Pulsed laser deposition and nanofabrication of mesoscopic devices based on cuprates and manganites

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Abstract
This thesis explores the growth, the nano-fabrication and the study of the magneto-transport properties of Superconductor/Ferromagnet/Superconductor (SFS) structures from complex oxides such as the high T_c superconducting cuprate YBa$_2$Cu$_3$O$_7$ (YBCO) and the ferromagnetic manganites La$_{2/3}$Ca$_{1/3}$MnO$_3$ and La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LCMO and LSMO), deposited with the pulsed laser deposition (PLD) technique. The present work has been possible thanks to the collaboration between the “Magnetism and Superconductivity” Group at the University of Fribourg, in Switzerland, and the “Experimentell Kondenserade Materiens Fysik” Group at Stockholm University, in Sweden.

Earlier, the two research groups in Fribourg and Stockholm had studied SFS structures from YBCO/LaMnO$_3$/YBCO multilayers with 20 nm thick ferromagnetic and insulating LaMnO$_3$ barriers, and obtained signs of an unconventional spin-triplet current across these structures. This finding motivated the present thesis work with a focus on two main aspects.

Firstly, to explore other candidate materials suitable as barriers and optimise their growth conditions as to maintain a large ferromagnetic moment and thus a high spin polarisation of the charge carriers. Secondly, to study what happens when the thickness of the ferromagnetic and insulating LaMnO$_3$ barrier is reduced well below 20 nm to enable larger supercurrents.

It has been shown for a series of YBCO/LCMO multilayers that the ferromagnetic moment of LCMO depends critically on the PLD growth conditions as well as on the thickness and even structural details of the YBCO layer on which they are grown. Furthermore, a protocol has been established to grow heterostructures with strongly ferromagnetic manganite layers embedded in thick YBCO layers by optimising the PLD growth conditions and by substituting the bottom YBCO layer with a Co and Ca substituted version of YBCO that has a tetragonal structure (tYBCO) instead of the orthorhombic one of plain YBCO.

Devices suitable for perpendicular magneto-transport measurements have been nano-fabricated from YBCO/manganite/YBCO multilayers with ~10 nm thick LCMO and LSMO layers as the F barriers. While no clear indications of a spin-triplet component of the superconducting order parameter have been obtained yet, a negative and hysteretic magneto-resistance has been observed that is indicative of a strong ferromagnetic order in the thin manganite barrier. The latter suggests a potential memory functionality of such structures that could be exploited in future spintronic memory devices.

Moreover, devices have been fabricated on SFS structures with a reduced thickness of the LaMnO$_3$ barrier of 10 nm and 5 nm. These samples were grown prior to the beginning of this PhD work using non optimised growth conditions, and it was found that the ferromagnetic properties of these LaMnO$_3$ barriers are strongly deteriorated. It remains to be seen whether the ferromagnetic order of such thin LaMnO$_3$ layers can be also recovered by using the optimised growth conditions as for LSMO and LCMO.

Keywords: cuprates, manganites, pulsed laser deposition, nano-fabrication, heterostructures.
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This thesis explores the growth, the nano-fabrication and the study of the magneto-transport properties of Superconductor/Ferromagnet/Superconductor (SFS) structures from complex oxides such as the high $T_c$ superconducting cuprate YBa$_2$Cu$_3$O$_7$ (YBCO) and the ferromagnetic manganites La$_{2/3}$Ca$_{1/3}$MnO$_3$ and La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LCMO and LSMO), deposited with the pulsed laser deposition (PLD) technique. The present work has been possible thanks to the collaboration between the “Magnetism and Superconductivity” Group at the University of Fribourg, in Switzerland, and the “Experimentell Kondenserade Materiens Fysik” Group at Stockholm University, in Sweden.

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It has been shown for a series of YBCO/LCMO multilayers that the ferromagnetic moment of LCMO depends critically on the PLD growth conditions as well as on the thickness and even structural details of the YBCO layer on which they are grown. Furthermore, a protocol has been established to grow heterostructures with strongly ferromagnetic manganite layers embedded in thick YBCO layers by optimising the PLD growth conditions and by substituting the bottom YBCO layer with a Co and Ca substituted version of YBCO that has a tetragonal structure (tYBCO) instead of the orthorhombic one of plain YBCO.

Devices suitable for perpendicular magneto-transport measurements have been nano-fabricated from YBCO/manganite/YBCO multilayers with $\sim$10 nm thick LCMO and LSMO layers as the F barriers. While no clear indications of a spin-triplet component of the superconducting order parameter have been obtained yet, a negative and hysteretic magneto-resistance has been observed that is indicative of a strong fer-
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Moreover, devices have been fabricated on SFS structures with a reduced thickness of the LaMnO$_3$ barrier of 10 nm and 5 nm. These samples were grown prior to the beginning of this PhD work using non-optimised growth conditions, and it was found that the ferromagnetic properties of these LaMnO$_3$ barriers are strongly deteriorated. It remains to be seen whether the ferromagnetic order of such thin LaMnO$_3$ layers can be also recovered by using the optimised growth conditions as for LSMO and LCMO.
Sammanfattning

Denna avhandling undersöker växten, nanofabrikationen och studien av magneto-transportegenskaperna hos Supraledare/Ferromagnet/Supraledare (SFS) strukturer av complexa oxider såsom kuprat hög-$T_c$ supraledare YBa$_2$Cu$_3$O$_7$ (YBCO) och ferromagnetiska manganiter La$_{2/3}$Ca$_{1/3}$MnO$_3$ och La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LCMO och LSMO), deponerade med puls-laserdepositionsteknik (PLD). Arbetet har varit möjligt tack vare samarbetet mellan ”Magnetism and Superconductivity”-gruppen vid universitetet i Fribourg, Schweiz, och ”Experimentell Kondenserade Materiens Fysik”-gruppen vid Stockholms universitet, i Sverige.

Tidigare har de två forskningsgrupperna i Fribourg och Stockholm studerat SFS-strukturer av YBCO/LaMnO$_3$/YBCO-multilager med 20 nm tjock ferromagnetisk och isolerande LaMnO$_3$-barrière och fått tecken på en okonventionell spintripletström genom dessa strukturer. Detta fynd motiverade detta avhandlingsarbet, fokuserat på två huvudsakliga aspekter.

Först, att utforska andra kandidatmaterial som är lämpliga som barrer och optimera deras materialväxtsförhållanden för att uppnå ett stort ferromagnetiskt moment och därmed en hög spinpolarisation hos laddningsbärarna. För det andra, studera effekterna av att tjockleken på den ferromagnetiska och isolerande LaMnO$_3$-barriären reduceras långt under 20 nm för att möjliggöra högre superströmmar.

Det har visats att för en serie YBCO/LCMO-multilager att det ferromagnetiska momentet för LCMO beror kritiskt på PLD-växtförhållanden, samt tjockleken, men även strukturella detaljer hos YBCO-skiktet på vilket de odlas. Vidare har ett protokoll upprättats för att odla heterostrukturer med starkt ferromagnetiska manganitlager inbäddade i tjocka YBCO-skikt genom att optimera PLD-tillväxtförhållanden och genom att ersätta det nedre YBCO-skiktet med en Co och Ca substituerad version av YBCO som har en tetragonal struktur (tYBCO) istället för den ortorombiska strukturen hos vanlig YBCO.

Enheter som är lämpliga för vinkelrätta magneto-transportmätningar har nanofabrikerats från YBCO/manganit/YBCO-multilager med 10 nm tjocka LCMO- och LSMO-lager som F-barriärer. Även om det inte har erhållits några tydliga indikationer på en spin-triplet-komponent i den supraledande ordningsparametern, har en negativ och hysteretisk magneto-resistans observerats, vilket tyder på en stark ferromagnetisk ordning i den tunna manganitbarriären. Det senare visar potentiell min-
nesfunktionalitet hos sådana strukturer, som skulle kunna utnyttjas i framtida spintroniska minnesenheter.

Dessutom har enheter tillverkats av SFS-strukturer med reduce-
rad tjocklek på LaMnO$_3$-barriären ner till 10 nm och 5 nm. Dessa
prover odlades innan detta PhD-arbete och använde icke-optimerade
växtförhållanden, vilket ledde till att de ferromagnetiska egenskaper-
na hos dessa LaMnO$_3$-barriärer är starkt försämrade. Det återstår att
se om den ferromagnetiska ordningen för sådana tunna LaMnO$_3$-skikt
också kan förstärkas med användning av optimerade växtförhållanden
som för LSMO och LCMO.
Zusammenfassung


In früheren Arbeiten haben beide Gruppen in Fribourg und in Stockholm bereits SFS Strukturen von YBCO/LaMnO$_3$/YBCO Multilagen mit einem 20 nm dicken ferromagnetischen LaMnO$_3$ Film untersucht, bei denen ein unkonventioneller spin-triplet Strom senkrecht durch die LaMnO$_3$ Barriere beobachtet werden konnte. Dieses Ergebnis motivierte die vorliegende Doktorarbeit, in der solche Strukturen in Hinblick auf zwei wesentliche Aspekte genauer untersucht wurden.

Zum einen wurden andere Manganate als geeignete Barriere untersucht und deren Wachstumsbedingungen optimiert, um ein grosses ferromagnetisches Moment und daher eine hohe Spin-Polarisation der Ladungsträger zu ermöglichen. Zum anderen wurde untersucht was passiert, wenn die Schichtdicke der ferromagnetischen und isolierenden LaMnO$_3$ Barriere deutlich unterhalb 20 nm verringert wird um so grössere Superströme zu ermöglichen.


Bauelemente für senkrechte magneto-transport Messungen wurden hergestellt aus YBCO/Manganat/YBCO Multilagen mit einer ~10 nm
dicken LCMO oder LSMO Lage als ferromagnetische Barriere. Auch wenn diese Ergebnisse nicht eindeutig auf eine spin-triplet Komponente des supraleitenden Ordnungsparameters hinweisen, wurde ein negativer und hysteretischer Magneto-Widerstand beobachtet, welcher ein Indikator für eine starke ferromagnetische Ordnung im dünnen Manganat Film ist. Solche Strukturen könnten demnach in zukünftigen spintropenischen Speichermedien eine Rolle spielen.

Schliesslich wurden aus YBCO/ LaMnO$_3$ /YBCO Multilagen mit einer reduzierten LaMnO$_3$ Schichtdicke von 10 nm und 5 nm, die bereits vor dem Beginn dieser Doktorarbeit hergestellt worden waren, SFS Nano-Strukturen hergestellt. Für diese stellte sich heraus, dass das magnetische Moment der LaMnO$_3$ Barriere sehr stark unterdrückt ist. Dadurch stellt sich die Frage ob, wie im Fall von LSMO und LCMO, die ferromagnetische Ordnung von solch dünnen LaMnO$_3$ Lagen ebenfalls mittels optimierter Wachstumsbedingungen verbessert werden könnte.
List of papers

This thesis compiles the work published on the papers:

I. Controlling the strength of ferromagnetic order in YBa$_2$Cu$_3$O$_7$/La$_{2/3}$Ca$_{1/3}$MnO$_3$ multilayers.

*Author’s contribution:* Deposited and characterised the samples. Conducted the VSM, XRD and XRR measurements and analysed the data. Contributed to writing the paper.

II. Memory-functionality superconductor / ferromagnet / superconductor junctions based on the high-$T_c$ cuprate superconductor YBa$_2$Cu$_3$O$_{7-x}$ and the colossal magnetoresistive manganite ferromagnets La$_{2/3}$X$_{1/3}$MnO$_{3+\delta}$ (X = Ca, Sr).
R. de Andrés Prada, T. Golod, O. M. Kapran, E. A. Borodianskyi, Ch. Bernhard and V. M. Krasnov.

*Author’s contribution:* Deposited, characterised and fabricated the samples. Conducted the measurements and analysed the data. Contributed to writing the paper.

III. Growth and Nanofabrication of All-Perovskite Superconducting / Ferromagnetic / Superconducting Junctions.
R. de Andrés Prada, T. Golod, C. Bernhard and V. M. Krasnov.

*Author’s contribution:* Fabricated the samples. Conducted the measurements and analysed the data. Wrote the first draft of the paper.
IV. Magnetic proximity effect and spin-polarization of the charge carriers in La$_{2/3}$Sr$_{1/3}$MnO$_3$/YBa$_2$Cu$_3$O$_7$/Alq$_3$/Co spin valves.
Under review.

Author’s contribution:
Deposited and characterised one of the samples. Participated in the data analysis.

V. Superconductivity and charge-carrier localization in ultra-thin La$_{1.85}$Sr$_{0.15}$CuO$_4$/La$_2$CuO$_4$ bilayers.

Author’s contribution:
Deposited two of the samples.
Papers not included in this thesis

VI. Structural, magnetic and electronic properties of pulsed-laser-deposition grown SrFeO$_{3-\delta}$ thin films and SrFeO$_{3-\delta}$ / La$_{2/3}$Ca$_{1/3}$MnO$_3$ multilayers.

Author’s contribution:
Participated in the data analysis.

VII. Granular superconductivity and charge / orbital order in YBa$_2$Cu$_3$O$_7$ / manganite multilayers.

Author’s contribution:
Participated in the deposition of some of the samples.
Abbreviations

ARPES  Angle-resolved photoemission spectroscopy
CMR   Colossal magneto-resistance
CVD   Chemical vapour deposition
EELS  Electron energy-loss spectroscopy
F     Ferromagnet
FEBID Focused electron beam induced deposition
FI    Ferromagnetic insulator
FIBID Focused ion beam induced deposition
FM    Ferromagnetic (in Chapter 1 is used for ferromagnetic and metallic)
FPGA  Field-programmable gate array
GMR   Giant magneto-resistance
HAADF High-angle annular dark field
HTSC  High temperature superconductor
ICP   Inductively coupled plasma
IR    Infrared
MFC   Mass flow controller
MR    Magneto-resistance
PCB   Printed circuit board
PCI   Peripheral component interconnect
PLD   Pulsed laser deposition
PNR   Polarised neutron reflectometry
PPMS  Physical property measurement setup
PR    Photoresist
PVD   Physical vapour deposition
PXI   PCI extension for instrumentation
RF    Radio frequency
RHEED Reflection high-energy electron diffraction
S, SC Superconductor, Superconducting
SEM   Scanning electron microscopy
SFS   Superconductor/ferromagnetic/superconductor
SLD   Scattering length density
STEM  Scanning transmission electron microscopy
SU    Stockholm University
UHV   Ultra-high vacuum
UniFr University of Fribourg
UV    Ultraviolet
VSM  Vibrating sample magnetometer
VTI  Variable temperature insert
XRD  X-ray diffraction
XRR  X-ray reflectivity

Material abbreviations

\textit{LCMO} \quad \text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3 \\
\textit{LMO} \quad \text{LaMnO}_3 \\
\textit{LSAT} \quad \text{La}_{0.33}\text{Sr}_{0.7}\text{Al}_{0.65}\text{Ta}_{0.35}\text{MnO}_3 \\
\textit{LSMO} \quad \text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3 \\
\textit{tYBCO} \quad \text{Y}_{0.8}\text{Ca}_{0.2}\text{Ba}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_7 \\
\textit{YBCO} \quad \text{YBa}_2\text{Cu}_3\text{O}_7
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Chapter 1

Introduction

The work of this thesis project has been performed in the framework of a collaboration between the University of Fribourg, in Switzerland, and Stockholm University, in Sweden.

The thesis is structured as follows. Chapter 1 describes the context of this work and the motivation for starting the project. Moreover, it summarises the essential properties of the ferromagnetic manganites and the cuprate high $T_c$ superconductors used in this thesis and details the geometry of the devices fabricated. Chapter 2 contains a description of the thin film deposition and the techniques that were used during the fabrication of mesoscopic devices. It also describes the different setups and techniques that were used to characterise these devices. Finally, Chapter 3 presents some of the obtained experimental results and provides a discussion of their interpretation and implications.

1.1 Motivation

Spintronics, or spin-electronics, is a technology that exploits not only the charge of the electrons but also their spin. This is typically achieved by using devices for which the electric resistance is sensitive to a certain spin polarisation of the current [1]. The field of spintronics has gained a renewed interest in the interaction between ferromagnetism and superconductivity. These are two strongly antagonistic phenomena, in particular when considering half-metallic ferromagnets for which the conduction bands are fully spin-polarised [2, 3]. In this case only a spin-triplet component of the superconductivity order parameter can penetrate deep into the ferromagnetic material and give rise to long-range proximity effects [4–7]. Various realisations of such a long-range
spin-triplet component have already been demonstrated when combining conventional superconductors, like Nb or Al, and ferromagnets, such as Fe, Co, or transition metal alloys \[8–10\]. The simultaneous control of both phenomena in multilayered devices may lead to fully spin-polarised supercurrents, which are of great interest for technological applications \[11–14\].

The research in the field of Spintronics based on high temperature superconductors, like the cuprates, and ferromagnetic materials such as the manganites is in comparison far less explored. The cuprates and manganites are members of the large family of complex oxides with exceptional physical properties that emerge due to strong electronic correlations. Factors such as strain, disorder, hole doping, external magnetic fields or finite thickness effects can strongly influence the interplay between the strongly coupled spin, orbital, charge and lattice degrees of freedom and lead to very different kinds of nearly degenerate ground states \[15–17\]. These correlated degrees of freedom give rise to different magnetic, electronic and orbital phases such as insulating, metallic, half-metallic or superconducting states, ferro-, antiferro- or canted antiferromagnetic phases or charge/spin/orbital ordered states \[18–20\].

Furthermore, the lattice parameters of these perovskite-type materials are typically rather well matched, which allows for the deposition of highly ordered thin film heterostructures of different oxides with atomic flat interfaces. Besides strain effects \[21–23\], the interface between two complex oxides can give rise to charge transfer, orbital reconstruction, and a modified magnetic exchange interaction \[24–30\]. Altogether, the complex oxides offer a great variety of interesting physical phenomena with great tunability, and allow for the deposition of epitaxial heterostructures at which various kinds of interface phenomena can be probed. This opens a multitude of possibilities for fundamental research of unusual states in matter, as well as for the implementation of these materials in devices with novel electronic and spintronic functionalities \[31–34\]. For instance, at the interface of complex oxide superconductor/ferromagnet (SF) structures and superlattices it has been shown that the ferromagnetic moment in the F layers can be strongly suppressed \[35–38\] whereas a sizeable magnetic moment is induced in the S layer \[39–43\].

Unfortunately, the above mentioned multitude of competing interactions and orders in the complex oxides and their tunability with various external factors has complicated the device-oriented research in
1.1. **MOTIVATION**

these materials. Besides, in comparison to their conventional superconducting and ferromagnetic counterparts, it is more critical to find fabrication techniques that do not deteriorate the crystalline structure of the oxides and lead to deoxygenation. This has hindered the research in complex oxides with device-oriented applications with respect to other conventional elements and alloys.

Despite of these difficulties, an important step toward the fabrication of devices made exclusively from complex oxides has been made in the context of a collaboration between the groups in Fribourg and Stockholm. They combined the skills in the deposition of high quality complex oxides with the PLD technique and their magnetic and spectroscopic characterisation by the group in Fribourg with the expertise in the nano-fabrication techniques and transport measurements by the group in Stockholm. In this collaboration, SFS structures composed of the high temperature superconductor YBa$_2$Cu$_3$O$_7$ (YBCO) and the ferromagnetic and insulating LaMnO$_3$ (LMO) were deposited with the PLD technique. Subsequently, device-like structures were nano-sculpted so the perpendicular transport across the 20 nm thick LMO barrier could be studied [44]. For these devices, signs of a long range proximity effect across the thick ferromagnetic barrier were obtained, which indicated an unconventional spin-triplet current across the ferromagnetic LMO barrier.

These promising first results provided the motivation for this thesis work for which the focus was on two main aspects.

Firstly, to modify the composition of the SFS structures. The materials employed as the F layer are hole doped versions of the previously used LMO that undergo an insulator-to-metal transition with an enormous decrease in resistance at $T_{\text{Curie}}$ known as colossal magnetoresistance (CMR), see Section 1.2.2. It is most crucial in these perovskites to achieve the largest ferromagnetic order possible and therefore a half-metallic state with a full spin polarisation of the charge carriers in the conduction band. In this sense, different factors were investigated related to the growth conditions of the heterostructures, such as the stoichiometric composition, the oxidation states and the role of defects in the ferromagnetic ordering of the F layers. The results obtained in this respect are published in Paper I [45].

Subsequently, SFS devices were nano-fabricated from multilayers with YBa$_2$Cu$_3$O$_7$ as the S layer and La$_{2/3}$Ca$_{1/3}$MnO$_3$ (LCMO) or La$_{2/3}$Sr$_{1/3}$MnO$_3$ (LSMO) as the F layer. The perpendicular transport through these heterostructures was found to be strongly influenced
by the ferromagnetic ordering in the manganites and the CMR effect, which resulted in a strong dependence of the resistance with an external magnetic field manifested by a hysteretic behaviour in the vicinity of zero field. This resistive bistability is published in Paper II [46], where we suggested its potential functionality as a ferromagnetic memory cell.

Secondly, to investigate the effect of reducing the thickness of the ferromagnetic LMO barrier. For this, two SFS structures were deposited with the same profile as in the former study, differing only in the thickness of the barrier (10 nm and 5 nm as compared to 20 nm in the first SFS structure). The obtained results are published in Paper III [47].

1.2 Introduction to perovskites

Figure 1.1 shows a sketch of a typical perovskite unit cell with the general formula ABO$_3$, where A and B are cations of different sizes and O is an oxygen anion that bonds the cations. The most extended representation of the unit cell of these materials locates the B cations (those with smaller ionic radii) at the corners of a cubic lattice, with the anions centred in the edges and the A cations sitting at the centre of the cube. Thus, the anions are located on the corners of an octahedron that encloses the small cations, as illustrated in Fig. 1.1. The inclusion

![Figure 1.1: Unit cell of a generic perovskite ABO$_3$. The oxygen ions form an octahedron that encloses the B cations.](image-url)
of cations with different oxidation states and ionic radii determines the structural, electronic and magnetic properties of the resulting material, making these compounds largely versatile and interesting. The properties of the perovskites strongly depend on the intra-unit cell geometry and, therefore, on the ionic radii disparity between the cations in the compound. The tolerance factor $f$ of the compound is a geometrical quantity defined as

$$f = \frac{d_{A-O}}{\sqrt{2} d_{B-O}}, \quad (1.1)$$

where $d_{Z-O}$ ($Z = A, B$) is the distance from the $Z$ site to the nearest oxygen [48]. It can be understood as the degree of lattice distortion, as it accounts for the lattice matching between the atomic AO and BO$_2$ planes that constitute the perovskite structure. When $f$ is close to 1 the stacking of the atomic planes is well matched, and the unit cell has the cubic lattice structure shown in Figure 1.1. As $f$ decreases, for $0.96 < f < 1$ the lattice distorts and becomes rhombohedral and, for $f < 0.96$, an orthorhombic coordination emerges [15]. The straight B–O–B bonds found in the cubic lattice bend as $f$ decreases, i.e. as the mismatch grows, and for the orthorhombic lattice the bond angle $\phi$ varies continuously with $f$ [20]. As it will be later discussed, the angle formed by the B–O–B bond strongly influences the magnetic exchange interactions.

In the case of manganites, or manganese oxide perovskites, the general formulation used is $\text{RE}_{1-x}\text{AE}_x\text{MnO}_3$, where the previous A cation is substituted on occasion either by a rare earth (RE) or by a divalent alkaline earth (AE), with the ratio between these two given by $x$. The Mn cations are those of smaller ionic radius and thus occupy the corners of the unit cell, while O remains as the bonding anion. The symmetric arrangement of the oxygen ions surrounding the Mn ions in an octahedral coordination induces a highly directional Coulomb interaction along the Mn–O directions, which is expressed in terms of a crystal field that strongly influences the electronic structure of the cation. This crystal field gives rise to a splitting of the five-fold degenerate Mn 3$d$ orbitals, since the orbitals oriented along the bond directions are of higher energy than those oriented along the diagonals. Thus, the Mn 3$d$ orbitals are split into three degenerate $t_{2g}$ levels for which the lobes are oriented along the diagonals, and two degenerate $e_g$ levels for which the lobes are oriented along the Mn–O bonds. Figure 1.2 represents schematically the crystal field splitting of the 3$d$ energy levels.
CHAPTER 1. INTRODUCTION

Figure 1.2: Level scheme of the 3d orbitals of a Mn$^{3+}$ ion in an octahedral oxygen environment. **Left panel:** The 3d orbitals of the isolated cation are degenerate. **Central panel:** the Coulomb repulsion due to the crystal field increases the energy of the two $e_g$ orbitals oriented along the bonding directions with respect to the three $t_{2g}$ orbitals that are oriented along the diagonals. **Right panel:** Jahn-Teller splitting of the $e_g$ levels as a consequence of a spontaneous octahedral distortion that reduces the energy of the occupied levels. Adapted from [48].

The electrons accommodate in these orbitals maximising the total spin $S$ due to Hund’s coupling. In the case of the cation Mn$^{3+}$ each $t_{2g}$ level is occupied by one electron with their spins aligned parallel, thus maximising $S$. The forth electron resides in one of the $e_g$ levels with its spin parallel to the spins of the electrons in the $t_{2g}$ levels. The energy of this forth $e_g$ electron can be reduced by spontaneous lattice distortions, which reduce the energy of one of the $e_g$ levels (that gets occupied) and correspondingly increase the energy of the other (which remains empty). This spontaneous symmetry breaking and distortion of the oxygen octahedron to lift the degeneracy of the $e_g$ levels, as shown in Figure 1.2, is known as Jahn-Teller effect. Besides Jahn-Teller distortions, which are driven by the minimisation of the electronic ground state energy, there exist also cooperative rotations of the MnO$_6$ octahedra that are structural driven and can further reduce the symmetry of the lattice.
1.2. INTRODUCTION TO PEROVSKITES

1.2.1 The parent compound LaMnO$_3$

The manganites studied in this thesis are LaMnO$_3$, La$_{2/3}$Ca$_{1/3}$MnO$_3$ and La$_{2/3}$Sr$_{1/3}$MnO$_3$. The former LaMnO$_3$ (denoted in the following as LMO) is often referred to as parent compound of the lanthanum manganites. The La/Mn ionic size mismatch leads to a tolerance factor for this compound of $f \sim 0.95$. The corresponding orthorhombic crystalline unit cell of LMO is presented in Figure 1.3, where the O anions have been removed to better visualise the octahedral distortions and rotations. The symmetry of the cell is reduced from cubic to orthorhombic, due to a rotation of the MnO$_6$ octahedron around the [1 1 0] axis in combination with the Jahn-Teller distortions [49]. The electronic configuration of the Mn cations is [Ar] 3$d^4$, or Mn$^{3+}$, equivalent to that shown in Figure 1.2. The combination of Jahn-Teller distortions and the large on-site Coulomb repulsion prevents the delocalisation of the $e_g$ electrons and binds them to the Mn sites, thus resulting in an insulating behaviour. Moreover, the $S = 2$ Mn$^{3+}$ cations couple via ferromagnetic superexchange along the crystallographic $ab$ planes, while antiparallel superexchange dominates along the $c$ direction. This leads to an $A$-type antiferromagnetic ordering of the moments in LaMnO$_3$ below a transition temperature of $T_N = 120$ K [49, 50].

![Figure 1.3: Extended unit cell of LaMnO$_3$ (dashed line). The O atoms at the vertices of the octahedra have been removed to better notice the distorted octahedral lattice. Solid lines indicate the pseudocubic unit cell.](image-url)
Hole doping this compound changes dramatically the described properties. The inclusion of electron vacancies in the $e_g$ levels in the form of Mn$^{4+}$ sites allows for the $e_g$ electrons to hop between neighboring sites. This intersite hopping occurs with a probability

$$t_{ij} \propto \cos(\theta_{ij}/2)$$

that depends on the relative angle $\theta_{ij}$ between the classical spins in the neighbouring $i, j$ sites. Therefore, the delocalisation of the $e_g$ electrons is maximal when the spins of the neighbouring Mn sites are oriented parallel, i.e. ferromagnetically aligned, as illustrated in Figure 1.4. This ferromagnetic interaction governed by the exchange of conduction electrons was first suggested by Zener, who termed it double exchange interaction [51, 52]. The given name stresses the importance of the O anions.

![Figure 1.4](image)

Figure 1.4: Sketch illustrating the double exchange mechanism. For two neighbouring Mn$^{3+}$ and Mn$^{4+}$ ions, the magnetic exchange is mediated by the O $2p_\sigma$ orbital oriented along the bonding direction. The electron in O $2p_\sigma$ with spin parallel to the $t_{2g}$ electrons on the right can jump to the Mn$^{4+}$ $e_g$ level, leaving behind a hole in O$^+$. The Mn$^{3+}$ $e_g$ electron can hop to O$^+$ only if its spin has the same orientation of the hole, i.e. the same orientation of the neighbouring Mn site (upper panel). This results in a net transfer of the $e_g$ hole in Mn$^{4+}$ to the left. If the spin orientations of the Mn sites are antiparallel (lower panel) the O$^+$ hole and the Mn$^{3+}$ $e_g$ electron have opposite spins and the exchange does not occur.
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in the exchange since, as depicted in Figure 1.4, the interaction is mediated by the O 2p orbitals. In particular, the angle $\phi$ of the Mn–O–Mn bond plays a fundamental role in the one-electron bandwidth $W$ (proportional to the hopping $t$) as the electron transfer between O 2p and Mn 3d states can be expressed by

$$t_{pd} \approx t_{pd}^0 |\cos \phi|,$$

where $t_{pd}^0$ is the hopping amplitude for the ideal cubic perovskite. Hence the transfer between neighbouring Mn 3d orbitals $t_{dd}$ is proportional to $t_{pd}^2$ and thus to $\cos^2 \phi$. Accordingly, the bandwidth $W$ decreases as the lattice mismatch increases, i.e. as the tolerance factor $f$ deviates from 1.

The double exchange interaction tends to delocalise the $e_g$ electrons and induce a metallic phase in the perovskites, and competes with the Jahn-Teller coupling that localises the electrons with collective deformations of the octahedral network. In the case of LaMnO$_3$, it has been demonstrated that it is possible to go from the discussed antiferromagnetic insulating state to a ferromagnetic metallic state by tuning the Mn/La ratio, which is equivalent to hole doping the material [49, 53–56]. However, the most commonly used mechanism for hole doping this compound is via the cationic substitution of La by divalent alkali earths, which is discussed in the next subsection.

1.2.2 Hole doped compounds: La$_{2/3}$Ca$_{1/3}$MnO$_3$ and La$_{2/3}$Sr$_{1/3}$MnO$_3$

Figure 1.5 depicts the phase diagrams of La$_{1-x}$Ca$_x$MnO$_3$ (left) and La$_{1-x}$Sr$_x$MnO$_3$ (right) as a function of the hole doping $x$, i.e. the addition of the divalent cations Ca$^{2+}$ and Sr$^{2+}$, respectively. In both compounds the AF coupling of the ferromagnetic $ab$ planes along the $c$ axis discussed for LaMnO$_3$ dilutes as the hole doping increases, evolving from a canted configuration of spins to a ferromagnetic and insulating (FI) phase, and then to a ferromagnetic and metallic (FM) phase which emerges at a doping level above $x \sim 0.17$. The $T_{Curie}$ of this FM phase steeply increases up to $x = 3/8$ for La$_{1-x}$Ca$_x$MnO$_3$ and $x = 0.3$ for La$_{1-x}$Sr$_x$MnO$_3$. Further hole doping these compounds decreases $T_{Curie}$ and, beyond $x = 0.5$, the FM phase gives way to an AF order that is accompanied by a charge ordered (CO) phase. The variety of phases that can be found upon hole doping these materials demonstrates the multitude of interactions that simultaneously compete in these struc-
tasures, making them of exceptional interest for fundamental research as well as for potential commercial applications.

The compounds studied in this work correspond to a doping level of $x = 1/3$ and, for convenience, in the upcoming $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ and $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ will be simply denoted as LCMO and LSMO, respectively. Both materials are located in the centre of the FM region of their phase diagrams, as indicated by the green vertical lines in Figure 1.5. These manganites present a theoretical magnetic saturation of $3.7 \mu_B/\text{Mn ion}$ and Curie temperatures of $T_{\text{Curie}} \approx 270 \text{ K}$ and $370 \text{ K}$ for LCMO and LSMO, respectively [57–62]. The large discrepancy in the Curie temperatures of these manganites can be explained considering the different atomic radius of $\text{Ca}^{2+}$ and $\text{Sr}^{2+}$. Indeed, upon the inclusion of $\text{Sr}^{2+}$ cations in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, the tolerance factor increases from $f \sim 0.95$ for $x = 0$ (corresponding to LMO, see Section 1.2.1) to $f \sim 0.98$ for $x = 1/3$. In such well-matched lattice the bandwidth $W$ is large since the Mn–O–Mn bonds are close to straight. The double exchange is strongly enhanced in materials with a large bandwidth, as discussed in the previous Section, and thus the double exchange dominates the ground state and a ferromagnetic configuration is found for LSMO even at room temperature.

Figure 1.5: Phase diagrams of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ (left) and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (right) as a function of the $\text{Ca}^{2+}$ and $\text{Sr}^{2+}$ content $x$, respectively. Green vertical lines mark the compositions used in this work, corresponding to $x = 1/3$. CO: charge/orbital ordering; FM: ferromagnetic metal; AF: antiferromagnetic; CI: spin-canted insulator; PI: paramagnetic insulator; PM: paramagnetic metal; AFM: antiferromagnetic metal. FI and/or CAF could be a spatially inhomogeneous states with FM and AF coexistence. From [15, 48].
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On the other hand, the addition of Ca$^{2+}$ cations has a reduced impact on the tolerance factor, which increases only to $f \sim 0.97$ for LCMO. In this distorted lattice the Mn–O–Mn bonds are not straight and the bandwidth is reduced. At high temperatures the spin configurations are largely disordered between Mn sites and, following equation (1.2), the effective hopping interaction is on average reduced. The ferromagnetic coupling via double exchange is thus blocked, and Jahn-Teller coupling dominates. At progressively lower temperatures the degree of spin disorder is reduced and the moments in the Mn sites gradually align favouring double exchange interactions. Finally, at $T_{\text{Curie}}$ the transition from PI to FM occurs.

Notably, the same mechanism that enables the double exchange interactions only for a ferromagnetic alignment of the on-site spins also strongly polarises the conduction band. Indeed, at the Fermi level there is only one spin polarisation that contributes to the conduction band while the hopping for the opposite polarisation is neglected (as schematically depicted in Figure 1.4). This effectively displaces the band of the neglected polarisation higher in energy, with one spin channel being metallic and the other insulating [63]. The materials with such spin splitting of the conduction bands are called half-metallic, and are naturally of great interest in spintronics.

![Figure 1.6: Extended unit cells of LCMO (left) and LSMO (right), highlighted by dashed lines. The O atoms at the vertices of the octahedra have been removed to better observe the distorted octahedral lattice. Solid lines indicate the pseudocubic unit cells (in the case of LSMO two pseudocubic unit cells are indicated).](image-url)
Moreover, the PI to FM transition described for LCMO can also be field induced. In the vicinity of $T_{\text{Curie}}$ it was found that the application of an external magnetic field aligning ferromagnetically the core spins of the Mn sites enables the $e_g$ electrons to gain kinetic energy and delocalise, thereby reducing the electric resistance by several orders of magnitude. This phenomenon was called colossal magneto-resistance (CMR) [64] to distinguish it from the giant magneto-resistance (GMR) observed in heterostructures from paramagnetic and ferromagnetic metals [65, 66]. The unit cells of LCMO and LSMO are plotted in Figure 1.6 (dashed lines), with the pseudocubic unit cell marked by solid lines. Note that the unit cell of LSMO is rhombohedral, corresponding to a tolerance factor close to 1. Interestingly, a similar rhombohedral structure should correspond to LCMO ($f \sim 0.97$) since, as it was mentioned in Section 1.2, the orthorhombic coordination emerges only for $f < 0.96$ [15]. Yet, the unit cell of LCMO is in fact orthorhombic [67, 68].

1.3 The high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

The high temperature superconductivity (HTSC) in the cuprates was first observed in the ceramic compound La$_{1-x}$Ba$_x$CuO$_4$ with an unprecedented $T_c$ of 30 K [69]. Later, it was discovered that the superconducting order parameter could survive up to 52 K upon the application of external pressure [70]. Substituting La by Y increases the chemical pressure in the lattice, leading to the realisation of an even higher $T_c$ of $\sim$ 90 K [71]. This new Y-Ba-Cu-O compound was later found to be YBa$_2$Cu$_3$O$_{7-\delta}$ [72].

The unit cell of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) corresponding to $\delta = 0$ is represented in Figure 1.7. It differs from the often called parent compound YBa$_2$Cu$_3$O$_6$ by the inclusion of one oxygen in the O(I) position. The structural feature common to the HTSC cuprates is the presence of edge-sharing CuO$_2$ planes separated by layers containing rare-earths and oxygen. It is agreed that the CuO$_2$ planes host the superconducting carriers, while in the case of YBCO the Cu-O chains separating the planes have the function of a charge reservoir. In the undoped YBa$_2$Cu$_3$O$_6$ the oxidation state of the Cu(II) cations contained in these planes is Cu$^{2+}$ and the corresponding electronic configuration is $[\text{Ar}] \ 3d^9$. The hopping of electrons between neighbouring Cu(II) sites is restricted by the strong on-site Coulomb repulsion between the elec-
1.3. THE HIGH \( T_c \) SUPERCONDUCTOR \( \text{YBa}_2\text{Cu}_3\text{O}_7-\delta \)

Figure 1.7: Unit cell of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \). The Cu-O chains develop as more O is added in the O(I) sites starting from the parent compound \( \text{YBa}_2\text{Cu}_3\text{O}_6 \). The CuO\(_2\) planes are highlighted in the central part of the unit cell.

electrons in the \( d \) orbitals. Moreover, the spins of the Cu\(^{2+}\) ions are antiferromagnetically coupled via superexchange through the O 2\( p_\sigma \) orbitals, making up for an antiferromagnetic and charge-localised (insulating) state [73]. Hence, an effective gap opens in energy splitting the \( e_g \) orbitals in two bands, one fully occupied with the 3\( d \) electrons and another unoccupied [17]. \( \text{YBa}_2\text{Cu}_3\text{O}_6 \) is thus a charge-transfer insulator, and in the Mott-Hubbard model the split bands are denominated lower Hubbard band (LHB) and upper Hubbard band (UHB), respectively, as depicted in Figure 1.8. On the other hand, the Cu cations occupying Cu(I) sites give their 4\( s^1 \) electron to the apical O(IV) oxygens and keep a closed electronic \( d \)-shell, thus having a minor contribution to the dc conductivity.

Figure 1.9 shows the general phase diagram of the cuprates as a function of the hole doping \( y \) in the CuO\(_2\) planes. In YBCO this hole doping can be achieved by a partial cationic substitution of Y\(^{3+}\) by Ca\(^{2+}\) [75], by pressure along the crystalline \( c \) direction or by the addition of oxygen to the lattice. The latter is more complicated in \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) than in other HTSC cuprates due to the presence of the Cu-O chains. The addition of oxygen ions in the lattice, which accommodate in the O(I) positions, affects primordially the oxidation of the
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Figure 1.8: The Mott-Hubbard model of a charge-transfer insulator, with the half filed 3d band splitting into the empty upper Hubbard band (UHB) and the full lower Hubbard band (LHB). Adapted from [74].

Cu(I) sites, introducing holes in the $e_g$ levels of the Cu-O chains. Only a certain portion of the introduced holes migrates to the CuO$_2$ planes affecting also the electronic structure of the Cu(II) sites. The amount of migrated holes with respect to the oxygen doping is ambiguous and non-lineal with the total oxygen introduced in the lattice [76, 77].

In the region $1 > \delta > 0.6$ (equivalent to $0 < y < 0.05$) the holes are predominantly introduced in the $e_g$ levels of the Cu(I) sites. However, the small amount of holes transferred from the Cu-O chains to the CuO$_2$ planes rapidly reduces the antiferromagnetic ordering. Below $\delta = 0.6$ (or above $y = 0.05$) the destruction of the antiferromagnetic ordering is complete, leading to a metallic phase and a sizable $T_c$. Therefore, the hole concentration in the CuO$_2$ planes controls the magnetic and electronic properties of the system.

It is interesting to note that the one-directional Cu-O chains develop a long-range coherence along the crystalline $b$ direction with the progressive addition of oxygen that results in a structural transition. For $\delta = 1$ the Cu-O chains are fully deoxygenated and there is a single hole per Cu(II) site, leading to a tetragonal and antiferromagnetic phase. In the limit case of $\delta = 0.6$ the Cu-O chains are sufficiently populated with oxygen in O(I) positions to develop a coherent assemble along the crystalline $b$ direction, which is elongated with respect to the
1.3. THE HIGH $T_c$ SUPERCONDUCTOR YBa$_2$Cu$_3$O$_{7-\delta}$

$a$ direction. Moreover, a small proportion of the holes in these Cu-O chains are transferred to the CuO$_2$ planes, sufficient to break the superexchange mechanism that results in the antiferromagnetic ordering. A new metallic, orthorhombic phase emerges at $\delta = 0.6$ ($y = 0.05$) with $a < b \ll c$. In thin films this long-range coherence can be suppressed by strain transfer from the substrate to the YBCO layer. However, there are evidences of a threshold thickness of $\sim 15$ nm above which the strain is relaxed and the YBCO layer recovers its orthorhombic unit cell [40, 79], often accompanied by the introduction of defects and stacking faults [80].

The superconducting underdoped region of the phase diagram extends between $\delta = 0.6$ and $\delta = 0.07$ (from $y = 0.05$ to $y = 0.15$). Here, a rapid increase in $T_c$ is observed up to $\delta \sim 0.4$ ($y \sim 0.11$) due to a larger transfer of holes into the CuO$_2$ planes, with $T_c$ reaching $\approx 60$ K [18]. The transfer of holes above $\delta \sim 0.4$ is less pronounced and results in a slower increase of $T_c$ up to the optimal doping, which corresponds to $\delta \sim 0.07$ ($y \sim 0.15$). For the optimally doped YBa$_2$Cu$_3$O$_{6.93}$ the $T_c$ is as high as 93 K [71, 72]. Further doping of YBCO above the optimal level leads to an overdoping effect that gradually reduces $T_c$. The fully

![Figure 1.9: General phase diagram for the HTSC cuprates as a function of the temperature and the hole doping of the CuO$_2$ planes $y$. Taken from [78].](image-url)
oxygenated YBa$_2$Cu$_3$O$_7$ falls therefore in the overdoped region, with $T_c \approx 90$ K. Despite of a strong confinement of the superconducting carriers to the CuO$_2$ planes (especially at lower doping values), the out-of-plane component of the resistivity has been found to exhibit a full superconducting transition with a complete drop to zero resistance at the same critical temperature as for the in-plane response [81].

1.4 Transport across SFS junctions

When a superconductor S and a normal metal N are adjacent to each other, the superconducting Cooper pairs can diffuse into the normal metal across the SN interface up to a certain length $\xi_n$. The latter parameter is known as the coherence length in the normal metal and depends on the Fermi velocity, the temperature and the disorder in the metal [12]. The diffusive penetration of superconducting Cooper pairs into the normal metal is denoted as the proximity effect, and was first formulated by Pierre-Gilles de Gennes in 1963 [82]. The pair in the metal is not an eigenstate but an evanescent state. If we consider a SN interface perpendicular to the $x$ direction, the induced wavefunction due to the penetration of pairs decays exponentially in the metal as

$$\Psi = \Psi_n \exp(-x/\xi_n),$$

where $\Psi_n$ is the order parameter at the interface. This exponential decay of the wavefunction in the metal is illustrated in the upper panel of Figure 1.10. Besides the diffusion of superconducting pairs in the metal, the electrons in the metal can also penetrate into the superconductor even if their energy is lower than the superconducting energy gap. This process, denominated Andreev reflexion, was demonstrated by A. F. Andreev in 1964 [83]. Here an electron with an energy close to the Fermi energy pairs with another electron of opposite spin in the normal metal, penetrating into the S as a Cooper pair. According to the conservation energy and momenta, the paired electron leaves behind a hole with the same energy as the first electron and opposite moment, which propagates in the metal as if it was reflected by the interface.

If we now place another superconductor at the opposite interface of the normal metal we construct a Josephson junction. The hole generated in the Andreev reflexion propagates across the metal until it reaches the second SN interface, where it converts back into an electron by destroying a Cooper pair and thus resulting in a transfer of electron pairs between superconductors. Moreover, if the thickness of
1.4. TRANSPORT ACROSS SFS JUNCTIONS

Figure 1.10: Schemes illustrating the proximity effect. **Upper panel:** The wavefunction of the pairs decays exponentially as they penetrate into the normal metal. **Lower panel:** If the normal metal is thin enough, two S layers separated by it can establish a phase difference in their order parameters due to the overlap of their wavefunctions in the metal. Adapted from [84].

The normal metal is smaller than the coherence length $\xi_n$, the wavefunctions of either superconductor overlap in the metal, as illustrated in the lower panel of Fig. 1.10, and a phase coherence is established between the superconductors.

The dc and ac Josephson effects demonstrate the occurrence of this coherence. In such a SNS junction, the dc Josephson effect shows that the supercurrent across the junction $I$ is a function of the difference of the macroscopic phases of the superconductors

$$I = I_c \sin(\varphi_1 - \varphi_2). \quad (1.5)$$

Here $\varphi_1 - \varphi_2$ is the phase difference between the macroscopic order parameters of the superconductors, and $I_c$ is the critical current of the junction. If the junction is now biased to a constant dc voltage $V$ the
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Figure 1.11: Diagram showing the change in momentum of two different singlets upon entering a F layer with a certain exchange field $h_{ex}$. **Upper panel:** $|\downarrow\uparrow\rangle$ singlet. **Lower panel:** $|\uparrow\downarrow\rangle$ singlet. The exchange field in the F layer alters the potential energy profile of the pair. The total energy is balanced by adjusting the kinetic energy of each electron by $\pm \Delta k_F$, inducing a finite moment $Q = \pm 2\Delta k_F$ in the pair’s centre-of-mass. Adapted from [86].

Phase difference varies with time, and an alternating current crosses the junction with a frequency

$$\frac{d(\varphi_1 - \varphi_2)}{dt} = \frac{2e}{\hbar} V.$$  \hspace{1cm} (1.6)

This is the ac Josephson effect. Together, the dc and ac Josephson effects demonstrate the macroscopic quantum nature of superconductivity and the existence of a macroscopic wavefunction common to the whole condensate. They were first predicted for SIS junctions (I = insulating layer) by B. D. Josephson in 1962 [85], who was awarded with the Nobel Prize in Physics in 1973.

The proximity effect described for a SN interface also takes place when the normal metal is substituted by a ferromagnetic metal F. However, the exchange field $h_{ex}$ present in the F layer adds an extra energy term $E_{ex}$ to the Cooper pairs as it establishes a preferential orientation.
of the spins. Let us consider a pair formed by an electron 1 of spin down and an electron 2 of spin up with equal moments of different sign $\mp k_F$, and an exchange field $h_{ex}$ in the F parallel to the spin up configuration, as depicted in the upper panel of Figure 1.11. Upon entering the F layer the electron 1 increases its potential energy by $E_{ex}$, the exchange field energy in F, while the electron 2 decreases its potential energy by the same amount. The pair keeps its energy equilibrium by decreasing the kinetic energy of electron 1 and increasing it for electron 2.

The moments of either electron change by $\Delta k_F$ so that the new kinetic energy compensates for the potential energy gained $E_{ex}$, and thus

$$\Delta k_F = \frac{E_{ex}}{\hbar v_F}, \quad (1.7)$$

where $v_F$ is the Fermi velocity. The centre-of-mass of the Cooper pair acquires a momentum $Q$

$$Q = k_1^\uparrow + k_2^\uparrow = 2\Delta k_F = \frac{2E_{ex}}{\hbar v_F}. \quad (1.8)$$

The wavefunction of eq. (1.4) that describes the proximity effect across a SN interface gains now an extra term due to the exchange field present in the F layer, and takes the form

$$\Psi_{\downarrow\uparrow}(x) = \Psi_f \exp(-x/\xi_f) \exp \left( \frac{2E_{ex}}{\hbar v_F} x \right). \quad (1.9)$$

If we consider now the opposite case with the spin of the electron 1 up and the spin of the electron 2 down (depicted in the bottom panel of Fig. 1.11) we can apply the same reasoning. In this case, the centre-of-mass of the Cooper pairs gains a total moment

$$Q = k_1^\uparrow + k_2^\downarrow = -2\Delta k_F = -\frac{2E_{ex}}{\hbar v_F}, \quad (1.10)$$

and the wavefunction takes the form

$$\Psi_{\uparrow\downarrow}(x) = \Psi_f \exp(-x/\xi_f) \exp \left( -\frac{2E_{ex}}{\hbar v_F} x \right). \quad (1.11)$$

In the condensate both pairs are equally probable, so the wavefunction of the proximity effect in a F layer is the superposition of both states:

$$\Psi(x) = \frac{1}{2} \left[ \Psi_{\downarrow\uparrow}(x) + \Psi_{\uparrow\downarrow}(x) \right] = \Psi_f \exp(-x/\xi_f) \cos \left( \frac{2E_{ex}}{\hbar v_F} x \right). \quad (1.12)$$
The total state of the Cooper pairs has an oscillatory decay as it travels through the F layers, as illustrated in Figure 1.12. The wavefunction oscillates in the F layer with a wavelength

\[ \lambda = \frac{\pi \hbar v_F}{E_{ex}}. \] (1.13)

It is important to note that the wavelength of the oscillations decreases as the exchange energy \( E_{ex} \) increases. Therefore, the decay of the superconducting states in the F layer is less abrupt for weakly spin-polarised ferromagnets, and gains in sharpness as the spin polarisation increases. In the limit case of a half-metal, the pairs do not enter the F layer and the proximity effect is forbidden. However, in the previous formulation we only considered Cooper pairs in a singlet state. It is easy to see that for the case of a triplet penetrating in the F layer the kinetic energy is not readjusted as a consequence of an unbalanced gain of potential energy, and thus \( Q = 0 \). This makes the diffusion into the F layer analogue to that of the SN case, and thus triplets penetrate over long distances across the SF interface.

Unfortunately, Cooper pairs in a triplet configuration of spins are far less probable than singlets due to the energy minimisation that

![Figure 1.12: Scheme illustrating the proximity effect in a ferromagnetic layer. The exponential decay of the order parameter gains an extra oscillatory term (see equation (1.12)). The wavefunction thus oscillates with a wavelength inversely proportional to the exchange energy in the F layer. Adapted from [84].](image-url)
occurs upon pairing electrons with opposite spin. The generation of such triplets was first predicted considering a SF interface at which the magnetisation in the F layer rotates in a spiral in a region close to the interface [87]. The spin quantisation was predicted to follow the spiral magnetisation and result in an equal-spin pair generated by triplet mixing with a long-range penetration into the ferromagnet. This has been experimentally realised using intrinsic properties of the F layer, such as conical ferromagnets [88] or magnetic inhomogeneities near the interface [89], and extrinsic in the form of multilayered arrangements of non-collinear magnetic structures [8, 9, 90, 91].

1.5 **Geometry of the mesoscopic devices**

The deposition of SFS heterostructures composed solely of complex oxides can be achieved by pulsed laser deposition (PLD). In this technique, the samples are deposited layer-by-layer on a perovskite substrate with similar lattice parameters to those of the materials to deposit. If the perpendicular transport across the heterostructure is to be probed, it is possible to choose a substrate doped with metallic impurities that can function as a bottom electrode. However, the appearance of pinholes in the layers increases as their thickness is reduced, and thus the substrate-electrode option is not suitable for structures with thin layers since the large planar surface probed (i.e. the total area of the substrate) increases the chances of measuring through pinholes. Instead, nano-fabrication techniques are typically used in conventional superconductors and ferromagnets to selectively deposit or remove parts of the samples and reduce the total area studied, thus minimising the occurrence of pinholes in the measurements.

![Figure 1.13: Example of a deposition – lithography – deposition – lift-off cycle. The areas at which a second deposition is not desired are covered with lithography. The lift-off of the resist takes away the layers deposited in the undesired areas.](image)
A standard nano-fabrication process is, for example, the deposition – lithography – deposition – lift-off cycle illustrated in Figure 1.13. Here the materials are selectively deposited during the second deposition thanks to the masking of certain areas of the sample with lithography. The resist used in this technique may later be removed in the lift-off, thus removing also the material deposited on top of it. This simple process may be further complicated by adding more intermediate steps, achieving a great flexibility. Besides, the use of conventional elements and alloys allows for selective etching of each material composing the sample, either by reactive ion etching (RIE) or wet etching using the appropriate gas or chemical solution, respectively. This further enhances the possibilities of the fabrication specially when combined with lithography, as it permits to selectively etch trenches in only certain layers while the others remain intact.

Working with complex oxides, however, is more complicated. The last few nanometers of a sample passivate and deoxygenate as soon as the sample is exposed to room conditions. Therefore, a fabrication cycle like the one proposed in Fig. 1.13 would lead to passivated interfaces and ruin the experiment. Moreover, the complex oxides are generally annealed in an O\textsubscript{2} high pressure to ensure the full oxygenation of the lattice. The annealing temperature, which must be sufficiently high to allow for the penetration of O\textsubscript{2} gas in the sample without activating the diffusion of the cations, is much lower than the deposition temperature (of 800 °C or higher) thus meaning that a second deposition on top of an already grown layer (exposed to room conditions and the chemicals used during the lithography) would lead to a further deterioration of the latter and reduce the deposition quality of the former. Finally, the multitude of elements that generally compose the complex oxides complicates the selective etching of only certain species and pushes inevitably toward a physical, non-selective etch (sputtering).

The description of the fabrication process and the techniques used to pattern, etch and sculpt devices in the PLD deposited SFS heterostructures is detailed in Section 2.1.2. The geometry of the fabricated devices is illustrated in Figure 1.14. Here, focused ion beam (FIB) is used to reduce the measurement area to a thin bridge of \(~275\) nm in width (upper panel), and two cuts interrupt the either S electrodes, respectively, ensuring that the current passes only across the F layer (lower panel). With this geometry the area probed in the F layer is small, reducing the probability of encountering pinholes. However, these nanometric cuts fall within the resolution limit of the FIB setup.
Figure 1.14: **Upper panel:** Top view of a bridge fabricated with FIB. The ion beam is used to define a narrow structure of ~275 nm. The transport across this bridge is limited to the upper S layer, as indicated by the white arrows in the inset scheme. **Lower panel:** Side view of a device, consisting on a bridge at which two sidecuts interrupt either S layer, thus ensuring that the transport in this device occurs only across the F layer delimited by the sidecuts. The white arrows in the inset scheme demonstrate the path followed by the current across such a device.

employed, demanding large S electrodes in order to safely “overcut” either S layer without taking the risk of cutting the totality of the heterostructure. The thickness of the S layers is therefore a critical factor during the nano-sculpting of the devices. After testing different thicknesses in SFS structures, it was decided that the minimum thickness of the S layers to work comfortably during the FIB sessions would be of 100 nm.
The deposition of SFS structures with such thick S layers entails a challenge when working with perovskites. In general, the superficial roughness increases with the thickness and complicates the subsequent deposition of a thin F layer. Moreover, the orthorhombicity that emerges in YBCO due to the long-range coherence of the Cu-O chains, as pointed in Section 1.3, cannot be constrained by substrate strain since the thickness of the S layer is far larger than the estimated critical thickness for the strain relaxation, of about 15 nm [40, 79]. This relaxation of the lattice is usually accompanied by defects and stacking faults [80] that further distort the surface at which the F layer is deposited. This is of fundamental importance, since the ferromagnetic phase emerges in manganites due to a double exchange interaction that strongly depends on the hopping probability and thus on the angles of the Mn–O–Mn bonds (see Section 1.2.1). All these difficulties have been addressed in this work, and in particular Section 3.1 expands the results published in Paper I on this matter.
Chapter 2

Experimental

This Chapter describes the experimental methods used to deposit and prepare the samples, as well as the techniques used for their characterisation. Section 2.1 outlines the sample preparation, subdivided in the deposition of the samples and the device fabrication. The latter applies only to those samples that were deposited with a SFS profile and showed promising results during their characterisation. Devices were only fabricated in a small portion of the samples deposited. Most of them, however, were means to get to those interesting structures, control and calibration samples or were deposited for fundamental physics exploration. Finally, Section 2.2 describes the characterisation techniques used during this work.

2.1 Sample preparation

The samples studied in this work were all deposited by means of pulsed laser deposition (PLD). The growth of the samples took place in the Physics Department of UniFr. The physical mechanisms involved in the PLD process, together with a description of the setup used are outlined in Section 2.1.1. Some of the samples were further processed in order to fabricate devices on them. The steps involved in this fabrication process are described in Section 2.1.2.

2.1.1 Pulsed laser deposition

PLD is the technique employed for the deposition of all samples that are studied in this thesis. This technique is part of the physical vapour deposition (PVD) family, which shares the common feature of using
solid targets with the same composition and stoichiometry as the material to be deposited, and differs on the physical procedure used to extract this material from the target. In PLD the growth is governed by plasma generation and manipulation, as it is in sputtering, but in a different manner. In PLD there is no power applied to electrodes, no electric field ionising the gas, and the plasma is not ignited all the time or all over the target. Instead, a pulsed laser is used to generate an intense pulse of light that is focused on the surface of the target. This laser pulse transmits its energy to the target, sublimating its surface and generating a plasma plume that carries the species of the target across the chamber as it expands. A substrate is located in the path of the plume, allowing for the condensation of the species as thin films.

The main advantages of this technique are the stoichiometric transfer from the target to the substrate and the localised generation of the plasma over the surface of the target, which translates in large deposition rates out of rather small sized targets and no need of target cooling. On the other hand, the plasma generated by the pulse is confined in a small lateral surface, and therefore the area at which a homogeneous growth is obtained is limited. The next subsections review the basic physical principles of PLD, and describe the setup that was used.

Deposition process

As mentioned previously, pulses of light generated by a laser are focused on the surface of the target, where they generate a plasma. The nature of the plasma thus depends on the interaction between the target and the light pulse. The photons mostly interact with the electrons in the target since the ions are too heavy to follow the frequency of the laser, usually centered in the near ultraviolet (UV). This interaction is confined to the optical penetration depth of the light into the target and the illuminated area, which in the present case is of about 3 mm$^2$. The large electric field of the intense laser pulse gives rise to a dielectric breakdown in the interaction volume.

The energy gained by the electrons is then transferred to the lattice via electron-phonon interaction, which vaporizes the material near the surface due to the large thermal energy gained. The main mechanism involved in this interaction is the disparity between the thermal diffusion length $l_t$ and the optical absorption length of the target. Indeed, when the optical absorption length is significantly larger than $l_t$ the lattice cannot dissipate the gained energy, heating up until ions are removed from the target surface. Only a small fraction (in the order of
µJ) of the total pulse energy (order of mJ) is required for this initial heating and evaporation of the target material. The larger portion of the energy absorbed is dissipated at later stages of the process during the dynamics of the plasma.

The vaporised material leaves the target as a directional plasma denominated plume that is composed of the various ions, electrons and neutral atoms formed by the recombination of electrons and ions. Coulomb forces make this plume expand as it travels perpendicular to the surface of the target due to recoil. The kinetic energy of the plasma that arrives to the substrate can vary from 1 to 500 eV depending on the laser fluency, the gas pressure in the chamber and the distance target-substrate. In general, energies around 100 eV result in sputtering on the substrate, and should therefore be avoided by controlling the parameters described.

The substrate is typically located in the trajectory of the plume. The species in the plasma arrive at the substrate as adatoms with an energy equivalent to the average kinetic energy of the plasma, which can be controlled as described previously. The adatoms diffuse over the surface until they reach a thermodynamically stable site where they bond chemically to the substrate and also to other adatoms. This leads to the nucleation of a film with the stoichiometry of the target. The deposition process is sensitive to several factors, like the rate of impingement of the plume, the kinetic energy of the plasma, the temperature of the substrate and the mobility of the adatoms. The latter is in turn affected by the chemical composition, roughness, crystallographic orientation and temperature of the substrate. The nucleation of the film is therefore a consequence of a non-equilibrium thermodynamic process and careful control of the growth parameters is essential.

**Experimental setup**

The PLD chamber is part of a larger custom built system at UniFr designed by SURFACE GmbH. A picture of the setup can be found in Figure 2.1. Three deposition chambers are directly attached to a transfer chamber, which allows for the deposition of heterostructures of complex oxides, organics and elemental metals by exchanging the samples from one chamber to another maintaining ultra-high vacuum (UHV) conditions. The deposition chambers are a PLD chamber equipped with an *in situ* reflection high-energy electron diffraction (RHEED) system for growth monitoring, a high temperature evaporation chamber for metals and a low temperature chemical vapour deposition (CVD) chamber for
organics. Also attached to the transfer chamber are a small chamber with a wobble-stick manipulator for the storage and mounting of mechanical shadow masks (not seen in the picture) and an UHV transfer port used to transfer the samples in UHV to other setups, for instance for angle-resolved photoemission spectroscopy (ARPES) measurements which are extremely surface sensitive.

The PLD chamber is equipped with an excimer KrF laser that produces laser pulses of 25 ns at a wavelength of $\lambda = 248$ nm. A series of mirrors guide the laser beam through a quartz window into the PLD chamber. A plano-convex lens with a focal length of 40 cm focuses the light pulses onto the surface of the target. After this lens, the laser footprint has a size of about $3 \text{ mm}^2$. Two pictures of the laser plume

Figure 2.1: Deposition setup in the Department of Physics at the University of Fribourg. The different deposition chambers are connected to a central transfer chamber accessible by a loadlock. This configuration allows for the deposition of heterostructures combining complex oxides, organics and metals.
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Figure 2.2: Plasma plume generated with an incident pulse of light of high intensity focused on a target. **Left panel:** side view. **Right panel:** top view. The path followed by the light pulse is indicated with a purple cone.

The path followed by the light pulse is indicated with a purple cone. can be seen in Figure 2.2, taken from different viewpoints in the PLD chamber at different angles.

The targets (up to five) are mounted in a carousel which enables them to be rotated and toggled thanks to a set of computer controlled motors. The substrates are glued on a stainless steel Omicron plate with silver paint, and mounted upside down in the PLD chamber at a distance of about 5 cm over the target. The substrate is heated from the back side of the Omicron plate using an infrared (IR) laser with a circular spot of about 4 mm in diameter. Its temperature is measured and controlled with a pyrometer also from the back. The deposition of the samples takes place in a dynamic pressure range between 0.1 mbar – 0.5 mbar. This dynamic pressure is achieved by a constant flow of gas into the chamber controlled by a mass flow controller (MFC) and a constant pumping of the gas by a turbo molecular pump through a bypass valve.

The deposition is monitored with a high pressure RHEED setup that consists of an electron gun (30 keV) and two differential pumping units, each connected to a turbo molecular pump. This differential pumping of the path followed by the electron beam allows to implement the RHEED technique despite of the large deposition pressures [92]. However, other alternatives can be used to monitor the deposition of atomic-flat layers at high pressures, such as ellipsometry [93]. A phosphorous screen located at the opposite side of the chamber displays the diffracted beam, which is recorded with a CCD camera. The column at which the Omicron plate is installed can be rotated and tilted...
to ensure the best alignment of the substrate with the electron beam. Figure 2.3 shows a scheme of the geometry inside the PLD chamber. The substrates used in the deposition of all the samples were commercial LSAT (0 0 1) substrates. LSAT is a cubic perovkite with the formula Sr\(_{0.7}\)La\(_{0.3}\)Al\(_{0.65}\)Ta\(_{0.35}\)O\(_3\). This oxide is commonly used in the deposition of heterostructures of cuprates and manganites thanks to the good matching of their crystal structures [39–42, 53, 94–98]. The substrates were heated up to the deposition temperature at a rate of 20 °C/min and maintained at the growth pressure and temperature for a minimum of 1 hour prior to the start of the deposition. After deposition, the samples were cooled down at a rate of 10 °C/min to 700 °C. At this temperature, the chamber was vented with 1 bar of O\(_2\) and the samples were rapidly cooled to the annealing temperature at a rate of 30 °C/min.

![Diagram of the geometry inside the PLD chamber.](image)

**Figure 2.3:** Diagram of the geometry inside the PLD chamber. The light pulse is focused on the surface of the target, generating a plasma plume that expands as it travels perpendicular to the target. The substrate, located on top of the plasma plume, is glued upside down on an Omicron plate and heated from the back. The electron gun is aligned glancing to the substrate surface. The pattern of the diffracted electrons is collected by a phosphorus screen.
2.1.2 Device fabrication

Some of the multilayers deposited by PLD have been further processed with nano-fabrication tools in order to obtain mesoscopic devices for magneto-transport experiments. The nano-fabrication techniques used are briefly described in the following subsections.

Gold coating

An additional gold coating layer was added to the oxide multilayers that would later be nano-sculpted. The purpose of this Au coating is to protect the samples from the forthcoming lithography and etching processes and the chemicals used in these techniques. This Au layer ranged in thickness between 50 nm and 100 nm, and was evaporated in the chamber labeled as “metal evaporation chamber” in Figure 2.1. The evaporation chamber and the PLD chamber are attached to the same transfer chamber, thus allowing the direct transfer from one chamber to another without breaking the vacuum. The evaporation chamber was pumped down to $9 \cdot 10^{-9}$ mbar with the Au loaded in an alumina crucible that is warmed up to 1525 °C at a rate of 1 °C min$^{-1}$. The Au was deposited on the surface of the sample at a rate of 0.1 Å s$^{-1}$, and monitored with a quartz crystal thin film deposition monitor. In this system it was observed that YBCO tends to deoxygenate as a result of the low base pressure and the thermal radiation from the Au source. In order to prevent this deoxygenation, the carrier plate containing the sample is in thermal contact with a liquid N$_2$ reservoir, which kept the sample temperature during the evaporation in the range between –27 °C and –87 °C. With this sample cooling procedure, no noticeable changes in the $T_c$ value of the YBCO were observed between the samples with and without Au, thus indicating that the oxygen loss of the YBCO layer has been avoided.

The adhesion of this capping layer to YBCO is rather poor, and it would peel off within a few seconds of treatment in an ultrasonic bath at a mild power. Its adhesion can be presumably improved by evaporating an intermediate layer of Cr, which is commonly used for this purpose. The main utility for the Au capping in these samples is protecting the top-most YBCO layer by avoiding direct contact with potentially harmful substances, such as the photoresist used in the optical lithography, the water used to stop the chemical reaction during development or the oxygen plasma used to clean off the photoresist remains. It also protects the samples during the baking of the pho-
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toressist and helps with grounding during the SEM sessions. Therefore, since this Au layer does not need to withhold mechanical stress, the capping deposited by these means served its purpose well.

**Optical lithography**

Optical lithography was used to define and connect large outer regions for contact pads and small central regions for device nano-sculpting. In this process the samples are coated in positive photoresist (PR), which is a polymeric organic material. This PR is photosensitive, and upon exposure to UV light it degrades and dissolves away in an aqueous base often denominated developer. The pattern is transferred to the

![Figure 2.4: The Canon PPC 210 projection mask aligner. Overlaid to the image is the path followed by the UV light generated by a mercury-lamp. The shadow projected by the mask is transferred to the PR-covered sample with the help of converging lenses.](image)
2.1. SAMPLE PREPARATION

Figure 2.5: **Lateral panels:** Pictures of two samples taken with an optical microscope of the Au capping layer and the transferred pattern in photoresist on top of it. **Middle panel:** Scheme of the samples with a detail on the central part, showing 6 horizontal fingers connected with a vertical central body. The devices are later fabricated in the horizontal fingers by means of focused ion beam.

surface of the sample by using a mask that covers certain parts of the photoresist, thus preventing its degradation during the UV exposure. Submerging the sample in developer washes away the degraded PR, thus remaining on top of the sample the pattern of the mask printed in photoresist.

Optical lithography, as well as the upcoming fabrication techniques, was performed in the Nanofabrication Facility located at the AlbaNova University Center in Stockholm. The samples were spin coated in photoresist and soft baked in a hotplate (100 °C, 60”). Spinning helps on getting a PR layer uniform in thickness while baking evaporates solvents, thus turning it more viscous and improving its adhesion. The exposure of the PR was done in a Canon PPC 210 projection mask aligner, at which the mask is placed on top of a set of converging lenses that transfer the shadow projected by mask. Figure 2.4 shows a picture of the Canon PPC 210, with the path followed by the light overlaid to it. The projection of the mask’s shadow was manually focused and aligned with the coated sample using a microscope. Once aligned, the sample was exposed to the $h$-line of the UV mercury-vapour lamp (404.7 nm) attached to the projection mask aligner. Upon exposure, the pattern was revealed in the PR by dissolving the exposed, degraded parts in
a strong base (MF-319). The chemical reaction was stopped by sub-
merging the sample in deionised water. Figure 2.5 shows pictures of
two samples with PR patterned on their surface.

**Etching techniques**

Etching techniques can be divided in two categories, depending on the
etcher and mechanism used. These are chemical etching and physical
etching. During a chemical etching process the etching agent reacts
chemically with the material, leading to volatile products and thus
leaving no traces of residue on the sample. During a typical physical
etch, however, the material is mechanically removed, generally sput-
tered away from the sample using a plasma. Here, a high power is
applied between two electrodes inside a chamber, creating a large elec-
tric field that ionises a low pressure gas between the electrodes. The
composition and pressure of the gas, the power applied to the elec-
trodes and the geometry of the chamber determine the properties of
the plasma. Besides physical etching, plasma can be also used for chem-
ical etching in a process called dry chemical etching, at which reactive
radicals generated in the plasma selectively etch certain compounds in
the sample.

In general, complex oxides are difficult to etch chemically due to
the high selectivity of the technique, the multiple elements these mate-
rials are composed of and their large anisotropy, which leads to uneven
etch ratios. For this reason, physical etching was the technique used
to etch the samples. This was done inside an Oxford Plasmalab 100
reactive ion etching (RIE) system, which has a temperature controlled
stage connected to a N₂ reservoir. Here, a high RF power is applied
between the electrodes while a constant flow of argon is set in the
chamber. The Ar⁺ ions accelerate toward the sample (located near the

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<td>Gas</td>
<td>Argon</td>
<td>Oxygen</td>
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<tr>
<td>Pressure</td>
<td>1 mTorr</td>
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<td>Gas flow</td>
<td>10 sccm</td>
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<td>RF power</td>
<td>300 W</td>
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<td>ICP power</td>
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<td>250 W</td>
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<tr>
<td>Temperature</td>
<td>-50 °C</td>
<td>Room temperature</td>
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Table 2.1: Etching settings used during the device fabrication.
2.1. SAMPLE PREPARATION

Figure 2.6: Pictures of the etching machines used. **Left panel:** Oxford Plasmalab 100 cryo-RIE system used for Ar sputtering. This setup is equipped with a liquid nitrogen inlet for cryogenic etching. **Right panel:** Oxford Plasmalab 80+ used for ashing of the photoresist with an oxygen plasma.

cathode), thus bombarding homogeneously the surface of the sample regardless of its composition. Sputtering is optimised by large powers and low pressures in the gas, which increase the mean free path of the ions as they accelerate toward the cathode. Inductively coupling the plasma (ICP) increases the degree of ionisation, thus enhancing the impingement rate in the sample. This etching process was used in the lithography patterned samples to sputter away those areas uncovered with photoresist. The parameters used can be found in Table 2.1. The etching process was done at a fixed temperature of \(-50^\circ\text{C}\), which prevents deoxygenation in the sample and minimises the hard-baking of the photoresist by the ions.

Besides physical etching, dry chemical etching was also used in the form of oxygen plasma to selectively target the photoresist. This process was used to remove strongly stuck on PR after Ar sputtering, and also right before the physical etch for a short time to ensure that no photoresist residue was left on the exposed areas after the development.
Since the process is meant to be driven by the chemical reaction between the plasma radicals and the photoresist, high pressures and low powers are used to reduce the energy of the impinging ions and minimise the physical sputtering on the samples. This oxygen dry chemical etching was done inside an Oxford Plasmalab 80+, and the parameters used can be also found in Table 2.1. Figure 2.6 displays pictures of both etching setups.

**Focused ion beam**

Focused ion beam (FIB) is an extremely versatile tool employed to selectively mill small areas in the samples. The milling consists of a beam of ions that are accelerated and focused on the sample, where they are used to mechanically sputter away material. Furthermore, the ions can be used to image using the secondary electrons emitted by the sample, but the degree of superficial degradation increases as the gallium is implanted on the sample. For imaging and navigation over the

![Focused ion beam setup](image)

**Figure 2.7:** The FIB setup at the Albanova Nanofabrication Facility. **Left panel:** A picture of the FEI Nova Nanolab 200 dual beam SEM–Ga$^+$ FIB system, with the e$^-$ and Ga$^+$ columns overlaid. **Right panels:** The interior of the FEI Nova showing the e$^-$ and Ga$^+$ columns. The use of 45° angled holders allows for both normal (upper panel) and glancing (lower panel) incidence.
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Figure 2.8: **Top left:** Picture of a contacted sample mounted on a PCB chip. **Top right:** Low magnification SEM image showing the central part of the sample. The wires contacting the larger pads in the sample are clearly visible. **Bottom right:** Intermediate magnification SEM image detailing the horizontal fingers defined with optical lithography at the central part of the sample. The central body is cut, isolating the horizontal fingers in three groups of two fingers. **Bottom left:** High magnification SEM image of one of the devices fabricated on the sample. *Inset:* scheme of the device with the only path defined for the current marked in white arrows.

sample, the FIB column is typically mounted inside a scanning electron microscope (SEM). Using electrons over ions for imaging minimises the damage, provided that the sample is properly grounded and thus the static charging due to the e-beam is not an issue.

An example of a setup like the described is the FEI Nova Nanolab 200 dual beam SEM – Ga\(^+\) FIB system shown in Figure 2.7. The Ga\(^+\) column is tilted 52° with respect to the e\(^-\) column, which sits on the vertical. This geometry is exploited by using 45° angled holders and choosing the right rotation angle, which together enable both normal and glancing incidence of the Ga\(^+\) ions on the sample with small tilts of the stage of 7°. This idea is depicted in the right panels of Figure 2.7.
Figure 2.9: Steps followed during the fabrication of SFS devices. The processes are arranged in columns corresponding, from left to right, to deposition, optical lithography, O$_2$ and Ar$^+$ etching and focused ion beam. The red arrows indicate the angle of incidence of the Ga$^+$ beam, while the white arrows show the motion of the current across the final device.

The FEI Nova was used during this work as the final step in the device fabrication. First, a current of Ga$^+$ ions of 100 pA was used in normal incidence to narrow the horizontal fingers defined with optical lithography into bridges (see Figs. 1.14 and 2.5). These bridges were further narrowed down with a current of 10 pA to their final width, which ranged between 700 nm and 200 nm. The reduced current allows for a more accurate polishing of the walls of the bridge.

The orientation of the beam with respect to the sample was then changed to glancing to perform two cuts that interrupt either S electrode in the bridge. Thus, with this method we define a single possible path for the electrical current to flow across the device; that is in a perpendicular motion through the manganite layer. On occasion the cut interrupting the uppermost YBCO was performed with normal incidence. Figure 2.8 shows in detail the horizontal fingers and the multiple locations at which the devices can be fabricated. The central body connecting the fingers is interrupted with FIB in order to isolate
the fingers in groups of two. This enables the simultaneous measuring of several devices at different locations avoiding any cross-talking. The FEI Nova system is also equipped with a gas injection system used for platinum deposition, induced either by the Ga$^+$ ions in focused ion beam induced deposition (FIBID) or by electrons in focused electron beam induced deposition (FEBID). A summary of the steps followed during the sample fabrication is schematically shown in Figure 2.9.

2.2 Sample characterisation

This Section describes the techniques used to characterise the samples deposited. X-ray diffraction and X-ray reflectivity were used to determine the structural and crystalline properties of the samples, and are introduced in Section 2.2.1. In Section 2.2.2 are described the physical property measurement system and, in particular, the vibrating sample magnetometry technique used for the magnetic characterisation of the samples. Finally, the temperature and field dependent transport properties of the nano-fabricated devices were probed in a closed cycle $^4$He cryostat introduced in Section 2.2.3.

2.2.1 X-ray diffraction and X-ray reflectivity

The crystalline phase and structural quality of the PLD-grown films was evaluated by means of X-ray diffraction (XRD) and X-ray reflectivity (XRR). Both measurements were performed with a four-circle diffractometer equipped with a rotating Cu-K$_\alpha_1$ anode (9 kW) from Rigaku. After passing a two-bounce Ge (2 2 0) monochromator, the X-ray beam reaches the sample with a certain incidence angle that can be varied either by rotating the X-ray source or by tilting the sample stage a certain angle $\omega$. The reflected or diffracted X-ray beam is then detected with a scintillation counter that can also be rotated around the sample. A sketch of the geometry described can be found in Figure 2.10, together with a picture of the Rigaku diffractometer.

The XRR data are typically recorded for very small (glancing) incident angles in the range of $\theta = 0^\circ$ to $3^\circ$ for which the measurement is most sensitive to the thin films and their interfaces. For angles below the reflection edge at $\theta < \theta_{crit}$ (which depends on the overall electron density of the sample), the X-ray beam cannot penetrate the sample and is fully reflected ($R(\theta) = 1$). For $\theta > \theta_{crit}$ the reflectivity falls off very rapidly ($R(\theta) \sim \theta^{-4}$) and typically exhibits intensity oscillations
from which the layer thickness and the roughness of the interfaces can be deduced. These are due to the constructive and destructive interference of the reflections from the interfaces between the layers with different scattering length densities. Provided that the scattering length density of the materials involved and the X-ray wavelength $\lambda = 1.54 \text{ Å}$ are known, this technique allows one to deduce the average thickness of each individual layer and its roughness.

Likewise, for the acquisition of XRD data we perform $2\theta-\omega$ scans typically in the range between $5^\circ$ to $120^\circ$. The mechanism behind the appearance of peaks in XRD is the diffraction of the photons on the periodic atomic lattice, following Bragg’s law of diffraction schematically illustrated in Figure 2.11. From the position of these peaks and their indexing, it is possible to reconstruct the lattice parameter of the crystalline direction that is contained in the plane of incidence. Consequently, from the shift of a given Bragg-peak or the appearance of new peaks with respect to the ones found in the corresponding bulk material it can be obtained information about the changes of the lattice parameter and/or symmetry that can arise in such thin films e.g. from strain effects due to their growth on a substrate with a different lattice parameter and/or symmetry. Furthermore, from the sharpness of the Bragg-peaks – their intensity and full width at half maximum – the crystallinity and coherence of the thin film can be assessed. For a

Figure 2.10: **Left panel:** A picture of the interior of the Rigaku system showing the four-circle diffractometer. **Right panel:** Scheme illustrating the geometry used in the X-ray measurements.
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Figure 2.11: Scheme illustrating Bragg’s law of diffraction. Intense Bragg-peaks are found in the detector due to the constructive interference of X-rays diffracted by different atomic planes in the sample. From the angular position of the Bragg-peaks and the wavelength of the X-ray $\lambda$ the distance $d$ between atomic planes can be inferred applying Bragg’s law for a given $n$ peak.

proper XRD scan, the angle $\chi$ needs to be aligned prior to the measurement with respect to a high intensity peak from the substrate. This minimises the signal losses due to misalignments between the detector and the plane of incidence of the photons. In most cases, the peak used for the $\chi$-alignment was the (0 0 2) peak of the LSAT substrate.

In the present work both the XRR and XRD techniques were used to characterise the thin films and multilayers. All PLD-grown samples were systematically probed with these techniques, from the control samples to the final multilayers. This constant feedback of structural information obtained from XRD and XRR proved to be of great importance in the optimisation of the PLD-growth parameters attending to structural quality, phase coherence, thickness and roughness of the thin films deposited.

2.2.2 Physical property measurement system

 Besides crystallographic analysis of the samples, their magnetic and magneto-transport properties were probed in a physical property measurement system (PPMS) by Quantum Design. This setup is equipped with a superconducting magnet that reaches fields up to $\pm 9$ T. During the transport measurements the samples were mounted and contacted in a puck that is installed at the bottom of the sample space. This space is surrounded by the He reservoir, which is used for cooling the magnet as well as for controlling the temperature of the sample space in the
Figure 2.12: **Left panel:** A picture of the PPMS setup used during this work, with the VSM motor installed at the top of the sample space. **Central panel:** Scheme of the interior of the PPMS, showing the transfer rod at the end of which the quartz rod is installed with the magnetic sample glued to it. **Right panel:** Detail of the bottom of the chamber. The sample is vibrated inside a pickup coil that registers an ac signal induced by the vibration of magnetic species inside of it.

range between 1.8 K – 400 K. The sample can be mounted in different orientations, thus changing the direction of the applied field with respect to the sample. The PPMS has an internal power supply, but it has occasionally also been modified to enable the use of an external Keithley multimeter for applying a bias to the sample and recording the response signal. The temperatures, fields and the data acquisition are all software-controlled.

For the dc magnetisation measurements, the vibrating sample magnetometer (VSM) option was used. A picture of the PPMS with the VSM motor installed is shown in Figure 2.12. The sample is glued on a quartz holder and mounted at the end of a transfer rod. Holders with different geometries allow for different sample orientations with respect to the field. The transfer rod is attached to an oscillating motor, which makes the sample vibrate at 40 Hz inside a pickup coil located at the bottom of the sample space. The movement of the magnetised samples inside the pickup coil induces an ac voltage in the coil with an amplitude that corresponds to its magnetic moment. Upon processing this signal with a lock-in technique, the moment is recorded in units of emu. Careful subtraction of all the undesired contributions to this
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signal including the substrate, sample rod or even the glue is crucial to determine the moment originating from the magnetic layers of the sample.

The intensity of the magnetic moment in emu is converted into $\mu_B$/magnetic ion knowing the total magnetic volume $V_{mag}$ and the volume of the unit cell of the magnetic layers $V_{uc}$ using the expression

$$m[\mu_B/\text{Mn}] = \frac{m[\text{emu}]}{\mu_B [\text{J} \cdot \text{T}^{-1}]} \cdot \frac{V_{uc}}{V_{mag}} \cdot 10^{-3} \left[ \frac{\text{J}}{\text{emu} \cdot \text{T}} \right].$$

(2.1)

2.2.3 Low temperature transport setup

The transport measurements on the nano-fabricated devices published in papers II and III were carried out inside a cryogen-free closed cycle $^4$He cryostat from Cryogenic Ltd. In this system, water cooled helium compressors liquefy the He that flows in a closed circuit. The liquefied He is collected in a pot, and allowed to flow and cool down the variable temperature insert (VTI) – inside of which the sample is located – upon its regulation through a needle valve. The He is then pumped and liquefied again, closing the cycle. The setup can reach temperatures of 30 K when the sample space is maintained in vacuum, and down to about 2 K when the space is filled with a few milibars of He acting as an exchange gas between the walls of the VTI and the sample. The cryostat is also equipped with a superconducting magnet that is kept at 5 K and reaches fields up to 17 T. The sample is inserted in the chamber using a rod with a rotatory sample stage that can rotate $\pm 135^\circ$, thus allowing for different field configurations. Furthermore, the insertion rod permits the electrical connection of the sample to the measurement setup and the monitoring of the temperature, the applied external field and the electric response. The rotatory stage is manipulated with a step-motor and is equipped with a temperature sensor and a heater for temperature control, as well as two Hall probes installed perpendicular to each other for sensing the field intensity and direction applied to the sample. Figure 2.13 shows a picture of the final portion of the insertion rod with the rotatory stage.

Prior to its installation inside the cryostat, the sample is glued on a plug-in PCB chip as the one displayed in Fig. 2.13. It is contacted to the gold-plated copper leads in the chip with aluminum wires using a wedge-bonder. A total of 20 contact leads are available on the chip, which arrive to the measurement setup as 10 channels of twisted pair
cables. In order to minimise the pick-up of electromagnetic noise, the samples are bonded using twisted pairs for $V^+V^-$ and $I^+I^-$. The sample is mounted in the rod by inserting the male pinhead connectors at the back of the plug-in to the female ones in the rotatory stage.

Figure 2.14: Picture of the 17 T closed cycle cryostat located in the Experimentell Kondenserade Materiens Fysik group laboratory. The cryostat appears in the foreground of the picture, with the electronics rack and the measurement monitorisation area placed in the background.
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The measurement setup is based on a National Instruments modular PXI (PCI eXtension for Instrumentation) controlled by a custom made LabVIEW environment. This system counts with analog-to-digital converts and field-programmable gate arrays (FPGA) for up to eight simultaneous lock-in measurements. The read-out voltages are measured using battery-driven differential preamplifiers, and the samples were in all measurements current biased and acquired in four point contact configuration. The current source consists of a waveform generator and an entrance resistance that is selected to be larger than the resistance of the sample. A resistance of 100 $\Omega$ is used to measure the current applied to the sample. A picture of the 17 T closed cycle $^4$He cryostat is shown in Figure 2.14.
Chapter 3

Results and discussion

3.1 Magnetic properties of YBCO/LCMO multilayers

This Section describes and expands the results published in Paper I. In particular, Section 3.1.1 describes the early results and phenomena found in the first YBCO/LCMO bilayers and trilayers deposited. Section 3.1.2 relates the implications of modifying the growth conditions, evaluated with polarised neutron reflectivity (PNR), scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS), in addition to standard characterisation techniques of XRD, XRR and VSM that are described in Section 2.2. The role of the bottom YBCO layer in the ferromagnetic ordering of the LCMO layer, and in particular its orthorhombic structure is discussed in Section 3.1.3. Finally, Section 3.1.4 elaborates on the complex spin-valve structures that can be realised when optimising the former parameters.

3.1.1 Magnetic properties of A-type YBCO/LCMO bilayers as a function of layer stacking sequence and YBCO layer thickness

A strong suppression of the ferromagnetic order in YBCO/LCMO bilayers was first encountered in the context of growing multilayers with the SFS structure described in Section 1.5, using YBCO as the S layer and LCMO as the intermediate F layer. At first glance, depositing a thin layer of LCMO on top of YBCO should be a relatively straightforward task. Indeed, much former work has been done on YBCO/LCMO bilayers and superlattices for which the interaction between supercon-
<table>
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<tr>
<th>Set A</th>
<th>Set B</th>
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<tr>
<td><strong>Temperature</strong></td>
<td><strong>Pressure</strong></td>
</tr>
<tr>
<td>825 °C</td>
<td>$P_{O_2} = 0.30 \text{ mbar}$</td>
</tr>
<tr>
<td>840 °C</td>
<td>$P_{O_2} = 0.34 \text{ mbar}$</td>
</tr>
<tr>
<td><strong>Laser fluency</strong></td>
<td><strong>Laser frequency</strong></td>
</tr>
<tr>
<td>2.00 J·cm$^{-2}$</td>
<td>2 Hz</td>
</tr>
<tr>
<td>1.42 J·cm$^{-2}$</td>
<td>7 Hz</td>
</tr>
<tr>
<td><strong>Post growth</strong></td>
<td></td>
</tr>
<tr>
<td>Pressure gradually increased at a constant flow of 200 sccm of O$_2$ while slowly cooling to 700 °C</td>
<td>Growth pressure maintained while slowly cooling to 700 °C</td>
</tr>
<tr>
<td><strong>In situ annealing</strong></td>
<td></td>
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<tr>
<td>485 °C for 1 hour</td>
<td>485 °C for 1 hour; then 400 °C for 1 hour</td>
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Table 3.1: Description of the two different types of PLD growth parameters that have been used in this work [45].

ductivity and magnetism was studied and a proximity effect on the manganite layer was discovered [36, 38, 42]. However, little systematic work has been performed toward depositing thin manganites on top of rather thick cuprates, yet obtaining a significant magnetic moment and a clear ferromagnetic behaviour of the manganite.

At first, single YBCO and LCMO layers were deposited on LSAT substrates using the same growth parameters for both materials. This set of growth conditions is in the following labelled as set A, and is described in Table 3.1. Figure 3.1 summarises the resistive and magnetic properties of the obtained YBCO and LCMO layers. Figure 3.1(a) shows the $R–T$ data for the YBCO single layer, which exhibits a metallic normal state response and a rather sharp superconducting transition in zero field with a superconducting onset of $T_c \approx 88.5$ K, reasonably close to the value of $T_c \sim 93$ K reported for the optimally doped bulk YBCO [71, 72]. In this regard, the set A of growth conditions seems to be appropriate for the deposition of YBCO layers with good superconducting properties. The $R–T$ data for the LCMO single layer in Fig. 3.1(b) demonstrates a strong PI to FM transition at $T_{Curie}$ as expected for this material, see Section 1.2.2. The resistance drops almost two orders of magnitude in zero field, from $R(220 \text{ K}) = 17.2$ kΩ down to $R(10 \text{ K}) = 200$ Ω. Furthermore, a strong magnetic response is measured in the LCMO layer, with a clear ferromagnetic transition in the dc $M–T$ curve at $T_{Curie} \approx 200$ K, see Fig. 3.1(c), and a saturation moment of 3.2 $\mu_B$/Mn ion at 10 K. The corresponding $M–H$ loop at
3.1. MAGNETIC PROPERTIES OF YBCO/LCMO...

Figure 3.1: Single layers of YBCO and LCMO deposited on LSAT with the set A of growth parameters. (a) $R-T$ curve of the YBCO single layer recorded applying an ac current of 10 $\mu$A. (b) $R-T$ curve of the LCMO single layer recorded applying an ac current of 10 $\mu$A. (c) dc $M-T$ curve for the LCMO layer measured while cooling in a magnetic field of 1000 Oe applied in-plane. (d) and (e) dc $M-H$ curves measured on the same LCMO layer at 10 K and 100 K, respectively, with the fields swept in-plane.

10 K in Figure 3.1(d) shows a hysteresis characterised by a coercive field of $H_{\text{coer}} \approx 80$ Oe and a remanence of $M_{\text{rem}} \approx 2.2$ $\mu_B$/Mn ion. With increasing field, the moment rapidly saturates to $\sim 3.2$ $\mu_B$/Mn ion, in good agreement with the theoretical saturation moment for bulk La$_{2/3}$Ca$_{1/3}$MnO$_3$ of $\sim 3.7$ $\mu_B$/Mn ion. The rather sharp reorientation in the hysteresis loop suggests that a coherent remagnetisation occurs over the sample as the field reaches $\pm H_{\text{coer}}$. The $R-T$, $M-T$ and $M-H$ curves in Figure 3.1 thus indicate that the set A is also adequate for the growth of a strongly ferromagnetic LCMO layer. As a reference for the discussion of the upcoming results on the YBCO/LCMO multilayers, Figure 3.1(e) also shows the dc $M-H$ loop at 100 K which has a saturation of $\sim 2.9$ $\mu_B$/Mn ion, a coercive field of $H_{\text{coer}} \approx 53$ Oe and a
remanence of $M_{rem} \approx 1.9 \, \mu B$/Mn ion. Overall, the YBCO and LCMO layers prepared with the A-type growth conditions show good metallic, superconducting and ferromagnetic properties.

Subsequently, two bilayers of YBCO/LCMO were deposited on LSAT using the same set $A$ of conditions, with the only difference between the bilayers being the stacking order. The samples are named according to the growth direction, with layer thickness given in units of nanometer. Accordingly, the bilayer with 15 nm of LCMO grown directly on the substrate and 15 nm of YBCO on top is labelled as LC-15/Y-15, while the one with the opposite stacking order is labelled as Y-15/LC-15. This formalism used to describe the structure profile of the multilayers will be maintained throughout this Chapter.

![A-type bilayers schematic](image)

Figure 3.2: Effect of the layer stacking sequence on the ferromagnetic properties of A-type bilayers. Upper panels: Schematics of the profiles of the bilayers LC-15/Y-15 (left) and Y-15/LC-15 (right). Lower panels: DC magnetic data obtained from the bilayers. (a) $M$–$T$ curves recorded while cooling in an in-plane magnetic field of 1000 Oe. (b) $M$–$H$ curves measured at 100 K with the field applied in-plane. A strong suppression of the ferromagnetic order in LCMO is observed when LCMO is deposited on top of YBCO. Adapted from [45].
The comparison of the magnetic properties of both bilayers in Figure 3.2 reveals surprisingly large differences. Indeed, the $M-T$ curve shown in Fig 3.2(a) demonstrates for the LC-15/Y-15 bilayer a strong ferromagnetic signal, with a clear ferromagnetic transition around 200 K and a saturation moment at 90 K that reaches about 2.75 $\mu_B$/Mn ion. Note that the superconducting response of the YBCO layer strongly affects the $M-T$ and $M-H$ data and makes it very difficult to obtain reliable information about the magnetic properties of LCMO at $T < T_c$. Therefore, the dc $M-T$ data are only shown at $T > T_c$ and the dc $M-H$ loops are taken at a temperature slightly above the $T_c$ of YBCO.

A clear magnetic hysteresis is observed for the LC-15/Y-15 bilayer at 100 K in Fig. 3.2(b), with a remnant magnetisation that amounts to $M_{rem} \approx 1.8 \mu_B$/Mn ion and a coercive field of $H_{coer} \approx 70$ Oe, and a total moment that reaches 2.81 $\mu_B$/Mn ion. This ferromagnetic signal is comparable to that obtained from the corresponding LCMO single layer shown in Fig. 3.1. In stark contrast, the bilayer Y-15/LC-15 shows a strongly suppressed magnetic signal with a moment that increases only gradually toward low temperature and shows no hint of a hysteresis in the dc $M-H$ curve. This indicates a strong suppression of the ferromagnetic moment of the LCMO layer that can only be attributed to the stacking order, i.e. to the circumstance that the LCMO is grown on top of the YBCO layer instead of the LSAT substrate.

Next, we studied how the ferromagnetic properties of a LCMO layer grown on top of a YBCO layer depend on the thickness of the latter. We prepared two A-type YBCO/LCMO/YBCO trilayers for which only the thickness of the bottom cuprate layer is varied. Following the described formalism to name the samples, the multilayer Y-15/LC-15/Y-30 is a trilayer with 15 nm of YBCO underneath the LCMO layer, while the trilayer Y-10/LC-15/Y-30 has only 10 nm. This minor difference was introduced to search for a possible influence of the strain relaxation of the YBCO layer (see Section 1.3). It is known that below a critical thickness YBCO remains strained to the crystalline structure of the substrate on which it is deposited (in this case, cubic LSAT). Above this threshold thickness of $d_{crit} \sim 10-15$ nm [40, 79], the strain relaxation sets in and gives rise to a number of structural defects and the recovery towards the orthorhombic crystalline structure of YBCO.

The dc VSM results on these trilayers are depicted in Figure 3.3, and indicate for Y-15/LC-15/Y-30 a very similar magnetic profile to that obtained for the bilayer Y-15/LC-15, with a gradual increase in the moment toward low temperatures and no clear sign of a ferromagnetic hys-
teresis. Surprisingly, the trilayer with the 10 nm thick bottom YBCO layer shows a typical ferromagnetic response with a spontaneous magnetisation emerging at $T_{\text{Curie}} \approx 180 \, \text{K}$ that amounts to $1.65 \, \mu_B/\text{Mn}$ ion at 90 K. The dc $M-H$ curve of this trilayer shows a clear hysteretic behaviour, with a saturation moment of $1.7 \, \mu_B/\text{Mn}$ and a coercive field and remanence of $H_{\text{coer}} \approx 40 \, \text{Oe}$ and $M_{\text{rem}} \approx 0.9 \, \mu_B/\text{Mn}$ ion, respectively. The fact that a seemingly moderate change in the thickness of the bottom YBCO has such a large impact on the magnetic properties of the LCMO layer on top suggests that the strain relaxation of the YBCO is playing an important role. This strain relaxation is known to restore the intrinsic orthorhombic structure of YBCO that emerges as

![Figure 3.3: Dependence of the ferromagnetic properties of LCMO on the thickness of the YBCO layer on which it is grown in A-type trilayers.](image)

**Upper panels:** Schematics of the profiles of the trilayers Y-10/LC-15/Y-30 (left) and Y-15/LC-15/Y-30 (right), deposited under the set $A$ of conditions. **Lower panels:** DC magnetic data obtained from these trilayers. (a) $M-T$ curves recorded while cooling in an in-plane magnetic field of 1000 Oe. (b) $M-H$ curves measured at 100 K with the field applied in-plane. The small change in thickness of the bottom YBCO has a surprisingly strong influence on the ferromagnetic ordering in the LCMO layer. Adapted from [45].
the one dimensional Cu-O chains develop a long-range order. Moreover, the strain relaxation in YBCO is usually accompanied by structural defects, such as screw dislocations and stacking faults, which in turn may affect the magnetic properties of the manganite as the VSM data suggests. In this sense, the trilayer with the 10 nm thick YBCO can be expected to remain almost fully strained by the LSAT, such that the in-plane structure is locked to that of the cubic LSAT and the one dimensional Cu-O chains cannot develop a long range order.

The effect of the strain relaxation in YBCO on the ferromagnetic properties of a LCMO layer grown on top has been further analysed by substituting YBCO with a cation substituted, tetragonal version of this cuprate. The results obtained are presented in Section 3.1.3.

3.1.2 Influence of the PLD growth parameters on the ferromagnetism of YBCO/LCMO multilayers

The strong suppression of the ferromagnetic order in the A-type grown YBCO/LCMO multilayers that are discussed in the previous Section 3.1.1 represents a significant drawback on the way to obtain SFS structures as those proposed in Section 1.5. Indeed, for the envisaged structures a thin ferromagnetic manganite layer needs to be grown on top of a 100 nm thick YBCO layer, whereas for the A-type multilayers in the previous Section the ferromagnetic response of LCMO is already entirely suppressed if it is grown on top of a 15 nm thick YBCO layer. Therefore, the PLD growth conditions have been re-examined and optimised as to obtain manganite layers that maintain a strong ferromagnetic response even if they are deposited on top of a thick YBCO layer. The result of this optimisation are the B-type growth conditions for which the parameters are listed on the right hand side of Table 3.1.

The most important difference in the optimised B-type conditions with respect to the original A-type conditions concerns the reduced laser fluency, which determines the kinetic energy of the species in the plasma plume as they arrive to the substrate, and the increased growth temperature which controls the mobility of the adatoms on the surface of the growing film.

In the following we compare the ferromagnetic properties of bilayers of YBCO/LCMO that were deposited with the different sets of A-type and B-type growth conditions. The magnetic properties of these bilayers have been investigated by means of dc magnetisation and polarised neutron reflectometry (PNR). Their structure and composition has been explored with XRD and for selected samples also
with scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS).

**DC magnetisation of A- and B-type YBCO/LCMO bilayers**

Figure 3.4 compares the magnetic response obtained with VSM for two Y-20/LC-30 bilayers that differ in the growth parameters used in their deposition. For the A-type bilayer (green line) there is once more a very weak ferromagnetic signal, similar to those in the previous Section, e.g. the A-type Y-15/LC-15 bilayer of Figure 3.2. The magnetic moment grows gradually as the temperature decreases, see Figure 3.4(a), reaching only 0.3 $\mu_B$/Mn at 90 K.

![Figure 3.4](image)

Figure 3.4: Dependence of the ferromagnetic properties of LCMO on the growth conditions for two bilayers with the same profile. **Upper panels:** Schematics of the profiles of the Y-20/LC-30 bilayers deposited under the set A (left) and set B (right) of growth conditions. **Lower panels:** DC magnetic data obtained from these bilayers. (a) $M$–$T$ curves recorded while cooling in an in-plane magnetic field of 1000 Oe. (b) $M$–$H$ curves measured at 100 K with the field applied in-plane. The strongly different magnetic profiles obtained from these bilayers is solely due to the different growth parameters used. Adapted from [45].
In stark contrast, the B-type bilayer (red line) shows a strong ferromagnetic response at $T_{\text{Curie}} \approx 210$ K with a moment of about 2.8 $\mu_B$/Mn at 90 K. A similar trend occurs for the $M$–$H$ curves of panel (b), where a pronounced hysteresis is evident for the B-type bilayer with a coercive field $H_{\text{coer}} \approx 140$ Oe, a remnant magnetisation $M_{\text{rem}} \approx 2.15$ $\mu_B$/Mn ion and a saturation moment that amounts to 2.8 $\mu_B$/Mn ion. On the contrary, no sign of a hysteresis is found for the A-type bilayer, with a moment that grows only gradually with field up to 0.3 $\mu_B$/Mn ion. Despite of the intermediate YBCO layer, the strength of the magnetic response of the LCMO in the B-type bilayer is comparable to the one obtained for the single LCMO layer that is deposited directly on the LSAT substrate, see Figure 3.1. This illustrates the relevance that the control of the deposition has on the properties of the manganite, playing a crucial role in the ferromagnetic suppression observed in the bilayers.

**Magnetic depth profiles of the A- and B-type YBCO/LCMO bilayers obtained with polarised neutron reflectometry**

The magnetic depth profile of the Y-20/LC-30 bilayers was probed by means of PNR. Figure 3.5 summarises the reflectivity curves obtained for both bilayers. First, reflectivity curves were obtained with neutron beams polarised with spin up and spin down configurations at 300 K. No difference was found in the reflectivity curves of either sample with respect to the spin polarisation of the beam, thus indicating that at this temperature the LCMO layers are not ferromagnetic (as expected). These curves served to determine the nuclear depth profile of the bilayers. The reflectivity data and the fit for the A-type (green symbols) and B-type (red symbols) bilayers at 300 K are shown in Figures 3.5(a) and (b), respectively. Next, the samples were cooled in an in-plane field of 0.46 T down to 90 K. At this temperature, the reflectivity curves were measured with neutron beams polarised in spin up and spin down configurations, represented in Figures 3.5(c) and (d). The temperature of 90 K was chosen because it is well below $T_{\text{Curie}}$ for LCMO, but still above the superconducting transition of YBCO below which additional contributions to the magnetic response may arise. For the A-type bilayer in panel (c), only a very weak splitting is seen between the spin-up and spin-down curves. To the contrary, for the B-type bilayer there is a pronounced splitting between the reflectivity curves for the different neutron beam polarisations, characteristic of a material with a large magnetic moment.
Figure 3.5: PNR data obtained from the A-type (in green) and B-type (in red) Y-20/LC-30 bilayers. (a) and (b) Reflectivity curves measured at 300 K. (c) and (d) Reflectivity curves measured at 90 K $\ll T_{Curie}$ for spin up and down polarisations of the neutron beam, after cooling the samples in an in-plane field of 0.46 T. Adapted from [45].

The data recorded at 90 K shown in Figs. 3.5(c) and (d) were fitted with the nuclear parameters obtained from the reflectivity curves at 300 K to construct the depth profile of the magnetic scattering length

| Layer   | Thickness (nm) | SLD $(10^{14} \text{m}^{-2})$ | $m$ $(\mu_B/\text{Mn})$ | Thickness (nm) | SLD $(10^{14} \text{m}^{-2})$ | $m$ $(\mu_B/\text{Mn})$
<table>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>LCMO₆</td>
<td>2.70 $\pm$ 0.25</td>
<td>3.65</td>
<td>0.10</td>
<td>1.90 $\pm$ 0.30</td>
<td>3.48</td>
<td>2.47</td>
</tr>
<tr>
<td>LCMO₅</td>
<td>8.00 $\pm$ 0.20</td>
<td>3.65</td>
<td>0.80</td>
<td>3.70 $\pm$ 0.40</td>
<td>3.60</td>
<td>2.74</td>
</tr>
<tr>
<td>LCMO₄</td>
<td>5.60 $\pm$ 0.26</td>
<td>3.50</td>
<td>0.64</td>
<td>8.00 $\pm$ 0.33</td>
<td>3.60</td>
<td>3.65</td>
</tr>
<tr>
<td>LCMO₃</td>
<td>7.50 $\pm$ 0.13</td>
<td>3.50</td>
<td>0.10</td>
<td>8.00 $\pm$ 0.32</td>
<td>3.60</td>
<td>3.60</td>
</tr>
<tr>
<td>LCMO₂</td>
<td>5.50 $\pm$ 0.30</td>
<td>3.65</td>
<td>0.00</td>
<td>7.50 $\pm$ 0.10</td>
<td>3.37</td>
<td>3.55</td>
</tr>
<tr>
<td>LCMO₁</td>
<td>7.00 $\pm$ 0.06</td>
<td>3.65</td>
<td>0.00</td>
<td>5.50 $\pm$ 0.20</td>
<td>3.37</td>
<td>2.50</td>
</tr>
<tr>
<td>YBCO₃</td>
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<td>4.20</td>
<td></td>
<td>6.30 $\pm$ 0.25</td>
<td>4.47</td>
<td></td>
</tr>
<tr>
<td>YBCO₂</td>
<td>5.00 $\pm$ 0.10</td>
<td>4.65</td>
<td></td>
<td>4.10 $\pm$ 0.10</td>
<td>4.74</td>
<td></td>
</tr>
<tr>
<td>YBCO₁</td>
<td>5.00 $\pm$ 0.10</td>
<td>4.65</td>
<td></td>
<td>10.00 $\pm$ 0.24</td>
<td>4.54</td>
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</table>

Table 3.2: Parameters used in the fit of the PNR data shown in Figs. 3.5 and 3.6. The LCMO and YBCO layers were subdivided in six and three layers, respectively. The data is organised in descending order from the outer-most LCMO sublayer (LCMO₆) to the inner-most YBCO sublayer (YBCO₁) [45].
Figure 3.6: Depth profiles of the nuclear (brown line) and magnetic (blue line) scattering length densities obtained from the fits to the reflectivity curves at 300 K and 90 K for the (a) A-type and (b) B-type bilayers. A reduced magnetic moment is found in the A-type over the entire LCMO layer, with a dead layer next to the interface with YBCO of ∼ 20 nm. On the contrary, the B-type bilayer shows a large magnetisation throughout the entire LCMO layer and only a weak reduction of its magnetic moment near the YBCO/LCMO interface. Adapted from [45].

The magnetic profile for the A-type bilayer confirms the strong suppression observed in the VSM measurements, and points out the existence of a dominant dead magnetic layer with a thickness of about 20 nm next to the YBCO/LCMO interface. For the B-type bilayer, however, the fit curves yield a large ferromagnetic moment over the entire thickness of the manganite, with a layer of 5.5 nm near the
YBCO/LCMO interface at which the moment is only weakly suppressed. The average magnetic moment of the LCMO layers amounts for the A-type bilayer to 0.46 $\mu_B$/Mn ion and 3.28 $\mu_B$/Mn ion for the B-type, both values agreeing with those deduced from the VSM data discussed in the previous Subsection.

**Structural properties of the A- and B-type bilayers studied with X-ray diffraction**

Figure 3.7 shows the XRD data at room temperature obtained from the same A- and B-type YBCO/LCMO bilayers that were discussed in the previous subsections. The panels in Fig. 3.7 compare the $\theta$–$2\theta$ scans using the same colour scheme for these bilayers: green for the A-type and red for the B-type. Regardless of the growth conditions, the XRD curves show narrow, intense (0 0 $l$) Bragg-peaks, indicating a uniform orientation of the layers along the crystalline $c$ axis direction. No impurity phases or traces of a misoriented fraction are found for either sample. Figure 3.8 displays the XRD data of both samples around the (0 0 1) Bragg-peak of LSAT. The main difference between both curves is related to a small shift of the centre of the diffraction

![Figure 3.7: Room temperature X-ray $\theta$–$2\theta$ scans of the A-type (green) and B-type (red) Y-20/LC-30 bilayers. Intense, narrow Bragg (0 0 $l$) peaks are found with no signs of impurity phases or misaligned fractions. The peaks of each material are labelled: L – LSAT; Y – YBCO; LC – LCMO. Adapted from [45].](image-url)
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Figure 3.8: Detail of the overlapping of the Bragg-peaks corresponding to LSAT (0 0 1), YBCO (0 0 3) and LCMO (0 0 1). The satellite oscillations in both samples indicate a long-range coherence of the crystalline planes. Adapted from [45].

peak for the A-type bilayer to a lower angle. Besides this, pronounced satellite peaks are found for both the A-type and B-type bilayers, revealing a high crystalline quality of YBCO and LCMO. From these results it can be concluded that the strong suppression of the magnetic moment found in the A-type bilayer is not related to a phase segregation or poor crystalline quality.

Scanning transmission electron microscopy and electron energy-loss spectroscopy on A- and B-type YBCO/LCMO samples

Four samples were investigated with STEM and EELS. These were the samples Y-15/LC-15 and Y-10/LC-15/Y-30 studied in Section 3.1.1, deposited under the set A of conditions and represented in Fig. 3.2 and Fig. 3.3, respectively; an A-type Y-15/LC-20 bilayer and a B-type Y-22/LC-30 bilayer. Figure 3.9 shows high-angle annular dark field (HAADF) STEM images of these samples. A common feature among the YBCO layers is the presence of stacking faults as double or even triple Cu-O chains that can be seen in the images as darker horizontal planes. Interestingly, these stacking faults are concentrated within
Figure 3.9: High angle annular dark field images obtained from A-type and B-type samples. (a) The Y-15/LC-15 A-type bilayer represented in Fig. 3.2. (b) The Y-10/LC-15/Y-30 A-type trilayer shown in Fig. 3.3. (c) An A-type Y-15/LC-20 bilayer. (d) A B-type Y-22/LC-30 bilayer. The interfaces are sharp and defect free, and a high degree of crystallinity is found for all LCMO layers. The only major defects are stacking faults due to the formation of double Cu-O chains that occur in the YBCO layers of all the samples.

the first 10-15 nm. Therefore, the appearance of stacking faults and the non-stoichiometric growth related to them may be strongly influenced by the relaxation of the strain transferred from the substrate, as discussed in Sections 1.3 and 3.1.1. Remarkably, for the B-type Y-22/LC-30 bilayer the seven uppermost unit cells of YBCO (next to the interface with LCMO) are essentially free of these stacking faults. This agrees with our interpretation that these defects are absent (or at least less frequent) after the strain has been completely relaxed. Regarding the LCMO layers, the images show interfaces that appear...
coherent and defect free, and a high degree of crystallinity that is comparable for all the samples.

The interface composition of these samples was studied with electron energy-loss spectroscopy (EELS). Figure 3.10 shows elemental maps and averaged elemental profiles corresponding to the A-type trilayer Y-10/LC-15/Y-30. Equivalent elemental maps corresponding to the A-type bilayer Y-15/LC-20 can be found in Figure 4 of Paper I [45]. The upper left panel in Figure 3.10 contains a high magnification HAADF image of the bottom YBCO/LCMO interface of the trilayer, with the area where the EELS spectra was analysed highlighted by a green rectangle. The ADF image and elemental maps were taken si-
multaneously within the marked rectangle, and are shown in the top right panel of Figure 3.10. These elemental maps were obtained from the analysis of the O $K$, Mn $L_{2,3}$, Ba $M_{4,5}$, La $M_{4,5}$ and Cu $L_{2,3}$ edges, from left to right. The atomic columns can be resolved from the high resolution ADF image, despite some spatial drift. The interfaces are defect-free, and no signs of interdiffusion are found in the vicinity of the interface with the exception of a bright red pixel that can be seen in the Cu $L_{2,3}$ elemental map of Figure 3.10, which is most likely a noisy pixel rather than a Cu atom.

The elemental profiles shown in the lower panel of Figure 3.10 were obtained by horizontal averaging of the two dimensional elemental maps. From these elemental profiles and from the elemental maps
the interfacial termination can be deduced. It can be seen that the final BaO faces a MnO$_2$ plane, as it is commonly observed for the YBCO/LCMO interface [40, 41, 99, 100]. However, in the case of the A-type Y-15/LC-20 bilayer a different, LaO-CuO$_2$ termination was also detected occasionally. The lack of statistics due to the highly local character of the technique does not allow us to determine the abundance of this LaO-CuO$_2$ termination, nor to exclude that it may also occur in other the other A-type and the B-type samples.

Figures 3.11(a) and (b) display two HAADF images of the YBCO/LCMO interfaces of the A-type Y-15/LC-20 bilayer and the B-type Y-22/LC-30 bilayer, respectively. Sharp interfaces and a high degree of crystallinity are once more observed for both samples. The yellow lines in the HAADF images mark the linescans at which the EEL spectra was obtained, represented in the panels (c) and (d) of Figure 3.11 for the A- and B-type bilayers, respectively. Three spectra are shown for each bilayer, corresponding to the LSAT (black), LCMO (blue) and YBCO (pink) layers. The absorption edges of O $K\alpha$, Mn $L_{2,3}$, Ba $M_{4,5}$, La $M_{4,5}$ and Cu $L_{2,3}$ indicate the presence of these elements in the corresponding layers. No indications of interdiffusion between the layers are found, with the exception of a small presence of Ba in the LCMO layer of the B-type Y-22/LC-30 bilayer, Figure 3.11(d), consequence of a minor ion mill damage during the sample preparation.

In particular, the intensity ratio between the Mn $L_3$ and $L_2$ absorption edges depends on the oxidation state of the manganese cations, and thus can be used for quantification [101]. Figure 3.12 details the vicinity of the Mn $L_{2,3}$ edge obtained from linescans across the LCMO layers of the A-type Y-15/LC-20 bilayer (in red) and the B-type Y-22/LC-30 bilayer (in black). Figure 3.12(a) shows the O $K\alpha$ edge around 530 eV and the Mn $L_{2,3}$ edge around 640 eV. The spectra have been offset in intensity for clarity. No clear differences can be noticed from the visual comparison of the Mn $L_3$ and $L_2$ edges. Yet, in Figure 3.12(b) it can be seen that the Mn $L_3$ edges of the A- and B-type LCMO layers do not overlap completely, indicating a different Mn $L_{2,3}$ intensity ratio and thus a different oxidation state of the manganese on either bilayer.

Figure 3.12(c) contains the mentioned Mn $L_{2,3}$ ratio calculated with a double-derivative method [102], obtained over the linescans indicated in Figs. 3.11(a) and (b) for the A-type (red circles) and the B-type bilayer (black squares). The scans commence at 0 nm, which corresponds to the LCMO layer starting from the interface. Note that the scanned line for the B-type spans only the first 10 nm and thus not
the entire thickness of the manganite layer. The disparity between the Mn $L_{2,3}$ ratios of the two bilayers suggests once more clear differences in the electronic properties of the LCMO layers. The Mn oxidation state corresponding to the Mn $L_{2,3}$ ratio, based on the calibration of bulk manganite samples, is shown as a double-axis in Figure 3.12(c). For the B-type bilayer the oxidation of the Mn cations is close to the value +3.3 that is expected for the nominal composition of La$_{2/3}$Ca$_{1/3}$MnO$_3$. On the contrary, the A-type bilayer has a significantly higher average value of about +3.5. This was also found for the other A-type samples studied, with Mn oxidation values ranging from +3.47 to +3.6. These significantly higher oxidation values suggest that the chemical compo-

Figure 3.12: (a) The O K and Mn $L_{2,3}$ absorption edges obtained from linescans on the LCMO layers of the A-type Y-15/LC-20 and the B-type Y-22/LC-30 bilayers. (b) Overlap of the Mn $L_3$ and $L_2$ edges of both bilayers. (c) Mn $L_{2,3}$ ratio across the LCMO layers (red circles for A-type, black squares for B-type). The position $L = 0$ marks the location of the YBCO/LCMO interface. The averaged Mn oxidation state for the B-type is close to the nominal value of +3.3, whereas for the A-type sample it is significantly higher with +3.5. Figure courtesy of N. Biškup and M. Varela, and partially adapted from [45].
position of the A-type samples deviates strongly from the stoichiometric La$_{2/3}$Ca$_{1/3}$MnO$_3$ of the target material. In the hole doping phase diagram of the La$_{1-x}$Ca$_x$MnO$_3$ system, a Mn oxidation of +3.5 is located around $x = 0.5$, and thus close to the border between the itinerant ferromagnetic state at $x < 0.5$ and insulating antiferromagnetic states with various kinds of charge and/or orbital orders at $x > 0.5$ (see Fig. 1.5). Here the ferromagnetic order is very unstable toward the formation of an AF and/or glassy magnetic state, which can explain the strong suppression of the ferromagnetic moment in the A-type bilayers. This pronounced increase in the oxidation state of the Mn atoms arises most likely from an off-stoichiometric cationic balance between the La and Mn ions, which has the effect of a net hole doping of the compound as discussed in Section 1.2.1 for the case of LaMnO$_{3+\delta}$.

In summary, the effect of using different growth conditions has been investigated with the VSM, PNR, XRD, STEM and EELS techniques. No significant differences were observed in the XRD data between the Y-20/LC-30 bilayers, which all showed a high degree of crystallinity with narrow and intense Bragg-peaks and no signs of misoriented regions or impurity phases. The dc VSM data showed a very contrasting magnetic behavior. A strong ferromagnetic signal was measured in the B-type bilayer, emerging at $T_{Curie} \approx 210$ K and reaching 2.8 $\mu_B$/Mn at 90 K, characterised by a clear hysteresis around zero field in the dc $M$–$H$ curves. Opposite to this, the A-type bilayer showed a strongly depressed ferromagnetism with a small magnetic moment at low temperatures and no sign of a hysteresis in the $M$–$H$ loops. The PNR results agreed with the VSM data, demonstrating for the A-type bilayer the existence of a dead magnetic layer next to the YBCO/LCMO interface with a thickness of about 20 nm. In comparison, only a weak reduction of the ferromagnetic moment near the YBCO/LCMO interface was found for the B-type bilayer. In both cases, the averaged value of the depth profile of the magnetic moment acquired with PNR agreed well with the magnitude of the moment deduced from the VSM data. Finally, the STEM images suggest that the LCMO layers are of comparably good crystalline quality, and the EELS elemental maps and profiles demonstrate that the YBCO/LCMO interfaces are atomically sharp and well defined with no clear signs of interdiffusion or chemical mixing. Stacking faults were found in YBCO terms of intergrowth of Cu-O double layers on all the samples regardless of the growth conditions. These stacking faults are more abundant in the strain relaxation region within the first 10-15 nm next to the substrate. The commonly observed
MnO$_2$–BaO–CuO$_2$ interfacial layer stacking sequence was found in all the studied samples, although the termination MnO$_2$–LaO–CuO$_2$ was also occasionally detected for one of the A-type bilayers.

The most important and remarkable result obtained from the latter techniques concerns the difference in the average manganese oxidation state between both sets of growth conditions, which for the B-type bilayer was close to the nominal value of $+3.3$ and for the A-type samples ranged between $+3.47$ and $+3.6$. In this regard, the LCMO layers of the A-type samples can be considered as a more strongly hole doped versions of the B-type LCMO. Provided that an excess oxygen concentration in the form of interstitial oxygen is typically not found in these materials, the additional doping originates most likely from an unbalanced La/Mn ratio as a consequence of a bad transfer of the stoichiometry of the target to the substrate. Possible reasons for such a deficient stoichiometric transfer are scattering effects between the species within the plasma plume or a re-sputtering of the adatoms in the surface of the substrate due to an excess energy. When comparing the two sets of growth conditions in Table 3.1 it can be seen that these effects should be stronger for the set A due to the higher laser fluency. Moreover, the lower substrate temperature used in the A-type depositions translates in a reduced diffusion of the adatoms in the substrate which can further enhance the re-sputtering effect.

This cation deficiency affects the ferromagnetic order within the LCMO in two ways. Firstly, the additional hole doping displaces the LCMO in the phase diagram towards the boundary with the antiferromagnetic and charge/orbital ordered states found for $x > 0.5$ (see Figure 1.5). Secondly, the Mn vacancies disrupt the Mn–O–Mn bonds through which the double exchange interaction gives rise to an itinerant ferromagnetic order (see Section 1.2.1), thus further reducing the effective bandwidth and favouring antiferromagnetic and/or glassy types of magnetic orders [15, 20, 53]

### 3.1.3 Orthorhombicity of YBCO and suppression of the ferromagnetic moment of LCMO

As was already mentioned in Section 3.1.1, the orthorhombic structure of the strain relaxed YBCO layers appears to have a strong influence on the ferromagnetic order of a LCMO layer that is grown on top of the YBCO. This effect was further explored by replacing the intermediate YBCO layer with a Co- and Ca-cosubstituted version Y$_{0.8}$Ca$_{0.2}$Ba$_2$Cu$_{2.8}$Co$_{0.2}$O$_7$ that has similar superconducting properties
3.1. MAGNETIC PROPERTIES OF YBCO/LCMO...

but maintains a tetragonal structure. In this cuprate, that in the following is referred to as tYBCO or tY, the Co$^{3+}$ ions reside on the Cu-O chains and introduce strong structural and electronic disorder. For bulk YBCO it has been shown that this gives rise to a transition from an orthorhombic to a tetragonal structure for a Co content $y > 0.15$. The Co content of $y = 0.2$ of tYBCO is adjusted to match the cubic lattice constant of LSAT of $a = b = 0.387$ nm [103]. In addition to the lattice disorder, Co$^{3+}$ ions introduce extra electrons and thus reduce the hole doping of the CuO$_2$ planes. This leads to a progressive decrease of $T_c$ as $y$ increases and eventually the absence of superconductivity at $y \geq 0.42$. To counteract this electron doping effect of the Co$^{3+}$, Ca$^{2+}$

Figure 3.13: **Upper panels:** Schematics of the profiles of the bilayers tY-30/Y-15 (left) and Y-15/LC-15 (right), deposited under the set A of growth conditions. **Lower panels:** DC magnetic data obtained from these bilayers. (a) $M$–$T$ curves recorded while cooling in an in-plane magnetic field of 1000 Oe. (b) $M$–$H$ curves measured at 100 K with the field applied in-plane. The sample with the intermediate tYBCO can be seen to develop a significantly stronger ferromagnetic order and a clearer hysteresis around the origin of the $M$–$H$ loop. Adapted from [45].
cations have been introduced substituting \( Y^{3+} \). For the tYBCO thin films with \( y = 0.2 \) and 20\% \( Ca^{2+} \) doping this leads to a reasonably high \( T_c \) value of \( T_c \sim 73 \text{ K} \).

The effect of using this tetragonal tYBCO over orthorhombic YBCO was tested for both sets of A- and B-type multilayers, described in Table 3.1. Figure 3.13 compares the previous A-type Y-15/LC-15 bilayer shown in Figure 3.2 with a A-type tY-30/LC-15 bilayer. It is clear that the bilayer with tYBCO exhibits a stronger ferromagnetic signal, despite of the circumstance that the intermediate tYBCO layer is twice as thick as the YBCO layer of the Y-15/LC-15 bilayer. The \( M-T \) curve of Figure 3.13(a) shows for the tYBCO sample a significantly larger moment that rises below \( T_{\text{Curie}} \approx 180 \text{ K} \). Furthermore, it exhibits a clear hysteresis in the dc \( M-H \) loop of panel (b) with a coercive field of \( H_{\text{coer}} \approx 55 \text{ Oe} \) and a remnant moment of \( M_{\text{rem}} \approx 0.14 \mu_B/\text{Mn ion} \). This enhancement of the ferromagnetic response that occurs despite of the larger thickness of the tYBCO layer, as compared to the one of the YBCO layer of the other bilayer, confirms that the orthorhombic structure of YBCO has a destructive influence on the ferromagnetic order of a LCMO layer that is deposited on top.

Figure 3.14 shows the VSM data obtained for two B-type trilayers, with the structures Y-100/LC-10/Y-100 and tY-100/LC-10/Y-100. The only difference between these trilayers concerns the substitution of the intermediate orthorhombic YBCO with tetragonal tYBCO. Note the large thickness of the intermediate cuprate layers of 100 nm, which in the case of samples deposited with the conditions A would yield no ferromagnetism at all for a 10 nm thick LCMO layer deposited on top. The dc \( M-T \) curves of Figure 3.14(a) show that with the B-type conditions a large ferromagnetic signal can be achieved in SFS structures such as these trilayers. A clear ferromagnetic transition can be seen for both samples at \( T_{\text{Curie}} \approx 200 \text{ K} \). However, the sample with tYBCO develops a magnetic moment that is almost two times larger than for the sample with YBCO, with the moment at 90 K reaching 1.75 \( \mu_B/\text{Mn ion} \) for the former and 0.9 \( \mu_B/\text{Mn ion} \) for the latter. A pronounced hysteresis is observed in both trilayers in the dc \( M-H \) curves of Fig. 3.14(b), but the tY-100/LC-10/Y-100 trilayer shows a larger saturation value (1.75 \( \mu_B/\text{Mn ion} \) vs 0.95 \( \mu_B/\text{Mn ion} \)), remanence (1.3 \( \mu_B/\text{Mn ion} \) vs 0.7 \( \mu_B/\text{Mn ion} \)) and a smaller coercive field (220 Oe vs 360 Oe).

The results obtained for the A- and B-type growth conditions help to understand the effect that the strain relaxation of the intermediate YBCO layers has on the ferromagnetic properties of the LCMO layers.
deposited directly on top. For the A-type bilayers it has been observed that tYBCO mitigates the strong ferromagnetic suppression that was originally found in the bilayers of Section 3.1.1, which indicated that the presence of the intermediate YBCO is detrimental for the ferromagnetic order in the manganite. The cationic substitution of Co for Cu removes the long-range order of the Cu-O chains, and thus avoids the strain relaxation that occurs in YBCO, which typically is combined with dislocations and other structural defects. The orthorhombic structure of YBCO affects the magnetic properties of LCMO even in the B-type trilayers, albeit the suppression of the ferromagnetic order is much weaker than for the A-type samples.
Combining the results in the previous Sections with these on tetragonal YBCO we can sketch a better idea as to why the ferromagnetic moment was completely suppressed in the first bilayers and trilayers of Section 3.1.1 samples. In Section 3.1.2 the combination of the magnetic, crystallographic and compositional analysis allowed to conclude that the LCMO layers in the A-type samples presented a high degree of crystallinity, suppressed magnetism and cationic imbalances in the La/Mn ratio. This off-stoichiometry directly affects the ferromagnetic ordering by effectively hole doping the material, and thus placing the material in the phase diagram closer to the antiferromagnetic or charge/orbital ordered states (see Figure 1.5). Moreover, the Mn vacancies disrupt the network of Mn–O–Mn bonds that is fundamental for the double exchange mechanism that stabilizes the itinerant ferromagnetic state as discussed in Section 1.2.1. This makes the FM order of the LCMO very sensitive to strain and disorder and thus to the structural details of the YBCO layer on which it is grown.

Indeed, it is known that the magnetic and electronic properties of La$_{1-x}$Ca$_x$MnO$_3$ in the vicinity of the FM–AF/CO phase boundary are very sensitive to defects and lattice distortions, which reduce the bandwidth and further decrease the ferromagnetic double exchange interaction. In this sense, an A-type YBCO/LCMO bilayer with a strain relaxed YBCO (and therefore with stacking defects) shall see its ferromagnetic order suppressed by its cationic imbalance and its enhanced sensibility to defects combined with a strain relaxed YBCO. On the other hand, this same sample with a defect free intermediate YBCO shall still be capable of recovering a moderate ferromagnetic ordering. This idea agrees with the results of Figure 3.13 when the strain relaxed YBCO is replaced by strain-free tYBCO.

On the other hand, B-type samples have demonstrated a high crystalline quality, large saturations in the ferromagnetic moment without magnetic dead layers and a nominal oxidation state for Mn of +3.3. A LCMO layer with this composition, well centred in the FM region of the phase diagram, is more robust magnetically than that close to the phase boundary and less sensitive to defects. B-type bilayers of YBCO/LCMO are therefore less dependent on the structural details of the intermediate YBCO (although not defect-proof), as observed in Figure 3.14 where a strain relaxed YBCO still demonstrates to impact the ferromagnetic properties of LCMO, and its substitution by tYBCO further enhances the ferromagnetic order of the manganite.
3.1.4 Multilayers with thin manganite layers embedded in thick YBCO layers

The suppression of the ferromagnetic order in thin LCMO layers grown on top of YBCO has been shown to depend strongly on the PLD growth conditions and also the orthorhombicity of YBCO. It remains now to explore the possibilities that the control and understanding of these mechanisms can offer. This has been investigated by the deposition of multilayers with two F layers embedded in thick S layers. The particular aim for these structures has been to obtain a spin-valve-like behaviour with thin LCMO or LSMO layers for which the magnetisation can be switched independently by an external magnetic field. The details of the set $B$ of growth parameters used for these multilayers are listed in Table 3.1; the effect of choosing these parameters was discussed in Section 3.1.2.

Figure 3.15 displays the magnetic response of corresponding thin single layers of LCMO and LSMO that are deposited under the B-type conditions directly on a LSAT substrate. The $M$–$T$ curves in Fig. 3.15(a) recorded while applying 1000 Oe in-plane show a strong FM response with $T_{\text{Curie}} \sim 225$ K for LCMO and $T_{\text{Curie}} > 300$ K for LSMO. The low temperature value of the ferromagnetic moment reaches 3.10 $\mu_B$/Mn ion for LCMO and 3.63 $\mu_B$/Mn ion for LSMO. A clear hysteretic be-

![Figure 3.15: Magnetic response of B-type grown single layers of LCMO and LSMO deposited on LSAT. (a) $M$–$T$ curves measured while applying 1 kOe in plane, showing a progressively increasing moment on LSMO with lower temperatures and a FM activation of LCMO at a temperature $T_{\text{Curie}} \sim 225$ K. (b) $M$–$H$ in-plane loop at 100 K, with a clear hysteresis around the origin and saturation values of 3.57 $\mu_B$/Mn ion for LSMO and 2.82 $\mu_B$/Mn ion for LCMO.](image)
behaviour in the in-plane $M-H$ magnetisation loop at 100 K is observed for both the LCMO and LSMO single layers, see Figure 3.15(b), with saturation moments of $2.82 \mu_B$/Mn ion and $3.57 \mu_B$/Mn ion for LCMO and LSMO, respectively. The coercive fields and remnant magnetisations amount to $H_{coer} \approx 72$ Oe and $M_{rem} \approx 2.35 \mu_B$/Mn ion for LCMO and $H_{coer} \approx 10$ Oe and $M_{rem} \approx 3.05 \mu_B$/Mn ion for LSMO. These values serve as upper limit for the thin layers embedded in a multilayer structure that are discussed below.

As it was mentioned previously, the goal is to deposit a superconducting spin-valve at which strong, independent FM layers display large moments with different coercive fields, so that the magnetic moment from either manganite layer can be individually oriented with an external magnetic field. As it was seen in Figure 3.15, the evolution with temperature, the magnetic saturation values and the coercive fields of LCMO and LSMO are different and, in this sense, using thin layers of LCMO and LSMO embedded in these structures may result in the de-

Figure 3.16: Multilayer M1. (a) Sketch of the multilayer structure and the layer thicknesses. (b) dc $M-T$ cooling the sample in 1 kOe in-plane. The grey line shows the extrapolated contribution of the LSMO layer to the total moment below the Curie temperature of LCMO. (c) dc $M-H$ in-plane loop at 90 K. The black curve shows the derivative of the magnetisation and thus the slope of the hysteresis curves. (d) $dM/dH$ curves at different temperatures.
sired independent magnetic reorientation of each individual layer. The results obtained from five multilayers with the structure described are compared next. The multilayers are labelled as M1–M5, with the manganites embedded in these structures separated by a thin YBCO layer in order to magnetically decouple their moments.

Figures 3.16–3.20 show the magnetisation data from these multilayers, with all the Figures sharing the same caption as that of Figure 3.16. The (a) panels of every Figure display a scheme showing the structure and thickness profile of each multilayer. The evolution of the magnetic moment with temperature, displayed in the panels (b), demonstrates a similar trend for all the multilayers with a finite magnetic moment already at room temperature due to the LSMO layer with $T_{\text{Curie}} > 300$ K, and an additional increase below $T_{\text{Curie}} = 205$ K – 220 K that marks the FM transition of LCMO. Overall, the $M$–$T$ curves of panels (b) indicate that the thin manganite layers keep their ferromagnetic character despite of being embedded in such a multilayer structure with a thick YBCO bottom layer. Note that the moment displayed in the plots is recalculated from the VSM data using equation (2.1) considering the total volume of the manganite layers in the sample. This means that at $T > T_{\text{Curie}}$ of LCMO the moment recalculated in $\mu_B$/Mn ion is normalised to all the Mn ions in the sample, obviating that LCMO is paramagnetic in this temperature range. As a reference to the eye, the observed monotonous increase of the moment attributed to LSMO is extrapolated to lower temperatures below $T_{\text{Curie}}$ of LCMO (in grey) in order to compare the contribution of each layer to the total moment measured in the $M$–$H$ curves. Panels (c) in Figures 3.16–3.20 display the in-plane hysteresis loops at 90 K (in gold) and the corresponding derivative $dM/dH$ plots (in black). The latter provide qualitative information about the sharpness of the field-induced reorientation of the magnetic moment of the manganite layers. Finally, panels (d) display $dM/dH$ curves at different temperatures above and below $T_{\text{Curie}}$ of LCMO.

Multilayers M1 and M2 differ on the thickness of the YBCO layer that separates the manganite layer (8 nm and 4 nm, respectively). M2 and M3 have the same thickness profile but for M3 the YBCO layers are replaced with tYBCO. For these three multilayers there is no clear sign of a separate switching of the magnetisation of the LCMO and LSMO layer (compare panels (c) and (d) of Figures 3.16, 3.17 and 3.18). Accordingly, these profiles do not seem to be suitable for the fabrication of spin-valve structures.
Figure 3.17: Multilayer M2.

Figure 3.18: Multilayer M3.
Interestingly, the contribution of LCMO to the total moment at 90 K ((b) panels) is small considering the extrapolated $M-T$ evolution for LSMO. Despite of the smaller coercive field observed in M3 due to the use of tYBCO over YBCO (as occurred in Figure 3.14), the magnetic reorientation is similar in these three multilayers. Indeed, both manganite layers in each structure orient their moments at very similar fields, thus resulting in a homogeneous realignment of the moments in the multilayers as if these consisted of a single ferromagnetic layer.

This suggests that either both FM layers are magnetically coupled, and therefore the reorientation of one layer precipitates the other, or that they are decoupled but have similar coercive fields. Should the latter be the case, decreasing the temperature further would result in a continuously increasing coercive field for the LCMO layer, which in turn may allow for an independent magnetic orientation in the FM layers. This idea, however, cannot be investigated in VSM due to the difficult interpretation of the magnetic data when YBCO goes superconducting, but requires of techniques at which the SC contribution can be subtracted, such as SQUID magnetometry. Another possibility would be to nano-sculpt devices in these multilayers to explore their perpendicular transport characteristics and the influence of the field in the resistance at low temperatures, as done in Papers II and III.

In clear contrast, the multilayers M4 and M5 in Figures 3.19 and 3.20 show signatures of completely independent ferromagnetic layers with different coercive fields, as can be seen in their corresponding (c) and (d) panels. In these multilayers the stacking order is altered, with LSMO being the manganite deposited directly on the thick cuprate bottom layer. This, together with using tYBCO as the bottom electrode, seems to allow for a LSMO layer that is magnetically very soft (as in M3) and a LCMO layer deposited over the thin intermediate YBCO layer with a larger magnetic moment and sufficiently larger coercive field such that its magnetisation can be switched independently from the one of the softer LSMO layer. In this regard, altering the stacking order directly influences the coercive fields, “hardening” LCMO and “softening” LSMO. This allows us to see a “two-step” hysteresis loop at 90 K and two peaks in the $dM/dH$ corresponding to the independent magnetic reorientation of LSMO at $\sim 50$ Oe and LCMO at $\sim 310$ Oe. Furthermore, by altering also the thickness ratio between both FM layers (as in M5, with LCMO twice as big as LSMO) the contribution from LCMO at 90 K is larger, and thus a clearer “two-step” hysteresis curve is achieved. It should be noted that this stronger effect is presumably
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Figure 3.19: Multilayer M4.

Figure 3.20: Multilayer M5.
3.2. TRANSPORT THROUGH $\text{La}_{2/3}\text{X}_{1/3}\text{MnO}_3$ ($\text{X: Sr, Ca}$)

occurring also for the M4 sample at lower temperatures, since the moment in LCMO at 90 K is not completely saturated yet (compare, for instance, the single layers in Figure 3.15). Therefore, at lower temperatures the contribution of LCMO to the total moment of the multilayer would be larger and thus produce a clearer step in the hysteresis due to the reorientation of the LCMO layer.

### 3.2 Perpendicular transport through SFS junctions with $\text{La}_{2/3}\text{X}_{1/3}\text{MnO}_3$ ($\text{X: Sr, Ca}$)

In the following the magneto-transport measured on devices fabricated on two trilayers with a SFS structure is discussed. These results were published in Paper II. The devices were nano-fabricated onto two SFS trilayers composed of complex oxide materials, at which the characteristics of the perpendicular transport through the F layer were measured. These trilayers were deposited with the B-type growth conditions described in Table 3.1. Following the formalism established at the beginning of Section 3.1.1, the trilayer labelled as LC_{10} has the structure Y-100/LC-10/Y-100, while the one denoted LS_{11} has the profile Y-100/LS-11/Y-100.

Firstly, the dc magnetisation data obtained via VSM from the unpatterned trilayers are plotted in Figure 3.21. Figure 3.21(a) shows

![Figure 3.21: DC magnetisation data obtained from the unpatterned SFS trilayers LC_{10} and LS_{11}. (a) dc M–T curves recorded while cooling in a 1 kOe in-plane field. (b) dc M–H hysteretic loops for the same trilayers recorded at 100 K (field in plane). The data confirm that the thin manganite layers embedded in thick YBCO layers exhibit a strong ferromagnetic response. Adapted from [46].](image-url)
that for the LC\textsubscript{10} trilayer a clear ferromagnetic moment arises below a Curie temperature of $T_{\text{Curie}} \sim 210$ K, whereas for the LS\textsubscript{11} trilayer a sizable ferromagnetic moment exists already at 300 K. In both cases, the ferromagnetic moment increases toward low temperatures, reaching at 90 K values of 0.95 $\mu_B$/Mn ion and 1.7 $\mu_B$/Mn ion for LCMO and LSMO, respectively. For both trilayers the magnetic moment is expected to keep increasing below 90 K, similar as in the single layers of Figure 3.15. However, for the trilayers the interpretation of the dc magnetisation curves below 90 K is complicated by the additional superconducting response of the YBCO layers. Therefore, only the data at 90 K or 100 K are reported here. For both trilayers, the dc $M$–$H$ loops at 100 K, Figure 3.21(b), show a clear hysteresis around the origin. This demonstrates that the embedded manganite layers have sizeable ferromagnetic moments whose orientation can be readily switched with an external magnetic field.

Next, devices with the geometry described in Section 1.5 were fabricated on these trilayers following the procedure detailed in Section 2.1.2. Figure 3.22 shows SEM pictures of the sculptured devices. The samples were then mounted in the 17 T cryostat setup described in Section 2.2.3 to study the transport characteristics across the thin manganite layer. Interestingly, for both samples a hysteretic behaviour was observed in the magneto-resistance ($MR$) curves. Figure 3.23 shows $R$–$H$ curves at different temperatures from a device fabricated on the LS\textsubscript{11} trilayer, with the field oriented in the plane. Except for the region close to the
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Figure 3.23: Magnetoresistance (MR) curves from a device fabricated on the trilayer LS$_{11}$, measured applying an ac current of 14 µA and an in-plane oriented magnetic field. Panels (a)–(d) show the MR-curves at 10 K, 65 K, 100 K and 115 K, respectively. The arrows indicate the direction of the field sweep. The change in sign in the slope is associated with the reorientation of the magnetisation of the LSMO barrier with the applied field. The sharp transition suggests a mono-domain type of switching. Adapted from [46].

origin, the resistance of the device decreases linearly as a function of the external field at temperatures above and below $T_c$. Near the origin, the MR curves show a characteristic hysteretic behaviour in terms of a sudden jump in the magnitude of the resistance and a related change in the sign of the slope. This abrupt change can be associated with a reorientation of the magnetic moment in the manganite barrier with the external field, which strongly influences the resistance through the device due to the CMR effect [64]. Note that the slope before and after the sharp change in resistance (at a given temperature) has the same absolute value, thus suggesting that the moment flips abruptly between the saturated values, and not in a progressive manner. The field at which the sign of the slope changes thus can be associated with the coercive
Figure 3.24: MR curves from a device fabricated on the trilayer LC.10 taken with an ac current of 100 µA and in-plane oriented field at temperatures of (a) 15 K, (b) 55 K, (c) 75 K, (d) 100 K, (e) 150 K and (f) 180 K. Arrows indicate the direction of the field sweep. The reorientation of the ferromagnetic barrier is not as sharp as for the device on LS.11. Adapted from [46].

field, $H_{coer}$, of the manganite barrier. This hysteretic behaviour is a strong indication that the ferromagnetic state of the thin manganite layer has been preserved during the fabrication processes. Moreover, the lack of intermediate steps in the flip of the moment suggests that the ferromagnetic barrier reorients with the field in a mono-domain fashion.
3.2. TRANSPORT THROUGH La$_{2/3}$X$_{1/3}$MnO$_3$ (X: Sr, Ca)

A qualitatively similar behaviour was observed in the $R$–$H$ curves for a device fabricated on the LC$_{10}$ trilayer, as shown in Figure 3.24. A linear decrease of the resistance is once more found for fields larger than $|H_{coer}|$, whereas the history of the field sweep determines the resistance found on the device for fields below $|H_{coer}|$. The magnetic reorientation in this case is not as sharp as for the device sculptured on LS$_{11}$ (see Fig. 3.23). Instead of a single-step switching behaviour, the device in LC$_{10}$ shows signs of a two-step reorientation with the external field. This could be related to the larger active area of the device in LC$_{10}$ compared to that in LS$_{11}$. As outlined in the caption of Figure 3.22, the dimensions of the devices are 700 x 275 nm$^2$ for the case of LC$_{10}$ and 560 x 275 nm$^2$ for LS$_{11}$. In this regard, the stepped switching of the ferromagnetic orientation in the device containing LCMO may arise due to the fact that the FM barrier is large enough to accommodate a second magnetic domain, for which the switching occurs at a slightly different magnetic field.

The hysteresis in the $MR$ curves involves a combination of the ferromagnetic moments of the manganite layer and the CMR effect. Indeed, the hysteresis reflects the finite coercive field at which the orientation of the magnetic moment of the ferromagnetic barrier in the device is switching. The measured change of the $MR$ results from the CMR effect which relates the resistance of the manganite layer to the degree of alignment of the spins in the Mn sites (see Section 1.2).

In the linear portions of the $R$–$H$ curves, $R(H)$ can be written as

$$R(H) = R(0) - \alpha |B(H)|,$$

where $R(0) = R(B=0)$, $B(H) = 4\pi M(H) + H$ and $\alpha$ is a constant coefficient. If we now consider the portions of the $MR$ curves at high positive fields for which $H > H_{coer}$ and $B > 0$, the magnetisation of the ferromagnetic barrier is thus saturated and $M(H) = M_s$. By inserting in eq. (3.1) the definition of $B(H) = 4\pi M(H) + H$, we can define the magnetisation in the barrier as

$$4\pi M_s = \frac{R(0) - R(H)}{\alpha} - H.$$

Extending the above assumption for all fields

$$4\pi M(H) = \pm \frac{R(0) - R(H)}{\alpha} - H,$$

where the sign depends on the sign of $B$. Using eq. (3.2) it is possible to reconstruct the $M$–$H$ hysteresis curves of the ferromagnetic barrier.
CHAPTER 3. RESULTS AND DISCUSSION

Figure 3.25: Comparison of the VSM data with the magneto-transport and the reconstructed hysteresis loops for LC_{10} (left) and LS_{11} (right). Upper panels: VSM hysteresis loops obtained from the unpatterned samples at 100 K. Middle panels: MR curves of the nano-fabricated devices at 100 K. Lower panels: $M$–$H$ loops reconstructed from the MR curves. The orange vertical lines mark the coercive fields obtained from the VSM data. Adapted from [46].

from the $R$–$H$ data. Two examples of reconstructed $M$–$H$ loops are shown in Figure 3.25 as obtained from the $R$–$H$ curves of LC_{10} and LS_{11} at 100 K that are displayed in Figs. 3.24(d) and 3.23(c), respectively. For comparison, the upper panels of Figure 3.25 show the hysteresis loops of the dc magnetisation measured with VSM on the unpatterned samples of Figure 3.21 in the same horizontal scale. The
3.2. TRANSPORT THROUGH $La_{2/3}X_{1/3}MnO_3$ (X: Sr, Ca)

Figure 3.26: Scheme illustrating the proposed functionality of the SFS devices as potential memory cells. Adapted from [46].

vertical lines mark the coercive field of the manganite layers as obtained from the VSM data and can be observed to match rather well the jumps in the $R-H$ curves and the reconstructed $M-H$ loops.

Furthermore, solving eq. (3.2) for $R(H)$ we have

$$R(H) = R(0) - \alpha H - 4\alpha \pi M_s. \quad (3.3)$$

Since the ferromagnetic barrier reorients its moment only for fields $H > H_{coer}$, in the hysteretic part of the curves there are two possible states of resistance depending on the relative orientation of $H$ and $M_s$. Indeed, due to the CMR effect a larger $|B|$ results in a smaller value of $R(B)$ (since $dR/d|B| < 0$) and thus when $M_s$ and $H$ are parallel $|B|$ is maximal and $R(B)$ is at its minimum. This suggests that a memory operation can be implemented with the devices shown in Figures 3.23 and 3.24 since, depending on the history of the magnetic field sweep, at a given value of the external field with $H < H_{coer}$ they exhibit two different resistance states. This idea is illustrated by the scheme in Figure 3.26, which shows that a small external field can lift the degeneracy of the resistance curves at $H = 0$ yielding two branches for which the magnetisation is either parallel or antiparallel with respect to $H$. For example, a small reading field $H_{read}$ gives rise to different values of $R$ at the points denoted as B(1) and C(0) in Figure 3.26.
At the point B(1) $M_s$ and $H_{\text{read}}$ are oriented antiparallel, and thus according to eq. (3.3)

$$R_1 = R(A) - 4\pi \alpha M_s + \alpha H_{\text{read}},$$

whereas at the point C(0) $M_s$ and $H_{\text{read}}$ are parallel, and hence

$$R_0 = R(A) - 4\pi \alpha M_s - \alpha H_{\text{read}}.$$

Consequently, a strong CMR effect is crucial in order to obtain a large readout signal, since the difference between $R_1$ and $R_0$ is determined by the CMR coefficient $\alpha$ according to $R_1 - R_0 = 2\alpha H_{\text{read}}$. Furthermore, the read-out signal can be enhanced by sequentially measuring at $-H_{\text{read}}$ (points C' and B'), thus increasing the fidelity of the device and potentially reducing the required magnitude of the read field.

The functionality of these devices as potential memory cells has several advantages. One is that the information is stored as a state of magnetisation, and thus is non-volatile. Besides, high $T_c$ value of the YBCO layers allows to operate memory at liquid nitrogen temperatures with high operation speed and low power dissipation, and makes it suitable for a superconducting digital exaflop computer for which it has been pointed out that “The main barrier to practical application is the lack of high-speed and low-power memory” [104]. Other advantages of this candidate for a memory cell are its scalability and simplicity, since the information is stored in a single F-layer that can be scaled down to mono-domain sizes. Furthermore, the operation of this potential memory cell is determined by the ferromagnetism and CMR of the manganite barrier, and thus its operation is limited to temperatures below $T_{\text{Curie}}$ and not below $T_c$. In this sense, the proposed memory cell can function both above and below $T_c$.

Several drawbacks prevent the presented structures from reaching a potential application. The resistances measured over a large variety of temperatures are yet too high to have a practical use, especially considering that the resistance splitting between the two states of the memory is small compared to the total resistance of the device, that is, $R(A) \gg R_1 - R_0$. In addition, the coercive fields of the FM barriers are yet too large, which in turn could limit the scalability of such a memory cell.

The presented devices can be considered as a first attempt on this matter, there exist many other oxide materials that may emerge as interesting candidates to substitute those used in these devices. An example of this is tYBCO, which was demonstrated in Section 3.1.3
to enhance the ferromagnetic ordering in the thin LCMO layers, thus potentially allowing to use a thinner manganite which would reduce the total resistance of the device. Besides, the coercive field necessary for the writing of states in memory cells as those proposed can be increased or reduced by the geometry and size of the device, which opens yet another way to improve the performance of these devices.

3.3 Perpendicular transport through SFS junctions with LaMnO$_3$

In the context of a former collaboration between the groups in Stockholm and Fribourg, SFS junctions with a 20 nm thick ferromagnetic insulating (FI) barrier of LaMnO$_3$ (LMO) were studied [44]. In the study of the current-voltage characteristics at $T < T_c$ three different regimes were observed. As a function of increasing bias voltage, the characteristics of the $I$-$V$ curves evolved from that of a current-blocked junction at $V \lesssim 0.3$ V to a Fowler-Nordheim type of tunnelling at $0.3$ V $\lesssim V \lesssim 1$ V. Furthermore, for a bias $V \simeq 1$ V a sharp jump of the current was observed and attributed to an excess current flowing across the junction.

Previously, two additional trilayers with a smaller thickness of the LMO barrier of 10 nm and 5 nm, respectively, were prepared but had not been further studied. In the context of this PhD project devices have been fabricated and measured on these samples, which also served as a training of the various techniques used in the device fabrication. This work has been published in Paper III. Discussed in the following are only the results that have been obtained from the SFS structures with the thinner LMO barriers (10 nm and 5 nm).

Figure 3.27 shows the $R$-$T$ curves obtained from a device fabricated on the sample with 10 nm of LMO. A clear superconducting transition is found at the various voltages and magnetic fields applied, indicative of a supercurrent passing through the device. In addition, an upturn of the resistance of the device can be seen around $T_{Curie} \sim 200$ K that can be associated with the transition of the LMO layer to a FI state. At temperatures below $T_{Curie}$ a certain magneto-resistance is observed when comparing curves with magnetic fields of 0 T (black) and 10 T in-plane (red) with the same current of $I_{ac} = 1$ $\mu$A. This $MR$ is negative, as expected for a CMR manganite. The right panel of Figure 3.27 shows in detail the low temperature range. The overall magnetic response of the 10 nm LMO layer appears to be rather weak.
CHAPTER 3. RESULTS AND DISCUSSION

Figure 3.27: $R$–$T$ curves recorded from a SFS device with a 10 nm thick LMO barrier under different field and bias conditions. A clear superconducting transition is observed at $T_c$. Inset: Detailed view of the low temperature response. Adapted from [47].

Finally, the curve in green shows the effect of combining a large bias with a field applied out-of-plane. The large drop in the resistance of the device found at $T_c$ indicates that the charge carriers are not tunneling across the LMO barrier. This idea is reinforced by the comparison of the curves at 1 $\mu$A (black) and 7 $\mu$A (blue) at low temperatures for which a larger applied current leads to a larger resistance, contrary to the trend that is expected for a tunneling process.

Figure 3.28: (a) $I$–$V$ characteristics of the SFS junction with 10 nm of LMO taken at different in-plane fields. (b) $R$–$H$ curves at 2 K measured with an ac current of 7 $\mu$A. Adapted from [47].
3.3. TRANSPORT THROUGH $\text{LaMnO}_3$

Figure 3.29: $R-T$ and $R-H$ data obtained from devices fabricated on the sample with a 5 nm thick LMO barrier. (a) $R-T$ curve of a device measured applying an ac current of 2 $\mu$A in zero field. (b) $R-T$ curve for a different device, which exhibits a small shift of the superconducting transition as an in-plane magnetic field of 10 T is applied and hardly any magneto-resistance in the normal state at $T > T_c$. (c) $R-H$ curves at 2 K measured with an ac current of 6 $\mu$A, exhibiting a positive MR. Adapted from [47].

Figure 3.28(a) shows the $I-V$ characteristics at 2 K for different magnetic fields applied along the in-plane direction. Features of a small Josephson current of about 10 $\mu$A can be seen, albeit it does not develop into a superconducting branch. Besides, the $I-V$ curves are not clearly affected by the external magnetic field, which agrees with the weak ferromagnetic response observed in the $R-T$ curves. The magneto-resistance of the device has been probed at low currents and is presented in Figure 3.28(b) for continuously increasing amplitudes of the magnetic sweep. A small modulation of the resistance is seen, but it is far from a clear Fraunhofer modulation. This is likely due to the complicated magnetic nature of the barrier.

The response obtained from the devices fabricated on the sample with the thinnest LMO barrier of 5 nm are presented in Figure 3.29. Panels (a) and (b) show the $R-T$ curves recorded for two different
devices. In both cases, despite of the different profile of the superconducting transition, the resistance falls to zero at $T < T_c$. Above $T_c$, there is no clear sign of an insulating behavior due to the formation of an FI state in the LMO layer nor is there any clear influence of an external magnetic field in the resistance, as can be seen from the red curve (6 $\mu$A, 10 T in-plane) in Figure 3.29(b).

The magneto-resistance of one of the devices is represented in Figure 3.29(c). It is not negative as it was found for the 10 nm LMO barrier but positive, characteristic of the response of the superconductors. Overall, the magnetism of this thin barrier seems to be even weaker than the one of the device with the 10 nm LMO. Nevertheless, the rather large resistance values that are observed at $T > T_c$ suggest that the current is flowing through the LMO barrier of the device (which does not develop a FI state) rather than through some nano-shortcuts due to defects in the barrier.

In summary, the FI properties of the LMO barriers have been observed to weaken as its thickness is reduced. As it was discussed for the case of YBCO/LCMO bilayers, presented in Section 3.1.1, the large thickness of the S layer on top of which the LMO layers are deposited may be one of the reasons for the weak ferromagnetic response. Moreover, the deposition parameters used during the growth of the present SFS structures may not be optimised for the deposition of thin F layers intended to be embedded in large S layers. As it was demonstrated in Section 3.1.4 it is possible to embed thin F layers of 10 nm, 8 nm and even 5 nm in SFS structures and obtain a sizable ferromagnetic signal thanks to the choice of the appropriate materials and growth conditions. It remains to be tested if the same protocol used in the deposition of LCMO and LSMO would also help to improve the ferromagnetic properties of the parent compound LMO.
Summary

The overall goal of this PhD thesis has been the fabrication of YBa$_2$Cu$_3$O$_7$ / manganite/ YBa$_2$Cu$_3$O$_7$ (SFS) structures to study their vertical magneto-transport properties across the ferromagnetic manganite layer. For this purpose, corresponding multilayers have been grown and characterised, mesoscopic structures have been nano-fabricated using lithography and focused ion beam techniques, and the vertical magneto-transport properties have been measured. This involved the use of multiple techniques such as PLD for the thin film growth, XRD, XRR, STEM and EELS for the structural characterisation, VSM magnetometry and PNR to study the magnetic properties, optical lithography and focused ion beam for the device nano-fabrication, and magneto-transport studies on the obtained devices.

The first step in this project, to grow YBCO/LCMO/YBCO multilayers with a thin but strongly ferromagnetic LCMO layer, already demonstrated to be a difficult task. Whereas it was rather straightforward to find suitable PLD growth conditions to obtain individual YBCO and LCMO layers with good superconducting and ferromagnetic properties, respectively, it turned out that the growth of corresponding YBCO/LCMO bilayers with a strong ferromagnetic response of LCMO is much more difficult. For the initial growth conditions (denoted as A-type) the ferromagnetic moment of the LCMO layers was strongly suppressed and, moreover, very sensitive to the structural details of the underlying YBCO layer, in particular to its orthorhombic distortion. Accordingly, the A-type recipe of the PLD growth parameters had to be revised and optimised to finally obtain YBCO/LCMO bilayers and multilayers with thin but strongly ferromagnetic LCMO layers.

This work has also provided some insight into the mechanism behind the suppression of the ferromagnetic order in the A-type YBCO/LCMO bilayers (or multilayers) that was not present, or at
least much weaker, for the corresponding B-type samples. For both types of samples, the XRD, STEM and EELS data suggested a similarly good structural quality with a high degree of crystallinity of the LCMO layers, atomically sharp and well defined interfaces with no clear signs of interdiffusion or chemical mixing and with the only detectable defects being stacking faults in the YBCO layers in the form of Cu-O double layers. Yet, a remarkable difference was observed in the average manganese oxidation state obtained with STEM-EELS, which yielded for the B-type bilayer a value close to the nominal one of $+3.3$, whereas for the A-type samples it ranged from $+3.47$ to $+3.6$. The increased Mn valence of the A-type LCMO was ascribed to an unbalanced La/Mn ratio that arises from a poor transfer of the stoichiometry of the target to the growing film on the substrate. The additional hole doping due to this cation unbalance weakens the ferromagnetic order of LCMO that is shifted in the doping phase diagram towards the boundary with antiferromagnetic and charge/orbital ordered states that compete with the FM order. Accordingly, the FM properties of LCMO become very sensitive to strain and disorder, and thus to the structural details of the YBCO layer on which it is grown.

To further explore the effect that the orthorhombic structure of plain YBCO has on the suppression of the FM order of A-type LCMO, the intermediate YBCO layer was replaced by Co– and Ca– substituted $\text{Y}_{0.8}\text{Ca}_{0.2}\text{Ba}_{2}\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{7}$ (tYBCO) with a tetragonal structure. This gave indeed rise to a resurrection of the FM order in the A-type grown tYBCO/LCMO bilayers and even for the corresponding B-type bilayers it strengthened the FM response. Using the B-type growth conditions and tYBCO instead of YBCO it was finally possible to realise spin-valve structures with very thin manganite layers (down to 5 nm) embedded in thick superconducting layers (~100 nm) with strong ferromagnetic moments that can be individually oriented and switched with an external magnetic field.

Subsequently, B-type SFS trilayers of YBCO/LCMO/YBCO and YBCO/LSMO/YBCO with thin F barriers (~10 nm) have been prepared and used in the nano-fabrication of mesoscopic devices and subsequent studies of the vertical magneto-transport. A pronounced hysteretic behaviour was observed in the magneto-resistance ($MR$) curves of these SFS devices that could be explained in terms of a change in the relative orientation of the magnetisation $M$ of the F barrier with respect to the external magnetic field $H$. Taking into account the well known colossal magneto-resistance properties of the manganites, which
relates the resistance of the manganite layer to the magnetic induction and thus to the alignment of the Mn spins, the \( M-H \) hysteresis loops of the F barrier have been reconstructed from the measured \( MR \) curves of the devices. These \( M-H \) loops revealed coercive fields that are very similar to the ones obtained from the dc magnetometry on the as grown multilayers (prior to nano-fabrication) and a sharp switching behaviour that is typical of a single (LSMO) or dual (LCMO) domain state of the F barrier. In the first place, these results demonstrate that the ferromagnetic order of the thin manganite barrier was indeed preserved during the fabrication processes. Moreover, it was shown that these devices enable a memory functionality for which the information is stored in the orientation of the magnetisation of the F barrier that can be read in terms of the device resistance upon the application of a small magnetic field \( H_{\text{read}} \).

Finally, in the initial stages of this PhD project, the nano-fabrication of devices and the of study their vertical magneto-transport properties has been attempted on YBCO/LaMnO\(_3\)/YBCO structures for which the LaMnO\(_3\) (LMO) acts as a ferromagnetic insulating barrier. The samples used were previously grown and first devices with rather thick LMO layers (20 nm) had been fabricated and studied as described in Ref. [44]. The task of the present work has been, besides the training of the various techniques, to realise similar structures with thinner FI barriers by reducing the width of the LMO layer to 10 nm and 5 nm. Unfortunately, it was found that this leads to a severe degradation of the ferromagnetic properties of the LMO barriers, i.e. for the devices with 10 nm (5 nm) thick LMO only a very weak (no sign of a) ferromagnetic response could be observed. Accordingly, the research on the YBCO/LMO/YBCO structures has not been further followed up.
Final conclusions and Outlook

The challenges proposed at the beginning of this work have been addressed. The transport across SFS structures with thinner LMO barriers demonstrated the difficulties that arise from the use of a geometry that strongly relies on thick S layers. The implementation of different magnetic perovskites in this structures would have been fairly straightforward if the optimisation of the ferromagnetic ordering in the thin F layers would have been disregarded. However, the challenge that presented the use of an intricate geometry and the emphasis deposited on obtaining large saturation moments in the manganite barriers led to structures with very interesting magnetic profiles at which the perpendicular transport shall be probed.

The control of the deposition and the understanding of the interactions between these strongly correlated materials widens the landscape of electronic devices, and opens new possibilities for spintronic heterostructures such as the multilayers shown in Section 3.1.4. The work compiled in this thesis is by no means a blind alley, and the conclusions arrived to do not attempt to establish whether this kind of materials will or will not see a commercial application. Rather, it attempts to emphasize the rich physical interactions that occur in these materials, as it has been known in the scientific community for decades, and establish some basic ideas on to the key factors for the manipulation of their properties.
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Appended papers