, V , induced in the coil by the changing flux is given by

$$V = -N \frac{d\phi_m}{dt} \quad (2.13)$$

Therefore the flux change can be obtained from the integral of the voltage

$$\Delta\phi_m = -\frac{1}{N} \int_0^{2\pi} dt V(t - t_0) \cos(\omega(t - t_0)) \quad (2.14)$$

where τ is the period of the oscillation.

The apparatus used in this project is a Quantum Design physical property measurement system (PPMS) VSM, which utilises a gradiometer coil configuration which consists of two oppositely wound coils, with the centre of oscillation positioned at the vertical centre of the pick-up coils. The maximum applied field is 14 T, supplied by a superconducting Niobium-Titanium solenoid and the temperature range for VSM measurements is 2 - 700 K with temperatures above 350 K accessible using the high temperature option.

2.3.2 SQUID magnetometry

The superconductive quantum interference device (SQUID) magnetometer is a highly sensitive (1×10^{-10} A m⁻² in DC and 1×10^{-12} A m⁻² in RF) instrument which is based

on a superconducting loop with one (RF SQUID) or two (DC SQUID) Josephson junctions. The Josephson junction is a structure which was theorised by B. Josephson [84, 85] and realised experimentally by P. Anderson and J. Rowell [86] which consists of a superconducting junction separated by an insulator, across which current can flow with no applied voltage. A superconducting loop can accommodate only an integer number of flux quanta $\Phi_0 = \frac{h}{2e}$ enclosed within the loop, and if an external field is applied then the loop will screen or increase the flux to the nearest integer by creating a circulating current. The sign of the circulating current changes with every $\Phi_0/2$ of flux which threads the loop, since it is more energetically favourable to increase the flux to the next higher value of $n\Phi_0$, rather than to screen it. If a current is pushed through the SQUID loop (DC operation), the voltage across the loop will oscillate as the external flux increases, with a period Φ_0 . In the flux-locked RF SQUID configuration, an LC circuit is coupled to the SQUID loop (with only one Josephson junction) inductively and RF current is used to measure the inductance of the circuit. External flux such as that introduced by a ferromagnetic sample will change the inductance, with a minimum and maximum corresponding to Φ_0 and $\Phi_0/2$ respectively. This is balanced by feedback electronics in the LC circuit in order to keep the flux threading the SQUID constant.

SQUID measurements are indirect, the flux from the sample is integrated by superconducting pick-up coils which are coupled to the SQUID. The arrangement is such that a superconducting coil magnet is used to produce high magnetic fields (5 T in the case of the SQUID used in this project). The sample is lowered into the detection coils, which are 4-turn gradiometer pick-up coils, situated inside the main coils which produce the applied field and are inductively coupled to the SQUID loop. In this project RF SQUID measurements are performed on a Quantum Design magnetic property measurement system (MPMS) 5XL.

2.3.3 Synchrotron X-Ray Techniques

The experiments are performed on a soft X-Ray beamline (ID32) at the European synchrotron radiation facility (ESRF) in Grenoble, France.

In the case of magnetic dichroism measurements (samples for both linear and circular dichroism experiments are mounted on a copper sample holder which is affixed to a rod which supports the signal line and can be rotated, and translated along 2 axes perpendicular to the beam. The sample is positioned directly in the beam path, in a chamber which is evacuated to ultra high vacuum. Two pairs of liquid helium-cooled superconducting coils are fitted to the chamber so that fields can be applied parallel and perpendicular to the beam direction. 4 T can be applied in the direction perpendicular to the beam, and 9 T can be applied along the beam axis. The X-Ray absorption spectra are collected by total electron yield (TEY), where the signal is given by the sample drain current which is needed to replace the electrons that are ejected to the vacuum level as a consequence of the x-ray absorption. The electron yield is normalised relative to a gold foil target.

In inelastic scattering measurements, the sample is mounted on a four circle goniometer along a linearly polarised X-ray path and diffracted X-rays are recorded on a 2D CCD camera cooled down by peltier cells to -80°C , after passing through energy dispersive X-ray optics. The geometry is discussed further in 2.3.3.3.

2.3.3.1 X-Ray Magnetic Circular Dichroism

The physical process of X-ray magnetic circular dichroism (XMCD) is the absorption of circularly polarised X-ray radiation by core electrons in selected elements at energies corresponding to transitions to unoccupied valence states. In measurements of transition metals the energies that correspond to the $2p$ to $3d$ transitions lie in the region between 400 - 900 eV. The strong spin-orbit coupling in the core level breaks the degeneracy of the $2p_{1/2}$ and $2p_{3/2}$ states and leads to two peaks in the absorption

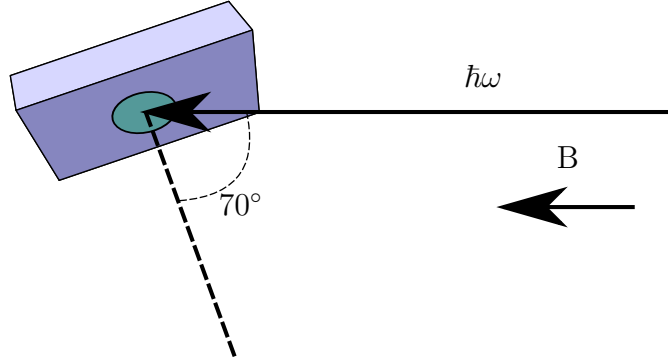


Figure 2.14: Illustration of the orientation of a sample during synchrotron X-ray absorption measurements, with the beam at 70° to the normal.

spectrum, namely L_2 and L_3 respectively in L -edge absorption spectroscopy. A typical XAS is shown in figure 2.15 (a).

The absorption of incident X-rays depends on the angular momentum of the electrons relative to the incoming X-ray if the orientation of spins is along the beam axis. More specifically, the absorption with left and right circularly polarized light will be different. The XMCD signal consists of the difference between these two XAS. In the case of thin films with in-plane magnetisation this can be achieved by rotating the sample so that the incident angle between the beam and the film normal is as close as possible to 90 deg. We went as far as 70° . A schematic illustrating the relative orientations of the applied field and the incident X-Ray beam to the sample is given in figure 2.14.

The extraction of spin and orbital angular moments from circularly polarised X-ray absorption spectra is a complex process of many manipulations of the raw spectra, shown in figure 2.15. Initially, a number of X-ray absorption spectra (XAS) are collected for both polarisations. Two average spectra are then obtained from the different polarisations, and are taken to be the absorption spectra $\mu_+(\omega)$ and $\mu_-(\omega)$ (in truth these are the energy dependent absorption coefficients, μ_+ and μ_- times some multiplication factor due to the resistivity of the sample/wire etc., but this is lost in normalisation anyway) for right- and left-handed circularly polarised light, where $\hbar\omega$ is the incident

photon energy (in eV). The isotropic XAS is then defined as

$$\frac{\mu_+ + \mu_-}{2} \quad (2.15)$$

and the XMCD spectrum is simply the difference $\mu_+ - \mu_-$ as shown in figure 2.15. To extract meaningful data from the XMCD spectra, the sum rules are applied as described in [87, 88]. The orbital and spin moments are obtained through the normalisation of the integrated dichroic signal of the absorption coefficients over the L_3 and L_2 edges by the integrated isotropic XAS after a background subtraction from the XAS described by the function

$$I(E) = I_0 \left\{ \frac{1}{2} + \frac{1}{3} \tanh \frac{(E - E_{L_2})}{\Delta} + \frac{1}{6} \tanh \frac{(E - E_{L_3})}{\Delta} \right\} \quad (2.16)$$

where E_{L_2} and E_{L_3} are the energies of the L -edges, Δ is a broadening term and I_0 is the signal above from the L_3 peak (at 660 eV for Mn). The spin moment are given in μ_B/hole by the formulae

$$m_o = -\frac{4 \int_{L_3+L_2} (\mu_+ - \mu_-) d\omega}{3 \int_{L_3+L_2} (\mu_+ + \mu_-) d\omega} (10 - n_{3d}) \quad (2.17)$$

$$m_s = -\frac{6 \int_{L_3} (\mu_+ - \mu_-) d\omega - 4 \int_{L_3+L_2} (\mu_+ - \mu_-) d\omega}{\int_{L_3+L_2} (\mu_+ + \mu_-) d\omega} (10 - n_{3d}) \quad (2.18)$$

Where n_{3d} is the number of electrons in the $3d$ orbitals of the species of interest. An extra factor of $(1 - \frac{7\langle T_z \rangle}{2\langle S_z \rangle})^{-1}$, where $\langle T_z \rangle$ is the expectation value of the magnetic dipole operator and $\langle S_z \rangle$ is equal to half of m_s in Hartree atomic units, has been omitted in equation 2.18, as it gives a very small correction to the spin moment in $3d$ metal in a cubic environment and with small $3d$ spin-orbit coupling [89].

2.3.3.2 X-Ray Magnetic Linear Dichroism

X-ray magnetic linear dichroism (XMLD) differs significantly from XMCD in that the dichroic absorption originates in the anisotropy of charge distributions due to spin-orbit

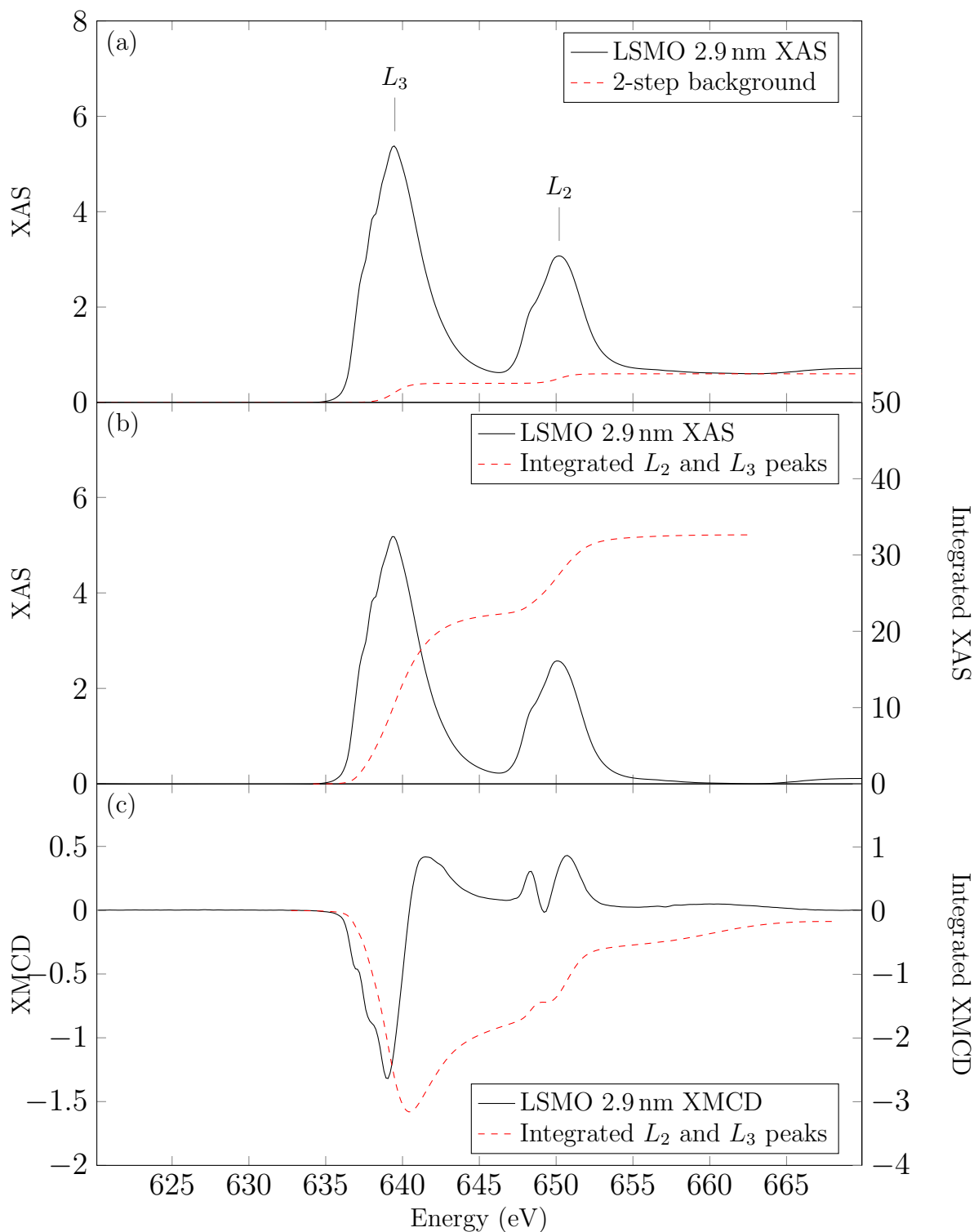


Figure 2.15: Operations performed on the Mn XAS spectra in the application of the sum rules for spin and orbital moment. (a) isotropic XAS spectrum of equation 2.15 and the two-step background to be subtracted, (b) integration of the L_2 and L_3 peaks of the isotropic XAS, and (c) integration of the dichroic signal.

coupling to the magnetic moment rather than the angular momentum contributed by its spin or orbital moment. It was first shown to be applicable to magnetic materials by G. van de Laan in 1986 [90]. In practice, XMLD experiments are performed using synchrotron X-rays which are linearly polarised parallel and perpendicular to the magnetic moment. In order to measure in-plane and out-of-plane directions, the angle of incidence is kept constant at 70° to the film normal. It is the interaction of the electric field of the X-ray with the charge anisotropy for a given energy which gives rise to absorption in XMLD. The probability of the core electrons of a given species absorbing incident linearly polarised photons is dependent on a number of factors. The primary contribution to the dichroism in linear dichroism is the orbital charge anisotropy, where a given energy level with lower than cubic symmetry will give a dichroic signal if one of the electric polarisation vectors is aligned with a direction of increased charge density. This is related to the occupancy of certain orbitals, for example d_{z^2} and $d_{x^2-y^2}$ will have different occupancy in an octahedrally coordinated transition metal in an oxide if there is a Jahn-Teller distortion. The second most significant contribution, though far smaller in magnitude than orbital charge anisotropy, is the charge anisotropy arising from the symmetry breaking effect of spin-orbit coupling in magnetic species. The magnitude of the dichroic signal is greatest when the electric field vector of a given polarisation is aligned with the magnetic axis, and has a $\cos^2(\theta)$ angular dependence, where θ is the angle between the electric polarisation vector and the magnetic axis [90]. Because this effect is proportional to the average square magnetic moment, it can also lead to dichroism in the XAS of antiferromagnetic materials such as NiO, where the cubic symmetry of the charge density in the paramagnetic state is lifted by the alignment of spins along any one of the of the $\langle 1\bar{2}1 \rangle$, $\langle \bar{2}11 \rangle$ and $\langle 11\bar{2} \rangle$ crystal directions through a spin-orbit interaction.

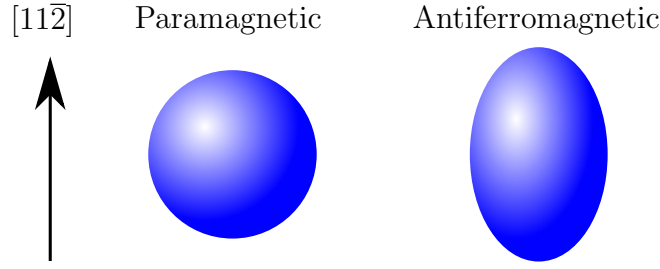


Figure 2.16: Distortion of the charge anisotropy in a cubic potential under the influence of spin orbit coupling in NiO.

2.3.3.3 Resonant Inelastic X-Ray Scattering

The process of resonant inelastic X-ray scattering (RIXS) utilises the resonance of a given ion at a given absorption edge to greatly enhance the inelastic decay cross-section of a photon. In this project, soft X-rays are used at the L_3 edge of Ni in NiO, an exemplar of type II antiferromagnetic order which is discussed later in section 5.0.1. In the simplest picture, taking NiO as the example, the process of RIXS consists of the absorption of an X-Ray photon which excites an electron from a p -orbital into the valence d -band, creating an electron-hole pair, followed by the radiative annihilation of the electron-hole pair. The difference in energy of the incoming and outgoing radiation is associated with the energy of the exciton subsequently created by this process. In essence, the final state can be an excited state of the ground state. A comprehensive review of inelastic scattering of X-rays is given in [91].

One of the advantages of RIXS is that the momentum transferred to a given exciton can also be measured. The momentum transfer $\mathbf{Q}$ is obtained from the change in X-ray photon momentum

$$\hbar\mathbf{Q} = \hbar\mathbf{k} - \hbar\mathbf{k}' \quad (2.19)$$

given incident and emitted X-ray wavevectors $\mathbf{k}$ and $\mathbf{k}'$ respectively. The sample is mounted on a four circle diffractometer, so as to allow for the selection of a range of

different crystalline directions, along which the momentum is transferred. The synchrotron provides a bright monochromated source of X-rays. The X-rays are incident on the sample at an angle ω and detected at 2θ , so as to probe a particular direction in reciprocal space. The X-rays diffracted from the sample are then dispersed (in vacuum) from a grazing incidence variable line spacing (VLS) spherical grating onto a CCD detector at a distance of about 12 m. The detector is operated at grazing incidence (20°) to compensate for the charge leakage between neighbouring pixels by matching the effective pixel size to the charge distribution caused by one photon shown schematically in figure 2.17 [91, 92]. The detector can be rotated laterally through 100° and from a scattering angle of 50° to 150° , allowing for the acquisition of an energy loss spectrum.

In the case of magnetic excitations, which are the focus of the work done here, single spin flip excitations are created at the L -edge due to the spin-orbit coupling of the $2p$ core hole [93]. The intermediate state of the excitation is characterised by a core hole in the $2p$ level split into two degenerate $j = 3/2$ and four degenerate $j = 1/2$ states. The core hole will be filled by a valence electron to return to the starting configuration by radiation of a photon. The final state can be the same as the ground state or an excited one. For example, in the excited state a spin flip could occur, requiring a change in the angular momentum of the emitted photon of $\Delta S = 1$ relative to the incident photon. The manifestation of this is a change in the energy and polarisation of the emitted photon. A bimagnon (2 magnons with a total angular momentum change of $\Delta S = 0$) and a double magnon ($\Delta S = 2$) can also be created in this process. The only requirement is the conservation of the total momentum, $\mathbf{Q} = \mathbf{K}_1 + \mathbf{K}_2$, where $\mathbf{K}_1$ and $\mathbf{K}_2$ are the wave vectors of the involved magnons and $\mathbf{Q}$ is the exchanged momentum of the X-rays. The observed double magnon momentum is band-like because there is a continuum of combinations of the transferred momentum which can satisfy the conservation rule.

Magnons are observed as peaks in the energy loss spectrum in the region of -0.1 eV from the inelastic peak.

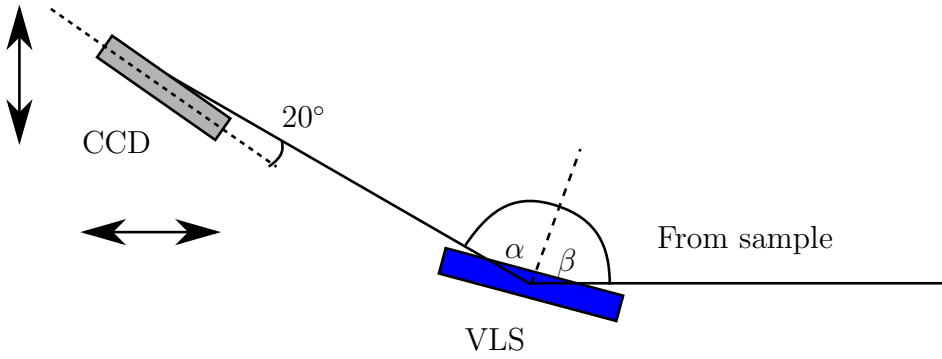


Figure 2.17: Schematic of the detector side of the RIXS configuration, adapted from Ghiringhelli *et al.*[92]

2.4 Transport Measurements

To evaluate the transport characteristics of some of the films and devices fabricated during this project, a number of techniques are used, including various Hall effect measurements, resistivity measurements and their temperature dependencies and tunnelling I - V curves. Here, the resistivity measurement and tunnelling I - V experiments are described, as they were used to obtain the data shown in the following chapters.

2.4.1 Resistivity

The measurement of resistivity in thin films is performed following the van der Pauw method [94, 95], where small titanium-gold contacts are deposited at four corners of square samples, contacted by silver wire bonded to the contacts by silver paste, as shown in figure 2.18. The measurements were performed using a LabView code to perform current sweeps between two contacts while simultaneously measuring the voltage generated on two separate contacts using a Keithley 2400 source meter connected via GPIB.

In the van der Pauw formulation the resistivity of a film of arbitrary shape and thickness d is given by

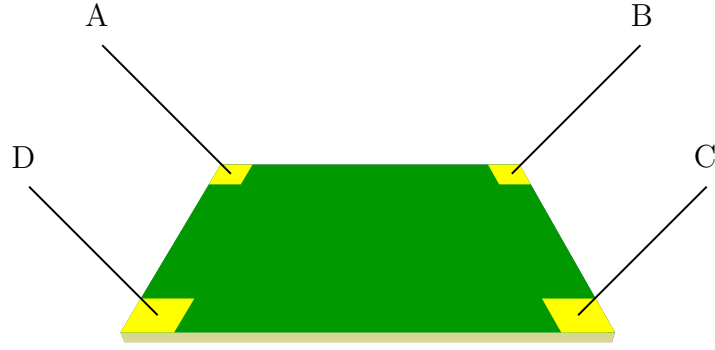


Figure 2.18: Illustration of the configuration of contacts for resistivity measurements by the van der Pauw method.

$$\rho = \frac{\pi d}{\ln 2} \frac{(R_{AB,CD} + R_{BC,DA})}{2} f \quad (2.20)$$

where $R_{hi,jk}$ is the resistance value associated with and applied current along $|hi|$ and a measured voltage along $|jk|$ where h, i, j and k denote the positions of the contacts at four adjacent points on the film respectively. The factor f is a function of the ratio $R_{AB,CD}/R_{BC,DA}$ and can be solved for using the relation

$$\frac{(R_{AB,CD} - R_{BC,DA})}{(R_{AB,CD} + R_{BC,DA})} = f \operatorname{arccosh} \left\{ \frac{\exp\left(\frac{\ln 2}{f}\right)}{2} \right\} \quad (2.21)$$

although for highly symmetric contact configurations it is typically close to unity. The numerical evaluation of this equation gives the dependence of the correction factor on the ratio of measured resistances and is shown in figure 2.19.

2.4.2 Tunnelling Electroresistance

The tunnelling electroresistance (TER) measurements performed during this work were done using a Keithley 2400 series voltage source controlled by a PC using LabView software which was also used in data acquisition. The devices tested were patterned using UV and electron beam lithographies by collaborators in Paul Scherrer Institut (PSI)

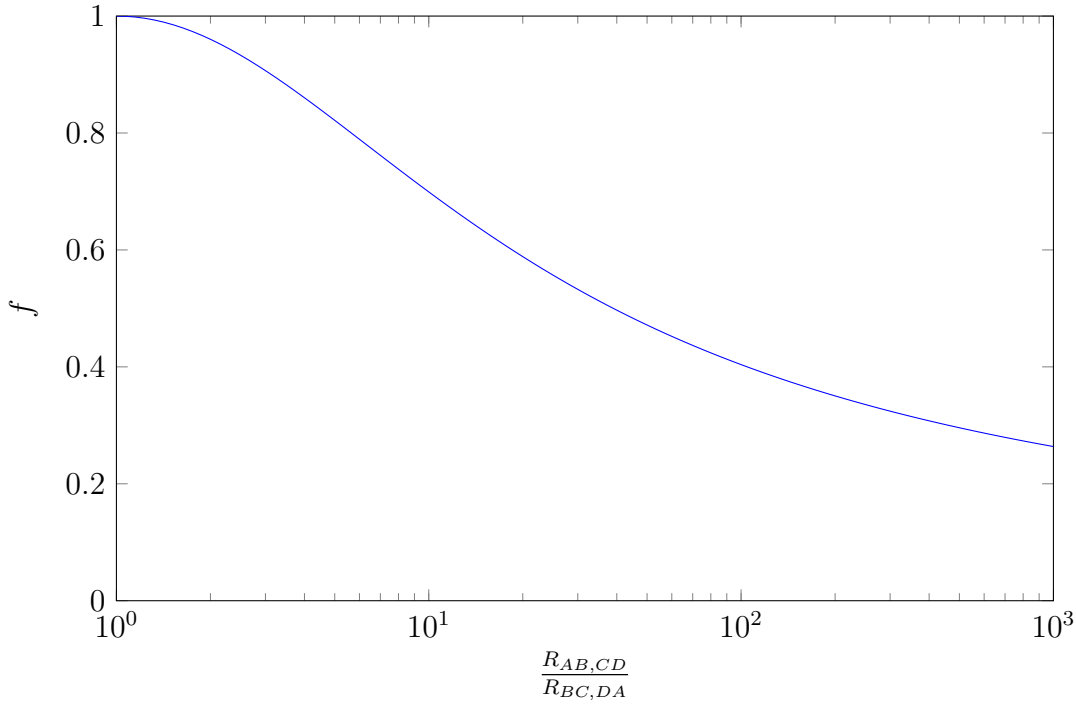


Figure 2.19: Plot of the correction factor for the van der Pauw formula (equation 2.21) against the ratio of measured resistances.

during the Interfacing Oxides project (IFOX) NMP3-LA-2010-246102. The devices were contacted using a precision probe-station.

2.5 Scanning Probe Microscopy

A number of scanning probe microscopies have been employed during this work, including contact and tapping mode atomic force microscopy (TM-AFM and AFM), magnetic force microscopy (MFM), conductive tip microscopy (CT-AFM), electrostatic force microscopy (EFM) and direct-piezoelectric force microscopy (DPFM). Here, the main techniques which relate to the results which are show in this thesis are described, namely AFM, TM-AFM, and DPFM.

2.5.1 Atomic Force Microscopy

The technique of atomic force microscopy is simple in principle and highly useful for the topographical characterisation of surfaces. The strength of the technique lies in

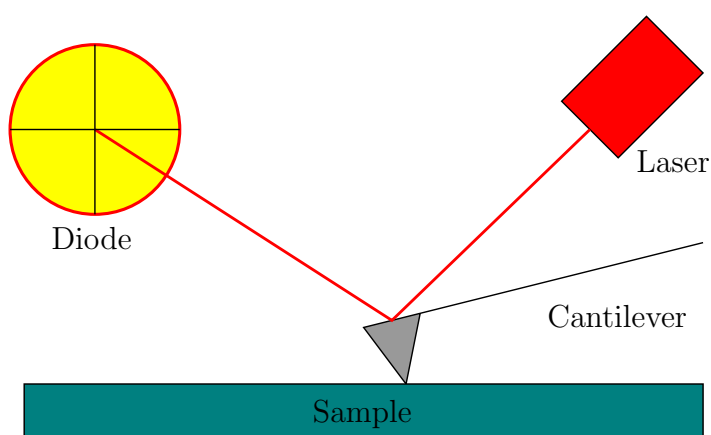


Figure 2.20: Schematic of an AFM apparatus.

the ability to measure minute deflections in the direction perpendicular to the surface which is being measured. The construction of an atomic force microscope as depicted in 2.20 consists of a small cantilever with a sharply defined tip etched at the end which is scanned across the surface which is to be characterised. Changes in the deflection of the cantilever which are caused by interactions with the surface are detected by reflecting light off the top surface of the cantilever (typically coated with gold or aluminium) and detecting that light with a photodiode. The diode is split into 4 quadrants, which allows the user to detect the deflection of the tip by the difference in voltage between either the top and bottom diodes or the left and right diodes, depending on the type of information which is required. There are two main modes of operation for AFM measurements, namely contact mode and tapping mode. In contact mode, the tip height is kept constant relative to the sample using feedback electronics to control a piezoelectric stepper which can raise or lower the sample height by a precise amount. In tapping mode the cantilever is oscillated close to the resonance frequency and when tip-sample interactions shift the resonance, the change in amplitude is used to infer the topography of the surface.

The two modes of operation in AFM correspond to regions in the profile of surface interaction energy, approximated by a Lennard-Jones potential

$$\Phi_{LJ} = \epsilon \left[\left(\frac{r_m^{12}}{r} - \frac{r_m^6}{r} \right) \right] \quad (2.22)$$

where $\Phi_{LJ}(r)$ is the potential at a tip sample distance r and ϵ is the depth of the potential well minimum at r_m . The interaction scales are shown in figure 2.21. Contact mode AFM is operated in the regime of repulsive force ($F = \frac{d\Phi}{dr}$ is negative) and tapping mode is operated in the attractive regime.

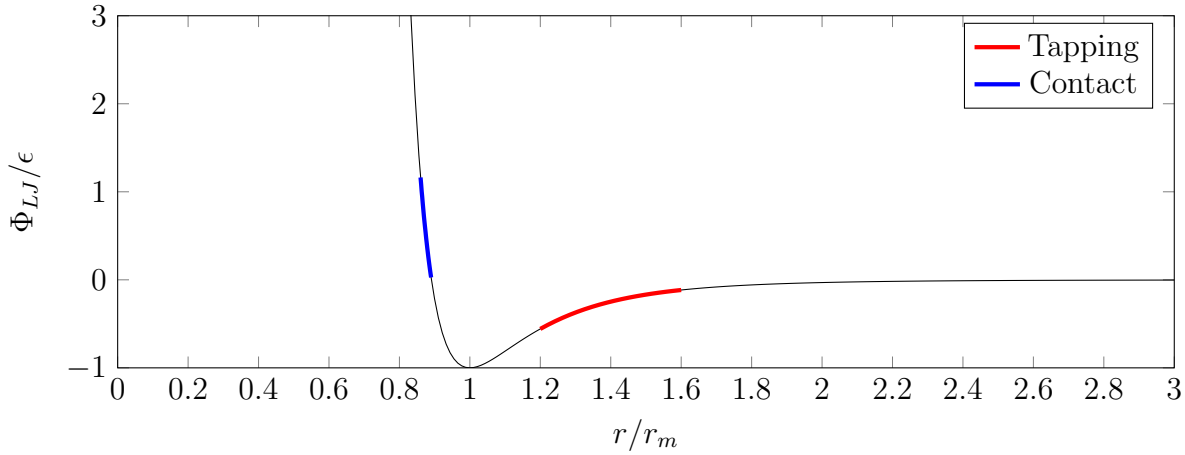


Figure 2.21: Lennard-Jones potential describing tip-sample interaction energy, and regions corresponding to contact and tapping mode AFM.

2.5.2 Electrostatic Force Microscopy

Electrostatic force microscopy (EFM) is the technique of imaging the electrostatic force gradients at the surface of a given ferroelectric sample. It utilises a metallised tip in contact mode, which is electrically grounded, and some electric contact below the ferroelectric layer, be it a metal thin film underlayer or a backside contact below the substrate. In the case of blanket thin films, the conductive underlayer is contacted using a diamond pen to scratch through the ferroelectric layer, and silver paint is used to bond a wire through the damaged region. The tip is first rastered over a defined area of the surface to create a topographic map of the surface as described in 2.5.1. The tip is then immobilised on the surface and a potential is applied between the metal layer and the tip coating to polarise the ferroelectric layer.

The required potential should be achieved when the electric field within the sample exceeds the coercive field of the ferroelectric which for ideal contact is

$$E_C = \frac{V_C}{t} \quad (2.23)$$

where t is the thickness of the film and V_C is the potential required to polarise the film. This is only true under the effective contact area of the tip, and the shape of the real electric field has some components parallel to the surface outside this area. Without a sufficiently stiff cantilever, however, the effective distance between the tip and the metallic underlayer may change under the electrostatic force of the applied potential as the cantilever is bent under this force. The electric field created between the tip and the metallic layer is like that created between two spatially separated charge densities; one in the shape of the tip, and another as an identical, oppositely charged image within the conductive underlayer. Therefore the region which is polarised is typically much larger than a circle with a radius equal to that of the tip radius of curvature.

Once the surface is polarised, which is marked by a sudden jump in the sample height (as perceived by the AFM feedback electronics) with a monotonically increasing applied potential, the applied potential is removed and the surface is again scanned in contact mode. The electrostatic potential of the polarised surface is added to the normal Lennard-Jones potential, which translates to an increased height in the topographical map.

In spite of the qualitative nature of this technique, it is a relatively quick experiment which is usefull in showing whether ferroelectric films can be reliably polarised and have persistent polarised states.

2.5.3 Direct-Piezoelectric Force Microscopy

Direct-Piezoelectric Force Microscopy (DPFM) is a technique in which a piezoelectric response to an applied mechanical ultrasonic excitation is directly measured. This

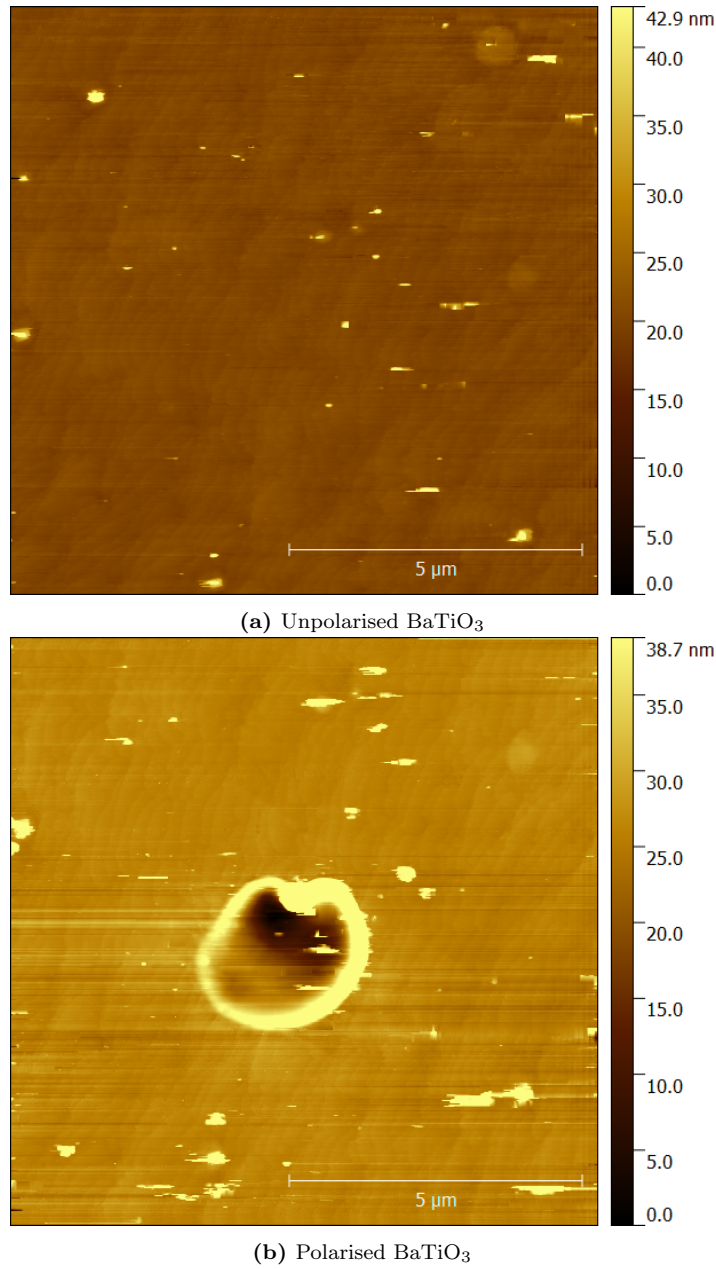


Figure 2.22: Electrostatic force microscopy of an (a) unpolarised and (b) polarised BaTiO₃ thin film.

was demonstrated in well-crystallised quartz by T. J. A. Mori, P. Stamenov and L. S. Dorneles [96]. It exploits the high spatial resolution of scanning probe microscopy and the large piezo signal that can be generated. In normal piezo-response force microscopy (PFM), an AFM is operated in contact mode, and an oscillating voltage is applied to the tip to generate a mechanical oscillation of the sample surface through the inverse piezoelectric effect. These oscillations are picked up through the amplified and lock-in

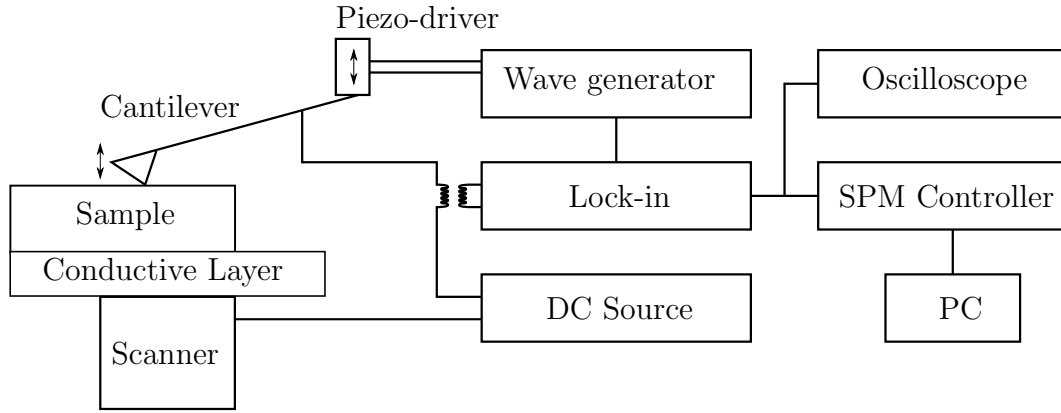


Figure 2.23: Schematic of a DPFM apparatus. Adapted from T. Mori *et al.*[96]

demodulated signal of the laser bridge. Extraction of the piezoelectric coefficients by PFM is difficult due to the effect of the feedback electronics of the AFM on the signals [97].

The apparatus used during this work is a Digital Instruments Nanoscope III Multimode SPM, utilising a metal coated tip in contact mode and the piezo driver used to oscillate the tip in tapping mode is driven using an external wave generator to provide the mechanical excitation. The electrical signal generated by the piezoelectric effect is read out by a synchronised lock-in amplifier, EG&G7265 and subsequently digitised by the SPM controller to allow simultaneous acquisition of the laser bridge signal and the direct piezoelectric signal. A DC voltage source is also used to apply bias to the tip, while protecting the AC circuitry using a linear air-gap transformer. A schematic of the apparatus excluding the feedback circuitry of the SPM itself is shown in figure 2.23.

Chapter 3

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$: Towards a Highly Spin-polarised Oxide Electrode

3.1 Introduction and Literature Review

In this section I will lay out the important results of the early investigations of the nature of the mixed valence manganites. Beginning with an account of the preparation of the solid solutions that lead them to being identified as the first ferromagnetic oxides, a key advance was the preparation of the oxides in thin film form during the 90's when there was much excitement about their 'colossal' negative magnetoresistance in the vicinity of the Curie temperature. The modern focus of perhaps the most famous of the mixed valence manganites, $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) as a potential candidate for oxide spintronics applications is then introduced as well as its applications in other areas of research.

3.1.1 The Mixed-valence Manganites

Mixed valence manganites have been the subject of numerous studies ever since their discovery in 1950, when they were the first known ferromagnetic oxides [98]. They are associated with Zener ferromagnetism attributed to double exchange, half-metallicity, a wide tunable range of Curie temperatures (T_C) and a huge negative magnetoresistance near T_C which was substantially bigger in thin films [99]. The mixed valence manganite families have interesting magnetic and electronic properties and potential for applications [100, 101], not least as electrodes for thin-film oxide and organic spin electronics [102–105]. The mixed valence manganites belong to the perovskite oxide family. The general formula of the perovskite oxides is ABO_3 , and in manganites the

perovskite A-site is occupied by a mixture of at least two species of different valence while the B-site is occupied by manganese. Therefore the general formula of the mixed valence manganites is $(X_{1-x}Y_x)MnO_3$, where X and Y are rare-earth and alkaline-earth or Pb^{2+} cations respectively.

The manganese cations, formally Mn^{3+} and Mn^{4+} , are octahedrally coordinated by oxygen, and the octahedra tend to exhibit Jahn-Teller distortion when occupied by Mn^{3+} $3d^4(t_{2g}^3 e_g^1)$, which is a spontaneous symmetry breaking distortion of the octahedra driven by the occupation of d -orbitals with electron density in particular directions, so as to decrease the overlap of these orbitals with the p -orbitals of the oxygen. The compositional phase diagrams exhibit phases with a wide variety of electronic structure, magnetic, charge and orbital order. Magneto-transport properties of the conducting mixed-valence manganites are strongly influenced by double exchange, where an e_g electron hops between adjacent Mn^{4+} $3d^3 t_{2g}^3$ cores. This is only permitted when the spins of the t_{2g}^3 Mn^{4+} cores on the two sites are aligned parallel.

The idea of double exchange was introduced by Zener in 1951 [106] in order to explain the empirical correlation of magnetic and transport phenomena found by Jonker and Van Santen in their original investigations of solid solutions of mixed valence manganites [98]. He describes the transfer of an electron from Mn^{3+} to O^{2-} and the simultaneous transfer of an electron from the O^{2-} to the Mn^{4+} in terms of two states

$$\begin{aligned}\psi_1 &: Mn^{3+}O^{2-}Mn^{4+} \\ \psi_2 &: Mn^{4+}O^{2-}Mn^{3+}\end{aligned}\tag{3.1}$$

corresponding to the before and after states of the double exchange, and the exchange integral

$$\int \psi_1^*(\mathcal{H})\psi_2 d\tau\tag{3.2}$$

giving the energy of the exchange. Here $\mathcal{H}$ is the hamiltonian of the system. The Mn multiplicity is maximised according to Hund's rule, therefore the integral is only nonvanishing if the spins of the d -shells of the ions are parallel. In other words, there is a large energy barrier to the electron double transfer if the Mn t_{2g} electron spins are not aligned on both sites with the hopping electron.

Transport in the mixed valence manganites is broadly governed by two phenomena. Below the Cuire temperature the transport can be viewed in an ideal crystal to be governed by the percolative spin-dependent hopping of electrons as described above by Zener double exchange. A different mechanism is proposed for transport above the Curie temperature which involves the magnetic polaron. This was first given a rigorous treatment by Kasuya in 1970 [107] who considered a large magnetic polaron. It is perhaps easiest to understand the existence of the magnetic polaron in terms of a change in free energy ΔF upon the addition of a single electron to an antiferromagnetic or paramagnetic crystal lattice, collectively visualised as a spherical polarised cluster of radius R as presented in Coey, Viret and Molnár's review [103]

$$\Delta F = \frac{E_0}{\gamma^2} - \frac{J_{sd}^2 \chi}{2\gamma^3}. \quad (3.3)$$

The first term in this expression represents the kinetic energy of the polaron, where a is the atomic radius, $\gamma = R/a$ and $E_0 = \hbar^2/2ma^2$ is the kinetic energy of the polaron wave in a periodic potential described by $\Psi(x) = Ae^{-i\vec{k}\cdot\vec{x}}$ given the reciprocal lattice vector $k = 1/a$. The second term is a magnetic binding (energy reducing) term which depends on the susceptibility χ and the exchange integral between the e_g conduction electrons and the localised t_{2g} core at each site, J_{sd} . One can see that given these two terms alone, the energy minimisation with respect to the polaron radius gives minima at either infinite radius or with vanishing R . The presence of dopants provides an oppositely charged site with which the electron can have an attractive Coulombic exchange, so we may add a term with a new γ -dependence, E_C/γ , where

$$E_C = \frac{e^2}{4\pi\epsilon_0} \frac{1}{a} \quad (3.4)$$

is the usual energy between two oppositely charged particles each of charge magnitude e given the vacuum permittivity ϵ_0 . The free energy equation now reads

$$\Delta F(\gamma) = \frac{E_0}{\gamma^2} - \frac{J_{sd}^2 \chi}{2\gamma^3} - \frac{E_C}{\gamma} \quad (3.5)$$

and has now a minimum in energy for finite R , allowing for the existence of a bound magnetic polaron. The polaron has a large effective mass and is only suitable to describe transport in doped manganites near the Curie temperature as it depends on the existence of non-collinear spins. Consequently the application of a magnetic field allows one to switch between the conduction mechanisms around the Curie point, which is the dominant phenomenon governing the colossal magnetoresistance of thin crystalline films of the mixed valence manganites, which is discussed further in section 3.1.2

Manganites with $x \approx 0.3$ exhibit the highest Curie temperatures and conductivity. The magnetic properties of thin films have recently been shown to be sensitive to the tilting of the network of interlinked, corner-sharing octahedra that make up the perovskite structure [108–110].

The structure of the mixed valence manganites deviates from the ideal cubic perovskite structure shown in figure 3.1 due to the combination of cation size, composition and Jahn-Teller distortions of the manganese oxide octahedra. Pollert *et al.* [111] discussed the microstructure of mixed valence manganites in terms of three separate factors. The first of these is the Goldschmidt tolerance factor, t , defined in terms of the A-site, B-site and oxygen ionic radii ($r_{A,B}, r_O$) by the equation

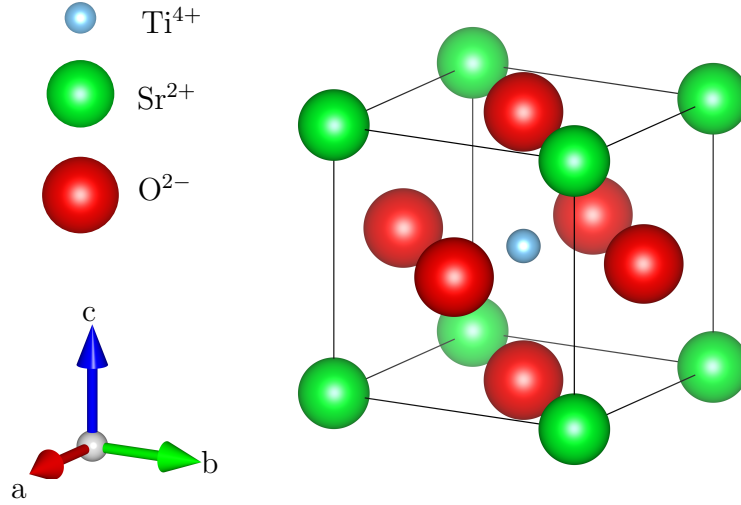


Figure 3.1: The ideal cubic perovskite structure of SrTiO_3 .

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (3.6)$$

is a measure of the steric effects of different cation and anions on the distortion of the perovskite structure from the ideal cubic $t = 1$ structure exemplified by SrTiO_3 . The cooperative Jahn-Teller distortion on Mn^{3+} sites (which itself is in competition with the electron hopping between Mn^{4+} and Mn^{3+}) represents the second factor. Finally there is the interatomic coulomb interaction between $3d$ electrons when there are Mn^{3+} and Mn^{4+} states present which leads to long range ordering of Mn sites of different valence known as charge ordering. The rhombohedral unit cell of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is shown in figure 3.2 using visualisation software by Momma and Izumi [112]. LSMO is commonly referred to in its pseudocubic representation of lattice parameter 388 pm.

The optimally doped $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) is rhombohedral and the octahedral tilt

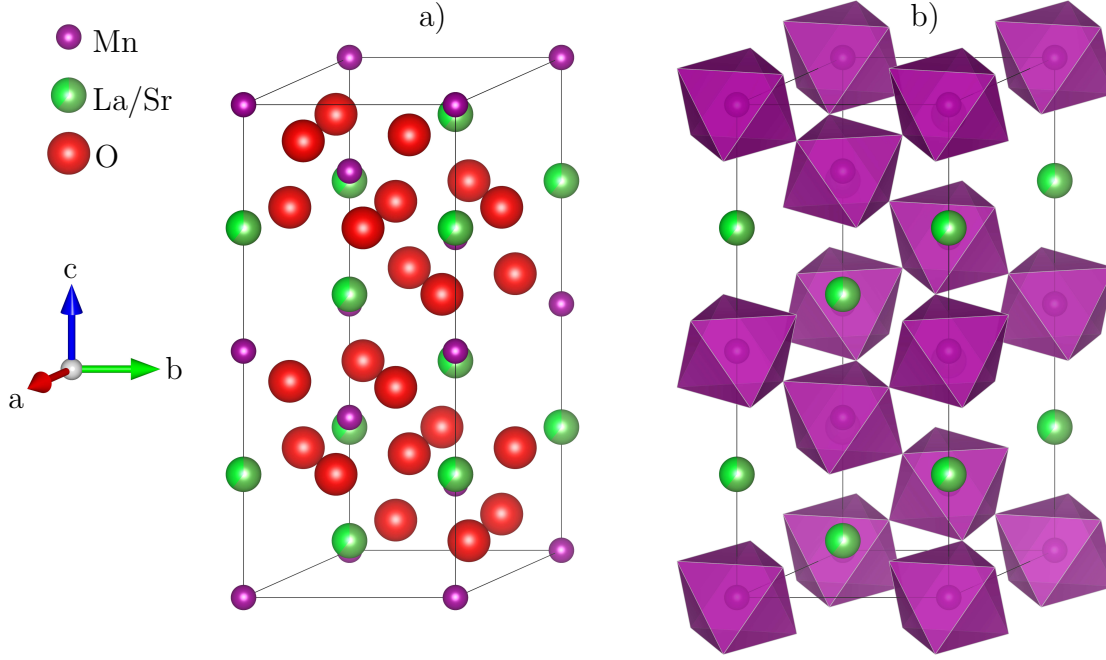


Figure 3.2: Diagram of the crystal structure of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ showing a) La/Sr, Mn and O positions and b) the corner-sharing oxygen octahedra about the Mn-sites.

system denoted by the Glazer [113] symbol $a^-a^-a^-$ and is described by the space group $R\bar{3}c$.

3.1.2 Thin Film Manganites

Interest in thin film mixed-valence manganites gained traction again in the early 90's with PLD-grown thin films, after the technique was developed for high T_{SC} superconducting oxide thin film growth. The growth of thin film LSMO was initially seen as a convenient ferromagnetic material to use in exploring the interaction between type-II superconductivity and magnetism, as it was a very well matched epitaxially with $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO). Researchers at the Hitachi research laboratory in Japan grew thin films of LSMO and LCMO (Ca on the A-site) sandwiched by YBCO layers [114–116]. They found that an enhanced proximity effect allowed a supercurrent to persist up to 62 K in 100 nm thick LCMO barriers between YBCO electrodes, and supercurrents were even measured in junctions with 500 nm thick LCMO barriers, although the critical current was dramatically reduced. The $\text{La}_{1-x}\text{Sr}_x\text{MnO}_y$ films grown by this

group exhibit the unusual effect of having antiferromagnetic or non-magnetic character at $x = 0.3$ which is the stoichiometry of LSMO which normally gives the best magnetic properties.

The focus of thin film growth shifted with the realisation of the large magnetoresistive effects in manganite films. Work by von Helmholt *et al.* [117], Chahara *et al.* [118] and Jin *et al.* [99] showed the famous huge, negative and isotropic colossal magnetoresistance (CMR) near the Curie temperature in well crystallised manganite films.

Once the techniques for the growth of the mixed valence manganites thin films had matured, the roadmap to device applications started to emerge, such as laid out in the paper by T. Venkatesan *et al.* in 1998 as part of a meeting on “Understanding and utilizing colossal magnetoresistance materials” [119]. Four main applications of manganites are laid out in this review; magnetic field sensors based on either the CMR effect, spin valve structure or microwave CMR sensors, electric field effect transistor-type devices (possibly utilising ferroelectric field effects) utilising a CMR channel, bolometric IR sensors using the metal insulator transition at the Curie temperature, and low temperature hybrid high temperature superconductor (HTS-CMR) devices. All of these applications are focused on thin film manganites, and some of the work in these areas, notably field sensors and bolometers, is ongoing [120, 121].

3.1.3 LSMO in Modern Research and Future Applications

As mentioned in section 3.1.2, LSMO and the broader family of manganites are still actively being researched as potential IR bolometers and magnetic field sensors. Perhaps the most successful applications of LSMO in recent years have been in the areas of solid oxide fuel cells, for which there are many examples of experimental and theoretical studies [122–124], solid oxide electrochemical reduction cells (for scrubbing nitrogen oxide emissions from diesel gasoline combustion engines) [125] and catalysis [126]. A basic diagram of a solid fuel cell is shown in figure 3.3.

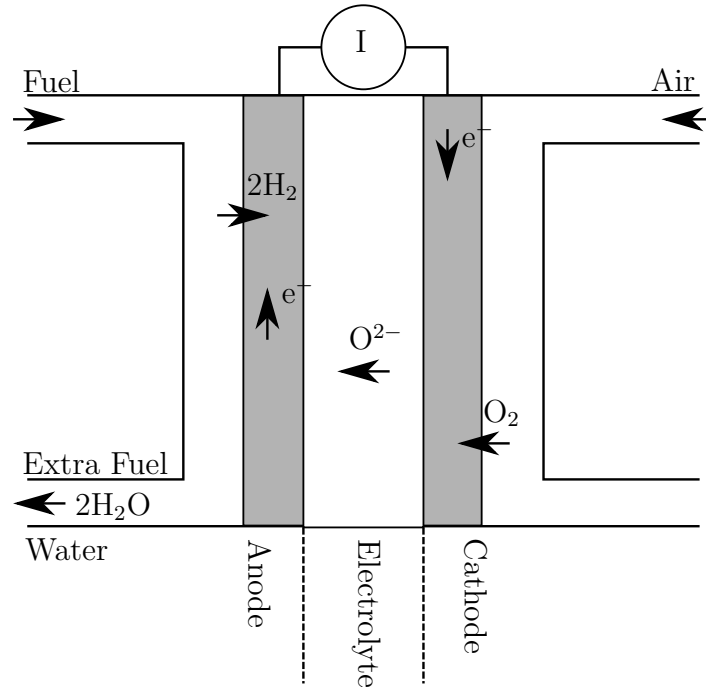


Figure 3.3: Simplified schematic of a solid fuel cell showing air and fuel (hydrogen) entering at the cathode and anode respectively, and the transfer of two electrons to each oxygen, which then travel through the electrolyte to combine with two reduced hydrogen ions at the anode to produce water.

In solid oxide fuel cells (SOFCs), where LSMO is used as the cathode material, the cathodic reaction involves the adsorption of molecular oxygen on the surface, followed by diffusion to the electrolyte, charge transfer and the incorporation of the ion to the electrolyte. In the case of LSMO, the oxygen adsorbs to the (001) terminated surface at the Mn sites in the case of MnO_2 termination and the hollow sites of the centres of the square array in the case of $\text{La}(\text{Sr})\text{O}$ termination [127]. The use of LSMO in SOFCs is generally limited to high temperatures of about 1000°C , where the oxygen sublattice anions are sufficiently mobile, although the structure and specific composition of the electrode materials can be manipulated to bring the operating temperature into the ‘intermediate temperature range’ of $500 - 700^\circ\text{C}$. Degradation of the cells is also an important factor, either by surface modifications or by thermomechanical cycling [128].

In the field of magnetism and spintronics, which is the focus of this work, LSMO has found its place as one of the ferromagnetic electrodes of choice for oxide spintronics and multiferroics, due to its Curie temperature being greater than room temperature,

its relatively good conductivity and the epitaxial match of LSMO with many other perovskite and spinel oxides. LSMO is used as a ferromagnetic electrode in many experimental oxide magnetic tunnel junctions (MTJ), and literature on these kinds of devices is plentiful [64, 129–131]. A fully magnetised volume of LSMO is theoretically half metallic due to the primary conduction mechanisms mentioned in section 3.1.1 requiring that hopping electron spins be aligned on adjacent sites. In spite of this the reported tunnelling magnetoresistance (TMR) at room temperature ($\approx 10\%$) typically does not exceed the giant magnetoresistance (GMR) of modern sensors and many values of TMR are reported at low temperature, far from the operating temperature range for consumer electronics.

There are likely a number of reasons for the strong temperature dependence of the TMR, but one of the most prominent barriers to robust room temperature TMR with a high resistance ratio is the ‘dead layer’ which has been reported at the surface and/or interface of thin LSMO films [51, 132].

3.1.4 Motivation

The motivation for this work is in the application of LSMO as a ferromagnetic electrode for oxide spintronics. A nominally fully spin polarised conductor which is epitaxially compatible with a wide range of other materials in the perovskite oxide family (and even other oxides and compounds) is highly sought after. If this was achieved, the focus of research could shift to the tailoring of electronic and magnetic properties of other materials in device structures, owing to the flexibility in the choice of constituents in isomorphic complex oxides. The problem of dead layers in LSMO is something which needs to be understood properly before there can be any hope of avoiding the associated constraints in future applications. The aim of my work in this chapter is to elucidate the nature of the dead layers and determine a practical route toward the minimisation of the dead layer effects, so that the field of oxide spintronics might progress to more exciting and useful applications.

3.2 Experimental Results

In this section the properties of the LSMO films on different substrates and their respective dead layers will be explored and discussed. The structural and magnetic properties of films will be presented, followed by the determination of the magnetic and electronic dead layer thickness. The nature of the dead layers will then be discussed with reference to the synchrotron X-ray data that was collected during this project.

3.2.1 Structure and Morphology of LSMO films

In this work, the effects of epitaxial strain imposed by the substrate on LSMO thin films are explored. To this end, LaAlO_3 (LAO), $\text{La}_{0.26}\text{Sr}_{0.76}\text{Al}_{0.61}\text{Ta}_{0.37}\text{O}_3$ (LSAT) and SrTiO_3 (STO) substrates were used, each imposing a different strain condition on LSMO under epitaxial growth conditions. The first of these substrates, LAO, is a rhombohedral perovskite and is often represented by the pseudocubic unit cell of lattice constant 379 pm. It imposes a large in-plane compressive strain on LSMO films grown in the pseudocubic (001) direction of -2.4% . LSAT is a cubic mixed perovskite which was developed as a substrate that can be fabricated at low cost due to its relatively low melting point and imposes a minimal amount of strain on superconducting cuprates and ferroelectrics. It has a lattice parameter of 387 pm and in the case of LSMO films grown in the (001) direction, it imposes a small compressive strain of -0.26% . STO is one of the most common single crystal oxide substrates used after sapphire and MgO and is usually used in the growth of perovskites. It has a cubic perovskite unit cell and a lattice constant of 391 pm and imposes a tensile strain on LSMO films grown in the (001) direction of 0.64% .

The thin films of LSMO grown by PLD for this study are well crystallised and oriented on the different substrates used, as can be seen in figure 3.4. The $(002)_{pc}$ LSMO peak can be seen close to the substrate (002) peak in all three cases, with Kiessig fringes clearly visible in films grown on STO and LSAT. In the case of LAO substrates, there

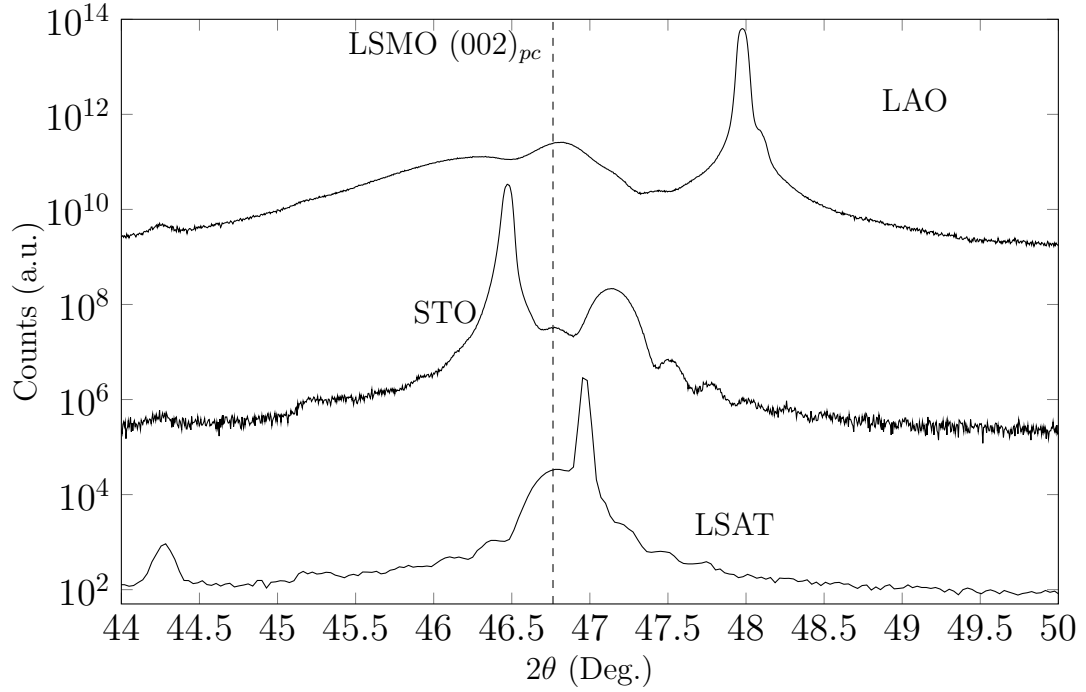


Figure 3.4: X-ray diffraction pattern of 20 - 30 nm thick films of LSMO on (001)-oriented LSAT, STO and LAO substrates. There is a well defined peak in the case of LSAT and STO, but there is strong shouldering in the case of LAO, indicating that the film is not entirely defect free and continuous.

is a peak at the bulk LSMO (002) position, but there is a large shoulder at lower angles. This indicates that while some of the film is strained, structural defects such as dislocations facilitate the relaxation of the structure towards that of bulk LSMO, while maintaining the (001) texture. The film thicknesses are in the range of 20 - 30 nm.

The misfit strains ϵ for LAO, LSAT and STO obtained from the nominal bulk lattice constants of the substrate and film materials by the formula

$$\epsilon = \frac{|a_{sub} - a_{film}|}{a_{sub}} \quad (3.7)$$

are $\approx -2.4\%$, $\approx -0.26\%$ and $\approx 0.76\%$, respectively, giving the highest strain on LAO. Here STO imposes tensile strain and both LAO and LSAT impose compressive strain. Reciprocal space mapping about the (113) direction of the substrates gives us further insight into the epitaxy of the films and allows us to estimate the average in-plane lattice parameter. In figure 3.5 one can see that in the cases of STO and LSAT substrates,

the x -component of the space lattice vector q_x is equal for the film and substrate peaks, indicating that the in-plane lattice parameters are equal, while the offset in q_z shows that some tetragonal distortion is induced to accommodate the conservation of volume of the unit cell.

In the case of LAO there are many structural defects which can accommodate the relaxation of the in-plane compressive strain imposed by the substrate, and this leads to a broad and ill-defined peak near the fully strained LSMO (113) peak, skewed towards the bulk peak position in figure 3.4. The resultant figure 3.5 (b) is further complicated by the apparent recrystallisation of the LAO substrate as seen in the optical microscope images in figure 3.6.

Comparing the images of LAO, STO and LSAT substrates after annealing under deposition conditions it appears that a major recrystallisation of the LAO substrate occurs. This would lead to many strain-relaxing defects at the interface of LSMO with LAO, and this could help to explain the bulk-like diffraction in figure 3.4.

The growth mode of LSMO is primarily the layer-by-layer mode, as inferred from the oscillations in peak intensity of the primary reflection of the RHEED pattern presented in figure 3.7. The decay of the envelope of the oscillations in the case of LAO and STO indicate that there is a transition to a more disordered surface after a certain thickness, of order 4 - 8 nm. The RHEED oscillations generated from films grown on LSAT, however, continue generally throughout the thickness of the film.

3.2.2 Magnetism in LSMO films

The magnetism of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ is probed by SQUID magnetometry and synchrotron X-ray magnetic dichroism, which allows for both the direct measurement of the full film and substrate net moments (SQUID), and the contributions from antiferromagnetic moments which are canted under high fields existing within the dead layer (XMCD).

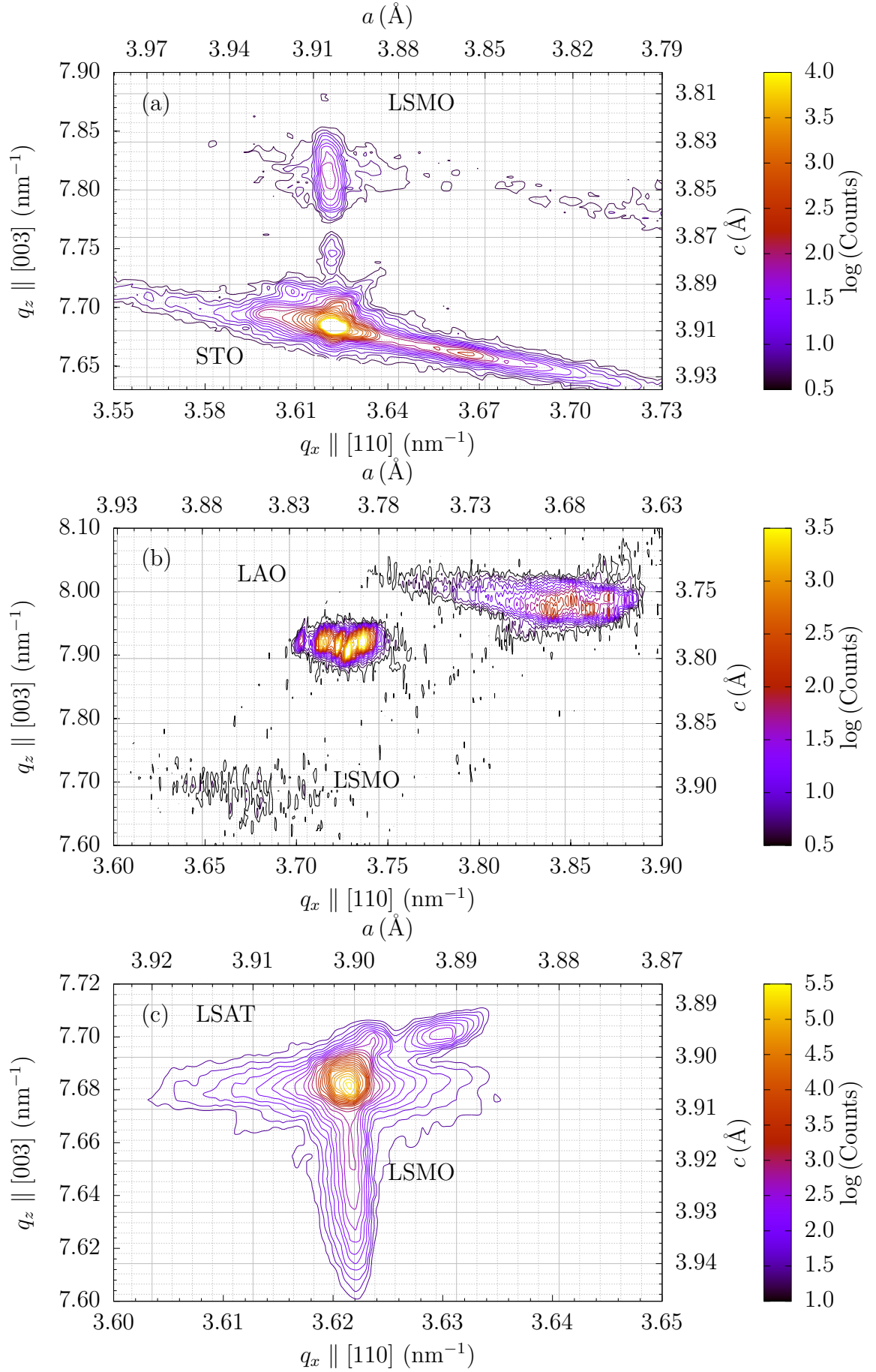


Figure 3.5: Reciprocal space maps about the (113) reflex of (a) STO, (b) LAO and (c) LSAT substrates showing the LSMO (113)_{pc} peak.

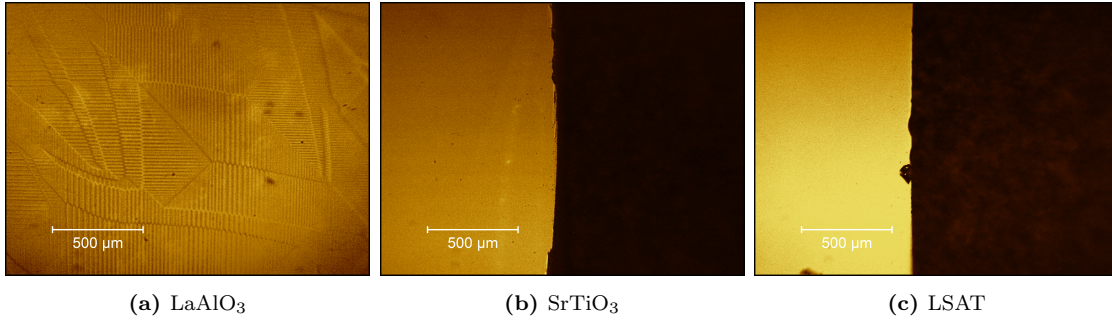


Figure 3.6: Optical images of blank LaAlO_3 , SrTiO_3 , and LSAT substrates used for the growth of LSMO thin films. The substrates have been treated under deposition conditions (700°C) for one hour prior to imaging. Note the multiple twins in LaAlO_3 .

Typical magnetisation curves for LSMO films of around 20 - 30 nm in thickness are shown in figure 3.8, along with the magnetisation curves of blank substrates of STO, LAO and LSAT which have been treated under the normal deposition conditions of LSMO. The magnetisation curves of the thin films display bulk-like saturation magnetisation of $M_s = 3.6 \mu_B \text{Mn}^{-1}$, close to the theoretical maximum bulk value of $3.7 \mu_B \text{Mn}^{-1}$. To get an accurate quantification of the magnetisation of the thinnest films of LSMO, it is necessary to subtract the contribution of the substrate from that of the film. As the thickness can be determined by first normalising the moments of both the blank substrates and the film/substrate combination to their respective surface areas, one can easily subtract the substrate signal as

$$\frac{m_{\text{film}}}{\text{Area}} = \frac{m_{\text{total}}}{\text{Area}} - \frac{m_{\text{substrate}}}{\text{Area}}. \quad (3.8)$$

The moment present in the blank substrates is shown in figure 3.8 (b) amounts to a few percent of that of the films illustrated in figure 3.8. This behaviour of substrates exposed to deposition conditions is consistent with previous studies in our group on the evolution of magnetism in d^0 SrTiO_3 substrates [133] and a number of other substrates [134]. The temperature dependence of the moment in LSMO films on different substrates is plotted in figure 3.9. It can be seen that the contribution of the substrate persists, independent of temperature, above T_C .

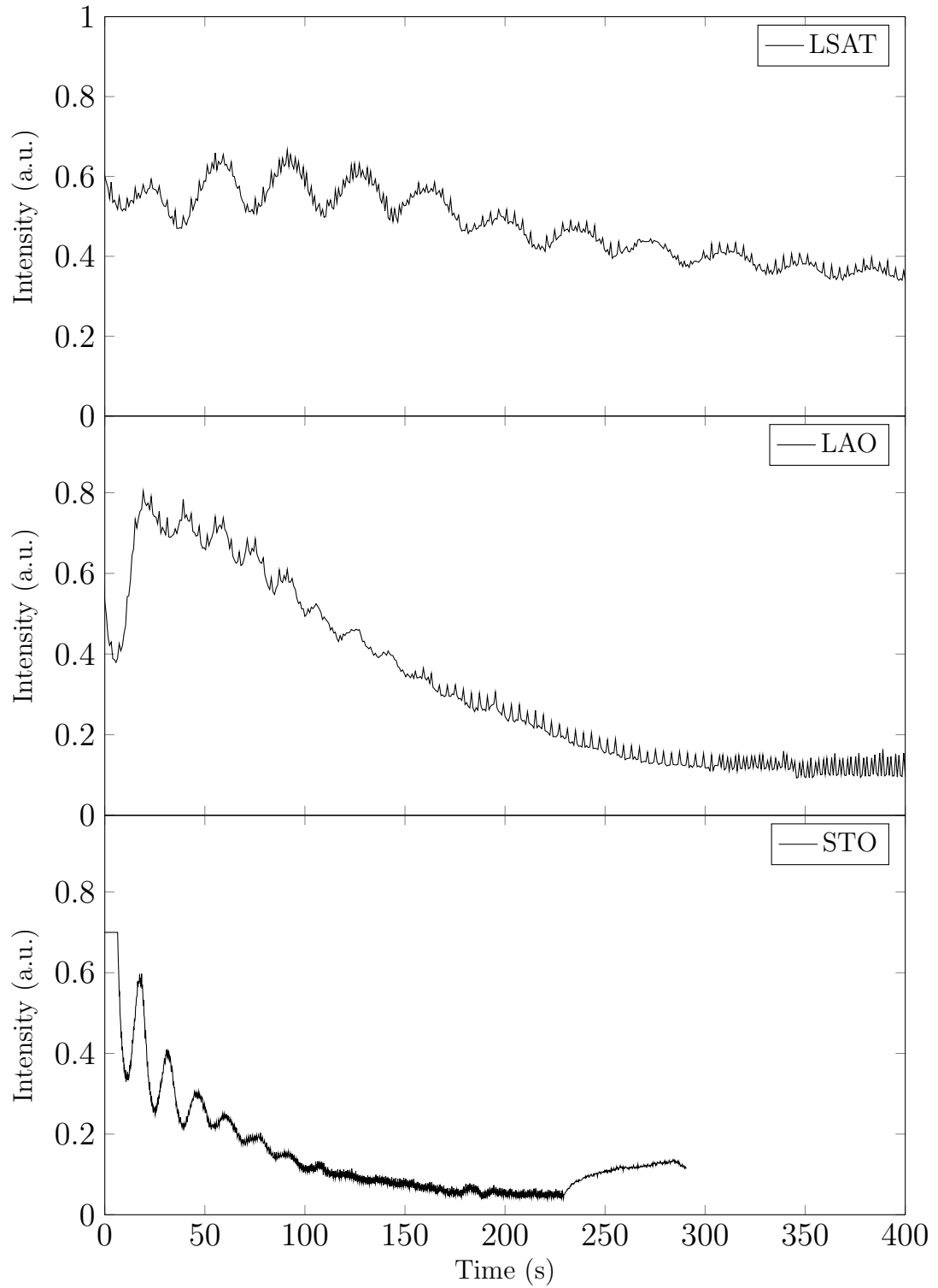


Figure 3.7: RHEED intensity during the initial deposition of 8.9 nm of LSMO on LSAT, 40 nm on LAO and 5 nm on STO.

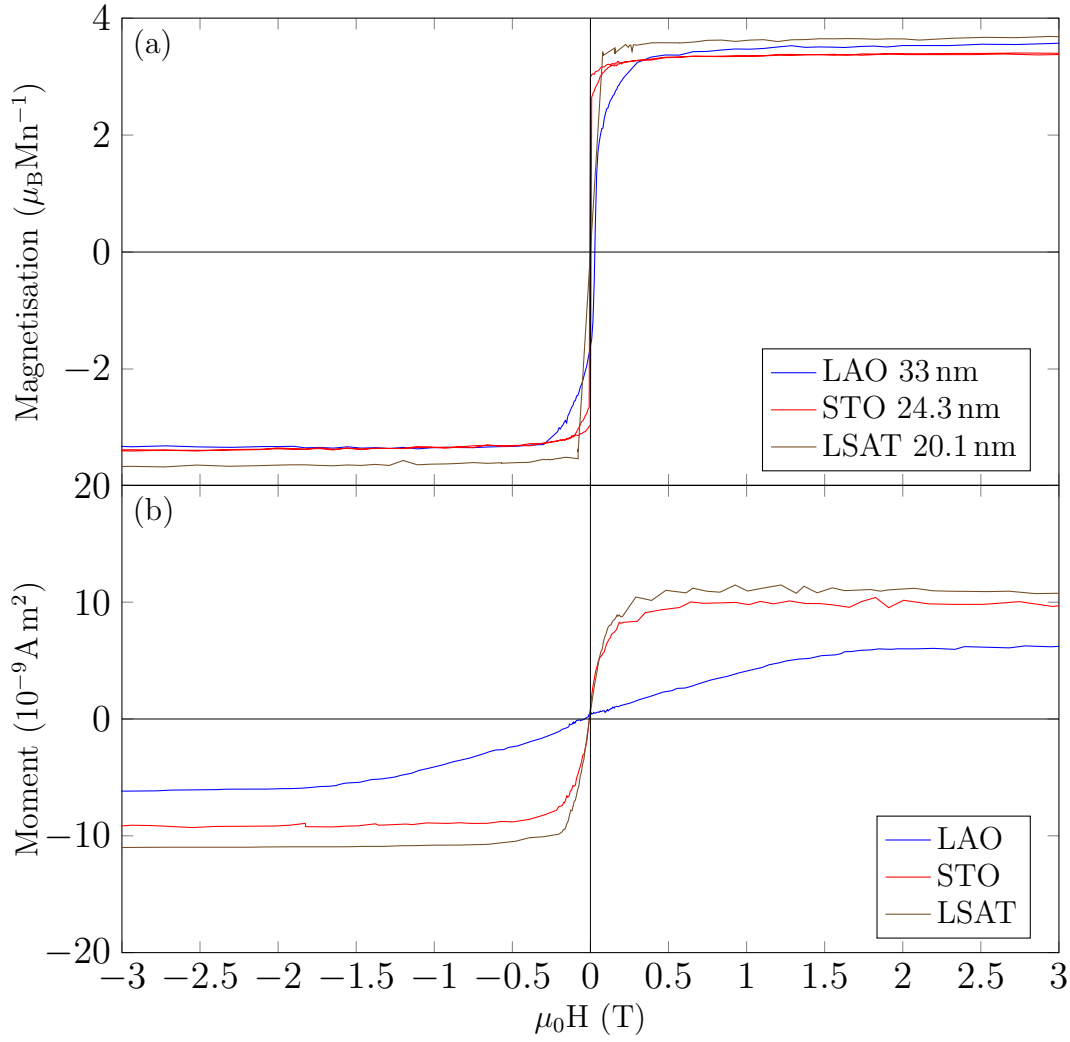


Figure 3.8: 4 K magnetisation curves (a) of LSMO on different (001)-oriented substrates, where the moments are of order $2 \times 10^{-7} \text{A m}^2$ and (b) of substrates exposed to the deposition conditions of LSMO of 700 °C, 0.3 mbar of oxygen for one hour.

The reduction in magnetic ordering temperature T_C is rapid with decreasing thickness at small thicknesses, and consistent with an Ising model of a simple cubic film [135]. Given a reduction in the mean coordination number z in a simple cubic lattice of spins, where

$$k_B T_C = z J_0. \quad (3.9)$$

with k_B the Boltzmann constant and J_0 the exchange constant of the Hamiltonian between two magnetic sites, the dependence of the mean coordination number on the

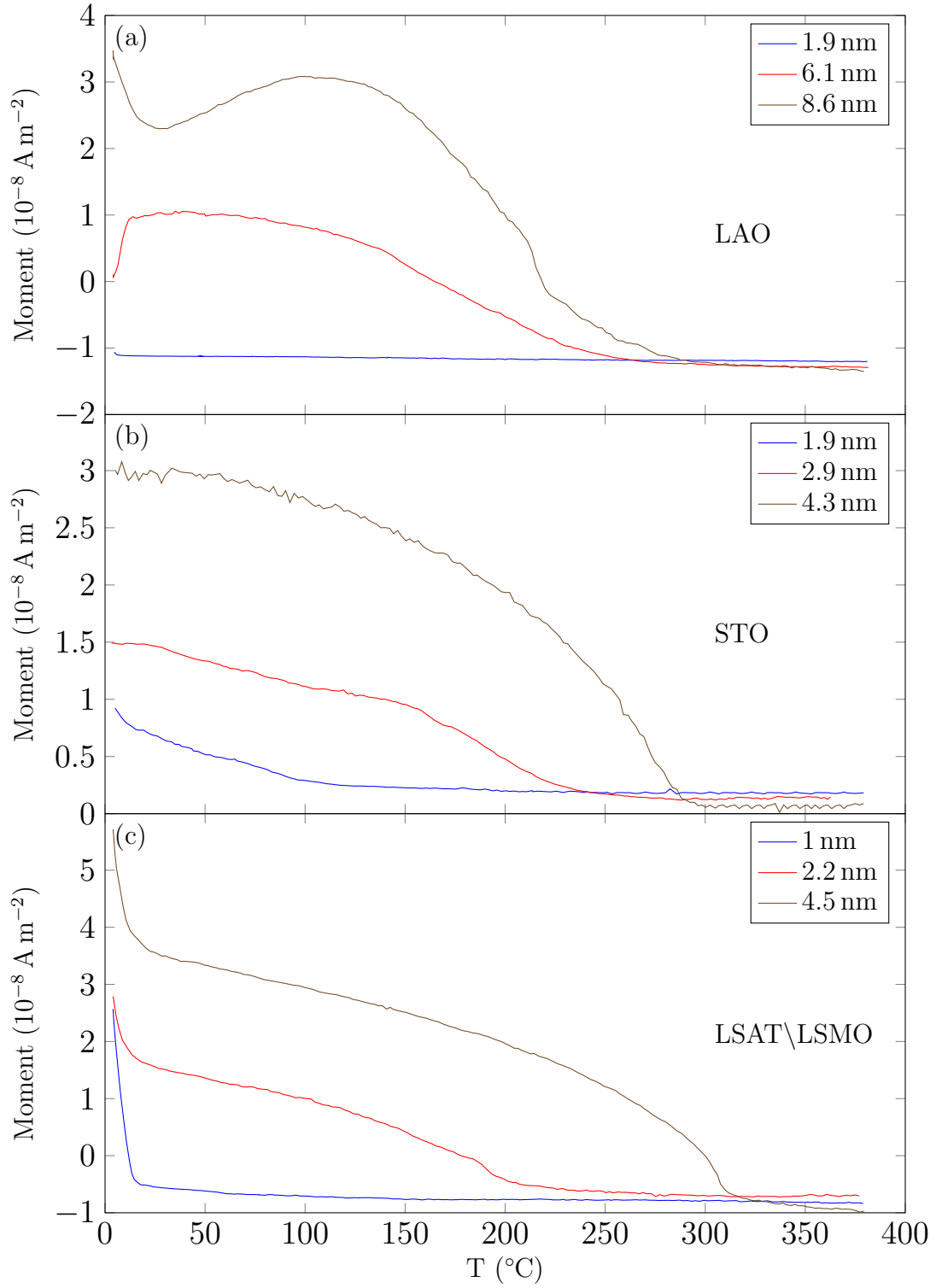


Figure 3.9: Temperature scans of the moment in (a) thin LSMO films on LaAlO_3 (b) SrTiO_3 and (c) LSAT in an applied field of 100 mT. The moment of the 1.9 nm thick film on LaAlO_3 indicates that at this thickness the LSMO film is entirely “dead”, and that the full negative moment is attributable to the diamagnetism of the substrate. An appreciable positive temperature independent moment is seen to persist above the Curie temperature in all three films on SrTiO_3 , which is attributed to the anomalous substrate magnetism mentioned in section 3.2.2. In the case of LSAT it is clear that the 1 nm thick film is below the dead layer thickness, which must be 3 unit cells or more.

number of layers goes as

$$\bar{z} = 6 - 2/n \quad (3.10)$$

Here n is the layer number. It is thus inferred that in the simplest case, one can model the phase transition temperature of a thin film to vary as $1/n$, ignoring the dead layer. More explicitly, the relationship between the Curie temperature and the number of ferromagnetically coupled layers in this model is given by combining equation 3.9 and 3.10,

$$T_C = J_0(6 - 2/n) \quad (3.11)$$

The Curie temperature is plotted as a function of layer number in figure 3.10. In the model, the limits of the bulk Curie temperature of 370 K and vanishing magnetism at a single magnetic layer are used. In truth, there are regimes for the existence of two-dimensional magnetic lattices [136], and indeed under certain conditions of strain, it is possible that Mn spins have a stronger exchange in the plane of the film than out of plane, but for a simple cubic Ising model the magnetic structure is three-dimensional.

3.2.3 Magnetic Dead Layer Thickness Determination

The thickness of the magnetic dead layer of LSMO films is determined by plotting the magnetisation M (corrected for the magnetism of the substrate) times the thickness d against the thickness. The intercept of this linear plot with the thickness axis should give the magnetic dead layer thickness, which is defined as the thickness at which there is no net magnetisation within the film. It does not distinguish between the free surface and the interface.

This method is displayed in figure 3.11, yielding dead layer thicknesses of (0.8 ± 0.3) nm, (1.5 ± 0.4) nm and (3.0 ± 0.4) nm for films grown on LSAT, STO and LAO. The dead

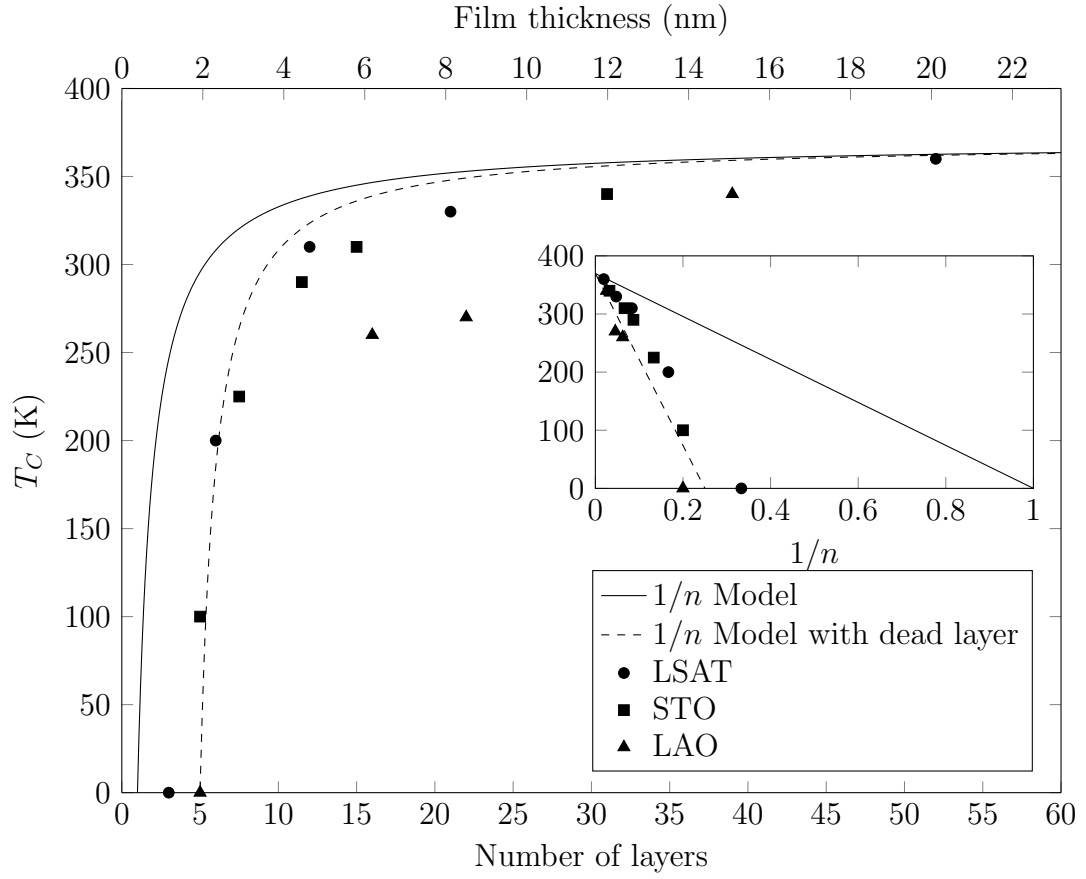


Figure 3.10: The Curie temperature of thin LSMO films plotted against thickness for different substrates and a simple $1/n$ model showing the approach to the bulk value of 370 K. A model correcting for a dead layer of 4 unit cells is also plotted. The inset shows a plot of $1/n$ against T_C for both models.

layer thickness appears to be intimately related to the strain of the film, with compressive strain induced by lattice mismatches of 0.26 % and 2.4 % on LSAT and LAO respectively and a tensile strain induced by a 0.64 % mismatch on STO.

3.2.4 Electronic Dead Layer Thickness Determination

The electronic dead layer in LSMO films is rather less reliably extracted from the room temperature sheet conductivity than the magnetic dead layer thickness is extracted from the magnetisation measured by SQUID magnetometry. The reason for this is that, apart from the dead layer contribution to the resistivity of films, there is also that of the surface scattering, which depends strongly on the roughness and thickness of the films. Figure 3.12 shows the thickness dependence of the sheet conductivity in

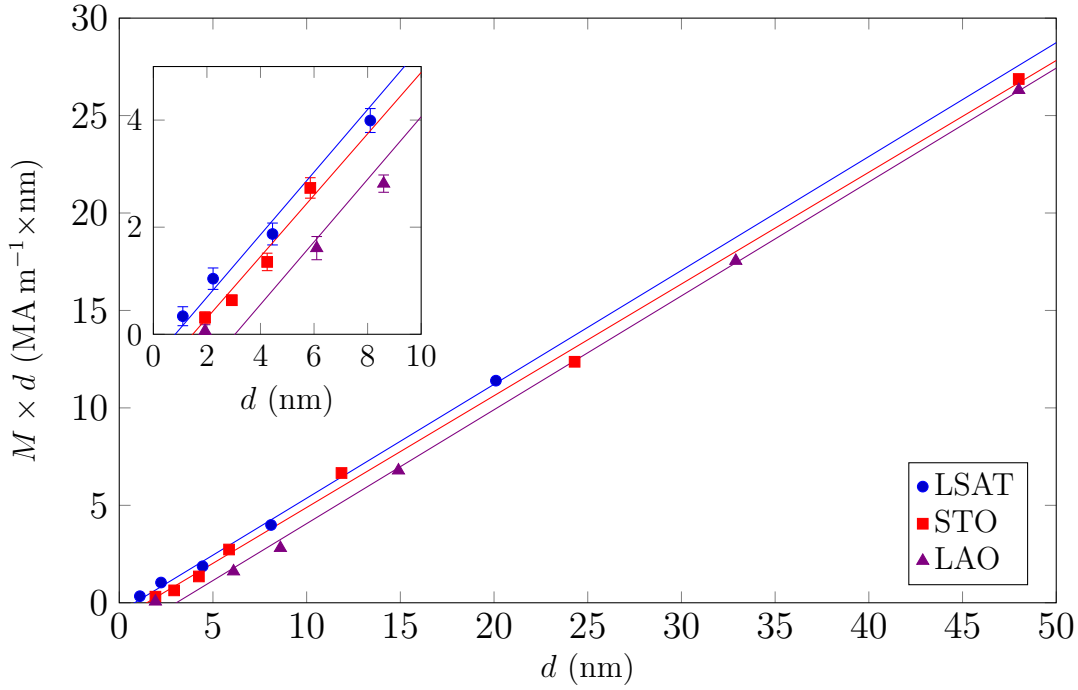


Figure 3.11: Plot to determine the dead layer thicknesses in LSMO on different substrates. A linear fit of the slope of each dataset gave dead layer thicknesses of 0.8, 1.5 and 3.0 nm for LSMO grown on LSAT, STO and LAO substrates respectively.

LSMO on LSAT, STO and LAO. Extrapolation is less certain than for the magnetic case, but the estimates are 3, 4 and 6 nm for LSAT, $SrTiO_3$ and $LaAlO_3$ substrates, respectively.

3.2.5 Nature of the Dead Layers

To examine the nature of the dead layers in LSMO, XMCD and XMLD were recorded at the ESRF synchrotron facility (beamline ID32). The XMCD signal at 5 K for different fields is shown in figure 3.13. These spectra were used to determine the orbital and spin magnetic moments associated with the Mn-site, although the orbital moment is insignificant compared to the spin moment, as expected for a transition metal in octahedral coordination when the orbital moments are quenched.

Table 3.1 shows the spin moments of Mn in the thin films obtained by the sum rules introduced in 2.3.3.1 under various conditions of field and temperature. The small coercivity of the LSMO films (≤ 20 mT), from figure 3.8) and the low field required to

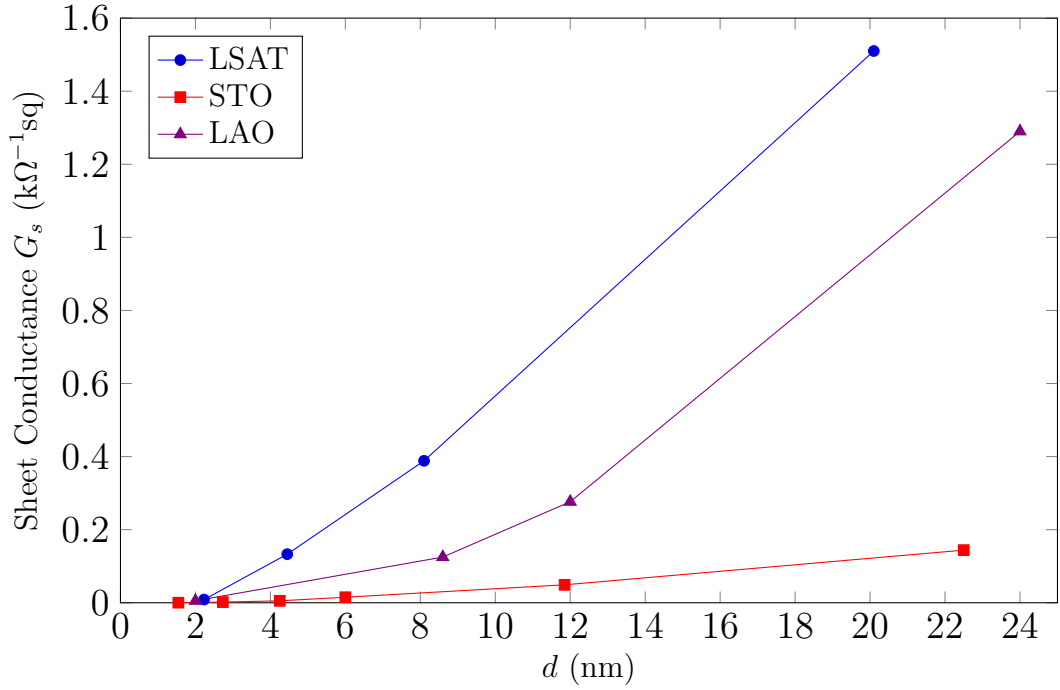


Figure 3.12: Plot to determine the electronic dead layer thicknesses in LSMO on different substrates.

saturate imply that there should be no appreciable increase in magnetisation beyond an applied field of 1 T. There is, however, an increase of the manganese moments in the case of all of the films in 9 T, indicating that there is some other source of magnetic moments which only comes into play at higher fields. One possible source of these additional moments aligned with the high external field is the canting of antiferromagnetic spins within the dead layer. The notion that the dead layer is antiferromagnetic rather than not ordered at all fits with the defining characteristics of the dead layer, namely the lack of net magnetic polarisation and a lack of conductivity in a nominally ferromagnetic conductor. The double exchange mechanism normally requires conductivity to operate, but it is possible for pairwise hopping to occur without long range percolation which could explain why the electrical dead layer is always thicker than the magnetic dead layer. While the lack of net magnetisation of the dead layer clearly fits with the antiferromagnetic picture, it is not so obvious why the conductivity would be destroyed by antiferromagnetism. Considering the mechanism of Zener double exchange described in 3.1.1, it becomes clear that the conduction of electrons by double

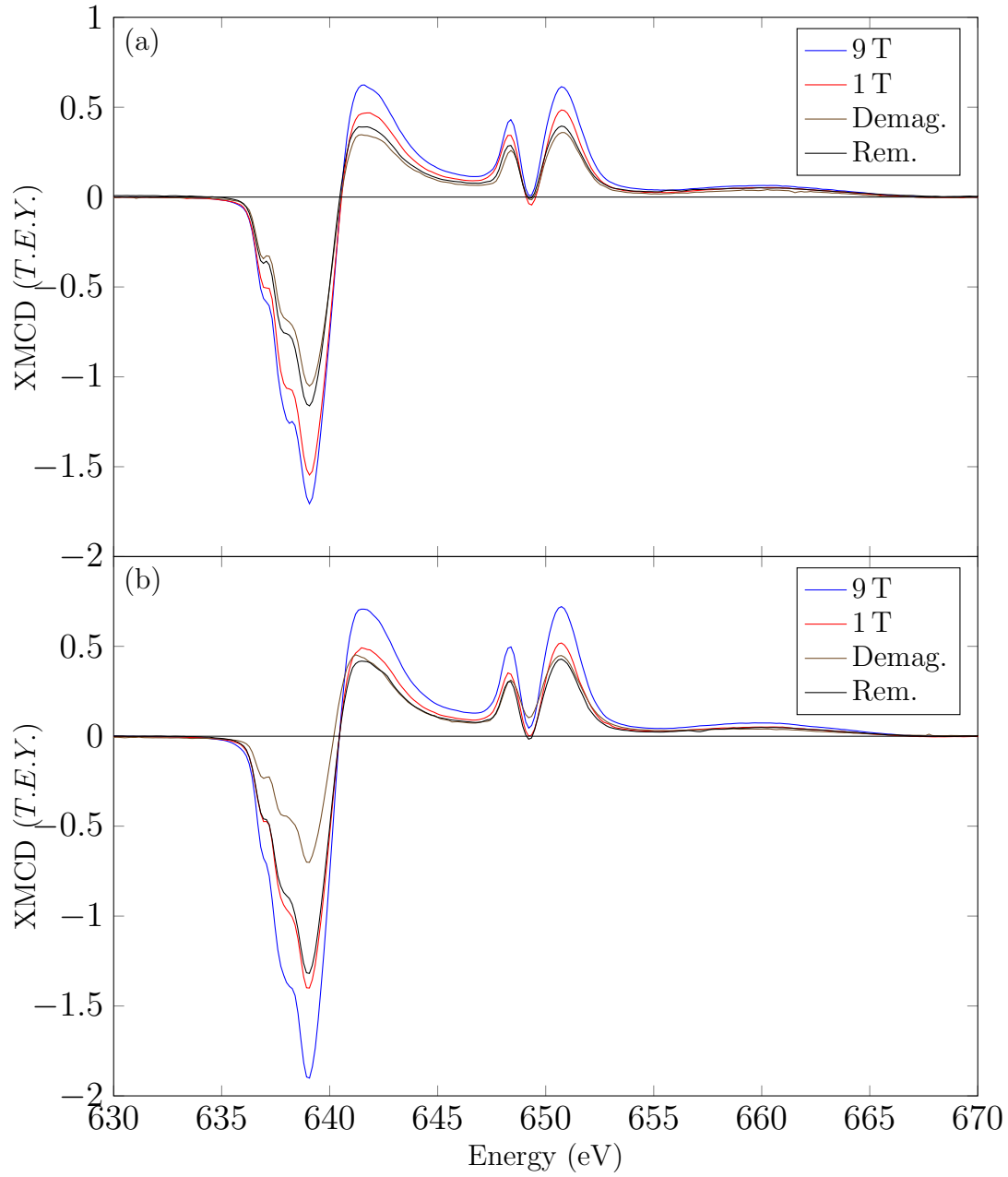


Figure 3.13: XMCD of (a) STO (2 nm) capped 3.9 nm and (b) 2.9 nm thick films of LSMO on STO in the demagnetised state, and under fields of 1 T and 9 T and at remanence.

Table 3.1: Mn-site spin moments from sum rule calculations on XMCD spectra for thin LSMO films grown on SrTiO₃ substrates.

Sample(nm)	T(K)	B(T)	$m_s(\mu_B/hole)$	$m_s(\mu_B Mn^{-1})$
2.9	5	1	0.20	1.28
2.9	5	9	0.25	1.59
2.9	5	0	0.16	1.01
2.9	300	1	0.02	0.13
2.9	300	9	0.10	0.61
2.9	300	0	0.00	0.01
3.9(Capped)	5	1	0.25	1.58
3.9(Capped)	5	9	0.31	1.93
3.9(Capped)	5	0	0.20	1.23
3.9(Capped)	300	1	0.06	0.40
3.9(Capped)	300	9	0.13	0.85
3.9(Capped)	300	0	0.01	0.07
1.9	5	1	0.09	0.56
1.9	5	9	0.17	1.06
1.9	5	0	0.02	0.16
1.9	300	1	0.00	0.01
1.9	300	9	0.04	0.23
1.9	300	0	0.00	0.02
24.3	5	1	0.20	1.29
24.3	5	9	0.23	1.45
24.3	5	0	0.18	1.14
24.3	300	1	0.09	0.59
24.3	300	9	0.13	0.83
24.3	300	0	0.07	0.47

exchange becomes impossible in an antiferromagnetic lattice. Note that the moments per Mn ($\approx 1 \mu_B$), even in the thicker films are much less than the average moment deduced from the film magnetisations ($2 - 3 \mu_B Mn^{-1}$). The X-ray measurements are made in total electron yield mode, where the top 3 - 4.5 nm is sampled, limited by the attenuation of electrons escaping the material, based on measurements of LCMO films by Ruosi *et al.* [137].

While antiferromagnetism of the Mn-site within the dead layer cannot be explicitly probed by XMCD, as the net absorptions of left and right circularly polarised X-rays are equal in this case, XMLD is sensitive to the charge anisotropy induced by antiferromagnetic order. Figure 3.14 shows the XMLD spectra obtained by the methods

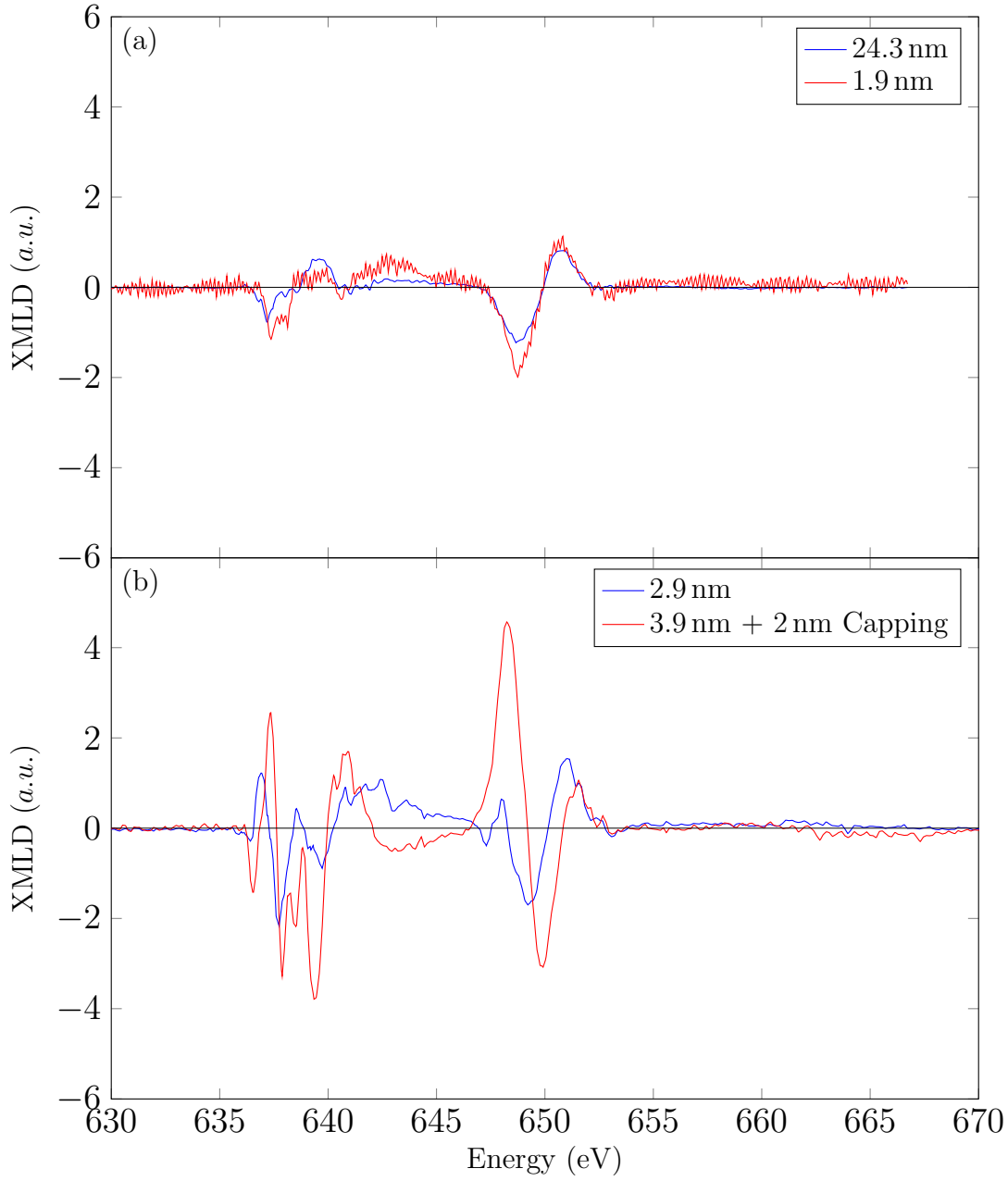


Figure 3.14: XMLD of (a) 24.3 nm and 1.9 nm and (b) 2.9 nm and STO (2 nm) capped 3.9 nm thick LSMO films.

outlined in section 2.3.3.2.

There is a linear dichroism signal in the case of all of the samples measured, and given a probe depth of $d \approx 4$ nm the full thickness of the dead layer is probed. It is interesting to note that the antiferromagnetic signal is present at the surface of the 24.3 nm thick film, and bears a striking resemblance to that of the 1.9 nm and 2.9 nm films. However,

the SrTiO₃ capped 3.9 nm LSMO film has a quite different structure, although the presence of the capping layer likely modifies the strain throughout the film, which is then clamped at both interfaces.

3.3 Discussion and Conclusion

The structural, magnetic and transport properties of LSMO thin films have been explored in this work. The films grown during this project exhibited high quality epitaxial growth when grown on LSAT and STO substrates, but had defective nature when grown on LAO, indicating that that growth of LSMO thin films is highly sensitive to strain. If we consider the magnetic data in terms of the strain induced by the substrate, it seems that the tensile strain of STO affects the thickness of the dead layer to a greater extent than the compressive strain of LSAT, which is an interesting result, especially in light of an old study of LSMO on MgO in our group where an even greater tensile strain ($\epsilon \approx 7.6\%$) leads to a very large dead layer of 10 nm [51]. Whatever the actual mechanism, it is apparent that the dead layer thickness is intimately related to the strain imposed by the film.

It is also found that there is a contribution to the observed net magnetisation, which could explain the reports of ultrathin films of an insulating magnetic phase of LSMO [138] and unusually high Mn moments [139], which comes from the substrate. This anomalous moment might be attributed to a half-metallic impurity band arising from oxygen vacancies in the substrate [133], given the increase in moment with annealing temperature up to 600 °C shown in [134]. The substrate magnetism exhibits little or no temperature-dependence. The effect is most pronounced in STO and LSAT, but is also present in LAO. Once this is taken into account the magnetism of the thinnest layers of LSMO can be understood.

The X-ray dichroism experiments performed in this work give us an interesting insight into the nature of the dead layers. The indication from circular dichroism is that

there is the capacity to recover some moment in the films with the application of high fields, within the probed volume. This is attributed to the canting of antiferromagnetic moments which exist in the dead layer, the existence of which is confirmed by X-ray linear dichroism. The actual mechanism of the formation of a dead layer presents an interesting problem. The mechanisms proposed by Huijben *et al.* [53], Valencia *et al.* [57] and Tebano *et al.* [52] represent the main theories to describe the origin of the dead layer. The first of these, exemplified by the Tebano paper, is the theory of orbital ordering, which relies on the splitting of the e_g levels with a distortion of the oxygen octahedra imposed by substrate strain in a Jahn-Teller scenario, to explain the non-conducting and antiferromagnetic nature observed. In this theory, a compressive strain imposed by the substrate should impose preferential occupation of the $(3z^2 - r^2)$ over the $(x^2 - y^2)$ d -orbital as illustrated in figure 3.15, following the analysis of the phase diagram of tetragonally distorted $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [140]. In this case, the dominant exchange between Mn sites in the plane of the film is superexchange, and double exchange in the perpendicular direction, giving C-type antiferromagnetic order. This can be understood in terms of the effective $d-d$ hopping integral t and the nearest neighbour exchange integral J_1 , which we express as $J_1 = \alpha t - \beta t^2$ ($\alpha, \beta > 0$), following from the discussion in [141], where α is the double exchange contribution and β is the superexchange contribution. In this formalism, as the Mn-Mn distance increases, t decreases and J_1 becomes larger along the axis of elongation. One can also consider the orbital degrees of freedom in this configuration, which are controlled by the lattice distortion. The e_g band is an antibonding state of $\text{Mn}(e_g)$ and $\text{O}(2p)$ orbitals, and a tetragonal distortion elongating the Mn-O bond will lead to preferential occupation of this orbital. Given a less than half filled e_g band, this leads to stronger double exchange between the more populated orbitals, in this case $(3z^2 - r^2)$. The converse can be said in the case of tensile strain, which leads to A-type antiferromagnetic order.

A second theory of the nature of the dead layer is that of structural and electronic phase separation, which is explained in Dagotto's review [100] and compared in Huijben's paper to that of orbital ordering. Essentially the randomly distributed structural

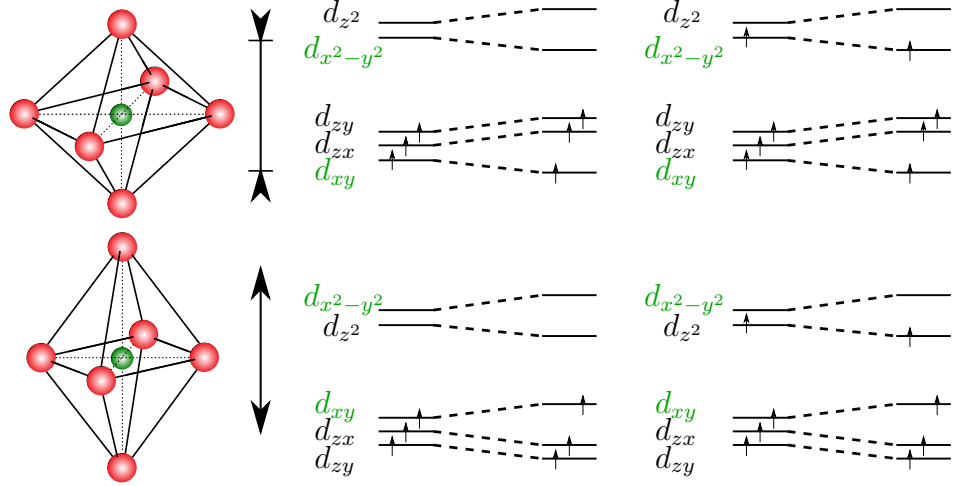


Figure 3.15: Illustration of the preferential occupation of d_{z^2} and $d_{x^2-y^2}$ under different conditions of strain and deformation of the oxygen octahedra in LSMO.

disorder imposed by the differing ionic charges and radii of A-site cations effecting the local Mn-O-Mn bond angles leads to randomised exchange between spins on Mn sites. This allows for the coexistence of clusters of antiferromagnetic and ferromagnetic domains near to the metal/insulator transition. The electronic phase separation is driven by a discontinuity in the density of carriers as the chemical potential is varied. At the point where the system is forced into this discontinuity, it exhibits spatially separated phases each exhibiting properties representing the extremes of the electronic densities. The reduction of carriers at the interface of the manganites should tend to favour a weakening of the ferromagnetic coupling between Mn ions, thereby increasing the relative importance of the antiferromagnetic interaction [142]. This is the driving force behind the electronic phase separation at the interface according to this theory.

The investigations of the dead layer reported here show that there is an antiferromagnetic layer at the surface of the LSMO films and perhaps the interface as well, although the exact energetic configuration of the interfacial dead layer may be different from the surface dead layer, as evidenced by the change in peak positions in the case of the XMLD of STO capped LSMO (figure 3.14). The situation may be as depicted in figure 3.16, with perpendicularly oriented spins at the surface dead layer, and in-plane orientations at the interface. It is likely that the surface layers of LSMO films can be

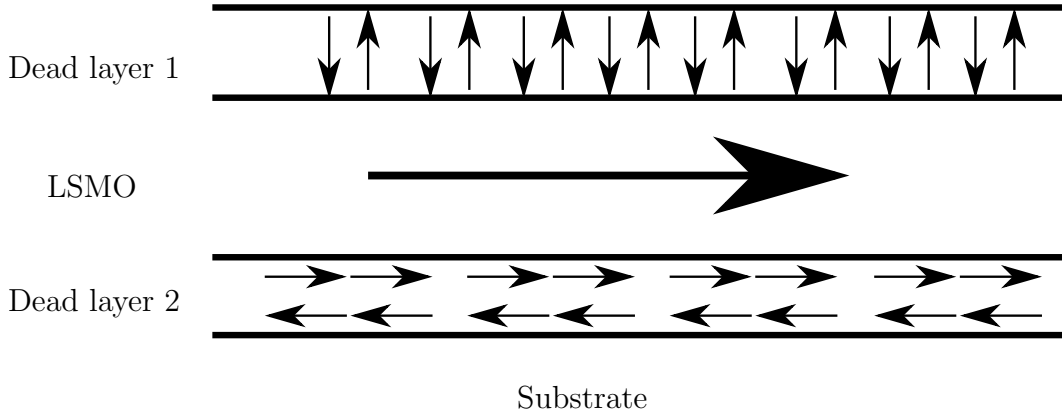


Figure 3.16: Schematic of the configuration of spins in the dead layer which is likely the case that gives rise to the XMLD results.

affected by defects such as oxygen vacancies and adsorbates which adhere to the surface between the sample fabrication and measurement, given the extended exposure to the atmosphere that the samples underwent. There was also no observed preferential occupation of the $(3z^2 - r^2)$ over the $(x^2 - y^2)$ orbitals in the XLD spectra, which agrees with the work of Huijben *et al.*. The evidence lends itself to the theory of electronic phase separation.

Chapter 4

CoFe₂O₄ & NiFe₂O₄: Insulating and Magnetostrictive Spinel Ferrites

4.1 Introduction and Literature Review

In this chapter the structural and magnetic properties of CoFe₂O₄ and NiFe₂O₄ are reviewed, and contemporary interest in their properties for applications is presented. I will then provide a motivation for the study of these materials in the context of spin filtering.

4.1.1 Ferrimagnetism in NiFe₂O₄ and CoFe₂O₄

The spinel ferrites, having the general formula MFe₂O₄, where M is a metal cation such as Co²⁺, Ni²⁺ and Fe²⁺, have the space group $Fd\bar{3}m$ and cubic spinel structure of AB₂O₄, consisting of a face-centred cubic array of oxygen ions with one tetrahedral and two octahedral sites per formula unit, and eight formula units per unit cell. The structure of the ferrites is usually ‘inverse’ because the A-sites contain tetrahedrally coordinated Fe³⁺ ions and the B-sites consist of an equal amount of octahedrally coordinated M²⁺ and Fe³⁺, whereas MgAl₂O₄ structure has the ‘normal’ spinel structure with only Mg²⁺ on the A-sites and Al³⁺ on the B-sites. The tetrahedral $8a$ sites have cubic $\bar{4}3m$ point symmetry and the octahedral $16d$ sites have trigonal $\bar{3}m$ point symmetry.

The ferrites are insulating and ferrimagnetic, with the exception of magnetite (Fe₃O₄) which is conductive. CoFe₂O₄, which is one of the two ferrites examined during this project, exhibits a high cubic anisotropy which is largely absent in the other spinel ferrites. The accepted lattice parameter of CoFe₂O₄ is 839.2 pm [143].

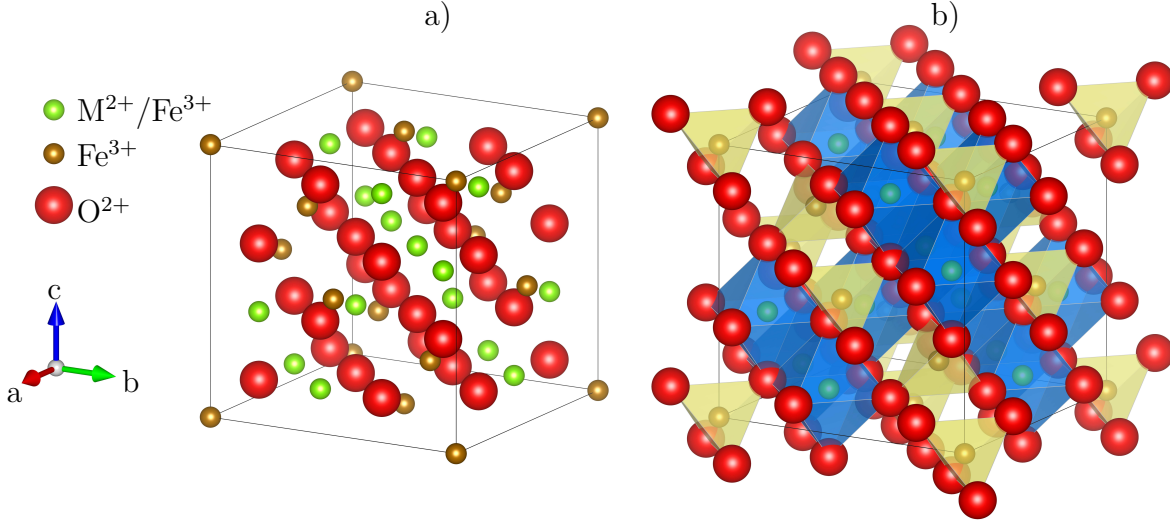


Figure 4.1: The structure of the cubic spinel ferrites showing (a) the atomic positions of the ions and (b) the octahedral and tetrahedral sites in the structure.

Fe^{3+} has $3d^5$ and is in a high spin state of $t_{2g}^3e_g^2$, $S = 5/2$ with a spin moment of $5\mu_B$, and high spin Co^{2+} $3d^7$ has $t_{2g}^5e_g^2$ configuration with $S = 3/2$ and a spin moment of $3\mu_B$. In B-sites, cobalt can also have a significant unquenched orbital moment of $\approx 0.6\mu_B$ [144–146]. This orbital moment is responsible for the strong cubic anisotropy $K_1^c \approx 290 \text{ kJ m}^{-3}$ along the easy $\langle 100 \rangle$ directions. Given the degenerate trigonal symmetry of the $\langle 111 \rangle$ directions for the octahedral sites, the spins of the Co^{2+} ions align along these directions, coupling to unquenched orbital moments. The ferrimagnetic Néel temperature of CoFe_2O_4 is 790 K [1].

The high magnetostriction of CoFe_2O_4 is another consequence of the unquenched orbital moment of Co^{2+} . The magnetostriction was originally measured by Bozorth in 1955 [147], who found a value of 885 ppm in $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$. This corresponds to a tetragonality $(a_\perp - a_\parallel)/a_{\text{bulk}}$ of about 0.1 %. This magnetostriction leads to a uniaxial anisotropy, upon imposing a strain ϵ along $\langle 100 \rangle$ given by [148]

$$K_U \approx (3/2)\lambda_{100}\epsilon E \quad (4.1)$$

where E is Young's modulus (C_{11}), 257 Pa [149] and λ_{100} is the magnetostriction

along the [100] directions. In the experimental work performed here, only the effective anisotropy can be determined, as there are many contributions to the strain in these epitaxial films.

As a result of the high magnetostriction, the strain imposed by a substrate on CoFe₂O₄ thin films has a large effect on the magnetic anisotropy [148, 151–156]. CoFe₂O₄ is thought to have potential as a candidate for perpendicular magnetic recording media [157] due to the fact that an appropriate substrate like MgO can be chosen so as to impose perpendicular anisotropy on the film. To estimate the perpendicular anisotropy from the magnetisation curves, the equation

$$K_U = K_{\perp} - K_S \quad (4.2)$$

is used, where $K_{\perp}$ is deduced from the area between the perpendicular and parallel curves based on the consideration that the energy needed to change that sample magnetisation by an amount dM is $\mu_0 H dM$ [158]. $K_S = -\frac{1}{2}\mu_0 M_s^2$ is the shape anisotropy.

Although the bulk magnetisation for CoFe₂O₄ is usually close to the theoretical bulk maximum 455 kA m^{-1} corresponding to $3.6 \mu_B \text{ f.u.}^{-1}$, the values reported for PLD grown thin films are very varied, as shown in table 4.1.

The second ferrite examined in this thesis is NiFe₂O₄. Bulk nickel ferrite, NiFe₂O₄ (NFO), is an insulator and is a soft ferrimagnet below 850 K with a relatively low magnetization of $2 \mu_B$ per formula unit. It again has the inverse structure with octahedrally coordinated Ni²⁺ $3d^8$ with $t_{2g}^6 e_g^2$ ions which have $S=1$ and much less unquenched orbital moment than CoFe₂O₄, leading to lower magnetostriction. It has a T_C of 865 K.

Unlike CoFe₂O₄ the magnetism of thin films of NiFe₂O₄ does not vary much from the bulk value of $\approx 330 \text{ kA m}^{-1}$

An interesting application proposed for CoFe₂O₄ and NiFe₂O₄ is as spin filtering tunnel barriers, such as was demonstrated by Moodera *et al.* in 1988 in the case of EuS tunnel

Table 4.1: Deposition conditions and magnetisations reported for CoFe_2O_4 in previous literature.

Substrate	Temp.(K)	Thickness(nm)	P_{O_2} (μbar)	M_s (kA m^{-2})	Ref.
MgO(100)	600	400	40	335	[159]
MgO(100)	800	400	40	426	[159]
STO/ CoCr_2O_2	600	140-430	1	380	[148]
MgAl_2O_4	500	65-900	1	?	[160]
MgO(100)	700	80	$1 \cdot 10^{-4}$	180-220	[161]
SrTiO_3 (100)	550	80	$1 \cdot 10^{-4}$	370	[161]
Al_2O_3 (0001)	800	40	2	?	[157]
SiO_2	550	33	2	260	[157]
SrTiO_3 (100)	500-700	70	0.1	?	[162]
MgAl_2O_4	175-690	200-220	13	450	[65]
MgO(100)	450	200	13	300	[163]
SrTiO_3 (100)	450	200	13	140/480	[163]
MgO(100)	?	13-100	70	260	[152]
SrTiO_3 (100)	?	13-100	70	390	[152]
BaTiO_3 (100)	?	13-100	70	210	[152]
LaAlO_3 (100)	?	13-100	70	280	[152]
MgO(100)	400	50-400	20	100-185	[153]
Pt(111)	550-750	247-290	90	180-220	[164]

barriers [165] after work by Esaki *et al.* showed magnetic field effects on tunnelling through insulating magnetic Eu-chalcogenide tunnel barriers in 1967 [166], where the high spin polarisation of the tunnel current was attributed to different barrier heights for different spin directions. Later Ramos *et al.* showed a spin polarised current of polarisation $P = 26\%$ through a CoFe_2O_4 barrier [9]. Recent theoretical work by Caffrey *et al.* suggested the existence of two different spin channels within the band gap for electrons tunnelling through NiFe_2O_4 and CoFe_2O_4 , which would be accessible by different band alignments with the electrode materials [167]. This will be further discussed in chapter 6 and it is one of the principles upon which a multiferroic device described in that chapter is based.

4.1.2 Motivation

NiFe_2O_4 and CoFe_2O_4 are interesting complex oxides because of their ferrimagnetic and insulating behaviour. The motivations for studying them have some overlap, in

that their magnetotransport properties both lend themselves to the spin-filtering application. CoFe₂O₄ has very large magnetostriction which could allow for control over the anisotropy by substrate induced strain; NiFe₂O₄ has a larger bandgap than CoFe₂O₄ which suggests it could be a more effective spin filter.

4.2 Experimental Results

In this section the experiments conducted to examine the magnetisation and magnetic anisotropy of CoFe₂O₄ are outlined, using careful analysis of the films strain under different conditions of strain and oxygenation using reciprocal space mapping (RSM), observing the changes in magnetic anisotropy by VSM and SQUID magnetometry and observing the Fe:Co ratio by energy dispersive X-Ray spectroscopy (EDX).

Deposition of high quality epitaxial films of NiFe₂O₄ with good magnetic properties by PLD is shown by XRD, AFM and SQUID magnetometry. The integration of NiFe₂O₄ into artificial multiferroic devices is discussed in chapter 6.

4.2.1 Structure and Morphology

The structure of CoFe₂O₄ and NiFe₂O₄ is investigated by XRD, RSM, AFM and RHEED to determine the quality of growth which is achieved. Symmetric XRD scans are performed on NiFe₂O₄ to ensure that films are oriented and crystallised. The surface of NiFe₂O₄ is examined by AFM to ensure that the films are smooth enough to be used as tunnel barriers. The strain in CoFe₂O₄ films is quantified under different conditions by RSM to better understand the magnetic data. The thicknesses of all films were determined by XRR.

4.2.1.1 CoFe₂O₄

The strain induced tetragonality in CoFe₂O₄ films grown on MgO substrates obtained by RSM as shown in figure 4.2. The in-plane lattice parameters of all films grown

on MgO were found to match that of the substrate ($2a_0 = 842$ pm), indicating a fully strained epitaxial film in all cases. The lattice parameters out of the film plane, however, were only well defined for the samples grown in vacuum $a_{\perp} = 837$ pm, with films grown at higher oxygen pressures showing a broadened distribution of $a_{\perp}$, which increased with oxygen pressure.

The CoFe₂O₄ films grown on MgAl₂O₄ have a large compressive 3.7 % lattice mismatch, which causes a large expansion of the unit cell perpendicular to the plane of the film. The RSM in figure 4.3 (a) illustrates how the inplane lattice parameter is poorly defined for CoFe₂O₄, although it clearly is influenced by the substrate. This is taken to indicate that there is a gradient of strain throughout the 46.5 nm thick film, but that there is a significant amount of the film which is heavily compressed by the substrate. The broad peak of the CoFe₂O₄ (226) reflection is centred at $a_{\parallel} = 831$ pm and $a_{\perp} = 850$ pm. This corresponds to an in-plane compression of 1 % and a similar expansion out of the film plane.

Films grown on LSAT have a less well-defined peak corresponding to CoFe₂O₄ (226), centred around $a_{\parallel} = 827$ pm and $a_{\perp} = 851$ pm, as can be seen in figure 4.3 (b). This indicates that there is also a large deformation of the unit cell which is not sustained throughout the 49.3 nm thick film.

4.2.1.2 EDX of CoFe₂O₄ Thin Films and Target

The Fe:Co ratio in four different thin films of CoFe₂O₄ deposited on MgO(001) and in the target used to deposit the films as measured by EDX are shown in table 4.2.

The analysis shows that the stoichiometry of the films deviates slightly from the bulk, becoming more stoichiometric during the deposition process, although this does not seem to correlate with the magnetisation of films.

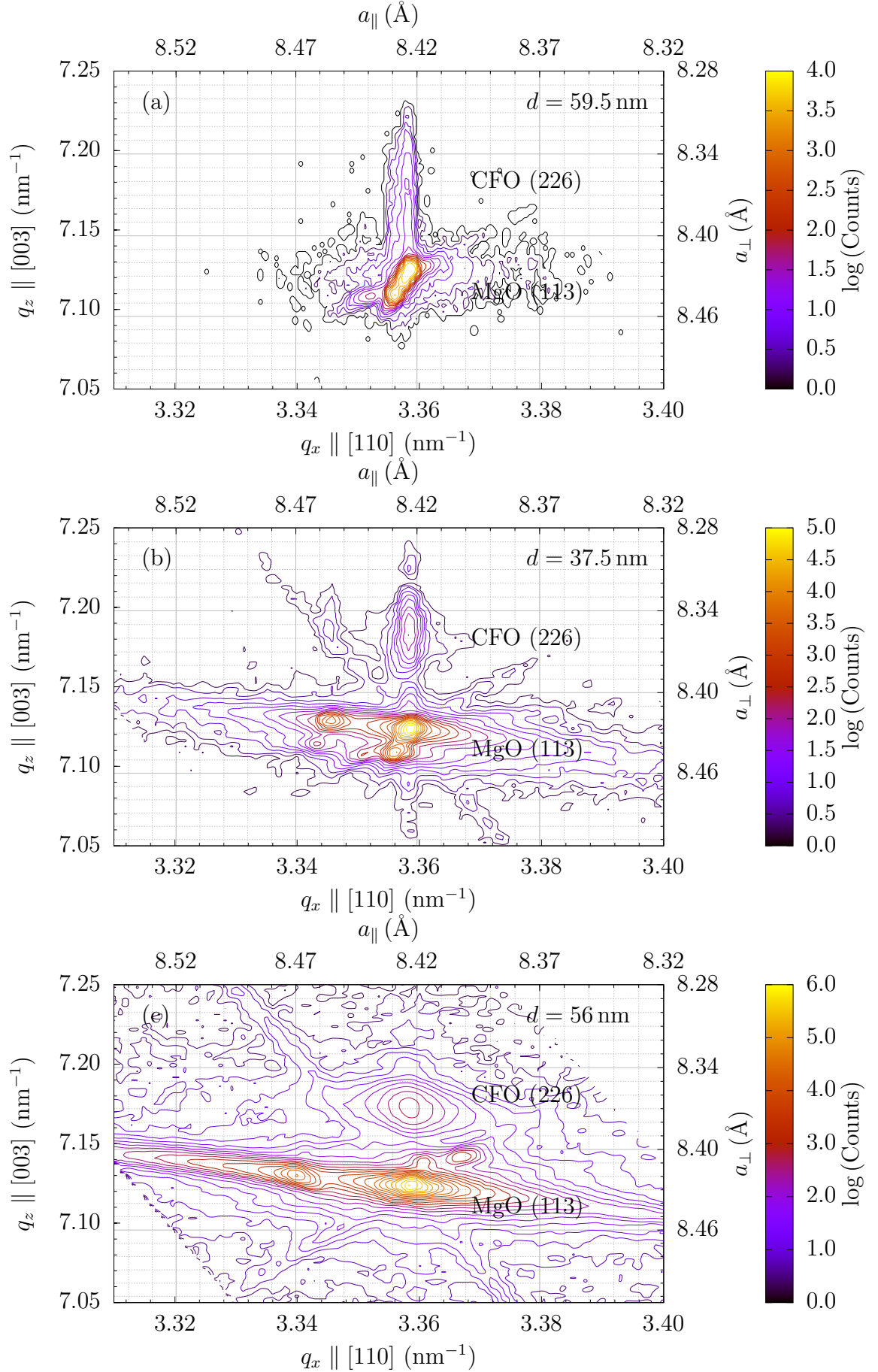


Figure 4.2: Reciprocal space maps about the (113) reflex of MgO under deposition conditions of 600 °C and a partial oxygen pressure of (a) 100 μbar , (b) 0.2 μbar and (c) vacuum showing the CoFe_2O_4 (226) peak.

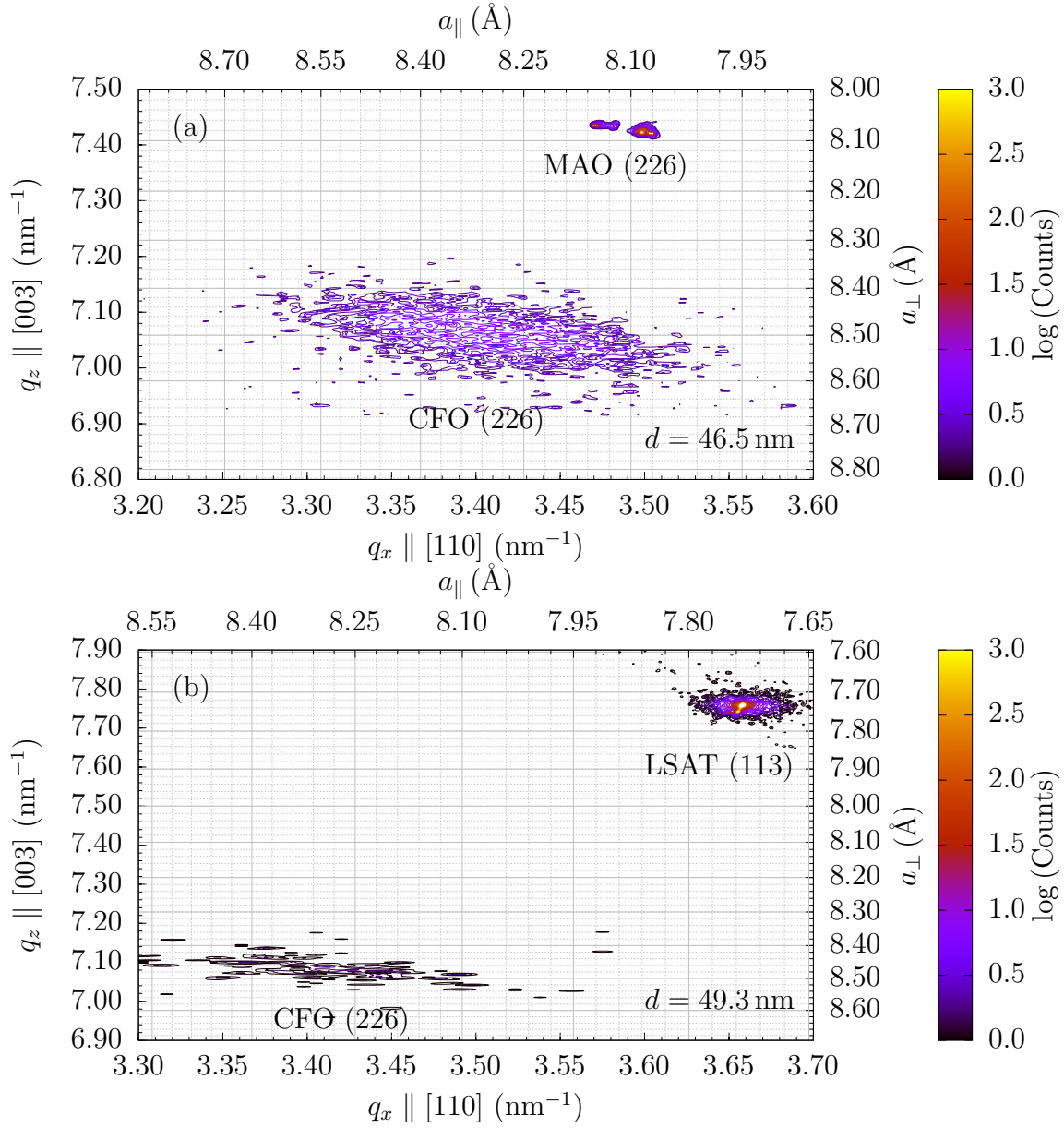


Figure 4.3: Reciprocal space maps about (a) the (226) reflex of MgAl_2O_4 and (b) the (113) reflex of LSAT under deposition conditions of 600 °C at vacuum showing the CoFe_2O_4 (226) peak.

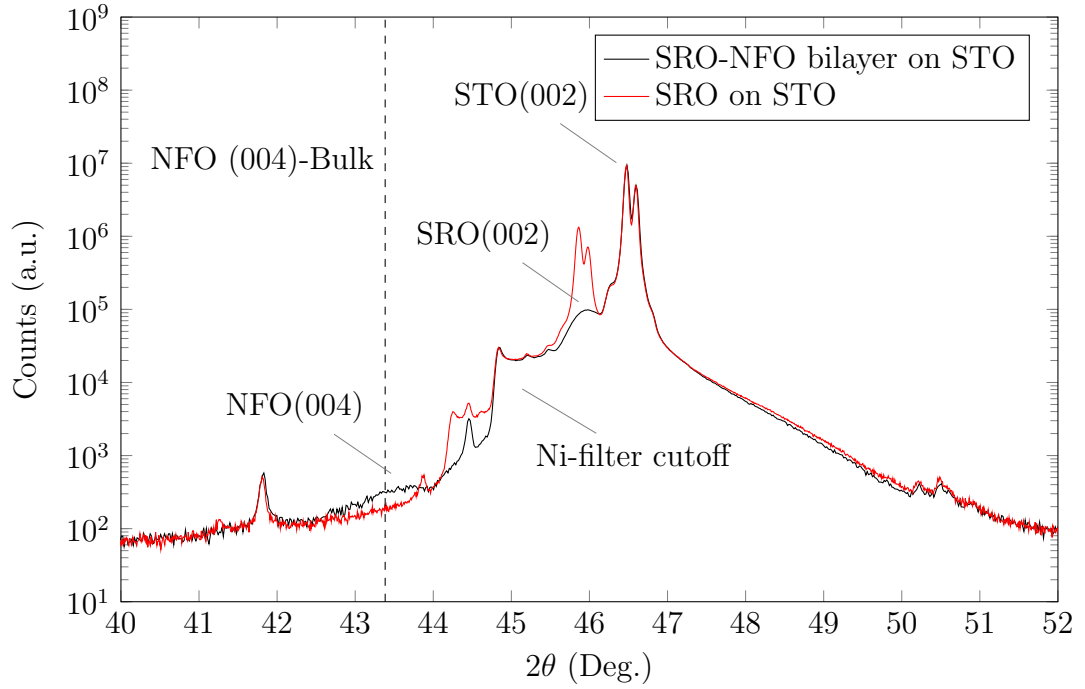
4.2.1.3 NiFe_2O_4

The XRD of 6 nm NiFe_2O_4 grown on 35 nm SrRuO_3 is shown in figure 4.4. This XRD was performed on a Phillips Panalytical (divergent source) diffractometer, and the peak near 45° can be attributed to the cutoff wavelength of the nickel-foil $\text{Cu}_{K\beta}$ filter.

The NiFe_2O_4 peak at 43.5° is of low intensity due to the low thickness of the film which also causes significant Scherrer broadening of the peak, due to its small thickness

Table 4.2: EDX analysis of Fe:Co ratios in CoFe_2O_4 samples. Ratios shown are the average of 5 separate scans for each sample.

Thickness (nm)	T_{subst}	P_{O_2} (μbar)	Fe:Co	Std. Dev.	M_s (kA m^{-1})
33.1	600	20	1.82	0.14	119
34	650	20	1.80	0.13	66
15	600	$< 10^{-3}$	1.70	0.23	387
56	600	$< 10^{-3}$	2.00	0.05	397
Target	-	-	1.96	0.02	455

**Figure 4.4:** XRD pattern of a SRO/NFO bilayer structure on STO (black line). The thickness of the NiFe_2O_4 layer is about 6 nm, which gives a very broad, low intensity peak. The red line is the XRD pattern of a single 100 nm thick SRO layer on STO for comparison.

limiting the dimensions of the crystallite size.

The AFM image in figure 4.5 is indicative of the epitaxial quality and low roughness of the thin NiFe_2O_4 films. The terracing of both the SrRuO_3 layers and the NiFe_2O_4 layers are visible. The SrRuO_3 layer has a much higher terrace step height (≈ 3 nm) than the unit cell parameter of NiFe_2O_4 layer (≈ 1 nm), due to the high growth rate of SrRuO_3 in this particular sample. The RMS roughness on the terraces is found to be of order 0.5 nm.

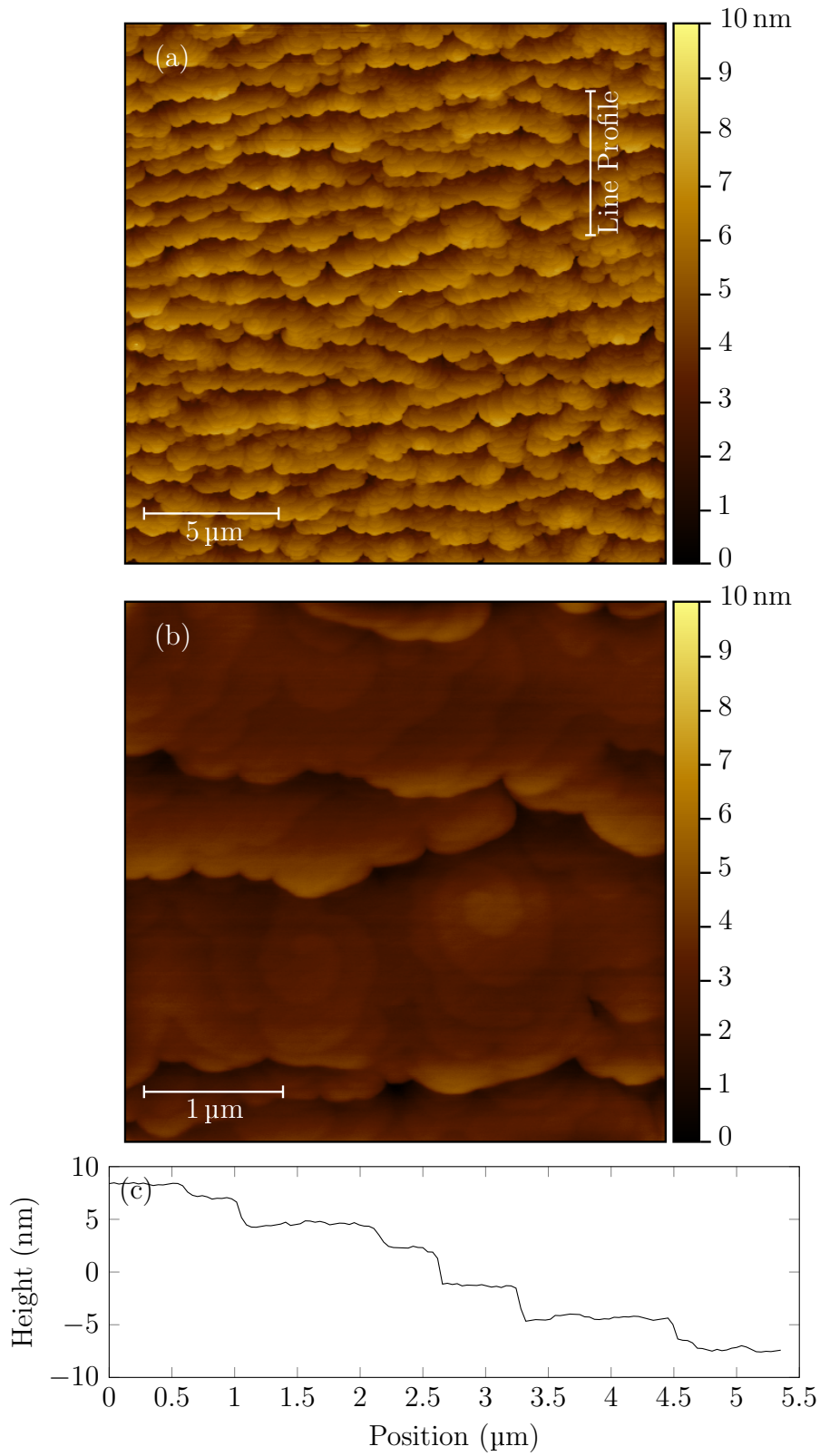


Figure 4.5: The surface of NiFe_2O_4 is shown here in AFM height contrast. The image was captured in contact mode, so as to obtain good resolution in height. (a) and (b) show the height-maps at different lateral scales and (c) shows the line profile indicated in (a).

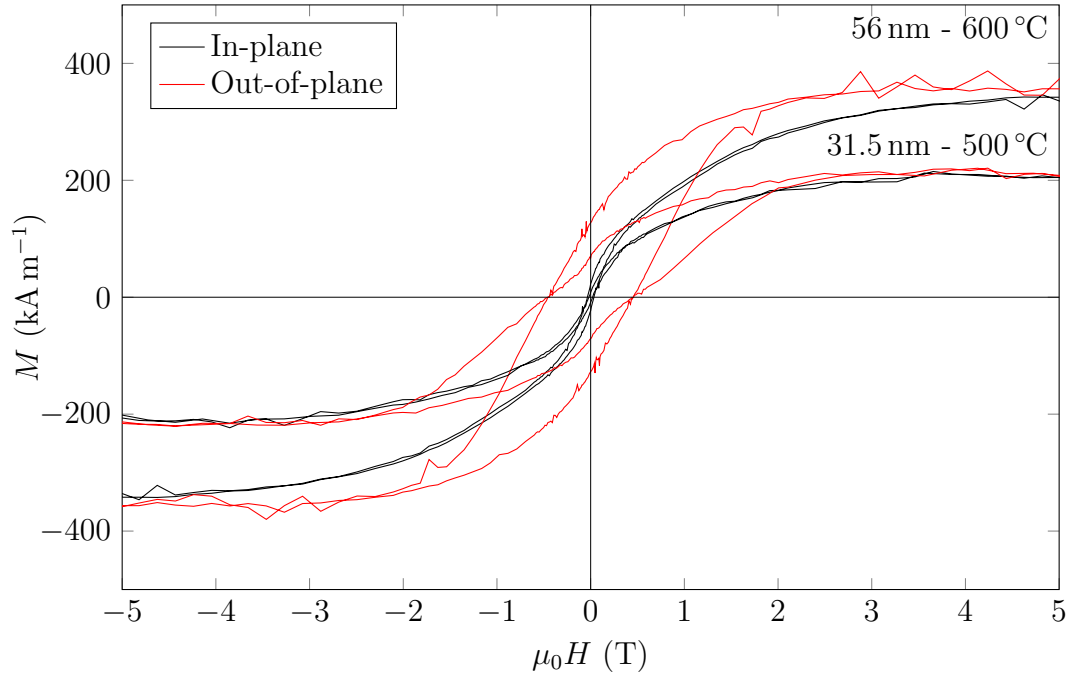


Figure 4.6: Room temperature magnetisation loops of CoFe_2O_4 thin films deposited on $\text{MgO}(001)$ at temperatures of 500°C and 600°C .

4.2.2 Magnetism

Experiments concerning the magnetic properties of CoFe_2O_4 and NiFe_2O_4 thin films are presented in this section. CoFe_2O_4 films are measured using SQUID and VSM magnetometry to show the effect of different deposition conditions and substrates on the magnetisation, and the magnetisation of NiFe_2O_4 is measured in a bilayer structure with SrRuO_3 and the temperature dependence of the moment in the structure is measured from 50 - 400 K.

4.2.2.1 CoFe_2O_4

The magnetisation of 31.5 nm and 56 nm CoFe_2O_4 films deposited in vacuum on MgO substrates at 500°C and 600°C respectively are shown in figure 4.6. The saturation magnetisation on both films is less than the bulk CoFe_2O_4 magnetisation of 455 kA m^{-1} measured for the PLD target used in the deposition of the films although there is a clear increase in the magnetisation at 600°C .

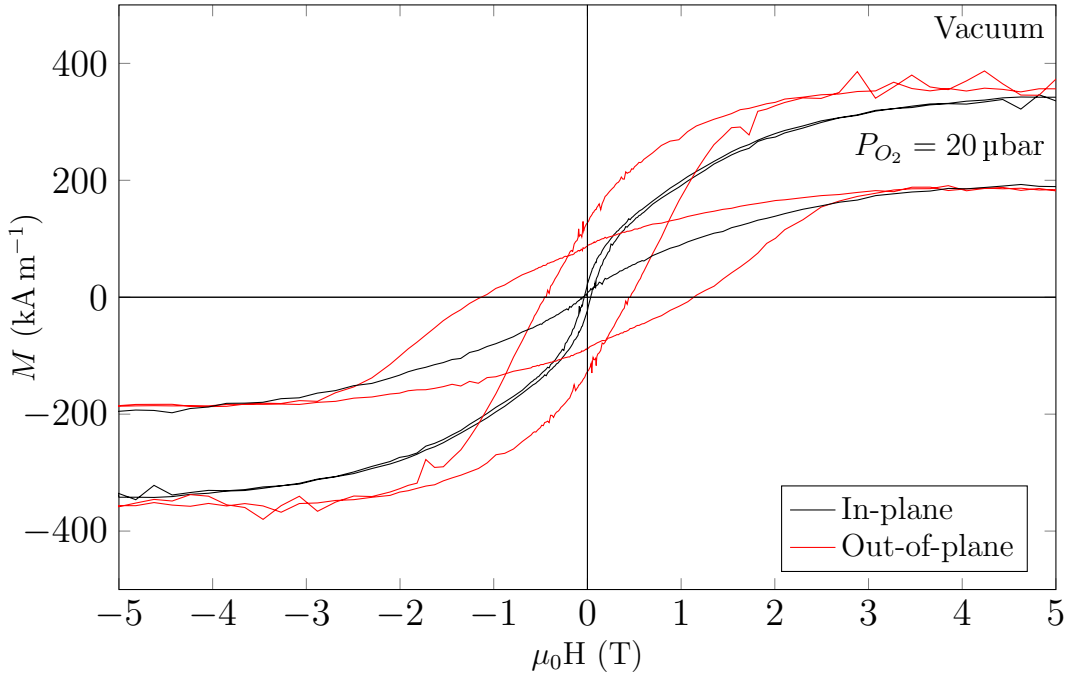


Figure 4.7: Room temperature magnetisation curves of CoFe_2O_4 thin films grown in vacuum and at $P_{\text{O}_2} = 20 \mu\text{bar}$, with the applied field both in the plane of the film and out, on MgO substrates.

The magnetisation curves for 56 nm and CoFe_2O_4 films grown on MgO substrates at 600°C in low and high oxygen pressures is shown in figure 4.7. The increased oxygen pressure decreases the magnetisation, and samples at higher oxygen pressures are further decreased, with samples grown at $100 \mu\text{bar}$ exhibiting saturation magnetisation as low as 60 kA m^{-1} , although this is also influenced by the lower Curie temperature. The pressure dependence of the saturation magnetisation is summarised in figure 4.8. The easy axis of magnetisation in these films is perpendicular to the plane and they have a large coercivity at low temperature, exceeding 5 T at 100 K.

The saturation magnetisation as a function of substrate temperature for films grown in vacuum and an oxygen pressure of $20 \mu\text{bar}$ is shown in figure 4.9. The moments of films grown in vacuum are consistently higher but in both cases the maximum lies at $T_S = 600^\circ\text{C}$. Increasing the fluence from 2.1 J cm^{-2} to 2.7 J cm^{-2} further increases the magnetisation of the films to 453 kA m^{-1} , as is shown in figure 4.10.

The easy axes of all films grown on MgO(001) are perpendicular to the film plane and

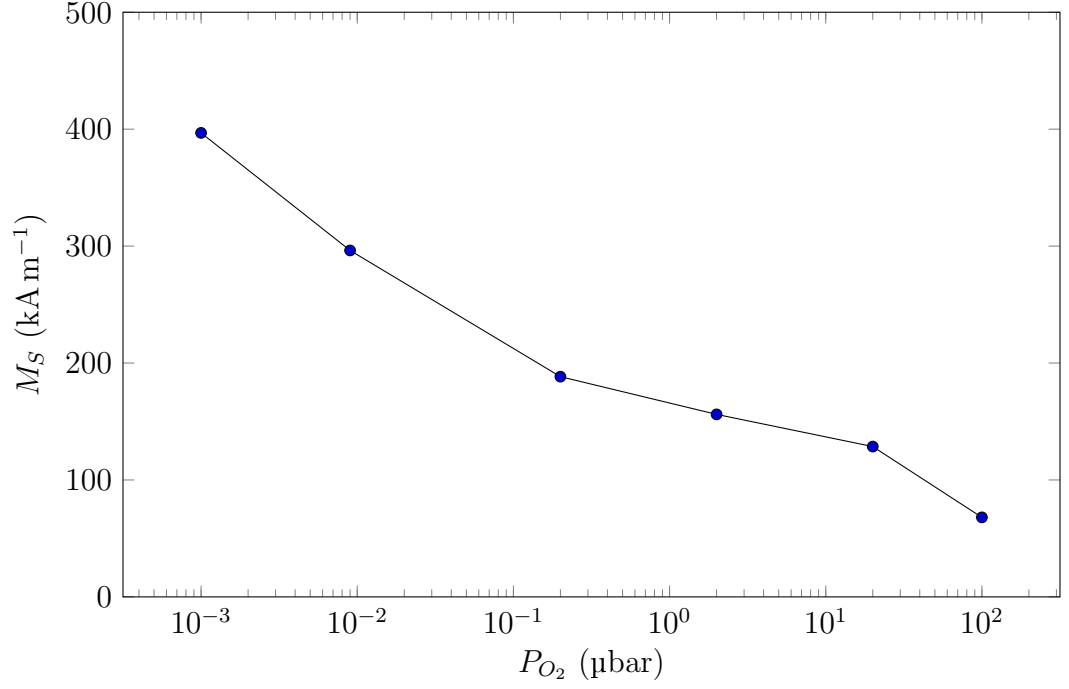


Figure 4.8: Room temperature magnetisation for CoFe_2O_4 films deposited on $\text{MgO}(001)$ at 600 K for a six different oxygen pressures with a constant laser fluence of 2.1 J cm^{-2} .

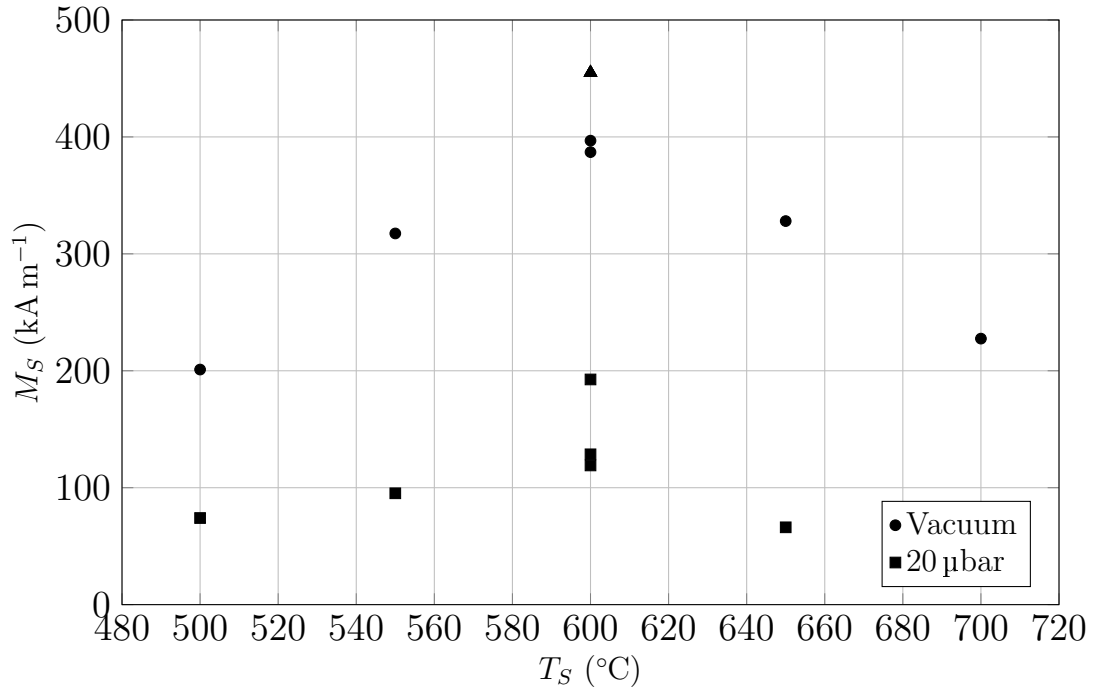


Figure 4.9: Magnetisation as a function of substrate temperature T_S for CoFe_2O_4 films deposited on $\text{MgO}(001)$ in vacuum and at 20 μbar measured at room temperature. The laser fluence used was 2.1 J cm^{-2} , except for the triangle (2.7 J cm^{-2}).

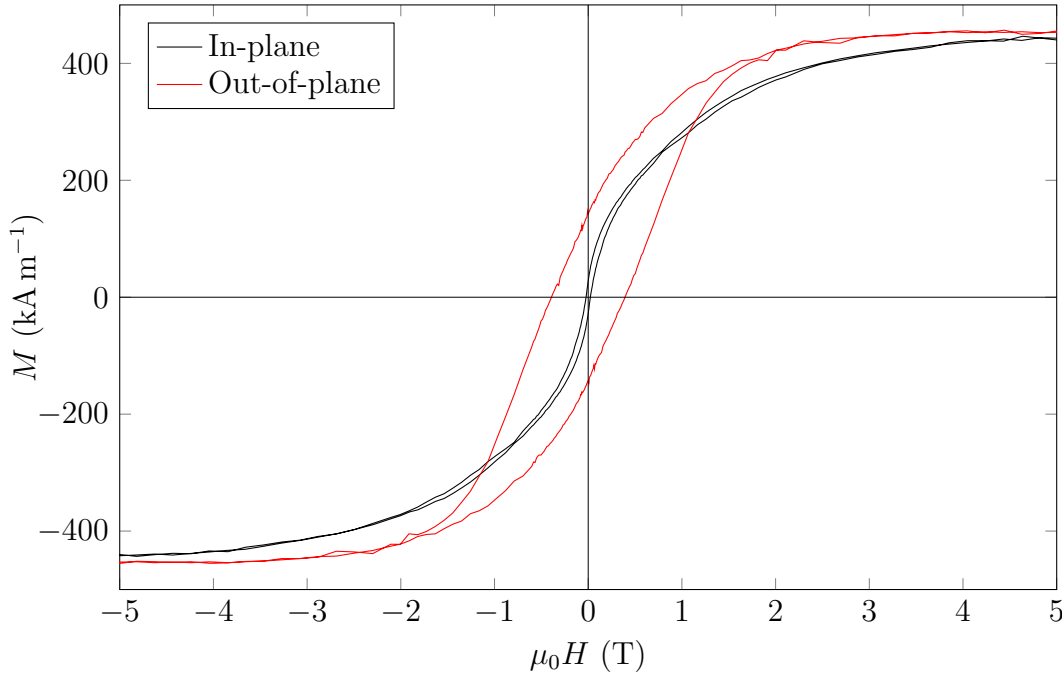


Figure 4.10: Magnetisation loops for CoFe_2O_4 grown at a substrate temperature of 600°C in vacuum using a laser fluence of 2.7 J cm^{-2} .

the coercivity in the high moment films reaches 400 kA m^{-1} , with low moment films showing even higher coercivity. Using equation 4.2, and the data in figure 4.6 an estimate of the intrinsic perpendicular anisotropy can be obtained. $M_S = 397\text{ kA m}^{-1}$ giving $K_S = -\frac{1}{2}\mu_0 M_S^2 = -99\text{ kJ m}^{-3}$ and the measured value of $K_\perp$ is 127 kJ m^{-3} . This gives a value of $K_U = 226\text{ kJ m}^{-3}$ which is smaller than values reported by Niizeki for samples with similar magnetisation curves using torque measurements [154] or estimates of anisotropy field $\mu_0 H_a = 2K_U/M_S$. Estimates of K_U from magnetisation curves that exhibit hysteresis can underestimate by up to 40% because of magnetic viscosity in the hysteretic direction, arising from the time dependence of the magnetisation process in a multidomain specimen.

The effect of different substrates on the magnetism of CoFe_2O_4 as measured by VSM is shown in figure 4.11. The in-plane compression imposed by the 3.7% mismatch of the MgAl_2O_4 substrate on a film grown in vacuum leads to a strong in-plane anisotropy of $K_U \approx -1.12\text{ MJ m}^{-3}$, which is much larger than the shape anisotropy $K_S = -62\text{ kJ m}^{-3}$. The anisotropy field is found to be 14 T and the anisotropy energy

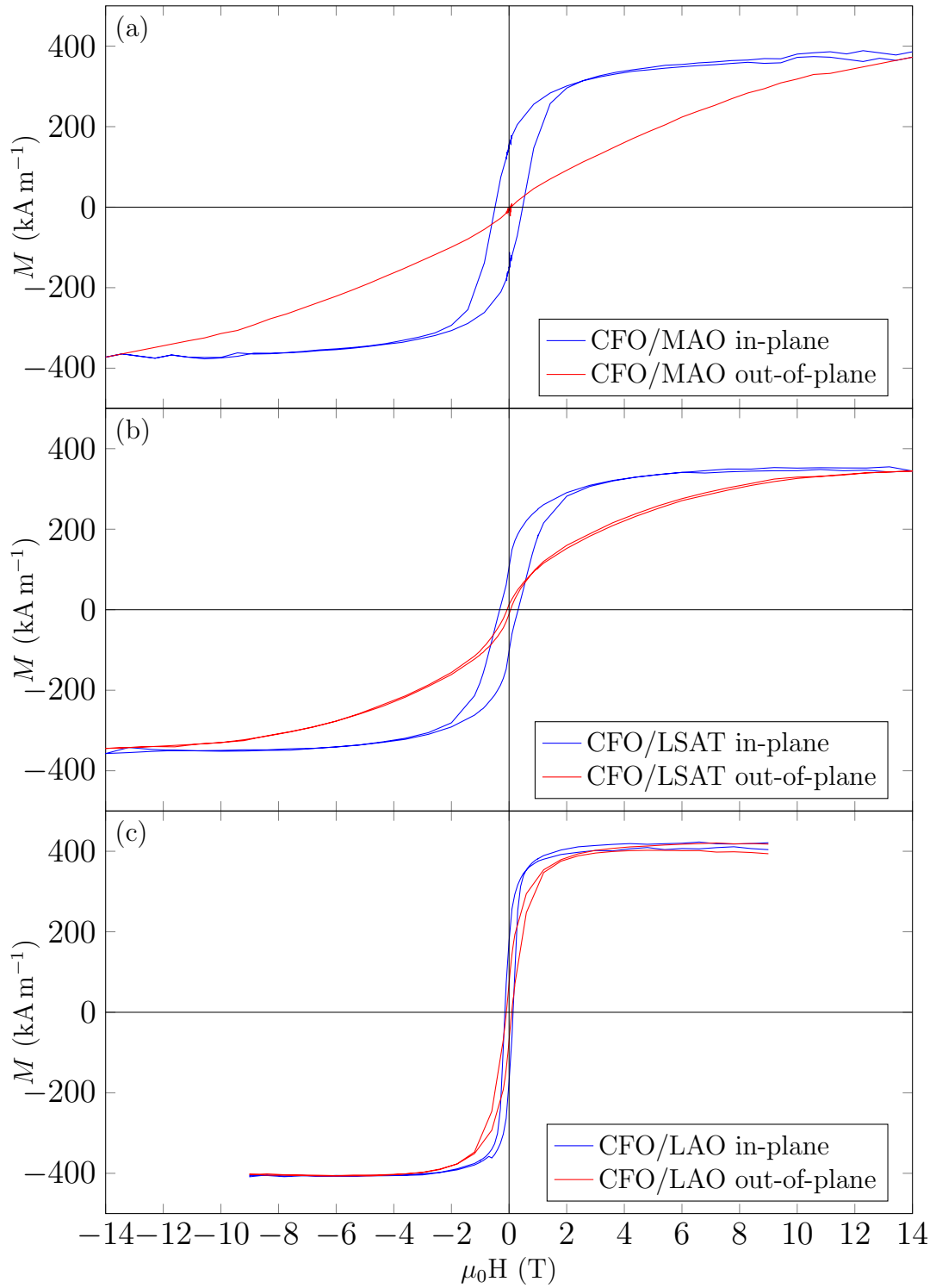


Figure 4.11: Magnetisation curves of CoFe_2O_4 thin films, with the applied field both in the plane of the film and out, on (a) MAO, (b) LSAT and (c) LAO substrates.

Table 4.3: Anisotropy of CoFe_2O_4 films deposited at 600 °C in vacuum on different (100)-oriented substrates. The line separates the parameters that are greater than or less than that of CoFe_2O_4 , 839 pm

Substrate	$a_{\perp}$ (pm)	Growth	M_S (kA m ⁻¹)	K_S (kJ m ⁻³)	K_U (kJ m ⁻³)	Anisotropy
TiO ₂	919	Unconstrained	413	-107	≈ 0	Shape, in-plane
MgO	842	Quasi- epitaxial	397	-99	226	Strain, perpendicular
MgAl ₂ O ₄	808	Oriented, Strained	317	-63	-1120	Strain, in-plane
SrTiO ₃	782	Oriented	183	-21	≈ 30	Strain, weakly perp.
LSAT	775	Oriented, Strained	270	-46	-650	Strain, in-plane
LaAlO ₃	758	Unconstrained	444	-123	≈ 0	Shape, in-plane

$-\frac{1}{2}\mu_0 H_a M_s$ is 2.2 MJ m⁻³. Films grown on LSAT substrate in vacuum have similarly high magnetisation and anisotropy, with $K_U = 0.65$ MJ m⁻³. A film grown on LAO, which exhibits an almost bulk magnetisation of 412 kA m⁻¹, has a very large mismatch of around 10 %, and so there is no epitaxy. In this film, the anisotropy is due to the shape, and there is negligible K_U contribution from epitaxial strain. This was also found to be the case for films deposited on TiO₂ (100) substrates which has a similar mismatch.

A summary of the lattice constants and anisotropy of CoFe_2O_4 films grown during this work is given in table 4.2, which includes data from films on SrTiO₃. SrTiO₃ is an unusual case. The film is oriented, but the magnetization is only 40 % of the bulk value. The perpendicular lattice parameter expands a little, but the net anisotropy is perpendicular to the plane, as for MgO, and is very weak. The effect of substrate strain is 20 – 40 times less than for MgAl₂O₄ or LSAT, and of opposite sign.

4.2.2.2 NiFe_2O_4

The magnetisation of a 6 nm thick film NiFe_2O_4 on 35 nm of SrRuO₃ as measured by SQUID magnetometry at room temperature is shown in figure 4.12. The moment from

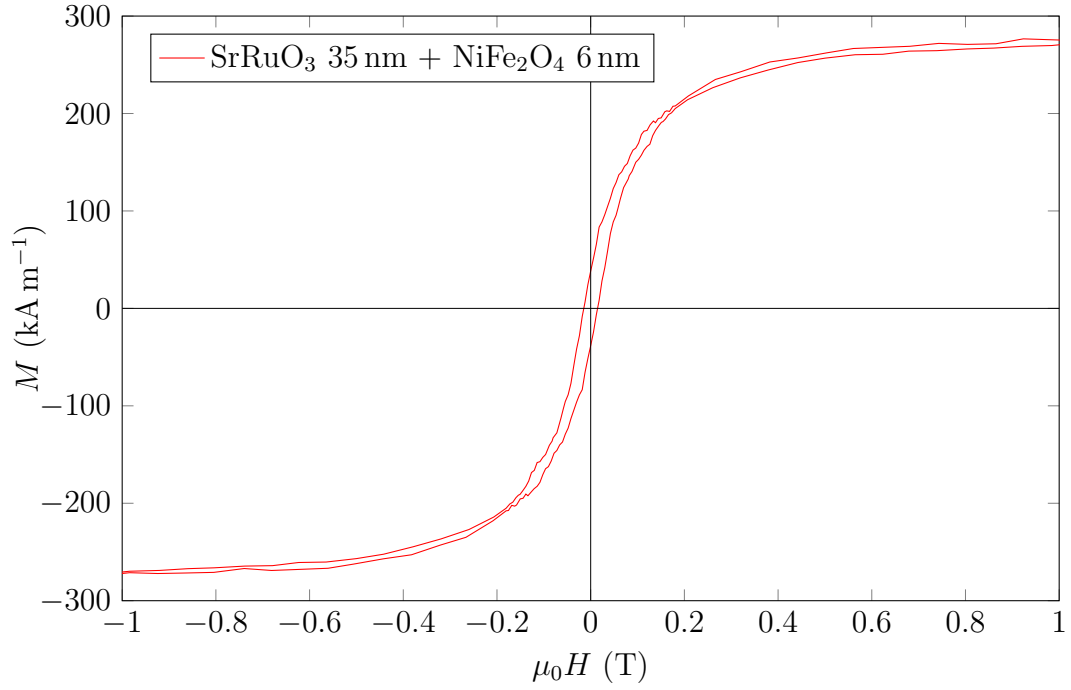


Figure 4.12: Room temperature SQUID M - H loop for thin NiFe_2O_4 grown on a SrRuO_3 layer on (001)-oriented SrTiO_3 . Opening of the hysteresis loop is likely due in part to the formation of magnetic structures at the $\text{NiFe}_2\text{O}_4/\text{SrRuO}_3$ interface.

the sample reaches about $4 \times 10^{-8} \text{ A m}^2$ corresponding to a magnetisation in NiFe_2O_4 of almost 300 kA m^{-1} which unlike CoFe_2O_4 , is close to the bulk value of 330 kA m^{-1} , despite the thinness of the film. As SrRuO_3 is paramagnetic at this temperature, its contribution and that of the substrate is accounted for by subtracting a linear slope. The coercivity of the NiFe_2O_4 film is 14.7 mT .

The temperature dependence of the magnetisation in an applied field of 100 mT is shown in figure 4.13. The reduction in moment of the SrRuO_3 film up to the Curie temperature of about 140°C is observed with about $2 \times 10^{-8} \text{ A m}^2$ of temperature independent moment remaining above this range up to at least room temperature attributed to the NiFe_2O_4 layer.

4.3 Discussion

The results that are obtained for films of CoFe_2O_4 on MgO and MgAl_2O_4 indicate that the magnetic anisotropy of the films is determined primarily by the substrate induced

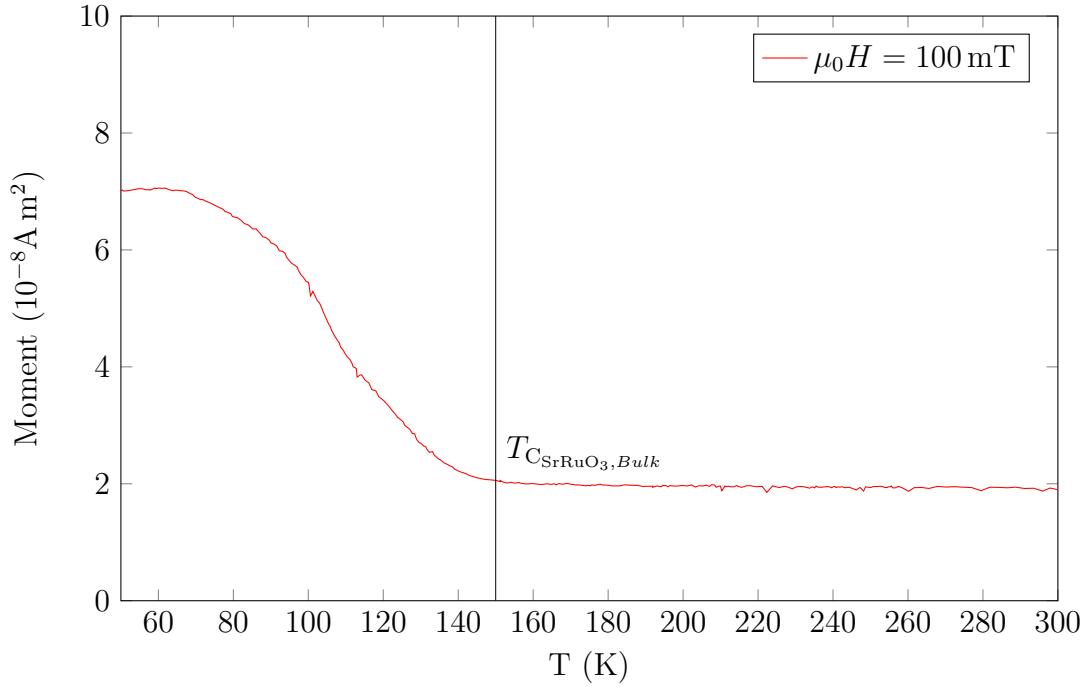


Figure 4.13: Temperature scan of the $\text{SrRuO}_3/\text{NiFe}_2\text{O}_4$ structure. Bulk T_C of SrRuO_3 is indicated.

strain, with these two substrates being good examples of the effect. The films grown on MgAl_2O_4 and LSAT both show a large spread in the $a_{\parallel}$ and $a_{\perp}$ parameters, but the in-plane anisotropy field is very large, reaching 14 T on MgAl_2O_4 . In the case of MgO , the films have strong perpendicular anisotropy due to the compressive strain imposed by the substrate.

This study shows that under good conditions of growth, CoFe_2O_4 films can reach magnetisations close to the bulk magnetisation of 455 kA m^{-1} on different substrates. Reports of the saturation magnetisation have been absent in much of previous literature, with magnetisations typically referred to normalised M_s values which are not referred to any given quantity. A summary of previous literature reporting deposition conditions and magnetisations of CoFe_2O_4 films is given in table 4.1.

The conclusion is that there is a small window of conditions for the growth of CoFe_2O_4 thin films by pulsed laser deposition, necessitating a temperature of 600°C and as high a vacuum as can be achieved, at least $1 \times 10^{-3} \mu\text{bar}$, where the magnetic properties behave like those of the bulk material. The results of the EDX analysis show reduction

in the Fe content, which for a ratio of Fe:Co of 1.8, would lead to a reduction of the moment to about 80 % of the bulk value, with any of the rearrangement of cations only increasing the magnetisation. The reasons for the major reduction in moment in otherwise fully strained and well crystallised films, such as those grown on MgO at high oxygen pressures are unclear, but one possibility is that there are antiphase boundaries within the structure which are created during deposition [8, 155, 168, 169]. Antiphase boundaries are a growth defect which occurs because of the differences in translational and rotational symmetry of the rock salt and spinel structures [170–172]. Where the lattice constant of the spinel layer spans two of those of a matched rocksalt oxide substrate, there is the possibility in two directions of two separate islands nucleating with a separation of $n + \frac{1}{2}$ spinel unit cells. The result of this is that there is an extra plane of antiferromagnetic B-O-B interactions at the interface between two crystallites. The more of these boundaries, the lower the net moment of the film. This explanation of the reduced moment does not strictly apply to MgAl₂O₄ substrates however, as the structural symmetries of the substrate are shared with the film, although there is still the possibility of antiphase boundaries arising due to the existence of misfit dislocations. The existence of antiphase boundaries is equally possible in NiFe₂O₄ thin films, as the SrRuO₃ layers upon which NiFe₂O₄ has successfully been grown also have lattice constants $a_{||} = 399.5$ pm smaller by about a factor of two.

Another explanation for the lowering of the moment is a non-collinear spin structure, such as that found in ZnFe₂O₄ at 15 K where the spins freeze in random directions, but this depends on the absence of A-site Fe³⁺. Bulk zinc ferrite has a normal spinel structure with Zn ions in the tetrahedral A sites and Fe ions in the octahedral B sites. Due to antiferromagnetic (AFM) superexchange interactions between B-B ions, bulk zinc ferrite is antiferromagnetic at $T_N = 10$ K. In the case of CoFe₂O₄ and NiFe₂O₄, the A-site Fe³⁺ ensures that there is a strong antiferromagnetic 135° A-O-B superexchange which determines the collinear Néel state [173].

The magnetisation seen in the NiFe₂O₄ thin films grown on SrRuO₃ approaches that of

the bulk value of $\approx 330 \text{ kA m}^{-1}$, indicating that there are likely no antiphase boundaries present in the film. The low roughness of the layers makes them compatible with thin tunnel barrier structures as implemented in chapter 6.

4.4 Conclusions

The main conclusion from the experimental work on CoFe_2O_4 is that the magnetism of thin films is highly dependent on oxygen pressure, temperature and substrate strain during deposition. At high oxygen pressures ($> 1 \times 10^{-3} \text{ }\mu\text{bar}$), low laser fluence ($< 2.7 \text{ J cm}^{-2}$) and temperatures either higher or lower than around 600°C , there is a significant reduction of moment. The high in-plane compressive strain of the MgAl_2O_4 and LSAT substrates was found to induce a huge in-plane anisotropy, and the tensile strain imposed by MgO induces a perpendicular anisotropy. In the case of NiFe_2O_4 , thin films can be successfully grown on SrRuO_3 layers retaining good magnetisation and crystal quality with low surface roughness, making it ideal for incorporation into a device structure.

The most plausible explanation for the reduction of moment in the CoFe_2O_4 films is in the Co spin state. In the bulk, Co^{2+} is in the high spin state which is stabilised by the trigonal crystal field at the distorted octahedral sites. The sites have $\bar{3}m$ symmetry due to the deviation of the O 32e site from the special position u from $3/8$ in the normal spinel structure. Strain due to the substrate could conceivably switch the Co^{2+} to a low spin state, $3d^7 t_{2g}^6 e_g^1$ which would give a spin $S = \frac{1}{2}$ and a spin moment of $1 \mu_B$. If there is some mixture of this phase with the high spin phase, magnetisations within the range $130 - 455 \text{ kA m}^{-1}$ are theoretically possible. Another possibility is that the normal spinel configuration is present, with Co^{3+} in the low spin $3d^6 t_{2g}^6$ arrangement giving $S = 0$. The net moment in this case is reduced to $1 \mu_B$ [174] and the Co^{3+} would sit on the octahedral B-sites.

Based on the experimental work presented here, $NiFe_2O_4$ presents a better option the purposes of building devices based on the spin filtering effects of the spinel ferrites. This is because it is less sensitive to the strain imposed by the substrate and exhibits good magnetic properties when grown on the perovskite $SrRuO_3$.

Chapter 5

NiO: An Antiferromagnetic Oxide as a Test Case for RIXS in Thin Films

5.0.1 Antiferromagnetism in NiO

Nickel oxide (NiO) constitutes a prototypical face-centered cubic (fcc) antiferromagnet, where Ni spins are coupled via the oxygen atoms by superexchange interactions and adopt a type-II spin arrangement for $T < T_N$. It crystallises in the rock-salt structure with a cubic lattice parameter of 417.5 pm, obtained from Rietveld analysis (see figure 5.3). The Ni^{2+} ions have a ground state $3d^8$ configuration with ${}^3A_{2g}$ symmetry and high-spin state due to the octahedral crystal field and electron-electron interactions, with two unpaired electrons giving a spin of $S = 1$. The magnetic configuration of NiO is determined by the exchange interactions of the nearest and next-nearest neighbour exchange interactions J and J' , the ferromagnetic 90° Ni-O-Ni and stronger antiferromagnetic 180° Ni-O-Ni superexchange interactions respectively. The Ni^{2+} coordination, spin structure and exchange interactions are shown schematically in figure 5.1. The antiferromagnetic structure of NiO was determined in the 50's experimentally [175, 176] and 70's theoretically [177]. Among all antiferromagnetic transition metal monoxides, NiO has the highest value of T_N (523 K). As a consequence, NiO could play a crucial role in addressing the challenge of increasing storage density in magnetic recording media by enabling magnetic stability at very low volumes far above room temperature. The spin structure consists of spins parallel to the $\langle 11\bar{2} \rangle$ in the (111) planes alternating along the $[111]$ direction. Without magnetic annealing, there are 24 equivalent domains, which consist of four twin domains for the $\langle 111 \rangle$ directions, three

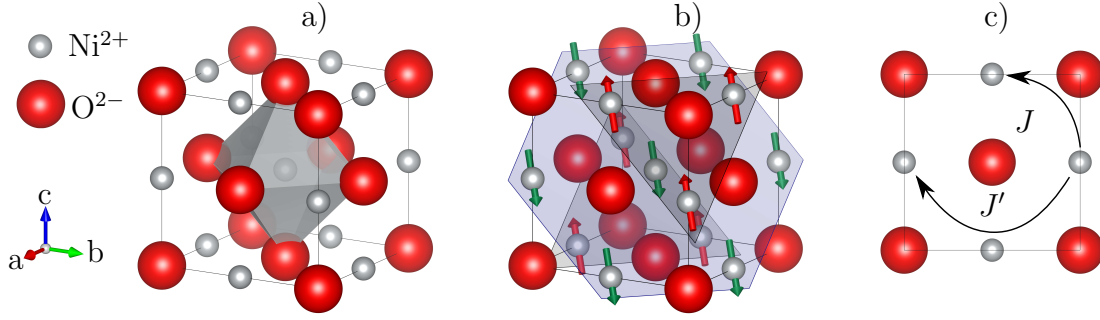


Figure 5.1: The structure of NiO showing (a) the octahedral O coordination of the Ni site, (b) the spin structure consisting of alternating anti-parallel $\langle 11\bar{2} \rangle$ oriented spins along the (111) direction and (c) the exchange between Ni ions in the (100) plane.

for the equivalent $\langle 11\bar{2} \rangle$ easy axes, and two equivalent spin directions along each of these.

NiO was used for exchange bias in early spin valve GMR structures [178, 179], but at room temperature the bias fields were quite low, possibly due to the absence of delocalised electrons, which increase the exchange bias interaction. Recently, thin films of NiO on SrTiO₃ have been shown to have ferromagnetic dislocations with high coercivities, which could have applications in the fabrication of nanoscale magnets [180]. There has been little work to determine how well the bulk antiferromagnetic properties of NiO are maintained in thin film form, as until now there are no methods of determining the exchange constants J and J' experimentally in thin films.

5.0.2 Motivation

The motivation for examining the properties of the insulating antiferromagnetic oxide NiO is rooted not only in finding suitable candidates for functional layers in oxide spintronic devices, but also because they present good model systems as proving grounds for novel instrumentation techniques. NiO is a very well understood type-II antiferromagnet which has been widely characterised. One of the motivations for this work was to show the capacity of the RIXS at ID32 in ESRF to map magnon dispersions in thin films, which has only reliably been done in bulk NiO by RIXS and INS prior to

this. It is also interesting to see how the behaviour of magnons compares between bulk and thin film NiO. The second reason to study thin films of NiO is motivated by the potential application of NiO as an exchange bias layer in all oxide spintronic device, although that remains a motivation for further work, and is not explored in this thesis.

5.1 Experimental Results

The structural and magnetic measurements of NiO thin films are presented here. XRD and RHEED demonstrate the high quality epitaxy that was achieved. RIXS showing the magnon dispersions along the [101] direction are shown, along with simulations and analysis performed in collaboration Dr. Davide Betto at ESRF.

5.1.1 Structure and Morphology

In this section, XRD patterns of the thin films of NiO are presented, along with Rietveld analysis of the XRD pattern of the PLD target used to grow the films. RHEED analysis of the initial growth of the films is also presented in order to understand the strain relaxation length scales.

5.1.1.1 NiO

The films of NiO deposited on MgO were highly oriented and fully strained, as can be seen in the XRD pattern in figure 5.2. The XRD scan was performed after post-annealing the NiO films in-field in ambient conditions, which is described in section 2.1.3.3.

The perpendicular lattice parameter of NiO is found to be 415.8 pm, which is less than the bulk value of 417.5 pm obtained by Rietveld analysis of the diffraction pattern of the target used in growing the film, shown in figure 5.3 which is intermediate between the reported values of 416.8 pm [181] and 418 pm [182].

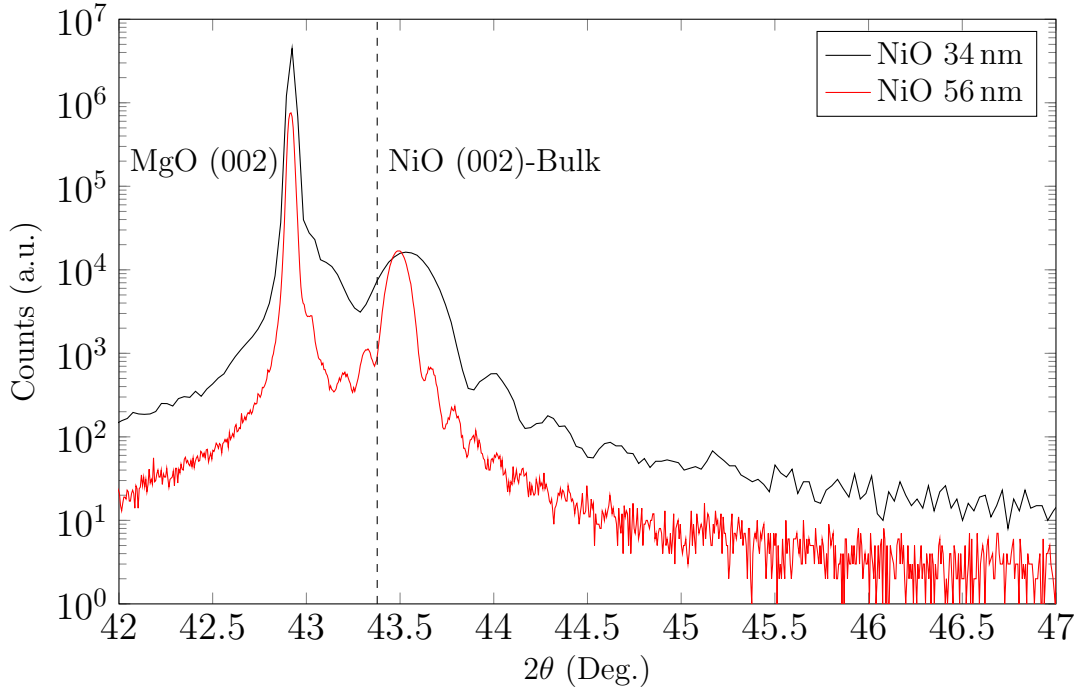


Figure 5.2: X-ray diffraction patterns from thin films of NiO grown to different thicknesses on MgO substrates. Kiessig fringes and a small linewidth in the thicker film indicates that there is ideal single crystal epitaxy in the films. The slight deviation from the bulk NiO peak position indicates that there is some strain in the film.

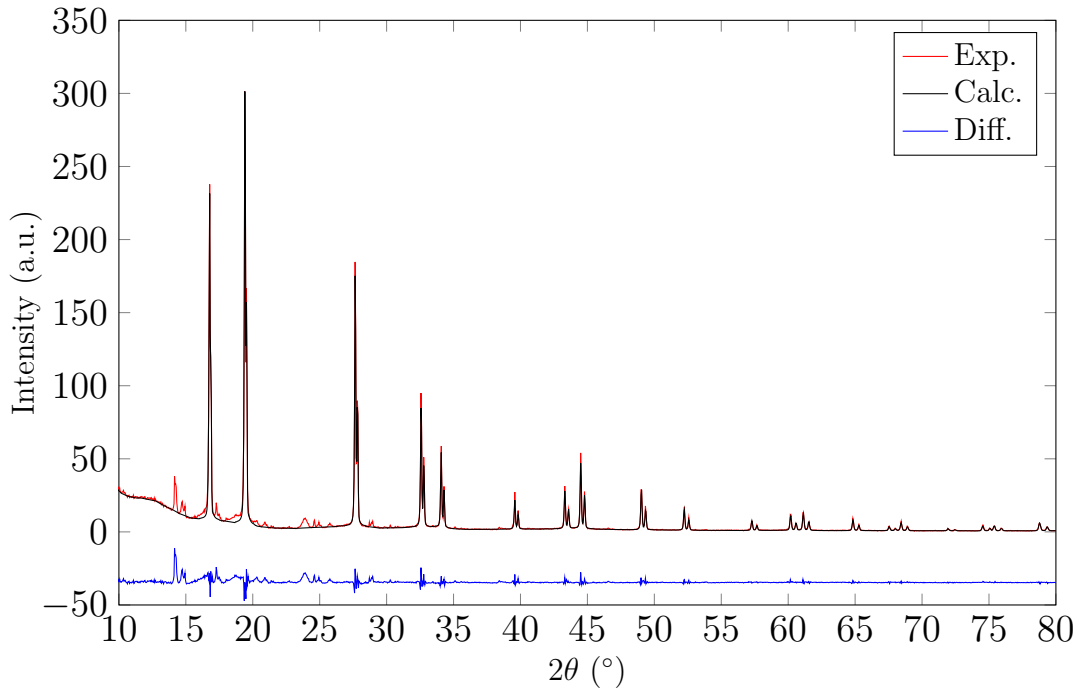


Figure 5.3: Rietveld fitting of the powder diffraction pattern of the NiO target used in the growth of thin films. The presence of peaks at low angles ($< 15^\circ$) corresponding to a spacing of 280 pm could be attributed to a small secondary phase of NiO_2 (space group $C12/m1$, $d_{(010)} = 281 \text{ pm}$) [183].

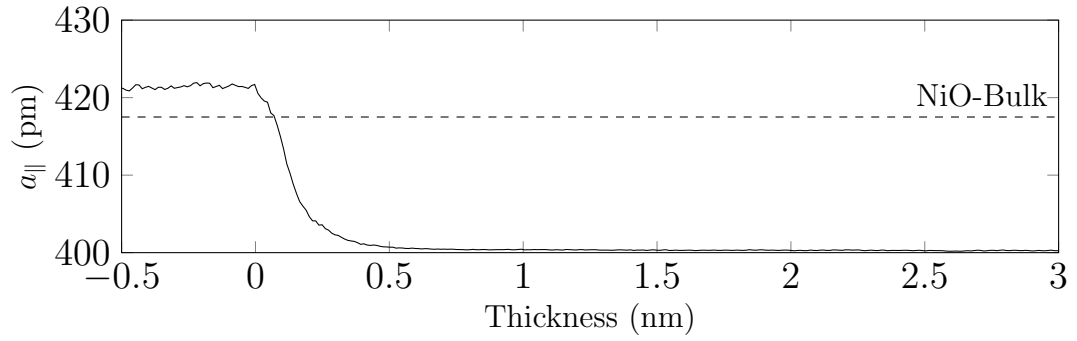


Figure 5.4: Evolution of $a_{\parallel}$ in NiO thin films during growth deduced from RHEED spot separation.

The lattice parameter of the MgO substrate is 421.1 pm, which in the case of perfect epitaxy corresponds to a tensile misfit strain of 0.85 % and would lead to $a_{\perp} = 410.4$ pm by volume conservation. It is therefore deduced that the strain is relaxed to some equilibrium in the first few layers of the film. This is supported by the evolution of the in-plane lattice parameter obtained from analysis of the peak positions of the RHEED diffraction during growth. The film appears to reach an equilibrium spacing by about 0.8 nm in thickness. The absolute value of the lattice spacing is calibrated to the substrate before deposition, but is highly sensitive to errors in the peak position caused by other effects such as Kikuchi lines and diffuse peaks at high oxygen pressure, and should only be taken as indicative of the film reaching equilibrium under deposition conditions when it is constant.

5.1.2 Magnon Dispersions in NiO Thin Films by RIXS

Typical XAS and RIXS spectra of a NiO thin film along the [101] axis is shown in figure 5.5, along with simulated transitions of octahedrally coordinated Ni^{2+} based on multiplet ligand field theory [184], broadened by convolution with Gaussians. The Ni has an effective occupation number of ≈ 8.2 due to charge transfer from the surrounding oxygen and the calculated transitions are the average of values obtained for all equivalent in-plane spin orientations.

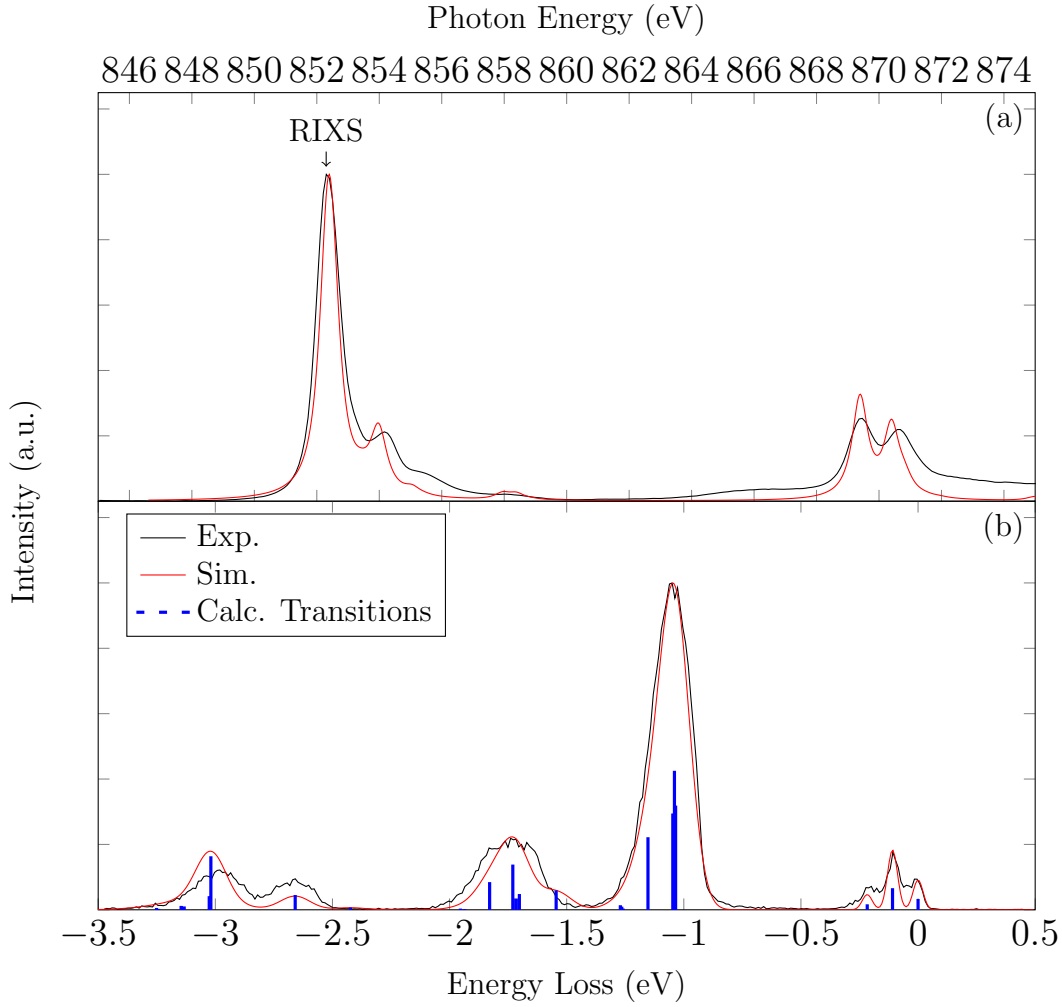


Figure 5.5: Experimental and simulated (a) absorption spectra and (b) RIXS at $Q = 8.3 \text{ nm}^{-1}$ along the $[101]$ direction for NiO thin films. The arrow indicates the energy at which the RIXS experiment was performed. The transitions have been convoluted with Gaussians to match the peak shapes.

The linear dichroic spectra of the films indicated that the films had preferential in-plane orientation of spins, in spite of the magnetic annealing treatment. None of the linear dichroism is thought to come from the charge distribution due to the symmetry of the crystal field, and is attributed to the magnetism through spin orbit coupling (see section 2.3.3.2).

The RIXS spectra as a function of Q along $[111]$ can be seen in figure 5.6 (a). The dd excitations at $-1, -2$ and -3 eV are well resolved, and are in agreement with previous literature [93, 185]. The single magnon peak, close to the elastic peak (relative phonon energy = 0 eV) is visible in figure 5.6 (b), with the double magnon peak at lower

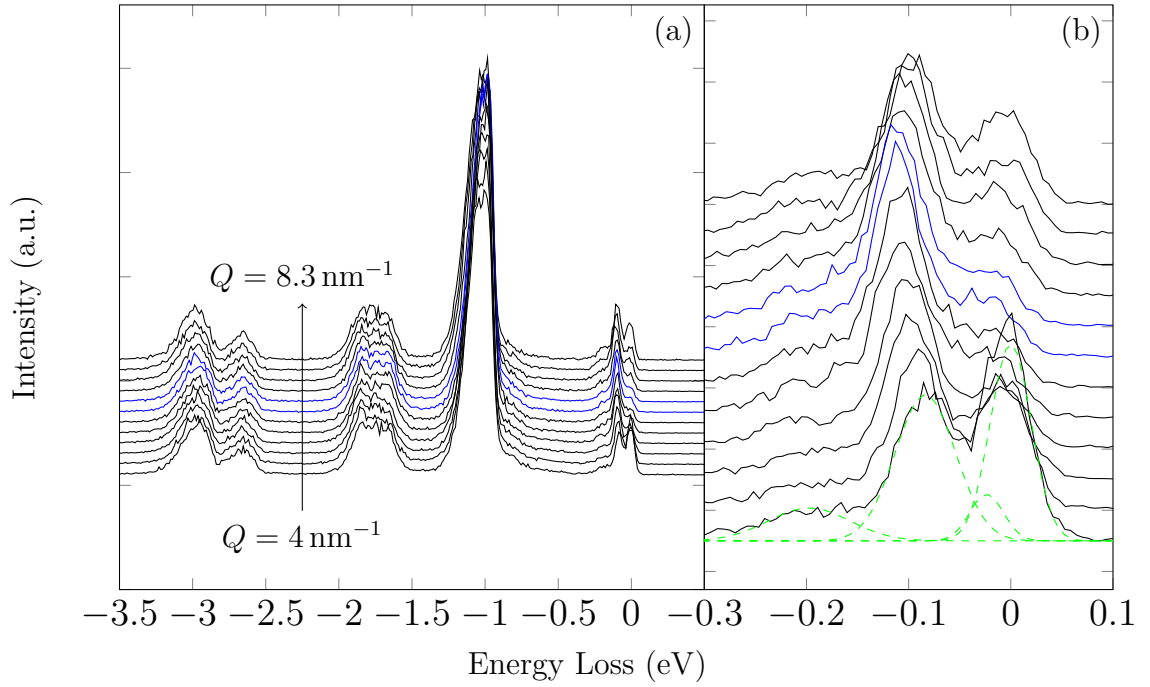


Figure 5.6: RIXS spectra using horizontally polarised X-rays (in the film plane) for a range of Q parallel to $[111]$. The extended relative photon energy is shown in panel (a) and the low energy part of the spectra are shown in (b). Blue spectra correspond to Q vectors at the zone boundary. The Gaussian curves used to find the peak positions are shown in green.

energy just about visible. The Gaussians fitted to the elastic, phonon single and double magnon peaks are marked by the dashed green lines.

From this picture of the inelastic scattering of X-rays, there is a clear dispersion of the single magnons in Q . This can be modelled using linear spin wave dispersion theory [186] as

$$\begin{aligned}
 E^2(Q) &= A^2 - B^2, \\
 A &= 6J' + 2JC_1, \\
 C_1 &= \cos \frac{1}{2}a_0(q_x - q_y) + \cos \frac{1}{2}a_0(q_y - q_z) + \cos \frac{1}{2}a_0(q_z - q_x), \\
 B &= 2J'C_2 + 2JC_3, \\
 C_2 &= \cos a_0q_x + \cos a_0q_y + \cos a_0q_z, \\
 C_3 &= \cos \frac{1}{2}a_0(q_x + q_y) + \cos \frac{1}{2}a_0(q_y + q_z) + \cos \frac{1}{2}a_0(q_z + q_x).
 \end{aligned} \tag{5.1}$$

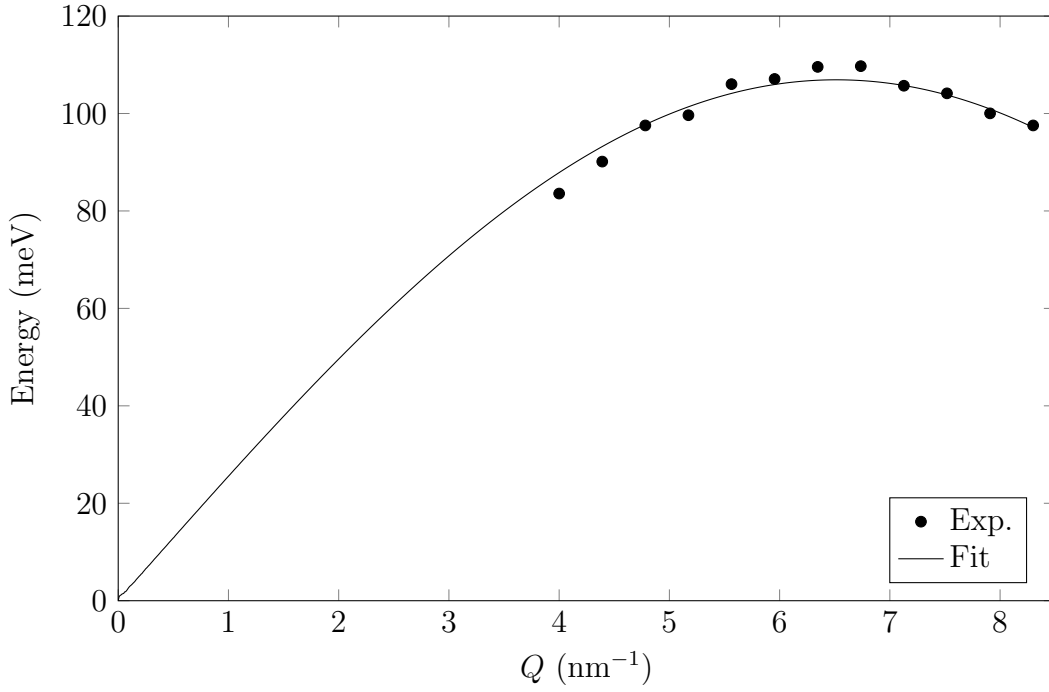


Figure 5.7: Single magnon dispersion along the [111] direction for NiO/MgO. The fit to the curve is obtained by linear spin wave theory, in the form of equation 5.7 [186].

where $a_0 = 417.7$ pm is the lattice parameter for NiO and (q_x, q_y, q_z) are components of the vector Q .

The fit to the experimental data for Q parallel to [111] is shown in figure 5.7. The values for J and J' predicted by this model are 0.4 meV and 17.5 meV respectively. After the least-squares fitting of data obtained for Q parallel to the [100], [101] and [111] directions to the linear spin wave model, the overall value of the next nearest exchange interaction J' was found to be 18.1(4) meV which is lower than that found by INS, 19 meV [186]. The value of J which was obtained after fitting dispersions along all directions is of order 19 meV. The Brillouin zone boundaries of the antiferromagnetic lattice along [001], [101] and [111] are at 7.5 nm^{-1} , 8 nm^{-1} and 6.5 nm^{-1} , respectively [187].

5.2 Discussion and Conclusions

The effort made here to both test the viability of using NiO as a test case for RIXS of thin films, and to provide an estimate of the exchange constants of the antiferromagnetic and ferromagnetic exchange interactions, respectively J' and J , the new capabilities of the beamline ID32 at the ESRF were utilised. An experimental resolution of 40 meV at the Ni L_3 edge was used, compromising between the highest resolution and counting time. The spin wave dispersion in different reciprocal lattice directions in thin-film samples has been precisely mapped, yielding $J' = 18.1(4)$ meV and $J \approx 1$ meV. The disparity between this and the bulk INS values mentioned in the previous section perhaps presents an interesting insight into the effect of the substrate. The misfit strain is of order 0.85 % represents an expansion along the [111] direction of 0.28 %, or about 2 pm. Because of the linear dependence of the transfer integral t on separation, and the t^2 dependence of the superexchange interaction one might expect this increased separation to lead to a reduction of J' by about 0.4 meV from the bulk value, which alone does not account for experimentally observed reduction. It might then be inferred that the reduction more likely comes from the properties of the films themselves, be it defects or the reduced dimensions of the films or a combination of these with the strain effect of the substrate. In summary, the results here present the key to being able to engineer the antiferromagnetism in NiO thin films and reliably quantify the interactions.

Chapter 6

BaTiO₃: Artificial Multiferroicity and Ferroelectric Thin Films

6.1 Introduction and Literature Review

The subject of this chapter is the ferroelectric oxide BaTiO₃ and the incorporation of ferroelectric materials into TMR/TER based devices for either two state memory devices or voltage controlled TMR for non-volatile low power, fast memory devices. I will initially introduce the concept of ferroelectricity in thin films, then give examples of BaTiO₃-based heterostructures in literature and provide a motivation for this work.

6.1.1 Ferroelectricity and Multiferroics

The two most useful properties of the electron from the point of view of devices are its spin ($\uparrow$, $\downarrow$) and its charge ($-e$). The field of electronics is concerned with the charge transport of the electron in the electric field, whereas in magnetism the magnetisation and magnetic fields are of interest. A third technologically significant field is spintronics, which is concerned with the transport of electron angular momentum and is usually manipulated with external magnetic fields or large currents. Another possible way of influencing magnetic properties is through electric fields by coupling ferroelectricity to magnetic order.

Ferroelectricity is named thus because of the similarity of the relationship between the electric polarisation and applied electric field in ferroelectric materials and the relationship between the magnetisation and applied magnetic field in ferromagnetic materials. One observes hysteresis in the polarisation curves of these materials. Electric

polarisation $\vec{P}$ is defined as the electric dipole moment per unit volume

$$\vec{P} = \frac{\delta \vec{p}}{\delta V} = \frac{\vec{p}_{unitcell}}{V_{unitcell}}. \quad (6.1)$$

and if we define the dipole moment $\vec{p} = q \cdot \vec{d}$ where q is the charge in a unit cell and $\vec{d}$ is the displacement vector defining the dipole, we can express the polarisation as

$$\vec{P} = \frac{q \cdot \vec{d}}{V_{unitcell}}. \quad (6.2)$$

Taking the unit vector parallel to the dipole moment $\vec{n}$ as a factor, and normalising the dipole length $|\vec{d}|$ by the parallel unit cell length a_0 ,

$$\vec{P} = \left(\frac{qd}{Aa_0} \right) \cdot \vec{n} \quad (6.3)$$

equation 6.3 gives us the expression of polarisation in terms of charge and area. To measure this property, we consider a capacitor structure such as the one shown in figure 6.1 and take the expression for the magnitude of the polarisation $P = \frac{Q}{A}$. The area A of the electrodes is known, and the charge Q can be calculated from a measured capacitance and an applied voltage, using the equation for capacitance

$$C = \frac{Q}{V}. \quad (6.4)$$

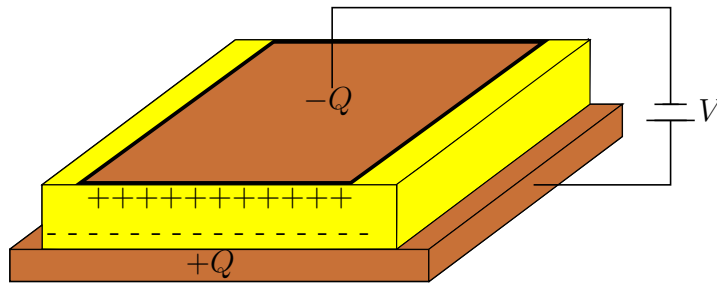


Figure 6.1: Schematic of capacitor structure for ferroelectric polarisation characterisation. The ferroelectric (yellow) is polarised between the two electrodes (amber)

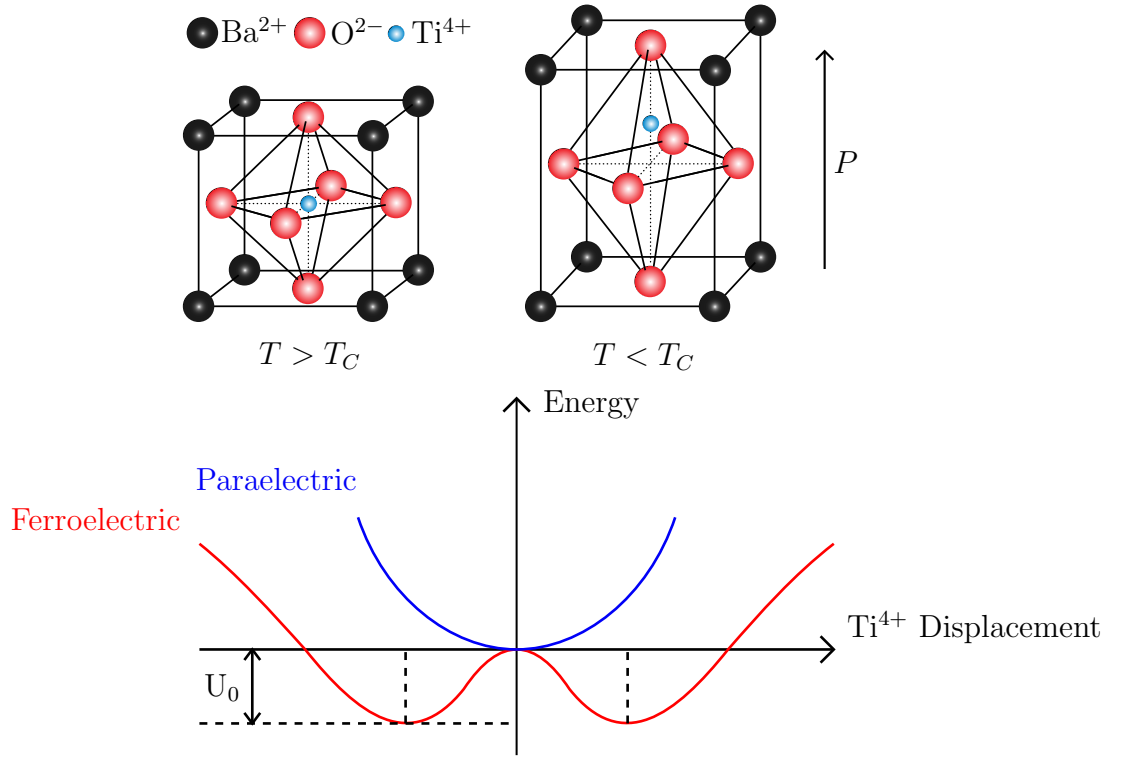


Figure 6.2: Microscopic distortions of the structure of BaTiO_3 and the associated energy diagram [188, 189]

The microscopic picture of polarisation is most easily understood in the example of BaTiO_3 as shown in figure 6.2, which is a tetragonally distorted perovskite below the ferroelectric Curie temperature at around 400 K, above which the structure becomes cubic and the material displays paraelectric behaviour. It can be seen that this distortion can only happen along high symmetry directions, and that this distortion necessarily makes ferroelectric materials piezoelectric.

The origin of macroscopic ferroelectricity was first phenomenologically described in terms of phase transformations after the theory of Landau in 1930 [190]. Landau theory of phase transformations was concerned with order-disorder transformations involving changes in crystal symmetry characterised by an order parameter and was constructed for second order phase transformations which are continuous in entropy at the transition point, but was extended by Devonshire in 1949 [191] to include first order transformations, of which ferroelectric phase transformations are an example. A

ferroelectric phase transformation can be described with polarisation P as the order parameter.

If we consider the thermodynamics of the ferroelectric transformation of cubic paraelectric to tetragonal ferroelectric ($m3m$ to $4/m\bar{m}$ symmetry, a uniaxial polarisation) like in the case of BaTiO_3 , in a stress free crystal, the free energy may be expressed in terms of a Landau potential, $\Delta A_L(P, T)$ and expand the free energy density as a Taylor series in powers of P . This free energy functional is an even function in polarisation, so it consists only of even powers of P :

$$\Delta A_L(P, T) = \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}\gamma P^6 + \dots, \quad (6.5)$$

where α, β and γ are expansion coefficients known as ‘dielectric stiffness’ coefficients, and are Taylor series as a function of temperature T themselves. Conventionally the first coefficient α takes the following form, giving the Curie-Weiss behaviour familiar to us from ferromagnetism:

$$\alpha = \frac{T - T_C}{\epsilon_0 C} \quad (6.6)$$

where T_C and C are the ferroelectric Curie temperature and constant, respectively, and ϵ_0 is the permittivity of free space. Above T_C , the Landau potential has a minimum only at $P = 0$ which corresponds to the cubic (and centrosymmetric) phase, which is paraelectric. Below T_C , there are two minima in the potential with polarisation, corresponding to the stable polarisation states of the non-centrosymmetric ferroelectric phase along the direction of tetragonal distortion [192].

6.1.2 BaTiO_3 in Device Structures

Major bottlenecks to the data-driven information technology sector today are the capacity, power consumption and read/write speeds of non-volatile memory components

in integrated systems. The current generation of commercial hard drives use Ørsted write-fields and tunnelling magnetoresistance (TMR) sensors (discussed in 1.2.1.2) which utilise the switching of stable magnetic states to store data. For high bit rates, such as in random access memory (RAM) complimentary-symmetry metal oxide semiconductor (CMOS) based storage is used for its high switching speed, but it is volatile memory and requires continuous power supply. This is one of the major driving forces behind the research into multiferroics, as researchers seek to combine the stability of magnetic memory with the speed and low energy cost of voltage control achievable in modern integrated circuitry. BaTiO₃ is a purely ferroelectric oxide, as it lacks any unpaired *d* or *f* electrons required for magnetism in transition metal oxides, and so is not intrinsically multiferroic and must be combined with ferro- or ferrimagnetic materials to achieve multiferroic functionality. In the last twenty years, there have been a number of high profile publications on artificial multiferroicity involving BaTiO₃, with two main approaches to the effect, namely strain mediated [193, 194] and electric field (charge) mediated [195–197] magnetoelectric coupling. Notably, many of the papers on magnetoelectric coupling by charge effects deal exclusively with *ab-initio* calculations, as it is notoriously difficult to create the perfect interfaces required, and even more difficult to reliably separate strain and charge effects. One example of an article which attempts to approach the problem using a combination of precise analytical techniques and calculation is the article by S. Valencia *et al.* [198] where the authors observe changes in the spin polarisation at the interfaces of Co/BaTiO₃ and Fe/BaTiO₃ with the ferroelectric polarisation of BaTiO₃ and attribute part of the magnetic moment to an induced spin on the Ti⁴⁺ site to a depth of a few unit cells in BaTiO₃. This moment is said to be due to hybridisation between Fe and oxygen atoms in the interfacial FeO layer which is formed naturally in the structure.

This project deals with the proposition that electrically addressable TMR-based storage could be a viable solution for a future generation of RAM, specifically the concept of voltage controlled TMR via artificially multiferroic tunnel barriers. The proposed device should consist of an all-oxide stack as shown in figure 6.3 consisting of a bottom

electrode of conductive SrRuO_3 , a tunnel barrier consisting of insulating ferrimagnetic NiFe_2O_4 and ferroelectric BaTiO_3 layers and a top ferromagnetic electrode of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. The operation of the device relies on the combination of the spin filtering effect (see 1.2.1.3) of NiFe_2O_4 with the ferroelectric effect of BaTiO_3 . Recent theoretical work performed in Stefan Sanvito's group at Trinity College Dublin suggests that the sign of spin filtering through NiFe_2O_4 depends on the energy of tunnelling states and that BaTiO_3 can alter the band alignment of the electrodes and hence alter the energy of these states [199, 200]. It is upon this basis that the project is conceived, though the potential for the device to function as a 4-state memory element based on electrical and magnetic field switching could also be explored.

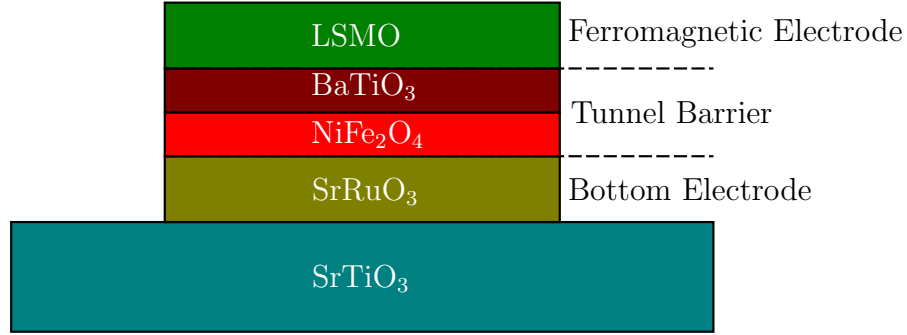


Figure 6.3: Illustration of the cross section of a multiferroic tunnel junction stack

6.1.3 Motivation

The motivation of this project is the demand for high frequency control of magnetic properties in oxides, to make them viable for integration into a future generation of integrated circuit (IC) technology. The realisation of either a stable electrically-writable magnetic bit or a 4-state memory device would be a major step towards this goal. The high polarisation of BaTiO_3 ($P \approx 0.26 \text{ C m}^{-2}$ [201, 202]) makes it a good candidate for interacting by ferroelectric field effects rather than piezoelectric effects, as compared with other piezoelectric ferroelectric materials such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ or $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$, which have high piezoelectric coefficients and may lead to excessive strains which can damage brittle oxide films.

BaTiO₃ is also epitaxially compatible with other perovskite and spinel oxides and has well-defined conditions for the growth of high quality single crystal films. These qualities make it an ideal candidate for interfacial magnetoelectric coupling, as a good control of the interface can be achieved in thin films of BaTiO₃ with other oxide films.

6.2 Experimental Results

In this section, the structural properties of three BaTiO₃ based structures will be discussed. The first is a simple blanket SrRuO₃/BaTiO₃ bilayer on SrTiO₃ (001) used to test the polarisability by EFM and DPFM (sections 2.5.2 and 2.5.3) of BaTiO₃ thin films, the second a trilayer of SrRuO₃/BaTiO₃/LSMO and the third a full multiferroic tunnel junction with a NiFe₂O₄/BaTiO₃ barrier. The ferroelectric polarisation of BaTiO₃ is examined qualitatively and a persistent polarisation and polarisability is shown and finally some transport properties of the multiferroic stack are shown.

6.2.1 Structure and Morphology of Films

As in chapters 3 and 4, the initial structural characterisation used to examine the structures used in this chapter are symmetric XRD scans and XRR, followed by AFM. In this project however, due to the length scales of critical aspects of the structures such as line edge roughness, tunnel barriers and misfit defects, SEM was employed and some TEM work was done by collaborators D. McLaren and K. O'Shea of the University of Glasgow.

6.2.1.1 SrRuO₃/BaTiO₃ Bilayers

The XRD pattern of BaTiO₃ on both SrTiO₃ substrates and SrRuO₃ layers is shown in figure 6.4. The extracted perpendicular lattice parameter from the 19 nm film representing a typical sample grown on SrTiO₃ is 420 pm. This deviation from the bulk tetragonal $a_{\perp} = 403.6$ pm implies that the film is strongly influenced by the substrate lattice parameter $a_{\parallel} = 390.5$ pm, inducing stronger tetragonality. In a film of

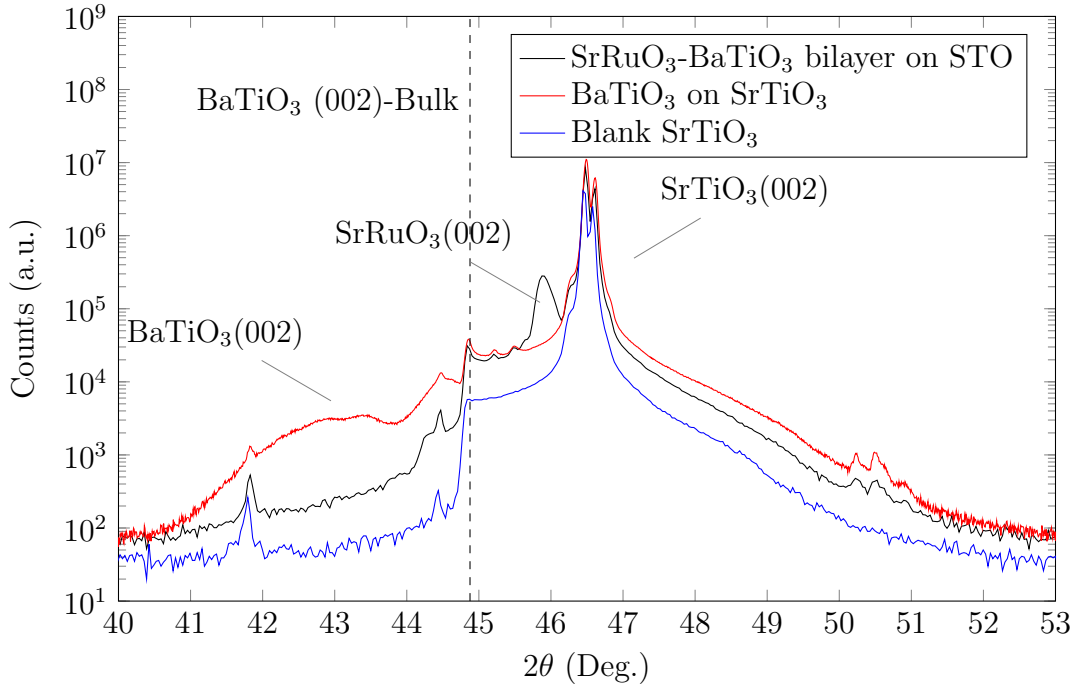


Figure 6.4: XRD pattern of a SrRuO₃/BaTiO₃ bilayer structure on SrTiO₃ (black line). The thickness of the BaTiO₃ layer is about 9 nm, which gives a very broad, low intensity (002) peak. The red line is the XRD pattern of a single 18 nm thick BaTiO₃ layer on SrTiO₃ for comparison.

9 nm thick BaTiO₃ on 63 nm SrRuO₃ the BaTiO₃ peak is not visible due to obscuration by other peaks, when compared to the film grown on blank SrTiO₃, although this film is found to be ferroelectrically polarisable, as discussed in section 6.2.2, indicating that it is of high quality.

6.2.1.2 SrRuO₃/BaTiO₃/LSMO Trilayers

The XRD pattern of a trilayer film of SrRuO₃/BaTiO₃/LSMO, with each layer at an approximate thickness of 20 nm, as measured with a parallelised source is shown in figure 6.5. Three clear peaks at $2\theta \approx 44.5^\circ$, 46° and 47.5° correspond to the (002) peaks of BaTiO₃, SrRuO₃ and LSMO, respectively, and again it is clear that the BaTiO₃ peak is significantly displaced by strain from the single crystal (002) position of 44.88° , shown by the dotted line in figure 6.4 which happens to coincide with the Cu_{K β} cutoff of the Ni foil filter used.

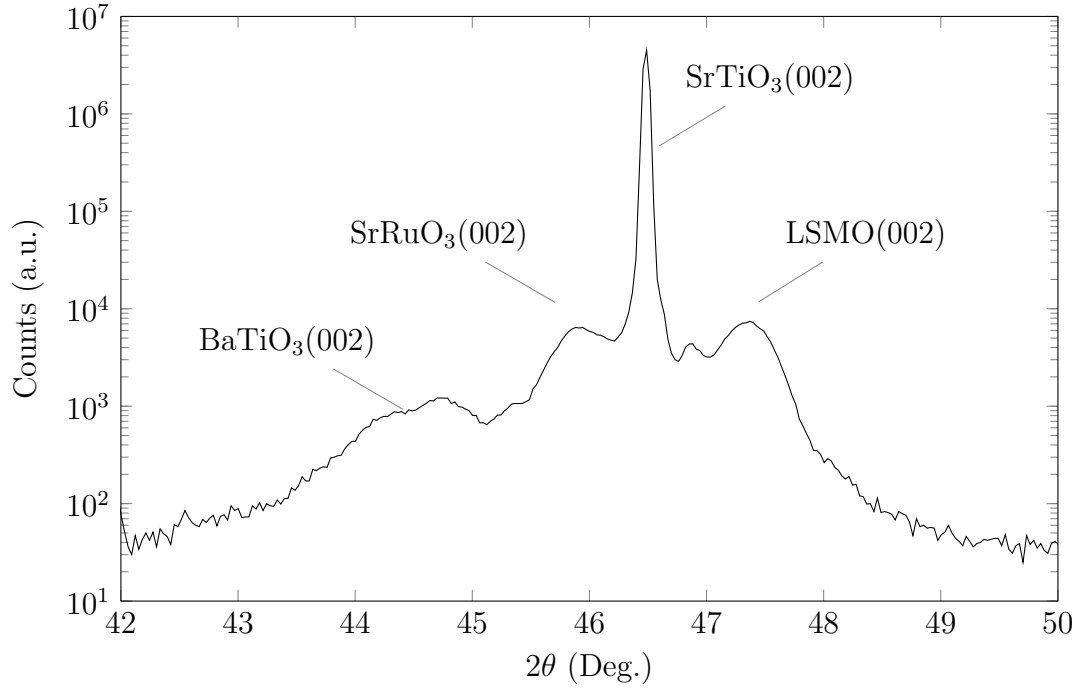


Figure 6.5: XRD pattern of a SrRuO₃/BaTiO₃/LSMO trilayer structure on SrTiO₃.

A number of these films were patterned by UV lithography and Ar-ion etching to form simple capacitor structures with millimeter-sized contacts, but were found to be shorted across the BaTiO₃ layer after patterning. SEM was used to examine the edges of the structure to determine the quality of the pattern in three different samples. As can be seen in figure 6.6, the lines of the pattern are not well defined, and in some cases there is a large amount of pitting. The images (a) and (b) from this figure are from the same sample, and a horizontal region of persistent charging can be seen, where a linear scan to adjust contrast and brightness was performed. This indicates that there is potentially large regions of the sample where there is no path for charge to compensate across the ferroelectric layer. Comparing the images (c) and (d) indicates that there may be some conditions which give more desirable results in terms of morphology, as the pitting in (d) is significantly reduced from that of (c). Unfortunately, an ideal etching condition could not be reached during the course of this experiment.

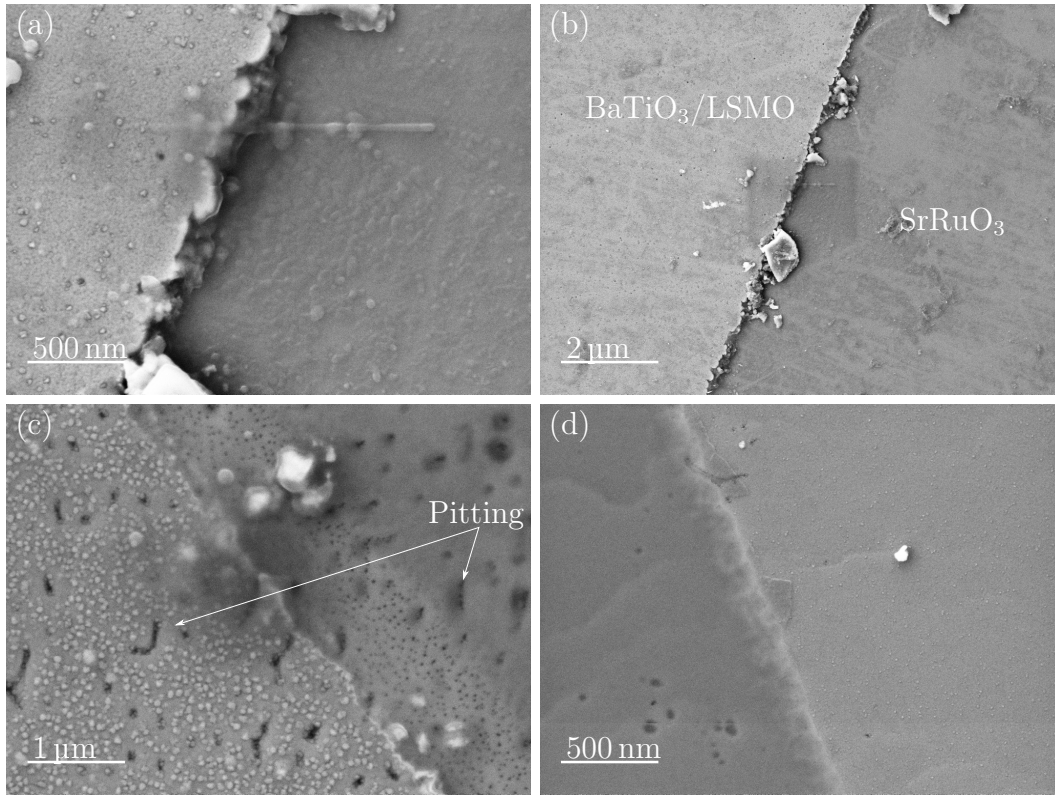


Figure 6.6: SEM images of the surface of a representative set of trilayer samples after ion milling to make it possible to address the bottom SrRuO₃ layer. The horizontal line in (a) and (b) is due to charging from the electron beam during a linescan to adjust contrast and brightness.

6.2.1.3 SrRuO₃/NiFe₂O₄/BaTiO₃/LSMO Stacks

A cross-sectional TEM image of the full device stack is shown in figure 6.7, although for the purposes of clearly showing the quality of the epitaxy of the barrier layers, this particular sample used a total barrier thickness of 10 nm whereas the thickness used for tunnelling devices was around 3 nm. The SrTiO₃/SrRuO₃ interface is sharp with some in-plane defects arising from steps on the substrate surface, but ultimately is of high quality. The interface of the 30 nm SrRuO₃ film with NiFe₂O₄ is also quite sharp, although there are a small number of misfit dislocations within the field of view at this interface, as well as at the interface with BaTiO₃, and there is also some mosaicity visible in the BaTiO₃ film. The crystallinity is recovered to a large extent in the 50 nm LSMO film, although there is a surface roughness of about 2 nm at the top surface of

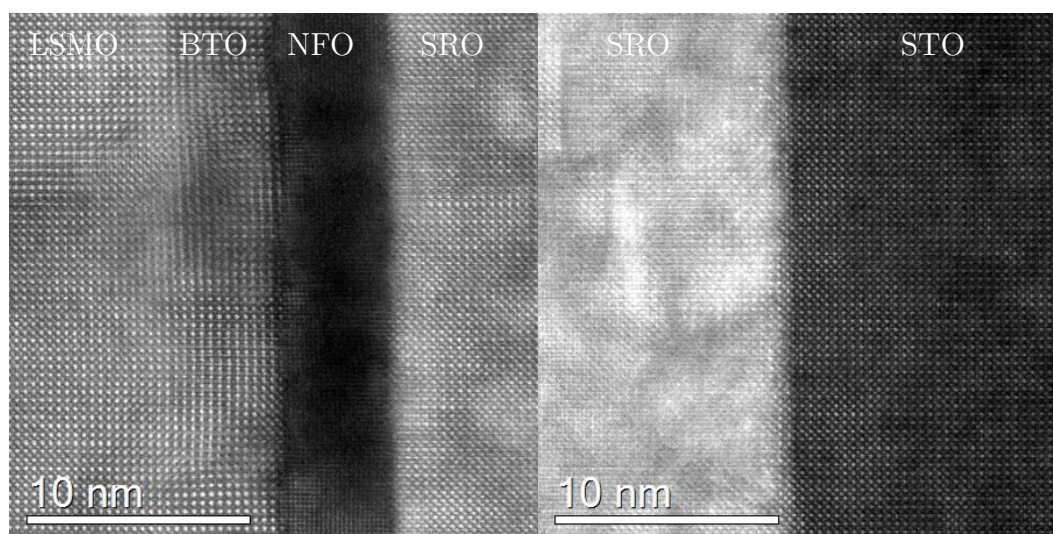


Figure 6.7: Cross sectional TEM images of the full stack and the interface of SrRuO₃ with the substrate.

the film, indicating that there may have been a transition to island growth from the nominally layer-by-layer growth indicated by RHEED.

6.2.2 Electrostatic Force Microscopy of SrRuO₃/BaTiO₃ Bilayers

The EFM images taken before and after polarisation of the 9 nm thick BaTiO₃ on a 63 nm thick SrRuO₃ electrode layer is shown in figure 6.8. The voltage applied between the AFM tip and the SrRuO₃ to switch the layer is 25 V, which corresponds to a maximum applied electric field of about 140 kV cm⁻¹. This is likely not a good estimate of the coercive electric field however, as the cantilever was likely deflected by the large electrostatic forces acting on it. The image of the polarised region supports this, in that there appears to be many more artefacts after the polarisation event, possibly due to damage to the tip. The EFM image shows that there is a persistent stable electrostatically charged region at the surface of the BaTiO₃ film after the application of an electric field. The shape of the polarised region in the EFM heightmap image is likely determined by a number of factors, primarily the shape of the tip and the distribution of electric field intensity between the tip and the electrostatic charge image created within

the conductive SrRuO₃ layer beneath the BaTiO₃ film. The PID feedback controls of the AFM apparatus attempt to follow lines of constant force between the tip and sample during each pass of the tip, and thus reflect inhomogeneity of the electrostatic repulsion forces within the polarised region.

6.2.3 Direct Piezo Force Microscopy of BaTiO₃ Films

The polarised surface of BaTiO₃ on SrRuO₃ electrode in an identical sample to that shown in figure 6.8 is shown in figure 6.9, contrasting the signals obtained with and without gain on the PID feedback loop used to correct the sample height in normal contact mode AFM operation. In figure 6.9 (f) the voltage generated by the acoustic vibrations of the tip as a result of the sample piezoelectricity can be seen. As it traces out the polarised region, it can be inferred that the polarised region is indeed piezoelectric. The effect of PID feedback in this case is to drown out most of the DPFM signal, as seen in figure 6.9 (c).

6.2.4 Transport in Patterned Devices

Repeated cycling of the room temperature I - V curve of a full device stack consisting of a SrRuO₃ bottom electrode, a NiFe₂O₄/BaTiO₃ barrier and a LSMO top electrode which has been patterned with $2 \times 2 \mu\text{m}$ junctions is shown in figure 6.10. In this sample the barrier layer consisted of 1.6 nm thick NiFe₂O₄ and 2 nm thick BaTiO₃, corresponding to two unit and five unit cells respectively. A clear hysteretic effect can be seen, indicating that there is perhaps a TER effect switching the structure between high and low resistance states, but it also seems to exhibit a gradual evolution in the low resistance state towards more metallic behaviour. In spite of this, the junction can reliably be returned to a high resistance state repeatedly with the application of a 1 s voltage pulse of 5 V.

The room temperature I - V characteristics of the patterned junction in different resistance states in a second sample with a 1.2 nm thick NiFe₂O₄ and 1.6 nm thick BaTiO₃

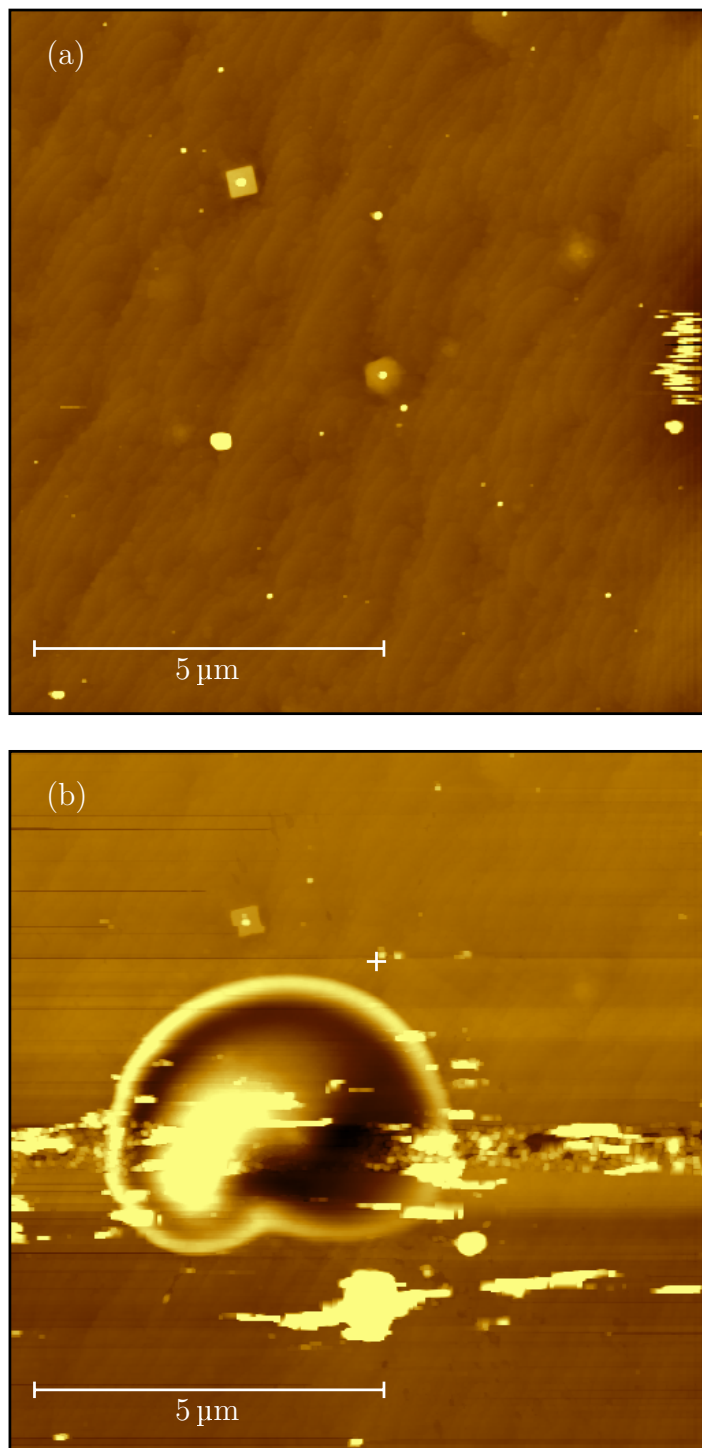


Figure 6.8: Electrostatic force microscopy images of the unpolarised (a) and polarised (b) BaTiO₃ surface.

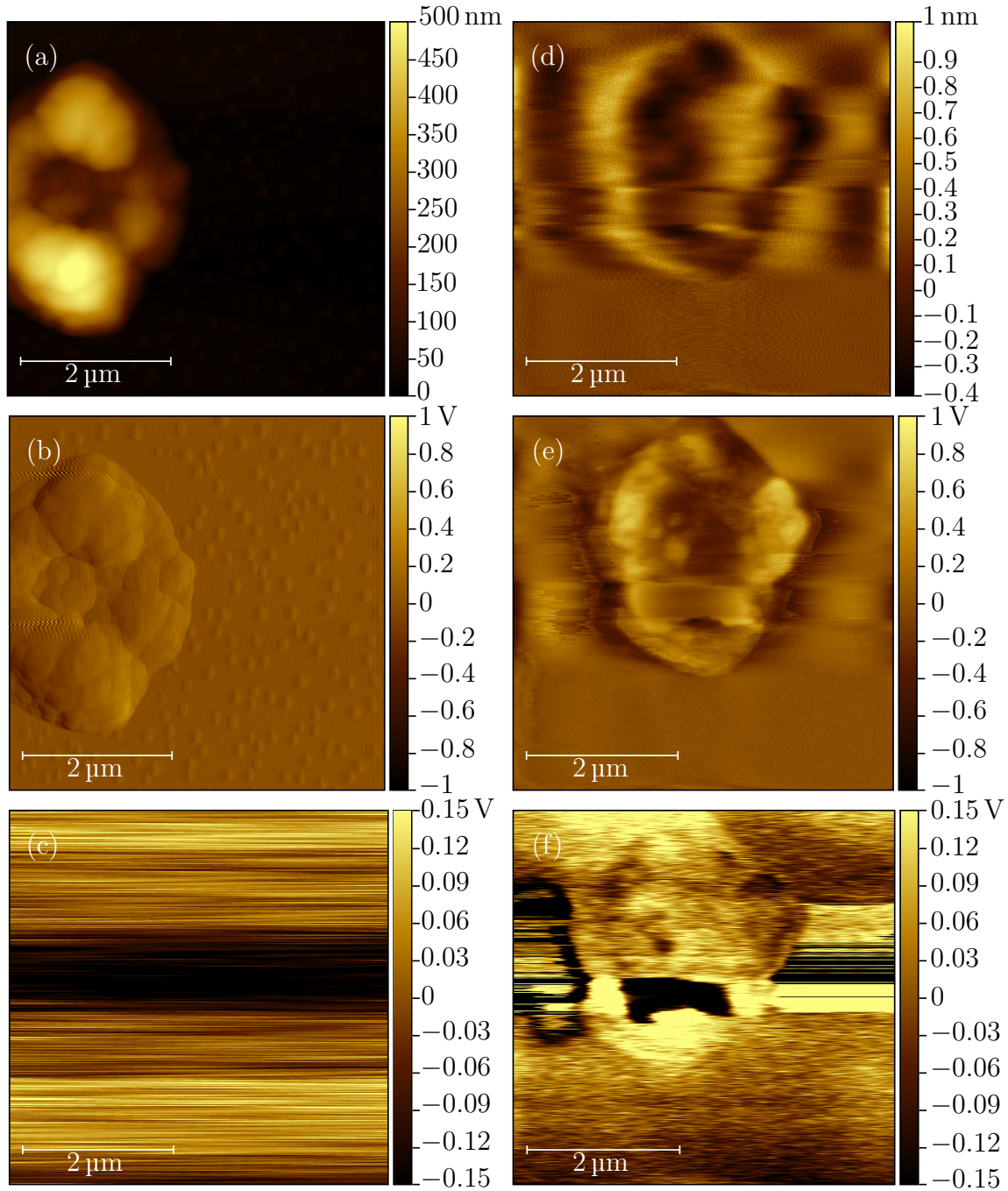


Figure 6.9: Direct piezo force microscopy images of the polarised $BaTiO_3$ surface for a $SrRuO_3/BaTiO_3$ bilayer on $SrTiO_3$. The images show the polarised region with (a,b,c) and without (d,e,f) PID feedback gain. The height-maps (a,d), deflection of the tip as detected by the AFM diode (b,e) and the piezo-response of the film (c,f) are shown.

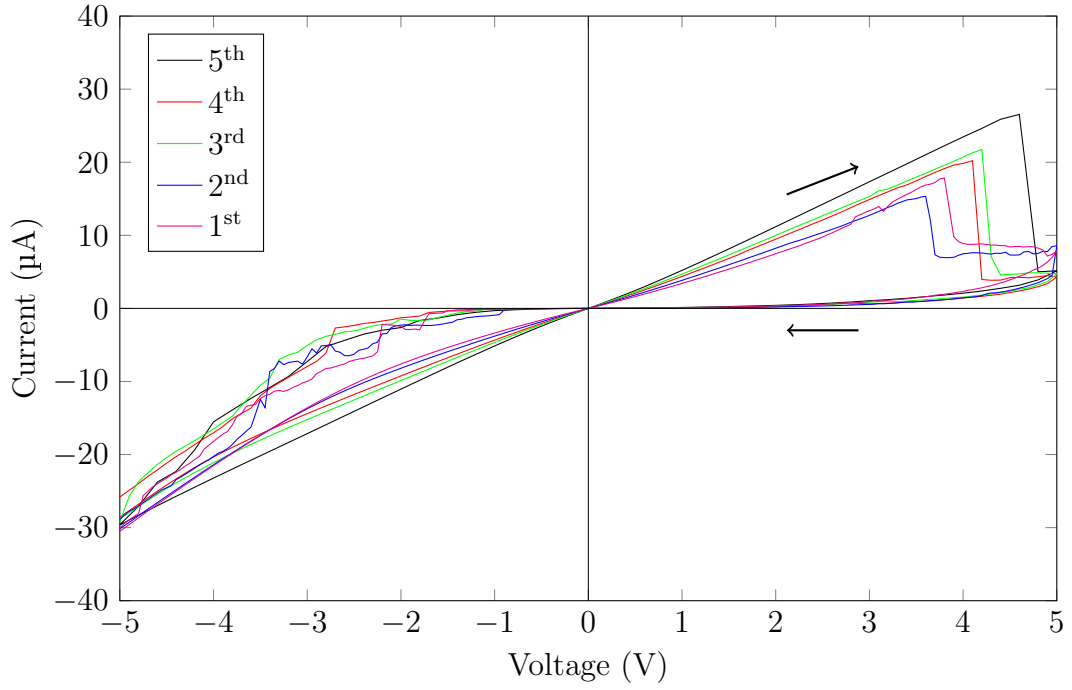


Figure 6.10: *I-V* characteristic of one of the patterned device stacks with a SrTiO₃ bottom electrode, NiFe₂O₄/BaTiO₃ barrier, and a LSMO top electrode on SrTiO₃ showing the evolution of resistance with repeated cycling.

barrier are shown in figure 6.11. To switch between states, a voltage step was applied to the junction in order to polarise the barrier. Two different voltages of 2 V and 6 V are shown in figure 6.11 (a) and (b) respectively. Interestingly, the effect of the polarity of the pulse is reversed between the two voltages. Figure 6.11 (c) shows the change in resistance on switching between the two states, which is roughly a factor of two.

6.3 Discussion and Conclusions

The results of this chapter establish that the growth of ferroelectric BaTiO₃, which can be reliably polarised in very thin film form, shown here down to a thickness of 9 nm, has been achieved. EFM and DPFM have been employed to show unambiguous electrostatic interaction in the former and piezoelectric response in the latter. These films are not ultrathin, but do approach the theoretical critical thicknesses of ferroelectricity in some reports prior to this of 2.4 - 5 nm [203, 204] although ultrathin ferroelectric

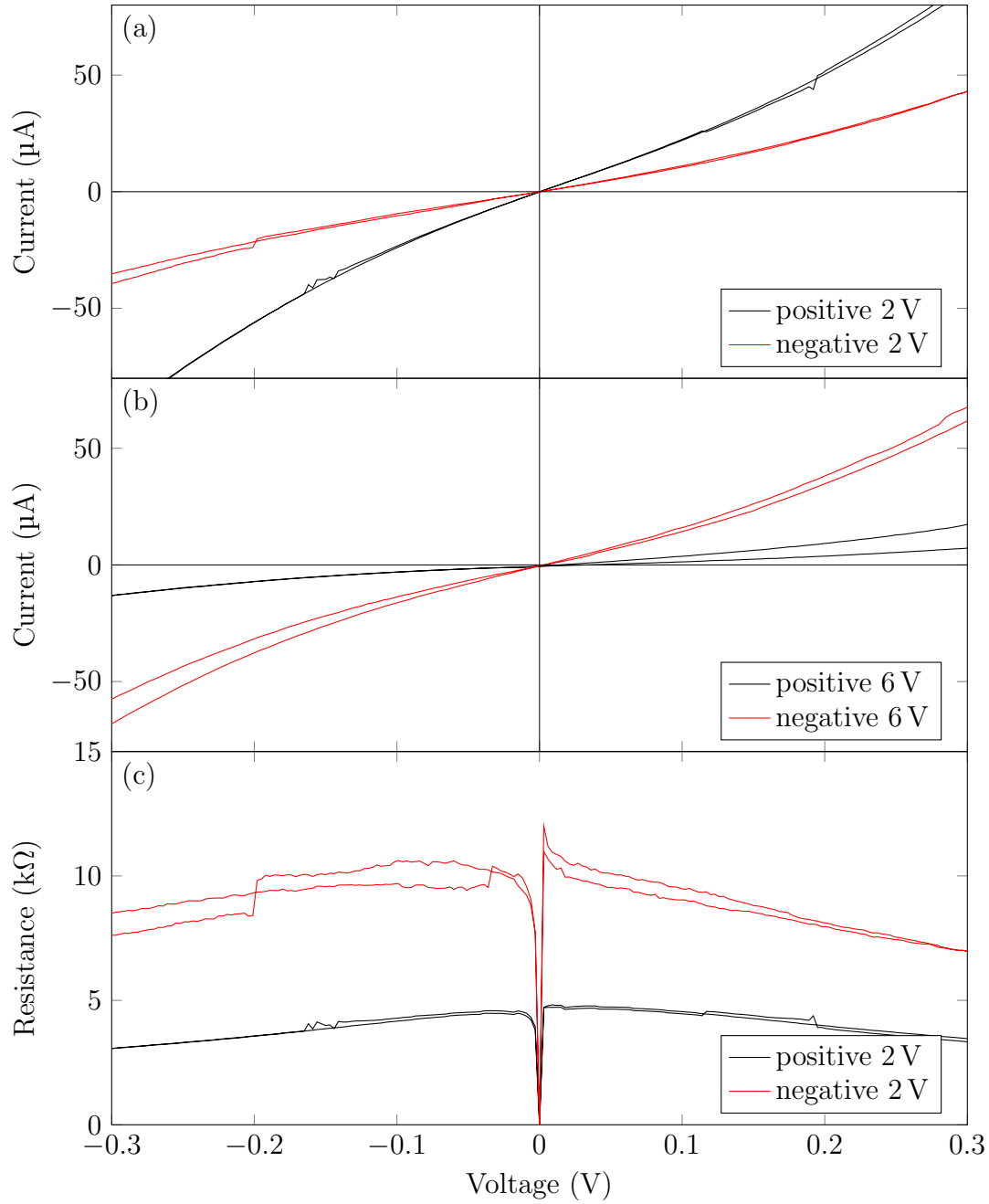


Figure 6.11: I - V characteristic of a patterned junction below the fields required for switching behaviour. There is a large switching voltage pulse ((a) 2 V, (b) 6 V) applied before measuring each curve. The resistance of the two states after the 2 V pulses is shown in panel (c).

BaTiO₃ layers have been shown before [205]. The results of this experiment are encouraging, and provide a basis for experiments on the ferroelectric field effect on magnetic oxides.

The trilayer capacitor structure of section 6.2.1.2 represents an attempt at the fabrication of ferroelectric field effect structure which could be used to observe the effect of polarisation on the presence of the intrinsic dead layer of LSMO. It is certainly conceivable that the process of the formation image charges in the LSMO film to partially compensate the depolarising field in BaTiO₃ (section 1.3.2) could effect the conditions required for the formation of the electronic phase separation (section 3.3). The method for preparing the structures has two main drawbacks which can explain the leakage across the BaTiO₃ layer, the first of which is easily overcome in principle; the Ar-milling process used to etch the oxides here resputters metal ions readily onto the structures being patterned, causing filaments to form between the electrodes. This can be avoided by introducing low-angle etching steps to remove this material, sacrificing only a small amount of the capacitor structure, but this requires the device become more elaborate, where many small junctions should be made so as to have redundancy and not to waste large areas of the blanket film. The second and somewhat more serious drawback is then revealed, as the SrTiO₃ substrates upon which these devices are patterned have a significant increase in their conductivity due to either Ar implantation or reduction of the surface with the liberation of the oxygen. Ideally, a reactive ion-etching recipe which is selective to particular layers would be used, such as the BCl₃ etch which has been used by collaborators from Paul Scherrer Institut (PSI) in Switzerland to pattern the device structures measured in section 6.2.4. Another method which could be utilised to etch is by a wet chemical processes, and this represents a potential route to the elimination of these drawbacks in future work.

The main result of this chapter is the electrical characterisation of fully integrated artificial multiferroic heterostructures. The structure of the heterostructure is that of an asymmetric ferroelectric tunnel junction (FTJ). The physics of electron transport

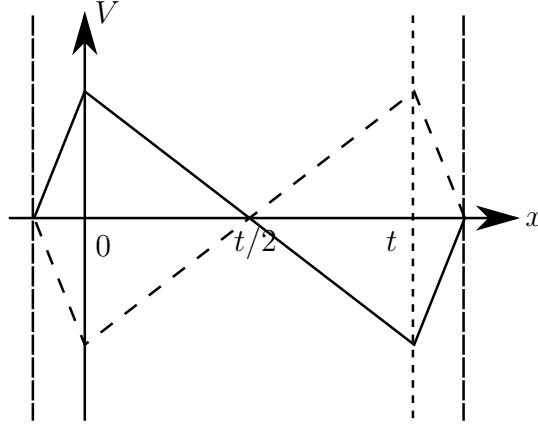


Figure 6.12: Potential profiles of the two possible polarisation states within the symmetric FTJ barrier of thickness t where x is the axis of electron propagation. Adapted from [206].

through the FTJ is described in the work of H. Kohlstedt *et al.* [206]. The description of the asymmetric junction in this work is well suited to the structure presented here. The profile of the ‘zigzag’ potential barrier in a symmetric ferroelectric junction is shown in figure 6.12. In this configuration, the depolarising field of the ferroelectric is screened symmetrically by the image charges induced in the electrodes, so that the average barrier height in either polarisation state is the same. Any change in tunnelling I - V curves is then due to piezoelectric effects, such as changes in the electron effective mass in the direction of the induced strain, changes in the conduction band edge effecting the electron wavenumber along the strain direction, and changes in the barrier thickness ($t = t_0 + d_{33}^* V$, where d_{33}^* is the effective piezoelectric coefficient along the direction of the applied voltage V). These effects give rise to changes in current density J (A m^{-2}) proportional to the second order in voltage V .

In an asymmetric junction, however, the profile of the potential barrier is not symmetric due to the different ability of the electrodes to screen the depolarising charges of the ferroelectric layer. In the simplest model provided by Kohlstedt, one electrode perfectly screens the depolarising charge of the ferroelectric and the other has a screening charge shifted from the ferroelectric by Δt , the potential profile is then approximated by that shown in figure 6.13. There are now two stable average barrier heights, $\bar{\phi}_1$ and $\bar{\phi}_2$ where $\Delta\bar{\phi} = \bar{\phi}_1 - \bar{\phi}_2$. The change in barrier height is approximated by

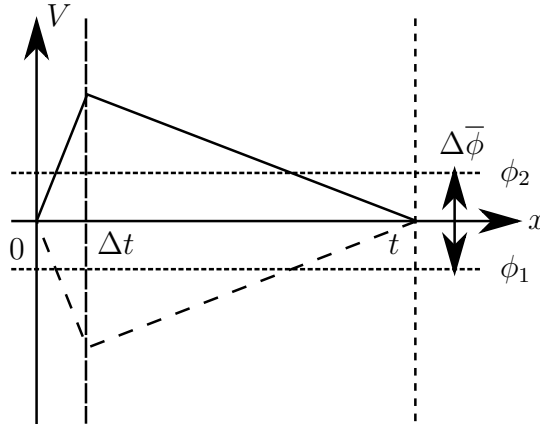


Figure 6.13: Potential profiles of the two possible polarisation states within the shorted asymmetric FTJ barrier with one electrode perfectly screening the depolarisation charge. Adapted from [206].

$$2\Delta\bar{\phi} \approx \frac{e|P_s|(t - \Delta t)}{[c_i(t - \Delta t) - \epsilon_0\epsilon_f]} \quad (6.7)$$

Where e is the electron charge, P_s is the saturation polarisation, ϵ_f is the dielectric constant of the ferroelectric and c_i is the interfacial capacitance (in units of F m^{-2}) [207], given by

$$c_i = \frac{\epsilon_0\sqrt{\epsilon_m}}{2\lambda_{TF}}. \quad (6.8)$$

The Thomas-Fermi screening length in LSMO is approximately $\lambda_{TF} = 0.2 \text{ nm}$ [40] and the dielectric constant is about $\epsilon_m = 4$ [208], giving $c_i = 44 \text{ mF m}^{-2}$. Using this value, and assuming $\epsilon_f \leq 300$, $\Delta t \ll t$ and $P_s = 0.26 \text{ C m}^{-2}$ gives a value of $\Delta\bar{\phi} \approx 80 \text{ meV}$ for a $\text{SrRuO}_3/\text{BaTiO}_3/\text{LSMO}$ junction with a 1.6 nm thick barrier. The presence of a 1.2 nm thick NiFe_2O_4 layer within the barrier further complicates the situation by increasing the asymmetry of the structure, but if the NiFe_2O_4 is taken into account as merely adding to the full barrier thickness, assuming the potential is roughly constant in the layer, then a change in barrier height of $\Delta\bar{\phi} \approx 150 \text{ meV}$ is obtained. Using the expression for the ratio of resistances in the high and low barrier states at low voltage derived from J. Simmons work [209] by Kohlstedt and given by

$$\frac{R_H}{R_L} = \frac{[4\pi t_0(2m_x^{*0})^{\frac{1}{2}}(\phi_0 - \Delta\bar{\phi})^{\frac{1}{2}} + h] \exp\left[-\frac{4\pi}{h}t_0(2m_x^{*0})^{\frac{1}{2}}((\phi_0 - \Delta\bar{\phi})^{\frac{1}{2}})\right]}{[4\pi t_0(2m_x^{*0})^{\frac{1}{2}}(\phi_0 + \Delta\bar{\phi})^{\frac{1}{2}} + h] \exp\left[-\frac{4\pi}{h}t_0(2m_x^{*0})^{\frac{1}{2}}((\phi_0 + \Delta\bar{\phi})^{\frac{1}{2}})\right]} \quad (6.9)$$

where h is Planck's constant and m_x^{0*} is the electron effective mass along the propagation direction, a ratio of 1.77 is obtained for $\Delta\bar{\phi} = 80$ meV and 2.91 for $\Delta\bar{\phi} = 150$ meV. The ratio of the resistances in the tunnel junction shown in figure 6.11 is around 2, indicating that the description of the junction lies somewhere between these models, but the behaviour is qualitatively similar to that of the asymmetric FTJ described in that work.

In conclusion, a ferroelectric tunnel junction has indeed been realised during this work and it only remains to be shown that there is coupling between the magnetic and ferroelectric properties to realise a full artificial multiferroic tunnel junction.

Chapter 7

Conclusions and Outlook

7.1 Conclusions

In this work the structural, magnetic and transport properties of LSMO thin films have been explored. The films were of high quality and displayed the desired bulk like magnetic properties in thick films. Strain induced by the substrate was found to influence the thickness of the interfacial dead layer to a large extent. The nature of the dead layer is found to be antiferromagnetic and it exists at both the free surface and interface, although the exact energetic configuration of the interfacial dead layer may be different from the surface dead layer. It is conceivable that the surface layers of LSMO films can be affected by defects such as oxygen vacancies and adsorbates which adhere to the surface between the sample fabrication and measurement. There was no observed preferential occupation of the $(3z^2 - r^2)$ over the $(x^2 - y^2)$ orbitals in the XLD spectra, which rules out to some extent the theory of orbital reconstruction. The evidence points to the theory of electronic phase separation as a means to explain the existence of the dead layer.

The magnetic anisotropy of CoFe_2O_4 is found to be determined primarily by the substrate induced strain, with both in-plane and out-of-plane orientations of the easy axis obtainable simply by the choice of substrate. Very high anisotropy fields of 14 T are obtained for in-plane orientations of the easy axis. This study shows that under good conditions of growth, CoFe_2O_4 films can reach magnetisations close to the bulk magnetisation of 455 kA m^{-1} on different substrates. This has been shown to be due to the sensitivity of CoFe_2O_4 films to the oxygen pressure during deposition. The most plausible explanation found for this effect in the CoFe_2O_4 films is changes in the Co spin state due to epitaxial strain.

The problem of changing spin states is not present in NiFe_2O_4 , as Ni^{2+} ($3d^8$) does not adopt a low spin state, making it the better choice for device applications such as that envisioned in this work. Its epitaxial compatibility with SrRuO_3 in thin film form, exhibiting low roughness while retaining the desired magnetic properties at low thickness and above room temperature make it ideal for incorporation into the artificial multiferroic structure of chapter 6.

The exchange integrals J and J' have been determined by analysis of the spin-wave dispersions in three dimensions in thin NiO films. The disparity between the bulk INS values and those found here are theorised to be due to strain effects imposed by the substrate during deposition. The results represent the key to being able to engineer the antiferromagnetism in NiO thin films and reliably quantify the interactions by RIXS.

The results of the investigations into the properties of PLD grown ferroelectric BaTiO_3 , show that it can be reliably polarised in thin film form down to a thickness of 9 nm. EFM and DPFM have been employed to show unambiguous electrostatic interaction in the former and piezoelectric response in the latter. The results of this experiment are encouraging, and provide a basis for experiments on the ferroelectric field effect on magnetic oxides. The devices based on BaTiO_3 patterned to form artificially multiferroic tunnel junctions have shown properties that closely match those of theoretical anti-symmetric ferroelectric tunnel junctions. In conclusion, it is believed that a ferroelectric tunnel junction has indeed been realised during this work and that it only remains to be shown that there is coupling between the magnetic and ferroelectric properties to realise a full artificial multiferroic tunnel junction.

In conclusion, and rounding up, this thesis represents advances in the understanding of the properties of five oxides which each have unique barriers to their implementation as components in oxide spintronic devices. The first of these, LSMO, can be incorporated as a magnetic electrode if the strain of the interfaces can be minimised. The evidence which points to the presence of electronic phase separation indicates that there is a large sensitivity of ultrathin films to external perturbations, as there is a competition between

phases. In the ferrites NiFe_2O_4 and CoFe_2O_4 , epitaxial films with optimised magnetic properties have been grown, overcoming the problem of reduced magnetisation and allowing for reliable control of the anisotropy in CoFe_2O_4 by substrate strain. The mapping of spin-wave dispersions in thin NiO films by RIXS has allowed for direct comparisons between bulk and thin film antiferromagnetic exchange constants, and represents a valuable insight into the dynamics of thin film antiferromagnets. Finally, the incorporation of ferroelectric BaTiO_3 into an all oxide tunnel junction represents a first step toward an electronically modulated magnetic tunnel junction.

7.2 Outlook

As mentioned in the previous section, the work here represents an insight into the materials that may well one day be used to build the oxide spintronics devices that will enable the next generation of data storage and sensor technology. However, before that goal is reached, it is worth mentioning a number of future objectives which should be envisaged. The first of these is the minimisation of the LSMO dead layer, and the path to this is clear if one is willing to accommodate the minimisation of strain by engineering the interfaces. In much the same way as LSAT substrates are tailored to minimise the strain effects on YBCO, substrates could also be tailored to do the same for LSMO. Another route to LSMO integration is through gradients in the Sr concentration. A more heavily $\text{Mn}^{3+/4+}$ doped interfacial layer could have the effect of decreasing/increasing the dead layer, although this may be more difficult to achieve than a tailored substrate or ideal buffer layer.

NiO remains an interesting material in it's own right, and is currently undergoing a revival in interest in the context of antiferromagnetic spintronics. The information obtained by the research shown in this thesis will surely play a part in the development of that field from the point of view of understanding the exchange interactions in increasingly complex adaptations of NiO thin films such as heterostructures and doped

films. The application of NiO as an exchange bias layer in all oxide heterostructures should be explored to elucidate the superexchange coupling across layers.

In terms of the ferrimagnets CoFe_2O_4 and NiFe_2O_4 , their applications are tied to those of BaTiO_3 in terms of this work. The contribution to the future of artificial multiferroics stemming from this work should involve measuring the magnetotransport of those devices mentioned in chapter 6, and fabricating similar devices based on $\text{CoFe}_2\text{O}_4/\text{BaTiO}_3$ tunnel junctions. The multiferroic coupling of CoFe_2O_4 and BaTiO_3 may in fact be interesting in terms of the modulation of anisotropy and damping by strain effects, as the work here has shown that CoFe_2O_4 has a colossal magnetoelastic coupling, which is maintained in thin films.

The achievements of this work will lay the foundations for adaptations of the materials described within, and are a significant contribution to the progress of oxide electronics as well as the understanding of some the mechanisms of those oxides.

Bibliography

- [1] J. M. D. Coey, *Magnetism and Magnetic Materials*, vol. 12. Cambridge University Press, 2010.
- [2] W. Thomson, “On the Effects of Magnetisation on the Electric Conductivity of Iron and Nickel,” *Proceedings of the Royal Society of London*, vol. 9, pp. 546–550, Jan. 1856.
- [3] T. R. McGuire and R. I. Potter, “Anisotropic Magnetoresistance,” *IEEE transaction on magnetics*, vol. 11, pp. 1018–1038, 1975.
- [4] M. N. Baibich, J. M. Broto, A. Fert, F. N. Van Dau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich, and J. Chazelas, “Giant magnetoresistance of (001)Fe/(001)Cr magnetic superlattices,” *Physical Review Letters*, vol. 61, pp. 2472–2475, Nov. 1988.
- [5] B. Dieny, V. S. Speriosu, S. S. P. Parkin, B. A. Gurney, D. R. Wilhoit, and D. Mauri, “Giant magnetoresistive in soft ferromagnetic multilayers,” *Physical Review B*, vol. 43, pp. 1297–1300, Jan. 1991.
- [6] M. Müller, M. Luysberg, and C. M. Schneider, “Observation of spin filtering in magnetic insulator contacts to silicon,” *Applied Physics Letters*, vol. 98, no. 14, p. 142503, 2011.
- [7] U. Lüdgers, M. Bibes, K. Bouzehouane, E. Jacquet, J. P. Contour, S. Fusil, J. F. Bobo, J. Fontcuberta, A. Barthélémy, and A. Fert, “Spin filtering through ferrimagnetic NiFe_2O_4 tunnel barriers,” *Applied Physics Letters*, vol. 88, no. 8, pp. 88–91, 2006.
- [8] S. Matzen, J.-B. Moussy, P. Wei, C. Gatel, J. C. Cezar, M. A. Arrio, P. Saintavit, and J. S. Moodera, “Structure, magnetic ordering, and spin filtering efficiency of $\text{NiFe}_2\text{O}_4(111)$ ultrathin films,” *Applied Physics Letters*, vol. 104, p. 182404, May 2014.
- [9] A. V. Ramos, T. S. Santos, G. X. Miao, M. J. Guittet, J. B. Moussy, and J. S. Moodera, “Influence of oxidation on the spin-filtering properties of CoFe_2O_4 and

- the resultant spin polarization,” 2008.
- [10] M. Chapline and S. Wang, “Room-temperature spin filtering in a $\text{CoFe}_2\text{O}_4/\text{MgAl}_2\text{O}_4/\text{Fe}_3\text{O}_4$ magnetic tunnel barrier,” 2006.
- [11] A. V. Ramos, M. J. Guittet, J. B. Moussy, R. Mattana, C. Deranlot, F. Petroff, and C. Gatel, “Room temperature spin filtering in epitaxial cobalt-ferrite tunnel barriers,” *Applied Physics Letters*, vol. 91, no. 12, pp. 2012–2015, 2007.
- [12] S. Matzen, J.-B. Moussy, G. X. Miao, and J. S. Moodera, “Direct evidence of spin filtering across MnFe_2O_4 tunnel barrier by Meservey-Tedrow experiment,” *Physical Review B*, vol. 87, p. 184422, May 2013.
- [13] W. H. Butler, “Tunneling magnetoresistance from a symmetry filtering effect,” *Science and Technology of Advanced Materials*, vol. 9, p. 014106, Apr. 2008.
- [14] H. Y. Hwang, Y. Iwasa, M. Kawasaki, B. Keimer, N. Nagaosa, and Y. Tokura, “Emergent phenomena at oxide interfaces,” *Nature Materials*, vol. 11, pp. 103–113, Jan. 2012.
- [15] W. F. Brown, R. M. Hornreich, and S. Shtrikman, “Upper Bound on the Magnetoelectric Susceptibility,” *Physical Review*, vol. 168, pp. 574–577, Apr. 1968.
- [16] G. T. Rado, J. M. Ferrari, and W. G. Maisch, “Magnetoelectric susceptibility and magnetic symmetry of magnetoelectrically annealed TbPO_4 ,” *Physical Review B*, vol. 29, no. 7, pp. 4041–4048, 1984.
- [17] J. Van Den Boomgaard, A. M. Van Run, and J. Van Suchtelen, “Magnetoelectricity in Piezoelectric—Magnetostrictive Composites,” *Ferroelectrics*, vol. 10, no. 1, pp. 295–298, 1976.
- [18] R. Schelkens, “Ferroelectric and Antiferroelectric Symmetry Groups,” *Physica Status Solidi (B)*, vol. 37, no. 2, pp. 739–743, 1970.
- [19] I. E. Dzyaloshinski, “A thermodynamic theory of “weak” ferromagnetism of antiferromagnetics,” *Journal of Physics and Chemistry of Solids*, vol. 4, pp. 241–255, Jan. 1958.

- [20] T. Moriya, “Anisotropic Superexchange Interaction and Weak Ferromagnetism,” *Physical Review*, vol. 120, pp. 91–98, Oct. 1960.
- [21] G. Dresselhaus, “Spin-Orbit Coupling Effects in Zinc Blende Structures,” *Phys. Rev.*, vol. 100, no. 2, pp. 580–586, 1955.
- [22] E. I. Rashba, “Properties of semiconductors with an extremum loop I. Cyclotron and combinational resonance in a magnetic field perpendicular to the plane of the loop,” *Soviet Physics, Solid State*, 1960.
- [23] E. I. Rashba, “Semiconductors with a loop of extrema,” *Journal of Electron Spectroscopy and Related Phenomena*, vol. 201, pp. 4–5, 2015.
- [24] A. Manchon, H. C. Koo, J. Nitta, S. M. Frolov, and R. A. Duine, “New perspectives for Rashba spin-orbit coupling,” *Nature Materials*, vol. 14, no. 9, pp. 871–882, 2015.
- [25] R. Ramesh and N. A. Spaldin, “Multiferroics: progress and prospects in thin films,” *Nature Materials*, vol. 6, pp. 21–29, Jan. 2007.
- [26] M. Bibes, “Towards a magnetoelectric memory Out of the scalar sand box,” *Nature*, vol. 7, pp. 425–426, June 2008.
- [27] W. C. Röntgen, “Über die durch Bewegung eines im homogenen elektrischen Felde befindlichen Dielektrikums hervorgerufene elektrodynamische Kraft,” *Annalen der Physik*, vol. 271, no. 10, pp. 264–270, 1888.
- [28] H. A. Wilson, “On the Electric Effect of Rotating a Dielectric in a Magnetic Field,” *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 204, pp. 121–137, Jan. 1905.
- [29] P. Curie, “Sur la symétrie dans les phénomènes physiques, symétrie d’un champ électrique et d’un champ magnétique,” *J. Physique*, vol. 3, pp. 393–415, 1894.
- [30] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*. Pergamon Press, Oxford, 1960.
- [31] I. E. Dzyaloshinski, “On the magneto-electrical effect in antiferromagnets,” *Journal of Soviet Physics JETP*, vol. 10, no. 3, pp. 628–629, 1960.

- [32] G. Catalan and J. F. Scott, "Physics and Applications of Bismuth Ferrite," *Advanced Materials*, vol. 21, pp. 2463–2485, June 2009.
- [33] I. Sosnowska, T. Peterlin-Neumaier, and E. Steichele, "Spiral magnetic ordering in bismuth ferrite," *J. Phys. C: Solid State Phys.*, vol. 15, pp. 4835–4846, 1982.
- [34] N. Farag, M. Bobeth, W. Pompe, a. E. Romanov, and J. S. Speck, "Rhombohedral LSMO films - a unique case of ferroelastic domain formation," *Physica Status Solidi (a)*, vol. 202, pp. R44–R46, Mar. 2005.
- [35] C. Jia, T. Wei, C. Jiang, D. Xue, A. Sukhov, and J. Berakdar, "Mechanism of interfacial magnetoelectric coupling in composite multiferroics," *Physical Review B*, vol. 90, p. 054423, Aug. 2014.
- [36] H. Zheng, "Multiferroic BaTiO₃-CoFe₂O₄ Nanostructures," *Science*, vol. 303, pp. 661–663, Jan. 2004.
- [37] S. Picozzi and C. Ederer, "First principles studies of multiferroic materials.," *Journal of physics. Condensed matter : an Institute of Physics journal*, vol. 21, p. 303201, July 2009.
- [38] C. Thiele, K. Dorr, O. Bilani, J. Rodel, and L. Schultz, "Influence of strain on magnetization and magnetoelectric effect in La_{0.7}A_{0.3}MnO₃ / PMN-PT(001) (A = Sr; Ca)," *Physical Review B*, vol. 75, p. 15, Feb. 2006.
- [39] N. Ashcroft and D. Mermin, "Solid State Physics," *Thomson Learning*, p. chap. 22, 1976.
- [40] X. Hong, A. Posadas, and C. H. Ahn, "Examining the screening limit of field effect devices via the metal-insulator transition," *Applied Physics Letters*, vol. 86, no. 14, pp. 1–3, 2005.
- [41] S. Zhang, "Spin-Dependent Surface Screening in Ferromagnets and Magnetic Tunnel Junctions," *Physical Review Letters*, vol. 83, pp. 640–643, July 1999.
- [42] H. M. Smith and A. F. Turner, "Vacuum Deposited Thin Films Using a Ruby Laser," *Applied Optics*, vol. 4, no. 1, p. 147, 1965.

- [43] D. Dijkkamp, T. Venkatesan, X. D. Wu, S. A. Shaheen, N. Jisrawi, Y. H. Min-Lee, W. L. McLean, and M. Croft, "Preparation of Y-Ba-Cu oxide superconductor thin films using pulsed laser evaporation from high T_c bulk material," *Applied Physics Letters*, vol. 51, no. 8, pp. 619–621, 1987.
- [44] B. D. Darwent, "Bond Dissociation Energies in Simple Molecules," 1970.
- [45] M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, "Atomic control of the SrTiO₃ crystal surface," *Science (New York, N.Y.)*, vol. 266, p. 1540, 1994.
- [46] G. Koster, B. L. Kropman, G. J. H. M. Rijnders, D. H. a. Blank, and H. Rogalla, "Quasi-ideal strontium titanate crystal surfaces through formation of strontium hydroxide," *Applied Physics Letters*, vol. 73, no. 20, p. 2920, 1998.
- [47] C. Neugebauer, "Condensation, Nucleation, and Growth of Thin Films," *Handbook of Thin Film Technology*, 1970.
- [48] W. K. Burton, N. Cabrera, and F. C. Frank, "The Growth of Crystals and the Equilibrium Structure of their Surfaces," *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 243, no. 866, pp. 299–358, 1951.
- [49] J.-H. Park, E. Vescovo, H.-J. Kim, C. Kwon, R. Ramesh, and T. Venkatesan, "Magnetic Properties at Surface Boundary of a Half-Metallic Ferromagnet La_{0.7}Sr_{0.3}MnO₃," *Phys. Rev. Lett.*, vol. 81, no. 9, pp. 1953–1956, 1998.
- [50] J. Z. Sun, D. W. Abraham, R. A. Rao, and C. B. Eom, "Thickness-dependent magnetotransport in ultrathin manganite films," *Applied Physics Letters*, vol. 74, no. 20, p. 3017, 1999.
- [51] R. P. Borges, W. Guichard, J. G. Lunney, J. M. D. Coey, and F. Ott, "Magnetic and electric "dead" layers in (La_{0.7}Sr_{0.3})MnO₃ thin films," *Journal of Applied Physics*, vol. 89, no. 7, pp. 3868–3873, 2001.
- [52] A. Tebano, C. Aruta, S. Sanna, P. G. Medaglia, G. Balestrino, A. A. Sidorenko, R. De Renzi, G. Ghiringhelli, L. Braicovich, V. Bisogni, and N. B. Brookes, "Evidence of orbital reconstruction at interfaces in ultrathin La_{0.67}Sr_{0.33}MnO₃

- Films,” *Physical Review Letters*, vol. 100, no. 13, pp. 2–5, 2008.
- [53] M. Huijben, L. W. Martin, Y.-H. Chu, M. B. Holcomb, P. Yu, G. Rijnders, D. H. A. Blank, and R. Ramesh, “Critical thickness and orbital ordering in ultrathin $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ films,” *Physical Review B*, vol. 78, no. 9, p. 094413, 2008.
- [54] C. Aruta, G. Ghiringhelli, V. Bisogni, L. Braicovich, N. B. Brookes, A. Tebano, and G. Balestrino, “Orbital occupation, atomic moments, and magnetic ordering at interfaces of manganite thin films,” *Physical Review B - Condensed Matter and Materials Physics*, vol. 80, no. 1, pp. 1–8, 2009.
- [55] T. Becker, C. Streng, Y. Luo, V. Moshnyaga, B. Damaschke, N. Shannon, and K. Samwer, “Intrinsic inhomogeneities in manganite thin films investigated with scanning tunneling spectroscopy,” *Physical review letters*, vol. 89, no. 23, p. 237203, 2002.
- [56] Z. Konstantinović, J. Santiso, D. Colson, A. Forget, L. Balcells, and B. Martíñez, “Self-organization processes in highly epitaxial $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ thin films grown on SrTiO_3 (001) substrates,” *Journal of Applied Physics*, vol. 105, no. 6, 2009.
- [57] S. Valencia, Z. Konstantinovic, D. Schmitz, A. Gaupp, L. Balcells, and B. Martínez, “Interfacial effects in manganite thin films with different capping layers of interest for spintronic applications,” *Physical Review B - Condensed Matter and Materials Physics*, vol. 84, no. 2, pp. 1–7, 2011.
- [58] J. C. Rojas Sánchez, B. Nelson-Cheeseman, M. Granada, E. Arenholz, and L. B. Steren, “Exchange-bias effect at $\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_3/\text{LaNiO}_3$ interfaces,” *Physical Review B - Condensed Matter and Materials Physics*, vol. 85, no. 9, pp. 2–6, 2012.
- [59] J. Nowotny and M. Rekas, “Defect structure, electrical properties and transport in barium titanate. III. Electrical conductivity, thermopower and transport in single crystalline BaTiO_3 ,” *Ceramics International*, vol. 20, no. 4, pp. 225–235, 1994.
- [60] D. Kan and Y. Shimakawa, “Controlled cation stoichiometry in pulsed laser

- deposition-grown BaTiO₃ epitaxial thin films with laser fluence,” *Applied Physics Letters*, vol. 99, no. 8, pp. 3–6, 2011.
- [61] M. Tachiki, T. Hosomi, and T. Kobayashi, “Room-Temperature Heteroepitaxial Growth of NiO Thin Films using Pulsed Laser Deposition,” *Japanese Journal of Applied Physics*, vol. 39, pp. 1817–1820, Apr. 2000.
- [62] Y. Kakehi, S. Nakao, K. Satoh, and T. Kusaka, “Room-temperature epitaxial growth of NiO(111) thin films by pulsed laser deposition,” *Journal of Crystal Growth*, vol. 237–239, pp. 591–595, Apr. 2002.
- [63] R. Yamauchi, Y. Hamasaki, T. Shibuya, A. Saito, N. Tsuchimine, K. Koyama, A. Matsuda, and M. Yoshimoto, “Layer matching epitaxy of NiO thin films on atomically stepped sapphire (0001) substrates,” *Scientific Reports*, vol. 5, no. 1, p. 14385, 2015.
- [64] B. B. Nelson-Cheeseman, F. J. Wong, R. V. Chopdekar, E. Arenholz, and Y. Suzuki, “Room temperature magnetic barrier layers in magnetic tunnel junctions,” *Physical Review B*, vol. 81, no. 21, p. 214421, 2010.
- [65] J. X. Ma, D. Mazumdar, G. Kim, H. Sato, N. Z. Bao, and A. Gupta, “A robust approach for the growth of epitaxial spinel ferrite films,” *Journal of Applied Physics*, vol. 108, no. 6, 2010.
- [66] C. N. Chinnasamy, S. D. Yoon, A. Yang, A. Baraskar, C. Vittoria, and V. G. Harris, “Effect of growth temperature on the magnetic, microwave, and cation inversion properties on Ni Fe₂ O₄ thin films deposited by pulsed laser ablation deposition,” *Journal of Applied Physics*, vol. 101, no. 9, pp. 2–5, 2007.
- [67] W. H. Bragg and W. L. Bragg, “The Reflection of X-rays by Crystals,” *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 88, pp. 428–438, July 1913.
- [68] H. M. Rietveld, “Line profiles of neutron powder-diffraction peaks for structure refinement,” *Acta Crystallographica*, vol. 22, no. 1, pp. 151–152, 1967.
- [69] H. M. Rietveld, “A profile refinement method for nuclear and magnetic structures,” *Journal of Applied Crystallography*, vol. 2, no. 2, pp. 65–71, 1969.

- [70] G. Malmros and J. O. Thomas, “Least-squares structure refinement based on profile analysis of powder film intensity data measured on an automatic microdensitometer,” *Journal of Applied Crystallography*, vol. 10, pp. 7–11, Feb. 1977.
- [71] C. P. Khattak and D. E. Cox, “Profile analysis of X-ray powder diffractometer data: structural refinement of $\text{La}_{0.75}\text{Sr}_{0.25}\text{CrO}_3$,” *Journal of Applied Crystallography*, vol. 10, pp. 405–411, Oct. 1977.
- [72] P. F. Fewster, “Reciprocal Space Mapping,” in *X-Ray and Neutron Dynamical Diffraction* (A. Authier, ed.), vol. 357, pp. 269–288, New York: Plenum Press, 1996.
- [73] L. G. Parratt, “Surface Studies of Solids by Total Reflection of X-Rays,” *Physical Review*, vol. 95, pp. 359–369, July 1954.
- [74] H. Kiessig, “Interferenz von Röntgenstrahlen an dünnen Schichten,” *Annalen der Physik*, vol. 402, no. 7, pp. 769–788, 1931.
- [75] V. Holy, J. Kubena, I. Ohlidal, K. Lischka, and W. Plotz, “X-ray reflection from rough layered systems,” *Physical Review B*, vol. 47, pp. 15896–15903, June 1993.
- [76] A. Ichimiya and P. I. Cohen, *Reflection High-Energy Electron Diffraction*. Cambridge University Press, 2004.
- [77] S. Nishikawa and S. Kikuchi, “The Diffraction of Cathode Rays by Calcite,” *Proceedings of the Imperial Academy*, vol. 4, no. 8, pp. 475–477, 1928.
- [78] S. Kikuchi, “Diffraction of cathode rays by mica,” *Proceedings of the Imperial Academy*, vol. 4, no. 6, pp. 271–274, 1928.
- [79] S. Kikuchi, “Further Study on the Diffraction Rays by Mica.,” *Proceedings of the Imperial Academy*, vol. 4, no. 6, pp. 275–278, 1928.
- [80] S. Kikuchi, “Diffraction of cathode rays by mica (Part III),” *Proceedings of the Imperial Academy*, vol. 7, no. 6, pp. 354–356, 1928.
- [81] S. Kikuchi, “The Diffraction of Cathode Rays by Mica (Part IV),” *Proceedings of the Imperial Academy*, vol. 4, no. 8, pp. 471–474, 1928.

- [82] S. Foner, “Versatile and sensitive vibrating-sample magnetometer,” *Review of Scientific Instruments*, vol. 30, no. 7, pp. 548–557, 1959.
- [83] D. O. Smith, “Development of a vibrating-coil magnetometer,” *Review of Scientific Instruments*, vol. 27, no. 5, pp. 261–268, 1956.
- [84] B. Josephson, “Possible new effects in superconductive tunnelling,” *Physics Letters*, vol. 1, pp. 251–253, July 1962.
- [85] B. Josephson, “Supercurrents through barriers,” *Advances in Physics*, vol. 14, pp. 419–451, Oct. 1965.
- [86] P. W. Anderson and J. M. Rowell, “Probable Observation of the Josephson Superconducting Tunneling Effect,” *Physical Review Letters*, vol. 10, pp. 230–232, Mar. 1963.
- [87] B. T. Thole, P. Carra, F. Sette, and G. Van Der Laan, “X-ray circular dichroism as a probe of orbital magnetization,” *Physical Review Letters*, vol. 68, no. 12, pp. 1943–1946, 1992.
- [88] C. Chen, Y. Idzerda, H.-J. Lin, N. Smith, G. Meigs, E. Chaban, G. Ho, E. Pellegrin, and F. Sette, “Experimental Confirmation of the X-Ray Magnetic Circular Dichroism Sum Rules for Iron and Cobalt,” *Physical Review Letters*, vol. 75, no. 1, pp. 152–155, 1995.
- [89] R. Wu, D. Wang, and A. J. Freeman, “Validity and the applicability of magnetic-circular-dichroism sum rules for transition metals,” *J. Appl. Physics*, vol. 75, no. 1994, p. 5802, 1994.
- [90] G. Van Der Laan, B. T. Thole, G. A. Sawatzky, J. B. Goedkoop, J. C. Fuggle, J. M. Esteve, R. Karnatak, J. P. Remeika, and H. A. Dabkowska, “Experimental proof of magnetic x-ray dichroism,” *Physical Review B*, vol. 34, no. 9, pp. 6529–6531, 1986.
- [91] L. J. P. Ament, M. Van Veenendaal, T. P. Devereaux, J. P. Hill, and J. Van Den Brink, “Resonant inelastic x-ray scattering studies of elementary excitations,” *Reviews of Modern Physics*, vol. 83, no. 2, pp. 705–767, 2011.
- [92] G. Ghiringhelli, A. Piazzalunga, C. Dallera, G. Trezzi, L. Braicovich, T. Schmitt,

- V. N. Strocov, R. Betemps, L. Patthey, X. Wang, and M. Grioni, “SAXES, a high resolution spectrometer for resonant x-ray emission in the 400-1600 eV energy range,” *Review of Scientific Instruments*, vol. 77, no. 11, 2006.
- [93] F. M. F. de Groot, P. Kuiper, and G. A. Sawatzky, “Local spin-flip spectral distribution obtained by resonant x-ray Raman scattering,” *Physical Review B*, vol. 57, no. 23, pp. 14584–14587, 1998.
- [94] L. J. van der Pauw, “A method of measuring the resistivity and Hall coefficient on lamellae of arbitrary shape,” 1958.
- [95] L. J. van der Pauw, “A Method of Measuring Specific Resistivity and Hall effect of Discs of Arbitrary Shape,” *Philips Research Reports*, vol. 13, no. 1, pp. 1–11, 1958.
- [96] T. J. A. Mori, P. Stamenov, and L. S. Dorneles, “Note: Direct piezoelectric effect microscopy,” *Review of Scientific Instruments*, vol. 86, p. 076102, July 2015.
- [97] H. Bo, Y. Kan, X. Lu, S. Peng, X. Wang, Y. Liu, W. Cai, R. Xue, and J. Zhu, “Influence of feedback parameters on ferroelectric domain imaging with piezoresponse force microscopy,” *Review of Scientific Instruments*, vol. 81, no. 4, 2010.
- [98] G. Jonker and J. Van Santen, “Ferromagnetic compounds of manganese with perovskite structure,” *Physica*, vol. 16, no. 3, pp. 337–349, 1950.
- [99] S. Jin, T. H. Tiefel, M. McCormack, R. A. Fastnacht, R. Ramesh, and L. H. Chen, “Thousandfold Change in Resistivity in Magnetoresistive La-Ca-Mn-O Films,” *Science*, vol. 264, no. 5157, pp. 413–415, 1994.
- [100] E. Dagotto, T. Hotta, and A. Moreo, “Colossal magnetoresistant materials: the key role of phase separation,” *Physics Reports*, vol. 344, no. 1-3, pp. 1–153, 2001.
- [101] M. B. Salamon and M. Jaime, “The physics of manganites: Structure and transport,” *Reviews of Modern Physics*, vol. 73, pp. 583–628, Aug. 2001.
- [102] V. Dediu, M. Murgia, F. Maticcotta, C. Taliani, and S. Barbanera, “Room temperature spin polarized injection in organic semiconductor,” *Solid State Communications*, vol. 122, pp. 181–184, Apr. 2002.

- [103] J. Coey, M. Viret, and S. Von Molnár, “Mixed-valence manganites,” *Advances in Physics*, vol. 48, no. 2, pp. 167–293, 1999.
- [104] L. E. Hueso, J. M. Pruneda, V. Ferrari, G. Burnell, J. P. Valdés-Herrera, B. D. Simons, P. B. Littlewood, E. Artacho, A. Fert, and N. D. Mathur, “Transformation of spin information into large electrical signals using carbon nanotubes,” *Nature*, vol. 445, pp. 410–413, Jan. 2007.
- [105] J.-W. Yoo, C.-Y. Chen, H. W. Jang, C. W. Bark, V. N. Prigodin, C. B. Eom, and A. J. Epstein, “Spin injection/detection using an organic-based magnetic semiconductor,” *Nature Materials*, vol. 9, no. 8, pp. 638–642, 2010.
- [106] C. Zener, “Interaction between the d-shells in the transition metals. II. Ferromagnetic compounds of manganese with Perovskite structure,” *Physical Review*, vol. 82, no. 3, pp. 403–405, 1951.
- [107] T. Kasuya, “Mobility of the antiferromagnetic large polaron,” *Solid State Communications*, vol. 8, no. 20, pp. 1635–1638, 1970.
- [108] D. Kan, R. Aso, R. Sato, M. Haruta, H. Kurata, and Y. Shimakawa, “Tuning magnetic anisotropy by interfacially engineering the oxygen coordination environment in a transition metal oxide,” *Nature Materials*, vol. 15, no. April, 2016.
- [109] A. Vailionis, H. Boschker, W. Siemons, E. P. Houwman, D. H. A. Blank, G. Rijnders, and G. Koster, “Misfit strain accommodation in epitaxial ABO_3 perovskites: Lattice rotations and lattice modulations,” *Physical Review B - Condensed Matter and Materials Physics*, vol. 83, no. 6, pp. 1–10, 2011.
- [110] Z. Liao, N. Gauquelin, R. J. Green, S. Macke, J. Gonnissen, S. Thomas, Z. Zhong, L. Li, L. Si, S. Van Aert, P. Hansmann, K. Held, J. Xia, J. Verbeeck, G. Van Tendeloo, G. A. Sawatzky, G. Koster, M. Huijben, and G. Rijnders, “Thickness Dependent Properties in Oxide Heterostructures Driven by Structurally Induced Metal-Oxygen Hybridization Variations,” *Advanced Functional Materials*, vol. 201606717, pp. 1–9, 2017.
- [111] E. Pollert, S. Krupička, and E. Kuzmičová, “Structural study of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ and $\text{Y}_{1-x}\text{Ca}_x\text{MnO}_3$ perovskites,” *Journal of Physics and Chemistry of Solids*,

- vol. 43, pp. 1137–1145, Jan. 1982.
- [112] K. Momma and F. Izumi, “VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data,” *Journal of Applied Crystallography*, vol. 44, no. 6, pp. 1272–1276, 2011.
- [113] A. M. Glazer, “The classification of tilted octahedra in perovskites,” *Acta Crystallographica Section B Structural Crystallography and Crystal Chemistry*, vol. 28, no. 11, pp. 3384–3392, 1972.
- [114] M. Kasai, T. Ohno, Y. Kanke, Y. Kozono, M. Hanazono, and Y. Sugita, “Current-Voltage Characteristics of $\text{YBa}_2\text{Cu}_3\text{O}_y/\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_y/\text{YBa}_2\text{Cu}_3\text{O}_y$ Trilayered-Type Junctions,” *Japanese Journal of Applied Physics*, vol. 29, pp. L2219–L2222, Dec. 1990.
- [115] Y. Kozono, M. Kasai, Y. Kanke, T. Ohno, M. Hanazono, and Y. Sugita, “Novel proximity effect between high- T_c superconductor and magnetic manganese oxide,” *Physica C: Superconductivity*, vol. 185–189, pp. 1919–1920, Dec. 1991.
- [116] T. Ohno, M. Kasai, Y. Kanke, Y. Kozono, and M. Hanazono, “Ferromagnetic resonance study on $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_z$ and $\text{YBa}_2\text{Cu}_3\text{O}_y/\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_z/\text{YBa}_2\text{Cu}_3\text{O}_y$,” *Solid State Communications*, vol. 81, no. 12, pp. 993–997, 1992.
- [117] R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, “Giant Negative Magnetoresistance in Perovskitelike $\text{La}_{2/3}\text{Ba}_{1/3}\text{MnO}_3$ Ferromagnetic Films,” *Physical Review Letters*, vol. 71, no. 14, pp. 2331–2333, 1993.
- [118] K. Chahara, T. Ohno, M. Kasai, and Y. Kozono, “Magnetoresistance in magnetic manganese oxide with intrinsic antiferromagnetic spin structure,” *Applied Physics Letters*, vol. 63, pp. 1990–1992, Oct. 1993.
- [119] T. Venkatesan, M. Rajeswari, Z. W. Dong, S. B. Ogale, and R. Ramesh, “Manganite-based devices: opportunities, bottlenecks and challenges,” *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, vol. 356, pp. 1661–1680, July 1998.
- [120] S. Balevicius, N. Zurauskiene, V. Stankevicius, T. Herrmannsdorfer, S. Zherlitsyn, Y. Skourski, F. Wolff-Fabris, and J. Wosnitzer, “CMR-B-scalar sensor application

- for high magnetic field measurement in nondestructive pulsed magnets,” *IEEE Transactions on Magnetism*, vol. 49, no. 11, pp. 5480–5484, 2013.
- [121] V. M. Nascimento, M. E. B. G. N. Silva, S. Liu, L. Manera, L. Méchin, and B. Guillet, “Optical and Electrical Characterizations of Uncooled Bolometers Based on LSMO Thin Films,” *Proceedings*, vol. 1, p. 634, Sept. 2017.
- [122] J. Sacanell, J. Hernández Sánchez, A. E. Rubio López, H. Martinelli, J. Siepe, A. G. Leyva, V. Ferrari, D. Juan, M. Pruneda, A. Mejía Gómez, and D. G. Lamas, “Oxygen Reduction Mechanisms in Nanostructured $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ Cathodes for Solid Oxide Fuel Cells,” *The Journal of Physical Chemistry C*, vol. 121, no. 12, pp. 6533–6539, 2017.
- [123] V. Sharma, M. K. Mahapatra, S. Krishnan, Z. Thatcher, B. D. Huey, P. Singh, and R. Ramprasad, “Effects of moisture on $(\text{La}, \text{A})\text{MnO}_3$ ($\text{A} = \text{Ca}, \text{Sr},$ and Ba) solid oxide fuel cell cathodes: a first-principles and experimental study,” *J. Mater. Chem. A*, vol. 4, no. 15, pp. 5605–5615, 2016.
- [124] A. L. Gavin and G. W. Watson, “Modelling the electronic structure of orthorhombic LaMnO_3 ,” *Solid State Ionics*, vol. 299, pp. 13–17, 2017.
- [125] Y. Zhang and J. D. Nicholas, “Barium Oxide (BaO) Infiltrated Lanthanum Strontium Manganese Oxide (LSM)-Gadolinium Doped Ceria (GDC) Solid Oxide Electrochemical Reduction Cells (SOERC) for Reduced Diesel NO_x Emissions,” *ECS Transactions*, vol. 78, no. 1, pp. 2381–2389, 2017.
- [126] W. S. Kim, G. Anoop, H. J. Lee, S. S. Lee, J. H. Kwak, H. J. Lee, and J. Y. Jo, “Facile synthesis of perovskite $\text{LaMnO}_{3+\delta}$ nanoparticles for the oxygen reduction reaction,” *Journal of Catalysis*, vol. 344, pp. 578–582, 2016.
- [127] Y. Zhou, Z. Lü, B. Wei, X. Zhu, X. Huang, W. Jiang, and W. Su, “Oxygen adsorption on the $\text{Ag}/\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (001) catalysts surfaces: A first-principles study,” *Journal of Power Sources*, vol. 209, pp. 158–162, July 2012.
- [128] H. Yokokawa, H. Tu, B. Iwanschitz, and A. Mai, “Fundamental mechanisms limiting solid oxide fuel cell durability,” *Journal of Power Sources*, vol. 182, no. 2, pp. 400–412, 2008.

- [129] F. Y. Bruno, M. N. Grisolia, C. Visani, S. Valencia, M. Varela, R. Abrudan, J. Tornos, A. Rivera-Calzada, A. A. Ünal, S. J. Pennycook, Z. Sefrioui, C. Leon, J. E. Villegas, J. Santamaria, A. Barthélémy, and M. Bibes, “Insight into spin transport in oxide heterostructures from interface-resolved magnetic mapping,” *Nature Communications*, vol. 6, p. 6306, 2015.
- [130] J. D. Burton and E. Y. Tsymbal, “Tunneling anisotropic magnetoresistance in a magnetic tunnel junction with half-metallic electrodes,” *Physical Review B*, vol. 93, no. 2, pp. 2–6, 2016.
- [131] T. Matou, K. Takeshima, L. D. Anh, M. Seki, H. Tabata, M. Tanaka, and S. Ohya, “Reduction of the magnetic dead layer and observation of tunneling magnetoresistance in $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ -based heterostructures with a LaMnO_3 layer,” *Applied Physics Letters*, vol. 110, no. 21, p. 212406, 2017.
- [132] S. Liang, J. R. Sun, J. Wang, and B. G. Shen, “Magnetic and conductive dead layer at the $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ – SrTiO_3 :Nb interface,” *Applied Physics Letters*, vol. 95, p. 182509, 2009.
- [133] J. Coey, M. Venkatesan, and P. Stamenov, “Surface magnetism of strontium titanate,” *arXiv preprint*, p. 1606.09422, 2016.
- [134] M. Venkatesan, P. Kavle, S. B. Porter, K. Ackland, and J. M. D. Coey, “Magnetic Analysis of Polar and Nonpolar Oxide Substrates,” *IEEE Transactions on Magnetics*, vol. 50, pp. 1–4, Nov. 2014.
- [135] G. A. T. Allan, “Critical temperatures of ising lattice films,” *Physical Review B*, vol. 1, no. 1, pp. 352–356, 1970.
- [136] C. Vaz, J. Bland, and G. Lauhoff, “Magnetism in ultrathin film structures,” *Reports on Progress in Physics*, vol. 71, no. 5, p. 056501, 2008.
- [137] A. Ruosi, C. Raisch, A. Verna, R. Werner, B. A. Davidson, J. Fujii, R. Kleiner, and D. Koelle, “Electron sampling depth and saturation effects in perovskite films investigated by soft x-ray absorption spectroscopy,” *Physical Review B*, vol. 90, no. 12, p. 125120, 2014.
- [138] H. Boschker, J. Kautz, E. P. Houwman, W. Siemons, D. H. A. Blank, M. Huijben,

- G. Koster, A. Vailionis, and G. Rijnders, “High-temperature magnetic insulating phase in ultrathin $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ films,” *Physical Review Letters*, vol. 109, no. 15, pp. 1–5, 2012.
- [139] H. Boschker, M. Huijben, A. Vailionis, J. Verbeeck, S. van Aert, M. Luysberg, S. Bals, G. van Tendeloo, E. P. Houwman, G. Koster, D. H. a. Blank, and G. Rijnders, “Optimized fabrication of high-quality $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ thin films considering all essential characteristics,” *Journal of Physics D: Applied Physics*, vol. 44, no. 20, p. 205001, 2011.
- [140] Z. Fang and K. Terakura, “Surface Magnetic Phase Diagram of Tetragonal Manganites,” *Journal of the Physical Society of Japan*, vol. 70, no. 11, pp. 3356–3361, 2001.
- [141] I. V. Solovyev and K. Terakura, “Zone Boundary Softening of the Spin-Wave Dispersion in Doped Ferromagnetic Manganites,” *Physical Review Letter*, vol. 82, p. 2959, 1999.
- [142] L. Brey, “Electronic phase separation in manganite-insulator interfaces,” *Physical Review B - Condensed Matter and Materials Physics*, vol. 75, no. 10, pp. 1–7, 2007.
- [143] E. H. Evans and B. Paretzkin, “Standard X-ray Diffraction Powder Patterns Library of Congress Catalog Card Number : 53-61386,” *Natl. Bur. Stand. (U.S.) Monograph 25, Section 9*, p. p. 81, 1971.
- [144] J. C. Slonczewski, “Origin of magnetic anisotropy in cobalt-substituted magnetite,” *Physical Review*, vol. 110, no. 6, pp. 1341–1348, 1958.
- [145] L. Braicovich, A. Tagliaferri, G. van der Laan, G. Ghiringhelli, and N. B. Brookes, “Sum Rules in X-Ray Resonant Raman Scattering: Recovering the Co Ground State Information in CoFe_2O_4 as a Test Case,” *Physical Review Letters*, vol. 90, no. 11, p. 117401, 2003.
- [146] J. A. Moyer, C. A. Vaz, D. A. Arena, D. Kumah, E. Negusse, and V. E. Henrich, “Magnetic structure of Fe-doped CoFe_2O_4 probed by x-ray magnetic spectroscopies,” *Physical Review B - Condensed Matter and Materials Physics*, vol. 84,

- no. 5, pp. 1–10, 2011.
- [147] R. M. Bozorth, E. F. Tilden, and A. J. Williams, “Anisotropy and magnetostriction of some ferrites,” *Physical Review*, vol. 99, no. 6, pp. 1788–1798, 1955.
- [148] Y. Suzuki, G. Hu, R. B. van Dover, and R. J. Cava, “Magnetic anisotropy of epitaxial cobalt ferrite thin films,” *Journal of Magnetism and Magnetic Materials*, vol. 191, no. 1-2, pp. 1–8, 1999.
- [149] Z. Li, E. S. Fisher, J. Z. Liu, and M. V. Nevitt, “Single-crystal elastic constants of Co-Al and Co-Fe spinels,” *Journal of Materials Science*, vol. 26, pp. 2621–2624, May 1991.
- [150] B. Schulz and K. Baberschke, “Crossover from in-plane to perpendicular magnetization in ultrathin Ni/Cu(001) films,” *Physical Review B*, vol. 50, no. 18, pp. 13467–13471, 1994.
- [151] W. Huang, J. Zhu, H. Z. Zeng, X. H. Wei, Y. Zhang, and Y. R. Li, “Strain induced magnetic anisotropy in highly epitaxial CoFe_2O_4 thin films,” *Applied Physics Letters*, vol. 89, no. 26, p. 262506, 2006.
- [152] A. K. Axelsson, F. Aguesse, V. Tileli, M. Valant, and N. N. McAlford, “Growth mechanism and magnetism of CoFe_2O_4 thin films; Role of the substrate,” *Journal of Alloys and Compounds*, vol. 578, pp. 286–291, 2013.
- [153] M. A. Tanaka, K. Harada, M. Takemura, K. Mibu, and J. Inoue, “Nonlinear strain dependence of magnetic anisotropy in CoFe_2O_4 films on $\text{MgO}(001)$ substrates,” *Journal of Applied Physics*, vol. 115, no. 17, pp. 2–5, 2014.
- [154] T. Niizeki, Y. Utsumi, R. Aoyama, H. Yanagihara, J. I. Inoue, Y. Yamasaki, H. Nakao, K. Koike, and E. Kita, “Extraordinarily large perpendicular magnetic anisotropy in epitaxially strained cobalt-ferrite $\text{Co}_x\text{Fe}_{3-x}\text{O}_4(001)$ ($x = 0.75, 1.0$) thin films,” *Applied Physics Letters*, vol. 103, no. 16, pp. 0–5, 2013.
- [155] H. Yanagihara, Y. Utsumi, T. Niizeki, J. Inoue, and E. Kita, “Perpendicular magnetic anisotropy in epitaxially strained cobalt-ferrite (001) thin films,” *Journal of Applied Physics*, vol. 115, no. 17, pp. 2–5, 2014.
- [156] J. A. Moyer, D. P. Kumah, C. A. Vaz, D. A. Arena, and V. E. Henrich, “Role

- of epitaxial strain on the magnetic structure of Fe-doped CoFe_2O_4 ,” *Journal of Magnetism and Magnetic Materials*, vol. 345, pp. 180–189, 2013.
- [157] J. H. Yin, J. Ding, B. H. Liu, J. B. Yi, X. S. Miao, and J. S. Chen, “Magnetic anisotropy and high coercivity of epitaxial Co-ferrite films prepared by pulsed laser deposition,” *Journal of Applied Physics*, vol. 101, no. 9, pp. 7–10, 2007.
- [158] M. T. Johnson, P. J. H. Bloemen, F. J. A. den Broeder, and J. J. de Vries, “Magnetic anisotropy in metallic multilayers,” *Reports on Progress in Physics*, vol. 59, pp. 1409–1458, Nov. 1996.
- [159] P. C. Dorsey, P. Lubitz, D. B. Chrisey, and J. S. Horwitz, “ CoFe_2O_4 thin films grown on (100) MgO substrates using pulsed laser deposition,” *Journal of Applied Physics*, vol. 79, no. 8, p. 6338, 1996.
- [160] G. Hu, J. Choi, C. Eom, V. Harris, and Y. Suzuki, “Structural tuning of the magnetic behavior in spinel-structure ferrite thin films,” *Physical Review B*, vol. 62, no. 2, pp. R779–R782, 2000.
- [161] W. Huang, J. Zhu, H. Z. Zeng, X. H. Wei, Y. Zhang, and Y. R. Li, “Strain induced magnetic anisotropy in highly epitaxial CoFe_2O_4 thin films,” *Applied Physics Letters*, vol. 89, no. 26, p. 262506, 2006.
- [162] P. Thang, G. Rijnders, and D. Blank, “Stress-induced magnetic anisotropy of CoFe_2O_4 thin films using pulsed laser deposition,” *Journal of Magnetism and Magnetic Materials*, vol. 310, pp. 2621–2623, Mar. 2007.
- [163] T. Dhakal, D. Mukherjee, R. Hyde, P. Mukherjee, M. H. Phan, H. Srikanth, and S. Witanachchi, “Magnetic anisotropy and field switching in cobalt ferrite thin films deposited by pulsed laser ablation,” *Journal of Applied Physics*, vol. 107, no. 5, pp. 1–7, 2010.
- [164] V. Madhav Kumar, A. Srinivas, A. Talapatra, S. Asthana, J. Mohanty, and S. V. Kamat, “Effect of deposition temperature on structural, microstructural and magnetic properties of CoFe_2O_4 thin films deposited by pulsed laser deposition,” *Journal of Materials Science: Materials in Electronics*, vol. 28, no. 1, pp. 446–453, 2017.

- [165] J. S. Moodera, X. Hao, G. A. Gibson, and R. Meservey, "Electron-Spin Polarization in Tunnel Junctions in Zero Applied Field with Ferromagnetic EuS Barriers," *Physical Review Letters*, vol. 61, pp. 637–640, Aug. 1988.
- [166] L. Esaki, P. J. Stiles, and S. V. Molnar, "Magnetointernal field emission in junctions of magnetic insulators," *Physical Review Letters*, vol. 19, no. 15, pp. 852–854, 1967.
- [167] N. M. Caffrey, D. Fritsch, T. Archer, S. Sanvito, and C. Ederer, "Spin-filtering efficiency of ferrimagnetic spinels CoFe_2O_4 and NiFe_2O_4 ," *Physical Review B - Condensed Matter and Materials Physics*, vol. 87, no. 2, pp. 1–7, 2013.
- [168] C. Gatel, B. Warot-Fonrose, S. Matzen, and J. B. Moussy, "Magnetism of CoFe_2O_4 ultrathin films on MgAl_2O_4 driven by epitaxial strain," *Applied Physics Letters*, vol. 103, no. 9, 2013.
- [169] J.-B. Moussy, S. Gota, A. Bataille, M.-J. Guittet, M. Gautier-Soyer, F. Delille, B. Dieny, F. Ott, T. Doan, P. Warin, P. Bayle-Guillevaud, C. Gatel, and E. Snoeck, "Thickness dependence of anomalous magnetic behavior in epitaxial $\text{Fe}_3\text{O}_4(111)$ thin films: Effect of density of antiphase boundaries," 2004.
- [170] D. T. Margulies, F. T. Parker, F. E. Spada, R. S. Goldman, J. Li, R. Sinclair, and A. E. Berkowitz, "Anomalous moment and anisotropy behavior in Fe_3O_4 films," *Physical Review B*, vol. 53, pp. 9175–9187, Apr. 1996.
- [171] J. M. D. Coey, A. E. Berkowitz, L. Balcells, F. F. Putris, and F. T. Parker, "Magnetoresistance of magnetite," *Applied Physics Letters*, vol. 72, pp. 734–736, Feb. 1998.
- [172] S. K. Arora, R. G. Sofin, and I. V. Shvets, "Magnetoresistance enhancement in epitaxial magnetite films grown on vicinal substrates," 2005.
- [173] C. M. Srivastava, G. Srinivasan, and N. G. Nanadikar, "Exchange constants in spinel ferrites," *Physical Review B*, vol. 19, no. 1, pp. 499–508, 1979.
- [174] R. G. Burns, *Mineralogical Applications of Crystal Field Theory*. Cambridge: Cambridge University Press, 2 ed., 1993.

- [175] C. G. Shull, W. A. Strauser, and E. O. Wollan, “Neutron diffraction by paramagnetic and antiferromagnetic substances,” *Physical Review*, vol. 83, no. 2, pp. 333–345, 1951.
- [176] W. L. Roth, “Neutron and optical studies of domains in NiO,” *Journal of Applied Physics*, vol. 31, no. 11, pp. 2000–2011, 1960.
- [177] Y. Yamamoto and T. Nagamiya, “Spin Arrangements in Magnetic Compounds of the Rocksalt Crystal Structure,” 1972.
- [178] B. Everitt, D. Wang, and J. Daughton, “Spin valves with NiO pinning layer,” *IEEE Transactions on Magnetics*, vol. 32, no. 5, pp. 4657–4659, 1996.
- [179] C. H. Shang, G. P. Berera, and J. S. Moodera, “Exchange-biased ferromagnetic tunnel junctions via reactive evaporation of nickel oxide films,” *Applied Physics Letters*, vol. 72, no. 5, pp. 605–607, 1998.
- [180] I. Sugiyama, N. Shibata, Z. Wang, S. Kobayashi, T. Yamamoto, and Y. Ikuhara, “Ferromagnetic dislocations in antiferromagnetic NiO,” *Nature Nanotechnology*, vol. 8, no. 4, pp. 266–270, 2013.
- [181] R. W. Cairns and E. Ott, “X-Ray Studies of the System Nickel-Oxygen-Water. II. Compounds Containing Trivalent Nickel,” *Journal of the American Chemical Society*, vol. 55, no. 2, pp. 534–544, 1933.
- [182] N. Smith, “The Structure of Thin Films of Metallic Oxides and Hydrates,” *Journal of the American Chemical Society*, vol. 58, no. 1, pp. 173–179, 1936.
- [183] J. M. Tarascon, G. Vaughan, Y. Chabre, L. Seguin, M. Anne, P. Strobel, and G. Amatucci, “In Situ Structural and Electrochemical Study of $\text{Ni}_{1-x}\text{Co}_x\text{O}_2$ Metastable Oxides Prepared by Soft Chemistry,” 1999.
- [184] M. W. Haverkort, M. Zwierzycki, and O. K. Andersen, “Multiplet ligand-field theory using Wannier orbitals,” *Physical Review B*, vol. 85, p. 165113, Apr. 2012.
- [185] G. Ghiringhelli, M. Matsubara, C. Dallera, F. Fracassi, R. Gusmeroli, a. Piazalunga, a. Tagliaferri, N. B. Brookes, a. Kotani, and L. Braicovich, “NiO as a test case for high resolution resonant inelastic soft x-ray scattering,” *Journal of Physics: Condensed Matter*, vol. 17, no. 35, pp. 5397–5412, 2005.

- [186] M. T. Hutchings and E. J. Samuelsen, “Measurement of spin-wave dispersion in NiO by inelastic neutron scattering and its relation to magnetic properties,” *Physical Review B*, vol. 6, no. 9, pp. 3447–3461, 1972.
- [187] G. Ghiringhelli, A. Piazzalunga, C. Dallera, T. Schmitt, V. N. Strocov, J. Schlappa, L. Patthey, X. Wang, H. Berger, and M. Grioni, “Observation of two nondispersive magnetic excitations in NiO by resonant inelastic soft-X-ray scattering,” *Physical Review Letters*, vol. 102, no. 2, pp. 2–5, 2009.
- [188] L. D. Landau and E. M. Lifshitz, *Statistical Physics*. Pergamon Press, Oxford, 1959.
- [189] A. Devonshire, “Theory of ferroelectrics,” *Advances in Physics*, vol. 3, pp. 85–130, Apr. 1954.
- [190] L. Lifshitz and E. Landau, *Statistical Physics*. Elsevier, 1980.
- [191] A. Devonshire, “XCVI. Theory of barium titanate,” *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, vol. 40, pp. 1040–1063, Oct. 1949.
- [192] A. Safari and E. K. Akdogan, *Piezoelectric and Acoustic Materials for Transducer Applications*. Boston, MA: Springer US, 2008.
- [193] S. Geprägs, A. Brandlmaier, M. Opel, R. Gross, and S. T. Goennenwein, “Electric field controlled manipulation of the magnetization in Ni/BaTiO₃ hybrid structures,” *Applied Physics Letters*, vol. 96, no. 14, 2010.
- [194] W. Eerenstein, M. Wiora, J. L. Prieto, J. F. Scott, and N. D. Mathur, “Giant sharp and persistent converse magnetoelectric effects in multiferroic epitaxial heterostructures,” *Nature Materials*, vol. 6, no. 5, pp. 348–351, 2007.
- [195] C. G. Duan, S. S. Jaswal, and E. Y. Tsybal, “Predicted magnetoelectric effect in Fe/BaTiO₃ multilayers: Ferroelectric control of magnetism,” *Physical Review Letters*, vol. 97, no. 4, pp. 13–16, 2006.
- [196] M. Fechner, I. V. Maznichenko, S. Ostanin, A. Ernst, J. Henk, P. Bruno, and I. Mertig, “Magnetic phase transition in two-phase multiferroics predicted from first principles,” 2008.

- [197] M. K. Niranjan, J. D. Burton, J. P. Velez, S. S. Jaswal, and E. Y. Tsymlal, “Magnetoelectric effect at the $\text{SrRuO}_3/\text{BaTiO}_3$ (001) interface: An ab initio study,” *Applied Physics Letters*, vol. 95, no. 5, pp. 1–4, 2009.
- [198] S. Valencia, A. Crassous, L. Bocher, V. Garcia, X. Moya, R. O. Cherifi, C. Deranlot, K. Bouzehouane, S. Fusil, A. Zobelli, A. Gloter, N. D. Mathur, A. Gaupp, R. Abrudan, F. Radu, A. Barthélémy, and M. Bibes, “Interface-induced room-temperature multiferroicity in BaTiO_3 ,” *Nature materials*, vol. 10, pp. 753–8, Oct. 2011.
- [199] N. M. Caffrey, D. Fritsch, T. Archer, S. Sanvito, and C. Ederer, “Spin-filtering efficiency of ferrimagnetic spinels CoFe_2O_4 and NiFe_2O_4 ,” *Physical Review B - Condensed Matter and Materials Physics*, vol. 87, p. 024419, Jan. 2013.
- [200] N. M. Caffrey, T. Archer, I. Rungger, and S. Sanvito, “Prediction of large bias-dependent magnetoresistance in all-oxide magnetic tunnel junctions with a ferroelectric barrier,” *Physical Review B - Condensed Matter and Materials Physics*, vol. 83, p. 125409, Mar. 2011.
- [201] J. D. Axe, “Apparent ionic charges and vibrational eigenmodes of BaTiO_3 and other perovskites,” *Physical Review*, vol. 157, no. 2, pp. 429–435, 1967.
- [202] J. Shieh, J. H. Yeh, Y. C. Shu, and J. H. Yen, “Hysteresis behaviors of barium titanate single crystals based on the operation of multiple 90° switching systems,” *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, vol. 161, no. 1-3, pp. 50–54, 2009.
- [203] J. Junquera and P. Ghosez, “Critical thickness for ferroelectricity in perovskite ultrathin films,” *Nature*, vol. 422, pp. 506–509, Apr. 2003.
- [204] Y. S. Kim, D. H. Kim, J. D. Kim, Y. J. Chang, T. W. Noh, J. H. Kong, K. Char, Y. D. Park, S. D. Bu, J. G. Yoon, and J. S. Chung, “Critical thickness of ultrathin ferroelectric BaTiO_3 films,” *Applied Physics Letters*, vol. 86, no. 10, pp. 1–3, 2005.
- [205] C. Li, L. Huang, T. Li, W. Lü, X. Qiu, Z. Huang, Z. Liu, S. Zeng, R. Guo, Y. Zhao, K. Zeng, M. Coey, J. Chen, Ariando, and T. Venkatesan, “Ultrathin

- BaTiO₃-Based Ferroelectric Tunnel Junctions through Interface Engineering,” *Nano Letters*, vol. 15, pp. 2568–2573, Apr. 2015.
- [206] H. Kohlstedt, N. A. Pertsev, J. Rodríguez Contreras, and R. Waser, “Theoretical current-voltage characteristics of ferroelectric tunnel junctions,” *Physical Review B - Condensed Matter and Materials Physics*, vol. 72, no. 12, pp. 1–10, 2005.
- [207] C. T. Black and J. J. Welser, “Electric-field penetration into metals: consequences for high-dielectric-constant capacitors,” *IEEE Transactions on Electron Devices*, vol. 46, no. 4, pp. 776–780, 1999.
- [208] X. Yin, M. A. Majidi, X. Chi, P. Ren, L. You, N. Palina, X. Yu, C. Diao, D. Schmidt, B. Wang, P. Yang, M. B. H. Breese, J. Wang, and A. Rusydi, “Unraveling how electronic and spin structures control macroscopic properties of manganite ultra-thin films,” *NPG Asia Materials*, vol. 7, no. 7, p. e196, 2015.
- [209] J. G. Simmons, “Generalized Formula for the Electric Tunnel Effect between Similar Electrodes Separated by a Thin Insulating Film,” *Journal of Applied Physics*, vol. 34, no. 6, pp. 1793–1803, 1963.

Presentations and Publications

- **Poster:** “Magnetisation of Undoped SrTiO_3 Crystals, and Other Pure Polar and Non-Polar Oxides”, *INTERMAG Conference*, Dresden, Germany, 2014
- **Poster:** “Oxide interfaces; Multiferroic Stacks as a First Attempt at Dual Control Tunnel Barriers and the Polar Catastrophe”, *European School on Nanoscience and Nanotechnology* Grenoble, France, 2014
- **Poster:** “Magnetisation of Undoped SrTiO_3 Crystals, and Other Pure Polar and Non-Polar Oxides”, *AMBER review*, Dublin, Ireland, 2015
- **Poster:** “Oxide interfaces; Multiferroic Stacks as a First Attempt at Dual Control Tunnel Barriers”, *European School of Magnetism*, Cluj Napoca, Romania, 2015
- **Poster:** “Magnetic Dead Layers in LSMO Revisited”, *INTERMAG Conference*, Dublin, Ireland, 2017
- **Publication:** M. Venkatesan, P. Kavle, S. B. Porter, K. Ackland, J. M. D. Coey “Magnetic Analysis of Polar and Nonpolar Oxide Substrates” *IEEE Trans. Magn.*, vol. 50, pp. 1-4, Nov. 2014.
- **Publication:** S.B. Porter, M. Venkatesan, P. Dunne, B. Doudin, K. Rode, J.M.D. Coey “Magnetic dead layers in $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ revisited” *IEEE Trans. Magn.*, vol. 53, pp. 1-4, Apr. 2017.
- **Publication:** D. Betto, Y.Y. Peng, S.B. Porter, G. Berti, A. Calloni, G. Ghiringhelli, N.B. Brookes “Three-dimensional dispersion of spin waves measured in NiO by resonant inelastic x-ray scattering” *Phys. Rev. B*, vol. 96, pp. 020409(R), Jul. 2017.
- **Publication:** F. Eskandari, S.B. Porter, M. Venkatesan, P. Kameli, K. Rode, J.M.D. Coey “Magnetization and Anisotropy of Cobalt Ferrite Thin Films” *Submitted for review: Phys. Rev. Mater.*, arXiv: 1709.09965, Sep. 2017.

- **Publication:** G.A. Boni, L. Hrib, S.B. Porter, G. Atcheson, I. Pintilie, K. Rode, L. Pintilie “Electrical properties of NiFe_2O_4 epitaxial ultra-thin films” *J. Mater. Sci.*, vol. 52, pp. 793-803, Sep. 2016.
- **Publication:** H. Kalhori, J.M.D. Coey, I.A. Sarsari, K. Borisov, S.B. Porter, G. Atcheson, M. Ranjbar, H. Salamati, P. Stamenov “Oxygen Vacancy in WO_3 Film-based FET with Ionic Liquid Gating” *Sci. Rep.*, vol. 7, pp. 12253, Sep. 2017.
- **Publication:** H. Kalhori, S.B. Porter, A.S. Esmaily, J.M.D. Coey, M. Ranjbar, H. Salamati “Morphology and Structural Studies of WO_3 Films Deposited on SrTiO_3 by Pulsed Laser Deposition” *Appl. Surf. Sci.*, vol. 390, pp. 43-49, Aug. 2016.
- **Publication:** J.F de Marneffe, L. Zhang, M. Heyne, M. Łukaszewicz, S.B. Porter, F. Vajda, V.D. Rutigliani, Z. el Otell, M. Krishtab, A. Goodyear, M. Cooke, P. Verdock, M.R. Baklanov “Vacuum ultra-violet damage and damage mitigation for plasma processing of highly porous organosilicate glass dielectrics” *J. Appl. Phys.*, vol. 118, pp. 133302, Oct. 2015.