LOW-ENERGY ELECTRONIC STRUCTURE AND FERMI SURFACE TOPOLOGY OF THE ITINERANT METAMAGNET Sr$_3$Ru$_2$O$_7$

By

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DISSERTATION
Submitted in fulfillment of the requirements for the degree

MASTER IN PHYSICS

at the

UNIVERSITY OF JOHANNESBURG

OCTOBER 2013

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Acknowledgements

The work presented in this dissertation was carried out in the electronic structure group based in the Physics Department at the University of Johannesburg. My scholarship was provided by the African Institute for Mathematical Sciences (AIMS) and the University of Johannesburg.

At the end of this MSc research program, I would like to thanks all the people who contributed to it.

First, my greatest thanks goes to my supervisor Dr. Emanuela Carleschi, and my co-supervisor Dr. Bryan P. Doyle for providing me with the opportunity to come to the University of Johannesburg and for their advices, guidance, support and encouragement during the last two years. Your assistance, corrections and comments during the analysis of data and writing up phases of this dissertation were very helpful. It was an honour to work with you, you are such great supervisors and wonderful people.

A special thanks goes to both the African Institute for Mathematical Sciences (AIMS) and the University of Johannesburg for granting me each with half of the bursary that supported me during my MSc research program.

I also thank my fellow postgraduate students in the Physics Department whom I have learned many new things from, namely Pius Rodney Fernando, Bernard Duah Asabere, Wisdom Nkosilathi Sibanda, Philip Musyimi and Marius Tchonang Pokaha. I also thank all the other fellow postgraduate students whom I have not mentioned here, and the academic and administrative staff in the Department of Physics of the University of Johannesburg for the warm research environment.

Finally, another special thanks goes to my family, especially to my parents, sisters and brothers for all the support and encouragement that they have shown me.
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Introduction

The way we live has been fundamentally changed by technological innovations based on optical, electronic and magnetic materials. Without the continuous increase of scientific understanding on phenomena that occur in materials, together with the processing and synthesis of materials, these technological revolutions would be impossible. Thus, the search of new materials is still the key driving force for the continuous blooming of modern technology.

In the last three decades, intensive search for new electronic materials was performed mainly in the 3d transition metal oxides (TMO) \[1\]. Scientists interests were focused on the study of these materials, because this category of materials have given rise to great sensation in condensed matter physics by presenting unusual electronic and magnetic phenomena such as high $T_c$ superconductivity and colossal magnetoresistance \[2, 3\]. These phenomena are caused by the strong electron-electron (e-e) correlation, which comes from the onsite Coulomb repulsion between the localised 3d orbitals electrons. Less attention was paid to the 4d TMO because their orbitals are more extended than the 3d orbitals and were thought to have smaller or insignificant e-e correlation effects \[4\]. However, with the discovery of numerous interesting electronic properties in 4d TMO, such as unconventional superconductivity \[5\], metal insulator transition \[6, 7\] and non Fermi liquid behaviour \[8\], new attention has been stimulated to this class of materials. The investigation on physical parameters such as charge transfer energy, Coulomb repulsion energy (U) and crystal field splitting energy of 3d and 4d TMOs, has revealed that although the U values of 4d TMO are smaller than those of 3d TMO, their charge transfer and crystal field splitting energies values are relatively large \[9\]. These large values show that the more extended 4d orbital electrons have weaker onsite U values ($\sim 1$ to $2 \text{ eV}$), but stronger hybridization energy W ($\sim 2$ to $5 \text{ eV}$) with the neighbouring O 2p orbitals \[9\]. In 4d TMO, when the ratio W/U is comparable, the competition between W and U energies give rise to wealthy and complex phases \[4\]. Therefore, any small perturbation such as an external magnetic field can easily tune the physical properties in the ground state \[4\]. Moreover, due to the small value of U, 4d orbitals become more important and the spin-orbit coupling is then significant \[10, 11\]. So far, a quite large quantitative studies have been performed on the 4d TMO series and the understanding of this type of materials remains at a qualitative level. The Ruddlesden-Popper (R-P) series of strontium ruthenates is one of the few class of materials that supplies a rare opportunity to study the strongly correlated electron systems in the 4d TMO.

The general chemical formula of the R-P series can be written as $D_{n+1}E_nM_{3n+1}$, where D and E are cations, M is an anion and n ($=1, 2, 3$ and $\infty$) is the number of consecutive layers of octahedra in the perovskite like-stack \[12\]. This series was initially referred to compounds with $\text{Sr}_3\text{Ti}_2\text{O}_7$-type or $\text{K}_2\text{NiF}_4$-type crystal structures and was first reported in the 1950s \[13, 14\]. This series of compounds present unusual electronic and magnetic properties due to the choice and stoichiometry of the anion M, the D and E cations.

With the discovery of unconventional spin-triplet superconductivity in $\text{Sr}_2\text{RuO}_4$ ($n=1$), the strontium ruthenates have raised a lot of attention, therefore inspiring high enthusiasm in exploring the Sr based R-P series with the general formula $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$. In this series, as the parameter n (here, n denotes the number of consecutive ruthenium oxygen ($\text{RuO}_6$) octahedra layers in the unit cell) increases from 1 to $\infty$, the number of nearest neighbouring $\text{RuO}_6$ octahedra also increases, depicting a systematic enhancement of the structure dimensionality. Thus, this series possesses an astonishing and distinctive dimensionality dependence of physical properties due to the strong interactions between the Ru ions \[5, 15\]. For instance, when n progress from 1 to $\infty$, the series is gradually driven from a paramagnet for $n=1$, to a metamagnetic paramagnet system for $n=2$, and then to a ferromagnet with metamagnetic
transition \((n = 3)\) [16]. The difference of physical properties with dimensionality and structure distortion in this system, make the R-P series an excellent system to investigate the interplay between lattice, orbitals, charges and spin degrees of freedom in the 4d TMO. The lattice distortions observed in this series remove the degeneracy between \(t_{2g}\) and \(e_g\) levels allowing hybridization between orbitals with different symmetry group [17].

The material studied in this dissertation is a double layered Sr\(_3\)Ru\(_2\)O\(_7\) \((n = 2)\) from the strontium ruthenate family. This project focuses in particular on the study of the near-Fermi-level electronic structure of Sr\(_3\)Ru\(_2\)O\(_7\), in order to understand the coupling between electronic and magnetic properties in this system [16]. The earlier work of Binz et al., has shown based on mean-field theory, that the metamagnetic behaviour in this system [18] can be understood as a result of the presence of van Hove singularities (vHS) (i.e., sharp peaks observed in the density of states (DOS)) in the proximity (\(\sim\) meV) of the Fermi energy [16] and associated to Fermi surface (FS) sheets of different symmetry. Recently, an analysis by density-functional theory of the low-energy electronic structure of the \(d_{xy}\) band dispersion of Sr\(_3\)Ru\(_2\)O\(_7\) has predicted a complex DOS with sharp features resembling vHS near the Fermi level associated to \(\gamma_2\) FS sheet [16, 18]. These complex DOS with vHS close to the Fermi level are favourable for magnetic instabilities by applying an external magnetic field, i.e., they favour the presence of the metamagnetism due to peaks near the Fermi level when an external magnetic field is applied. More recently, Allan has suggested another vHS associated to the \(\alpha_2\) FS sheet with the \(d_{xz, yz}\) orbital character [19] as predicted Refs. [18, 20].

In this work, Angle Resolved Photoemission Spectroscopy (ARPES) was used to probe the FS and the band dispersions of this compound. By means of ARPES we were able to determine the symmetry and location on the FS of the vHS associated to different FS sheets.

In literature, there are only two published experimental ARPES reviews by Tamai et al. and Allan et al. on Sr\(_3\)Ru\(_2\)O\(_7\) [19, 21], and the outcomes of Tamai’s paper are in agreement with density-functional calculations cited above [16, 18]. In particular, Tamai and coworkers extracted two sharp peaks (located at \(-4\) meV and \(-1\) meV below the Fermi level) in the \(d_{xy}\) DOS of Sr\(_3\)Ru\(_2\)O\(_7\). These two peaks are related to a Fermi surface pocket centred at the \(X\) point, but due to a broad experimental resolution in comparison with the width of these peaks, others vHS were not detected in this work. Thus, a possibility of presence of other vHS associated to different FS sheets cannot be excluded. The \(d_{x^2-y^2}\) bands dispersion can also possibly reveal a complex density of state with vHS close to the Fermi level for both lattice distortions and the interlayer coupling in Sr\(_3\)Ru\(_2\)O\(_7\) cause a strong reorganization of the electronic charge in the RuO\(_6\) octahedra by allowing \(t_{2g} - e_g\) hybridization [17]. In this work, we therefore focus on a detailed analysis of the Fermi surface mapping and band dispersions analysis of Sr\(_3\)Ru\(_2\)O\(_7\) in order to locate and determine the symmetry of the vHS in the DOS associated to different Fermi surface sheets.

This dissertation is divided into six chapters together with two appendixes and is organized as follows.

Chapter 1 begins with an introduction section 1.1 that gives a detailed discussion on strongly correlated electron systems since the material studied in this project belongs to this class of material. Section 1.2 presents a general overview on transition metal oxides. Section 1.3 exhibits a brief literature survey on the previously reported physical properties of three members of the Sr Ruthenates series namely Sr\(_2\)RuO\(_4\) \((n = 1)\) in section 1.3.1, Sr\(_4\)Ru\(_2\)O\(_{10}\) \((n = 3)\) in section 1.3.2 and SrRuO\(_3\) \((n = \infty)\) in section 1.3.3. A rich and more detailed literature review of the previously reported physical properties of Sr\(_3\)Ru\(_2\)O\(_7\) is then given in section 1.4 in order to explain in details the contribution of this work. Finally, the scope of this study is presented in section 1.5.

Chapter 2 talks about the theoretical description of ARPES which is the experimental technique used
in order to acquired data presented in this dissertation. After a brief introduction exhibits in section 2.1, the principle of ARPES is presented in section 2.2. This section discusses in more detailed some relevant aspects such as the conservation of energy and parallel component of the electron momentum in a solid. This section also shows the derivation of expressions of momentum $K$ inside the vacuum and its relationship with the momentum $k$ inside the solid. A detailed theoretical description of a photoemission process is described in sections 2.3 and 2.4, which are the commonly theoretical approaches used in order to approximated the photoemission intensity. Section 2.5 describes the link between the measured photoemission intensity and the spectral function. In this section, the spectral function is represented through the Green’s function. Section 2.6 deals with the explanation of self energy since it holds all information due to the particle interaction effects. This section talks about the photoemission linewidth and inverse lifetime and introduces also the Lorentzian line shape that is frequently used in the process of data analysis. A theoretical description of the effects of the photoemission matrix elements on the measured ARPES spectra is described in section 2.7. An introduction on the effect of electron correlation observed in ARPES spectra is presented in section 2.8 with the help of some results taken from the literature. From these examples of electronic systems, one can see that unusual renormalization and kinks observed in photoemission spectra is due to the electronic coupling to a bosonic mode such as phonons or magnetic excitations.

Chapter 3 starts with a short introduction in section 3.1, followed by section 3.2 which describes the non-trivial experimental aspects of ARPES based on the use of synchrotron radiation and of the state-of-the-art Scienta electron energy analyser. A detailed explanation on how a 2D image colour map acquired with a Scienta R4000 spectrometer is presented in section 3.3. In this section the way to extract two standard curves (momentum distribution curve and energy distribution curve), which are used frequently in order to analyse the 2D image colour map, is also shown. The floating zone technique used in order to acquired high quality $\text{Sr}_3\text{Ru}_2\text{O}_7$ samples used in this work is explained in section 3.4 together with the cleavage procedure.

Chapter 4 begins with an introductory section 4.1 followed by section 4.2 that gives information on the experimental settings used in the process of acquiring high resolution cuts and Fermi surface maps presented in this work. The procedure used in order to determine the Fermi energy level of the experimental measured ARPES spectra is presented in section 4.3. This section also exhibits how to determine the experimental energy resolution achieved during the experiment, pass energy of the analyser and the type of polarization used to construct the Fermi surface maps presented in this dissertation. Section 4.4 shows a detailed description of the method used in order to determine the first Brillouin zone of $\text{Sr}_3\text{Ru}_2\text{O}_7$ compound. Section 4.5 presents a possible construction of the complex Fermi surface map of $\text{Sr}_3\text{Ru}_2\text{O}_7$ from its parent compound $\text{Sr}_2\text{RuO}_4$. In this section we are also comparing the shape of Fermi surface sheets of all Fermi surface maps of $\text{Sr}_3\text{Ru}_2\text{O}_7$ presented in the literature. A clear explanation on how to reconstruct Fermi surface maps from raw experimental data is given in section 4.6. Section 4.7 presents the experimental measured Fermi surface maps of $\text{Sr}_3\text{Ru}_2\text{O}_7$ acquired in this work. In these Fermi surface maps, only three Fermi surface sheets are well resolved. A careful analysis of these experimental Fermi surface maps obtained in this work have revealed some new bands which are not predicted by the theory together with distortions on these maps and details of these distortions are given in section 4.8. With the presence of these distortions in our experimental FS maps, we use a common method in literature, i.e., we symmetrised FS maps in order to get a periodicity and to more understand our maps. Finally the summary of the chapter is presented in section 4.9.

Chapter 5 presents in depth analysis and discussion of the electronic band structure of $\text{Sr}_3\text{Ru}_2\text{O}_7$ from ARPES experiment. This chapter begins with an introductory section 5.1 followed by section 5.2 which describes and gives the difference between the linear horizontal and vertical polarizations exploited during
the ARPES experiment. The effect of matrix elements observed on band dispersions and Fermi surface maps of Sr$_3$Ru$_2$O$_7$ is also discussed. Analysis of the ARPES resolved Fermi surface sheets of Sr$_3$Ru$_2$O$_7$ is presented in section 5.3. In this section we observed a new Fermi surface sheet named $u$ band which has not been predicted by the theory. This section also shows that the $\delta$ Fermi surface sheet is an electron pocket while $\alpha_1$ and $u$ band are hole pockets. Section 5.4 presents the line shape analysis of Sr$_3$Ru$_2$O$_7$. Section 5.5 focuses on the kink energies observed on the band dispersions of Sr$_3$Ru$_2$O$_7$. These kinks are compared to a previous Raman spectroscopy study and lattice dynamic calculations taken from Ref. [15]. The renormalisation effect observed on the band dispersion is presented in 5.6. Section 5.7 presents the analysis of bands that exhibits a complex density of states near to the Fermi energy level. These complex density of states is expected to give rise to Van Hove singularities near the Fermi level.

Chapter 6 presents the summary of the phenomena observed on Sr$_3$Ru$_2$O$_7$ and suggests some future work.

Appendix $A$ explains in more details the mechanism of metamagnetism observed in localised systems which is based on spins-flop or spins-flip reorientation. It also describes a mechanism of metamagnetism observed in itinerant metamagnetism which is based on the Stoner model. In this model, the metamagnetism is attributed to sharp peaks (often called van Hove singularities) in the density of states close to the Fermi level.

Appendix $B$ describes in more details the concept of quantum criticality and shows how it occurs in Sr$_3$Ru$_2$O$_7$ compound.
1. Magnetic and Electronic Properties of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \)

1.1 Introduction

Strongly correlated electron systems defined as those in which the individual electron-electron (e-e) interactions need to be taken into account to explain their properties, represent one of the most fascinating branches of condensed matter physics. Unusual behaviour observed in the \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) compound are mostly due to the strong e-e interactions present in this system. These strong e-e interactions are observed when the overlap of atomic orbitals of different atoms is much less than the on-site e-e Coulomb repulsion \[23\]. Correlated materials normally possess incomplete filled \( d \) or \( f \) electron shells showing narrow energy bands \[24\].

The most general form of the Schrödinger equation which describes thoroughly the electrons and ions in a solid is given by equation 1.1:

\[
\hat{H}\Psi = E\Psi, \tag{1.1}
\]

where \( \hat{H} \) is the Hamiltonian of the system, \( \Psi \) is the many-body wave function of all electrons in the metal and \( E \) is the energy of the state \( \Psi \). In order to fully describe the system, the Hamiltonian \( \hat{H} \) in equation 1.1 should not be only written based on the kinetic and potential energy of the particles that constitute the system but must also take into account the potential energy of their interactions.

By including only the dominant interactions, the Schrödinger equation (1.1) for the \( N \)-particle wave function of all \( N \) electrons in the metal can be rewritten in the following form:

\[
-\sum_{j=1}^{N_e} \frac{\hbar^2}{2m_j} \nabla_j^2 \Psi + \sum_{j<k} V_{ee}(r_j - r_k)\Psi - \sum_{\alpha=1}^{N_i} \frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2 \Psi + \sum_{\alpha<\beta} V_{ii}(r_\alpha - r_\beta)\Psi + \sum_{i,\alpha} V_{ei}(r_i - r_\alpha)\Psi = E\Psi, \tag{1.2}
\]

where \( m_j \) is the mass and \( r_j \) is the position of the \( j^\text{th} \) particle. The subscripts “\( e \)” and “\( i \)” stand for electron and ion respectively. The first term in equation 1.2 represents the kinetic energy of the electrons, while the second term \( V_{ee} \) represents the electron-electron interaction. The third term is the kinetic energy of the ions while the fourth \( V_{ii} \) is the ion-ion interaction. The last term \( V_{ei} \) is the electron-ion interaction. The Greek subscripts represent ions and the Roman subscripts represent electrons. The potentials \( V_{ee}, V_{ii} \) and \( V_{ei} \), are given by the following formulas \( V_{ee} = \frac{e^2}{|r_j-r_k|} \), \( V_{ii} = \frac{Z_\alpha Z_\beta e^2}{|r_\alpha-r_\beta|} \) and \( V_{ei} = \frac{Ze^2}{|r_i-r_\alpha|} \), where \( Ze \) and \( e \) are the ionic and electronic charges, respectively.

Equation 1.2 becomes impossible to solve as the number of particles in the system becomes large. The ground state of multi-electron atoms can be deduced only if some approximations are made. Depending of the problem that we are solving, such approximations may be the local-density approximation (LDA) of density functional theory or the Hartree-Fock approximation (HFA) \[25\]. Their accuracy varies with what is being calculated. For example, for the spin polarisation in Li and in the 1s shell HFA is more accurate than LDA, while in the 2s shell the LDA is rather better than the HFA \[26\]. In addition the HFA approximation is more preferable than LDA for the Mott insulators \[27\], while the combination of LDA with spin-orbit coupling is more accurate for some 4d systems such as \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) \[21\]. It is important to note that LDA is based on the assumption that the potential of the exchange correlation must strongly depend on the electron density at a given point in space, while HFA is based on the expansion of the wavefunction in single Slater determinants. For more informations about these
approximations, references [24, 25, 26, 27, 28, 29] can be consulted. The Hartree-Fock approximation cannot be used in the case that e-e correlation leads to complicated many-body effects, but the single particle approximation knows a remarkable success in describing several properties of solids, despite the presence of the e-e interaction. This remarkable success has an explanation in the Fermi liquid theory of Landau [30, 31, 32]. Here the one electron approximation is replaced by a quasi-particle description of electron pairs specifying the elementary particle-hole excitations in the vicinity of the Fermi level in the theory of Landau. We can conclude that when we are dealing with many-body interactions, a given particle and the surrounding cloud of interacting particles are considered as one particle and this one particle is called a quasi-particle [33, 34, 35, 36]. Figure 1.1 provides an illustration of the concept of a quasi-particle. In this theory the properties of a system of interacting particles are considered to be qualitatively the same as for a non-interacting system [37]. For instance this behaviour is observed when the mass of the non-interacting electron is many times smaller than the mass of the quasi-particle [38]. The ideal example of this is called heavy fermion materials where the quasi-particles mass is increased to hundreds of times higher than the original non-interacting electron mass by the complex many-body effect.

Some unusual and remarkable phenomena in strongly correlated systems are Mott insulating behaviour [39, 40, 41], Kondo-insulating and heavy fermion behaviour in $f$ electron systems [33, 35, 42], high temperature superconductivity in cuprates [1], unusual magnetic behaviour such as metamagnetism transition in layered ruthenates [43, 44] and quantum critical behaviour in rare earth intermetallic compounds [45]. Many transition metal oxides belong to the class of strongly correlated materials and the compound of this study is a member of the transition metal oxides family.

This chapter starts by an introduction in section 1.1, followed by section 1.2 which presents a general overview on transition metal systems since the compound of this study which is Sr$_3$Ru$_2$O$_7$ belongs to this class of materials. Section 1.3 presents general physical properties of different strontium ruthenates members of the R-P series. Section 1.4 focuses on the literature review of the bilayer compound Sr$_3$Ru$_2$O$_7$ followed by the scope of this dissertation in section 1.5.

1.2 General Overview on Transition Metal Oxides

Transition metal oxides (TMO) are defined as a category of materials that contain transition metal (TM) elements and oxygen. In these materials the valence electrons are mostly constituted of metal $d$ shells interacting with O $2p$ states. Since the discovery of high temperature superconductivity in cuprates by Bednorz and Müller [1], the layered TMO have become one of the most extensively studied groups of
materials in the field of condensed matter physics. Many TMO belong to the class of strongly correlated materials. The R-P series \((\text{Sr}_{n+1}\text{Ru}_{n}\text{O}_{3n+1})\) is a very interesting family of TMO because of the plethora of electronic and magnetic properties that they display. The overall properties of these materials are governed by the electronic structure with \(d\) orbitals from the TM ions, which is energetically close to the \(p\) orbitals on the oxide ions, enabling considerable interactions between these two species. In these kind of materials, the orbital degree of freedom through strong coupling with charge, spin and/or lattice degrees of freedom plays an important role in generating the large variety of electronic and magnetic states. The rich nature of the \(d\)-block elements has granted physicists the power to design materials with unusual and novel properties [6].

The structural building block of many TMO is the perovskite structure. Any material with the same type of crystal structure as calcium titanium oxide (\(\text{CaTiO}_3\)) is called perovskite. This compound was named after the Russian mineralogist L. A. Perovski and was discovered by Gustav Rose in 1839 from samples found in the Ural Mountains of Russia [46]. The ideal perovskite crystal structure with the general chemical formula \(\text{ATO}_3\) is cubic and of space group \(P m \bar{3} m\) (see Figure 1.2). According to the common description of the ideal perovskite structure \(\text{ATO}_3\), "A" and "T" are cations (\(A =\) alkaline earth or lanthanide cation, and \(T =\) transition metal cation) and "O" is an anion. A atoms are located on the corners of the cubic cell, the T atom is located in the centre of an array of corner shared \(\text{TO}_6\) octahedra, and oxygen occupies the centre of the faces see Figure 1.2. A and T atoms both form a cubic close packed array. The position of the atoms in the perovskite structure are given in detail in Table 1.1.

Table 1.1: Atomic positions for the idealized perovskite structure in space group \(P m \bar{3} m\).

<table>
<thead>
<tr>
<th>Site</th>
<th>Wyckoff position</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>A cation</td>
<td>1a</td>
<td>(0, 0, 0)</td>
</tr>
<tr>
<td>T cation</td>
<td>1b</td>
<td>(1/2, 1/2, 1/2)</td>
</tr>
<tr>
<td>O anion</td>
<td>3c</td>
<td>(1/2, 1/2, 0) (1/2, 0, 1/2) (0, 1/2, 1/2)</td>
</tr>
</tbody>
</table>

Note: Wyckoff positions denote by a number and a letter, tell us where the atoms in the crystal can be found. The letter is called Wyckoff site while the number is called multiplicity of the site. More details about Wyckoff positions can be found in Ref. [47].

It should be noted that in the ideal perovskite structure each T-O bond is of equal length, and the T-O-T bond angle is equal to 180° [48].

Most of the perovskite structures do not have a cubic symmetry because they are distorted. There are different types of distortions such as distortions of the \(\text{TO}_6\) octahedra, T cation displacements, and tilting of the \(\text{TO}_6\) octahedra. The most common type of distortion is the tilting of the \(\text{TO}_6\) octahedra...
which results in structures of lower symmetries. Various systems have been developed by Woodward \[49\] and Glazer \[50\] to describe such distortions and the space group associated with them. The main driving forces beyond such transformation are the sizes and charge differences on the A and T sites. The stability of the perovskite structure depends on the radii of the ions in the crystal and is relatively independent of the valency. This is described by the tolerance factor \( t \), \[51, 52, 53, 54\] given by the formula:

\[
t = \frac{t_{AO} + 1}{\sqrt{2(t_{TO} + 1)}},
\]

where \( t_{AO} = \frac{r_A}{r_O} \) and \( t_{TO} = \frac{r_T}{r_O} \), with \( r_A \) radius of the A ion, \( r_T \) radius of the T ion, and \( r_O \) is the radius of the \( O^{2-} \) ion. The tolerance factor \( t \) is equal to 1 for an ideal perfect cubic perovskite. Many perovskite show deviations from \( t = 1 \) due to the variations in ionic radii of various ions and may not even have a cubic structure. These deviations from \( t = 1 \) show the level of lattice distortion. Goldschmidt \[54\] showed that perovskite structures are stable within the range \( 0.78 < t < 1.05 \). The lower values of \( t \) (\( t<1 \)) indicate A-site cations which favour rotations and/or tilting of the TO\(_6\) octahedra. Thus, the different values of the tolerance factor show us that most perovskite TMO deviate from the perfect cubic structure and show distortions.

Lifting of the Orbital Degeneracy

Orbital degeneracy is an important source of complex behaviour in \( d \)-electron systems, and depends on the local chemical environment of the TM. TMO present interesting orbital-related phenomena, for instance, orbital-driven ferroelectricity in manganese oxide \[55\], orbital-selective Mott-transition in \( \text{Ca}_2\text{Sr}_x\text{RuO}_4 \) \[56, 57, 58, 59\] and orbital-dependent superconductivity in \( \text{Sr}_2\text{RuO}_4 \) \[60, 61\]. A common case to consider in TMO is the octahedral environment, where a transition metal ion \((3d/4d/5d)\) sits at the centre of an octahedron with an oxygen ion on each corner. If one considers the oxygen anions as point-like charges, the \( O^{2-} \) ions produce a crystalline electric field which lifts the degeneracy of the five \( d \)-electron valence orbital in the TMO cation \[2, 62\]. The splitting of the \( d \) orbitals into two manifolds, i.e., the \( t_{2g} \) orbitals \((d_{xz}, d_{yz} \text{ and } d_{xy})\) and \( e_g \) orbitals \((d_{z^2} \text{ and } d_{x^2-y^2})\) is due to the crystal field that arises mainly from electrostatic repulsion between the electrons in the \( d \) orbitals of the TM and those in the \( 2p \) oxygen orbitals in an octahedral symmetry. Crystal field determines the energy gap between the \( t_{2g} \) and \( e_g \) orbitals. Therefore, the split between the two sets of orbitals \( e_g \) and \( t_{2g} \) is called \( \Delta_O \) (see Figure 1.4)\(^1\). It should be noted that in \( 4d \) TMO the \( 4d \) orbitals are more expanded and thus the crystal field splitting is usually larger than the exchange splitting (defined as the difference in energy between the corresponding spin up and spin down subbands \[24, 63\]). Consequently, in an octahedral environment they are generally in a low-spin configuration in which all the \( t_{2g} \) bands are lower than the \( e_g \) bands. In other words, the triplet degenerate \( t_{2g} \) orbitals have lower energy because their orbital lobes lie off-axis from the oxygen atoms \( p \) orbitals see Figure 1.4.

Not all TO\(_6\) compounds are sitting in an undistorted octahedral environment, some of them are sitting in a tetragonal environment, depending on the distortion of the TO\(_6\) compound. For example the octahedron represented in Figure 1.3(a) can undergo tetragonal distortions, i.e., the octahedron can be elongated or compressed in the \( z \)-axis (see Figure 1.3(b) and 1.3(c)). This kind of distortion is frequently observed in compounds with \( \text{Cu}^{2+} \) \((d^9)\) ions. Therefore, some TO\(_6\) compounds are sitting

\(^1\)The crystal field splitting \( \Delta_O \) depends on both the metal ion and the nature of the ligands.
Figure 1.3: Illustration of the crystal field splitting for a $d^4$ ion in octahedral and tetragonal environments: (a) non-distorted octahedron, (b) elongated octahedron, (c) compressed octahedron. (b) and (c) show the tetragonal distortions also known as Jahn–Teller distortions on the $d$ orbitals in an octahedral environment. (d) In a regular tetrahedron the splitting of the $d$ orbitals is inverted compared to that of an octahedron. Since a tetrahedron does not present a centre of inversion, the $t_{2g}$ and $e_g$ orbitals are replaced by the $t_2$ and $e$, respectively, without the parity label $g$. $\Delta_T$ denotes the crystal field splitting energy of the tetragonal environment (see the green arrow). Figure reproduced from [65].

in a regular tetrahedron, and in this case the splitting of the $d$ orbitals is inverted$^2$ compared to that of an octahedron, i.e., $t_{2g}$ orbitals have higher energy levels compared to $e_g$ orbitals. The crystal field splitting $\Delta_T$ (see Figure 1.3(d)) of the tetragonal environment is smaller than the one of the octahedral environment $\Delta_O$, i.e., $\Delta_T = \frac{4}{9} \Delta_O$, because there are less ligands in the tetrahedral complex and none of them point directly at $d$ orbitals. This situation is observed in some compound in the $3d$ state like chromium Cr (see Figure 1.3(d)). In this figure, the Cr$^{2+}$ ($3d^4$) ion possesses 4 unpaired electrons because $\Delta_T$ is less than the energy required for spin pairing. In this figure also $t_{2g}$ and $e_g$ are replaced by $t_2$ and $e$ respectively without the parity label $g$ due to the fact that in a tetrahedron there is no centre of inversion. For example in the electronic structure of $3d$, the Hund coupling energy ($\sim 3$ eV) is larger than the crystal field splitting ($1 - 2$ eV) between the $t_{2g}$ and $e_g$ states, inducing the appearance in some cases of a high-spin configuration [23]. For example Ref. [64] shows how in LaSrMnO$_4$, the exchange splitting of $e_g$ states is sufficiently wide to place the $t_{2g}$ band above the $e_g$ band.

The shape of the orbitals of $4d$ TMO are quite different from those of $3d$ TMO. This difference is due to the fact that the $3d$-electron systems usually have a small overlap and narrow bandwidth due to the

$^2$In a regular tetrahedron, none of the orbitals point directly at the ligands, but some of them ($t_2$) are oriented so that they point more closely towards the ligand positions and therefore electrons in the $t_2$ orbitals are higher in energy than those in the $e$ orbitals.
Section 1.3. Physical Properties of Sr Ruthenates $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$

The fundamental building block of the strontium Ruddlesden-Popper (R-P) series is the perovskite structure shown in Figure 1.2. In this series, the cation A = Ruthenium (Ru), the cation T = Strontium (Sr) and the anion O = Oxygen (O). After this general overview on the transition metal oxides, the review of the physical properties of the Ruddlesden-Popper series is given in the following sections.

### 1.3 Physical Properties of Sr Ruthenates $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$

All compounds in the R-P series possess Ru ions in the $4+\,$ electronic configuration (i.e., $4d^4\,$) and have Fermi surfaces with strong $4d_{xy}$, $4d_{xz}$, and $4d_{yz}$ orbital character derived from the Ru states hybridized with O $2p$ states [17]. Sections 1.3 and 1.4 will describe how the trend in the R-P series of strontium relatively small radial extent of the wave function with respect to the lattice parameter. While in the $4d$-electron systems the electronic correlations are expected to be weaker due to larger spatial extent of their wave function [23]. Due to the complexity of the $4d$ orbitals shapes (they possess eight and not four lobes like the $3d$'s), only the $3d$-orbitals have been presented in Figure 1.4.

In the case of the strontium ruthenates such as $\text{Sr}_2\text{RuO}_4$, $\text{Sr}_3\text{Ru}_2\text{O}_7$, and $\text{Sr}_4\text{Ru}_3\text{O}_{10}$, the anion Sr can be assigned an oxidation state of $2^+$, which leaves this anion in the chemically inert closed shell configuration ($[\text{Kr}]$). Oxygen atoms are always in $2^-$ filled shell state corresponding to a $[\text{He}]\,2s^22p^6$ configuration. Therefore, the ruthenium atoms are found in a $4^+\,[\text{Kr}]\,4d^4$ state. Relative to this present analysis, we can see that, the electronic properties of these compounds are due mainly to the contribution of the four Ru$^{4+}$ $4d$ electrons even if it has been shown that the contribution of Sr is not negligible [66].

The four Ru$^{4+}$ $4d$ electrons occupy the $t_{2g}$ orbitals (the $t_{2g}$ triplet state can accommodate six electrons or 3 pairs ($\uparrow\downarrow$)), but they are partially filled in the $4d^4$ configuration. Since the crystalline electric field is larger than the Hund’s rule coupling [67], the $e_g$ orbitals stay empty (see Figure 1.4). Thus the Fermi surface for this type of compounds is formed by $t_{2g}$ bands (if no distortion of the octahedra are observed). For a transition metal ion that has less than four $d$ electrons, its $d$ electrons will only occupy the $t_{2g}$ levels if only the crystal field effect is considered (e.g. V and Ti, both in a $3d^3$ ground state) [68]. For the case where the transition metal ion has more than three but less than eight $d$ electrons, the way in which electrons will fill the $t_{2g}$ and $e_g$ orbitals is determined by the competition between the crystal field and the Coulomb repulsion between $d$ electrons [68, 69].

Figure 1.4: The schematic electronic configurations of Ru$^{4+}$, with the relevant valence state $4d^4$. The crystal field of the O$^{2-}$ ions splits the five $4d$ states into the $e_g$ doublet and $t_{2g}$ triplet subshells. The $t_{2g}$ and $e_g$ energy located at lower and higher energy levels respectively, and their occupancies (left). The crystal field splitting energy $\Delta_0$ is presented by the red arrow. 3$d$ orbitals were chosen for illustration because $4d$ orbitals are more complex to visualise (right).
ruthenates is towards a three dimensional ferromagnetic order when increasing the number of Ru ions in the unit cells. Due to its fascinating properties, this series has known intensive studies. A detailed discussion of the physical properties of Sr ruthenates in the R-P series is provided in sections 1.3 and 1.4.

1.3.1 Sr$_2$RuO$_4$ ($n=1$)

The first member of the strontium R-P series is the single layer ruthenate Sr$_2$RuO$_4$. This material is called single layer because it has only one RuO$_2$ layer in the unit cell, as shown in Figure 1.5(a). This figure shows the ideal representation of the Sr$_2$RuO$_4$ crystal structure obtained with the perfect body centred tetragonal crystal structure, of space group symmetry I$4/mmm$ [73], with fourfold rotational and inversion symmetry. Its lattice parameters are $a = b = 3.862$ Å and $c = 12.722$ Å. [74]. This compound was first synthesised by Maeno et al. [5] because it is isostructural to La$_{2-x}$Sr$_x$CuO$_4$ (see Figure 1.5(a) and 1.5(b)), which is the first high-$T_c$ cuprate superconductor discovered by Bednorz et al. with $T_c \approx 30$ K [1]. Sr$_2$RuO$_4$ compound has gained vast popularity because it was the first non-cuprate TMO to show superconductivity, at $T_c \approx 1.5$ K [5]. This discovery has led to intense theoretical and experimental work up to now on the unconventional nature of its superconductivity. The two materials Sr$_2$RuO$_4$ and La$_{2-x}$Sr$_x$CuO$_4$ are highly two dimensional. Both are oxides with conduction which occurs in partially filled $d$ bands that are strongly hybridized with the oxygen $p$ orbitals [75]. Despite the structural similarity between the two materials, they have different electronic and magnetic properties. For instance, La$_{2-x}$Sr$_x$CuO$_4$ and most cuprates have a single Cu $3d_{x^2-y^2}$ - O$_{2p}$ band at the vicinity of the Fermi energy while Sr$_2$RuO$_4$ has 3 bands with Ru$^4$ $d_{xy}$, $d_{yz}$, $d_{xz}$ - O$_{2p}$ character crossing the Fermi level [76].

The superconductivity in Sr$_2$RuO$_4$ is highly sensitive to disorder: an impurity amount of tens of parts per million will rapidly suppress the superconducting phase [77]. It has been shown that the critical temperature $T_c$ of Sr$_2$RuO$_4$ reaches a maximum of 1.5 K in clean samples [77]. Further studies indicate that the properties of Sr$_2$RuO$_4$ deviate strongly from the BCS standard model of s-wave superconductivity$^5$ and there are good proofs that Sr$_2$RuO$_4$:

$^5$The observation of a strong suppression of $T_c$ by non-magnetic impurities [77] and lattice defects [78] is the key signature of the non-s-wave superconductivity in Sr$_2$RuO$_4$. 

Figure 1.5: (a) Illustration of Sr$_2$RuO$_4$ crystal structure and the in-plane representation of the RuO$_6$ octahedra. The basal unit cell is shown by the dark blue square. (b) Representation of La$_{2-x}$Sr$_x$CuO$_4$ crystal structures. Both crystal structures are tetragonal with space group I$4/mmm$. If the La atoms are replaced by Sr atoms and the CuO$_2$ planes are replaced by RuO$_2$ planes, then these structures are identical. Figure partially reproduced from [70, 71, 72].
Section 1.3. Physical Properties of Sr Ruthenates $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$

Figure 1.6: (a) The $d_{yz}$, $d_{xz}$ and $d_{xy}$ orbitals including their dispersions $E(K)$ and Fermi surfaces expected from tight binding models using $\text{Sr}_2\text{RuO}_4$ hopping parameters. (b) Unhybridised bands from the single layer compound obtained by adding the Fermi surfaces from the three $d_{yz}$, $d_{xz}$ and $d_{xy}$ orbitals. (c) Hybridised single layer bands form the Fermi surface of $\text{Sr}_2\text{RuO}_4$. Figure reproduced from [19, 71]. Fermi surfaces of $\text{Sr}_2\text{RuO}_4$: Fermi surface as determined from Angle Resolved Photoemission Spectroscopy (ARPES) (d), Local Density Approximation (LDA) (e) and de Haas-Van Alphen experiments (HVA) (f). Figures adapted from [84, 88, 89]. The three Fermi surface sheets $\alpha$, $\beta$ and $\gamma$ were resolved in all LDA calculations, ARPES spectra, de HVA maps and in Figure 1.6(c).

- presents unconventional superconducting behaviour with a spin-triplet pairing [5, 79, 80, 81, 77, 82];
- exhibits time-reversal symmetry-breaking of the orbital part of the pair wavefunction [83];
- possesses line nodes in the gap function [83];
- shows quasi 2D Fermi liquid behaviour with heavy $d$-electron masses (whose quasiparticle properties have been measured with high accuracy [84, 85]) in the ab-plane close to a ferromagnetic instability [86] with a highly anisotropic electronic conductivity [79, 87];
- shows no sign of magnetic ordering from room temperature down to very low temperatures and several other interesting properties that can be found in the literature.

The electronic structure and the Fermi surface (FS) of $\text{Sr}_2\text{RuO}_4$ have been extensively studied in order to clarify its FS topology in the normal state. ARPES [88, 90], de HVA [89] and quantum oscillation measurements [84, 85] were carried out on $\text{Sr}_2\text{RuO}_4$ and present a well defined FS according to a Fermi liquid metal, in agreement with LDA calculations [91, 92] and to the FS map constructed from that of the $\text{Sr}_2\text{RuO}_4$ via a simple argument [71] (see Figure 1.6). The Fermi surface (FS) topology of $\text{Sr}_2\text{RuO}_4$ is composed of three quasi cylindrical bands (Fermi surface sheets) deriving from the $t_{2g}$ orbitals in Ru ions. These three Fermi surface sheets are: $\alpha$, $\beta$ which derives from the $d_{xz}/d_{yz}$ orbitals, and $\gamma$ which derives from the $d_{xy}$ orbital. $\alpha$ is centred at the $X$ point of the first Brillouin zone and is a hole-like sheet, while $\beta$ and $\gamma$ which are centred at the $\Gamma$ point of the first Brillouin zone are electron-like. Note that the FS obtained by dHVA experiment provides additional 3D information on the detailed shapes of the $\alpha$, $\beta$, and $\gamma$ sheets (see Figure 1.6(f)).

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4 One speaks about the Fermi surface from the simple argument, when all Fermi surfaces of $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals are adding together and cross each other see Figure 1.6(b). Thus by taking into account the anticrossing of bands, hybridisation gaps will arise and the sheets will reconnect into closed surfaces and form the Fermi surface map see in Figure 1.6(c). These informations were taken in Refs. [71, 93].
Recently, Matzdorf and coworkers have found using low-energy electron diffraction (LEED) that the oxygen octahedra in Sr$_2$RuO$_4$ located in the topmost layer, are rotated by $5.5^\circ$. This rotation causes the $\sqrt{2} \times \sqrt{2}$ reconstruction of the primitive cell and its rotation by $45^\circ$ with respect to the original orientation [94, 95]. Due to this rotation, every FS sheet (from the bulk) has its surface counterpart. Zabolotnyy et al., [96] have shown that the FS map of Sr$_2$RuO$_4$ is more complex (see Figure 1.7(a)) with the splitting of the $\beta$ band into two sheets, i.e., in $\beta_1$ and $\beta_2$ (see the inset of Figure 1.7(a)) and an additional new surface state (see Figure 1.7(a) around the X points). They have suggested that this splitting is caused by Rashba coupling [96]. This splitting is most notable along the diagonal of the Brillouin zone (BZ) and the value of the momentum splitting between the two bands ($\beta_1$ and $\beta_2$) is presented in Figure 1.7(b) and 1.7(c). The surface reconstruction (see Figure 1.7(a) around the X point) appears to replicate over the entire surface by the translation vector $\Gamma X$. Figure 1.7(a) shows that the spectra result from a superposition of bulk and surface states. Zabolotnyy et al., have also shown that all bands ($\beta$, $\gamma$ and $\alpha$) are doubled [96] and this has been confirmed by Ref. [97] by plotting the momentum distribution curves (MDCs) obtained by integrating a 10 meV region below the Fermi energy $E_F$ (see Figure 4.4 of Ref. [97]). More information concerning detailed studies of Fermi surface and the electronic band structure of Sr$_2$RuO$_4$ can be found in [79] and in many other articles and books related to this compound [79, 84, 88, 89, 96, 97].

**Figure 1.7:** (a) FS map of Sr$_2$RuO$_4$ presenting the three FS sheets $\alpha$, $\beta$ and $\gamma$ and the splitting of the $\beta$ FS sheet in $\beta_1$ and $\beta_2$ (see the inset). Value of the momentum splitting between the two features $\beta_1$ and $\beta_2$: (b) Extracted of the momentum distribution curve (MDC) dispersion for the energy momentum cut at $\varphi = 45^\circ$ and momentum splitting at the Fermi level. The square symbols denotes the MDC peak positions for the two features. (c) The black line represents the fit to the function $A \cos(\varphi) + B$. Figure reproduced from [96].

1.3.2 Sr$_4$Ru$_3$O$_{10}$ ($n = 3$)

The triple layered ruthenate Sr$_4$Ru$_3$O$_{10}$ is the third member of the strontium R-P series and has three layers of RuO$_6$ octahedra per unit cell. Its lattice parameters were determined by Crawford et al. by using X-ray diffraction measurements on flux grown single crystals of Sr$_4$Ru$_3$O$_{10}$. They found that the lattice parameters of this compound are: $a \approx b = 3.90$ Å and $c = 28.57$ Å and its crystal structure is orthorhombic with $pbam$ space group symmetry [98] (see Figure 1.8(a)). This compound is a structurally distorted ferromagnet with a Curie temperature $T_c = 105$ K. It has been proved by Iliev et al. that two different distortions take place in the Ru-O-Ru angle planar octahedra. The RuO$_6$ octahedra of the inner layers are rotated by an average angle of $11^\circ$, while the octahedra in the outer two layers in the
Section 1.3. Physical Properties of Sr Ruthenates $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$

Figure 1.8: Comparison of the crystal structures of the triple-layered and infinite-layered strontium ruthenates. (a) $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ ($n = 3$) and (b) $\text{SrRuO}_3$ ($n = \infty$), they belong to an orthorhombic space group $Pbam$ and $Pbnm$, respectively. Figure adapted from [70].

unit cell are rotated in the opposite direction by an average angle of $\sim 5.6^\circ$ (see Figure 10 in Ref. [15] that shows the representation of these rotations). The presence of such distortions in this compound shifts the crystal structure of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ from being tetragonal to orthorhombic [15].

The earliest analyses of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ reported conflicting properties because of impurities. The experiment on the flux grown crystal of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ performed by Cao et al. [99], have shown that the ferromagnetic transition is followed by an additional magnetic transition at $T_M \simeq 50$ K (see Figure 2(b) in Ref. [99]). This compound also presents a saturated magnetic moment of $\sim 1.0\mu_B/\text{Ru}^{4+}$, directed principally along the $c$ axis, with very unusual anisotropic properties under applied magnetic field [98, 99]. It has been proved that the magnetic state below $T_M$ depends on the field orientation [98, 99]: when the field is apply in-plane ($H \parallel ab$) the magnetisation curve $M$ shows only a weak cusp at $T_C$, and a pronounced peak at $T_M$, with a small irreversibility (see Figure 3 in Ref. [99] and 1.9(a)). Contrarily, when the field is applied along the $c$ axis ($H \parallel c$), the magnetisation curve $M$ presents a sharp increase below 50 K and its hysteresis becomes large, always with ferromagnetic behaviour along the $c$ axis (see Figure 2(a) in Ref. [99]). Gupta et al. [100] proposed that this transition is associated with the tilted orientation of the Ru magnetic moments. Thus, the tilted Ru moments are ferromagnetically aligned along the $c$ axis when the temperature range is $T_M < T < T_C$, but no net in-plane ordering for an in-plane field is observed. It was shown that for $T < T_M$ the moments are locked into a tilted antiferromagnetic configuration for in-plane fields less than 2 $T$, while for in-plane fields higher than 2 $T$, the moments are locked into a tilted ferromagnetic configuration. These observations on the ferromagnetic behaviour along the $c$ axis were confirmed by magnetic and transport measurements performed on a floating zone (FZ) grown single crystal [101]. More recently, Granata et al. [102] have investigated by means of the neutron scattering diffraction the magnetic properties of the triple layered $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ at zero field. They have found that there are no signatures of long range antiferromagnetic order or ferromagnetic compound in the $ab$ plane.

Measurements of the isothermal magnetisation reveal a metamagnetic transition accompanied by significant hysteresis at about 2 $T$ for $H \parallel ab$ (see inset 1 in Figure 1 in Ref. [101] and 1.9(b)). Figure 1.9(b) confirms the presence of the sudden superlinear rise in magnetisation defined as metamagnetism.
Section 1.3. Physical Properties of Sr Ruthenates $\text{Sr}_n\text{Ru}_{n+1}\text{O}_{3n+1}$

Figure 1.9: (a) Temperature dependence of the magnetic moment at 10 Oe and (b) magnetic field dependence of the magnetic moment of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ at 4 K with magnetic field applied along the ab-plane.

in a high-purity $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ single crystal around 2.2 T. Very unusual transport properties have been observed for the in-plane resistivity $\rho_{ab}$ around this metamagnetic transition, which is shown by a sharp change between $\sim 1.75$ $T$ and $\sim 2.5$ $T$ presenting a remarkable nonmetallic temperature dependence within the transition regime (see Figure 3 in Ref. [101]) and extraordinarily sharp steps as the field sweeps down through the transition (see inset 2 in Figure 1 in Ref. [101]). This nonmetallic behaviour in transport properties within this field range is probably due to scattering off the boundaries of the ferromagnetic domains.

Investigations on the electronic structure of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ are underway in our group. More information about the physical properties of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ can be found in [15, 100] and in many other articles.

1.3.3 $\text{SrRuO}_3$ ($n = \infty$)

The infinite layered ruthenate $\text{SrRuO}_3$ is the last member of the strontium R-P series and is a three-dimensional compound. $\text{SrRuO}_3$ has perovskite structure shown in Figure 1.8(b). The earlier works on $\text{SrRuO}_3$ have revealed that this compound is a ferromagnetic conductor with $\rho = 2.75 \times 10^{-4}$ $\Omega$cm at room temperature and a Curie temperature $T_C \approx 160$ K (see Figures 1.10(a) and 1.10(b)), and it may present also momentum space magnetic monopoles [104, 105, 106, 107]. G. Cao et al., have shown that $\text{SrRuO}_3$ has a saturated magnetic moment of $\sim 1.6\mu_B$/Ru for $T < T_C$ [110]. The resistivity measurements performed by Mackenzie and coworkers in high quality thin films of $\text{SrRuO}_3$ have revealed that the resistivity of this compound is proportional to $T^2$ below approximately 10 K. Therefore, it was concluded that the ground state of $\text{SrRuO}_3$ is a Fermi liquid [111]. Two Fermi surface sheets with quasiparticle masses 4.5 and 6.1 $m_e$ were determined in the previous Shubnikov-de Haas oscillations measurements [112]. Alexander and coworkers [113] reported de Haas-van Alphen oscillations in a single crystal of $\text{SrRuO}_3$, their results have indicated at least six fundamental frequencies of oscillation with the confirmation of the effective masses of the two FS sheets given above [113]. A detailed study of the Fermi surface of $\text{SrRuO}_3$ was presented by Santi and Jarlborg [114]. Figures 1.10(a) and 1.10(b) present the temperature dependence of magnetisation of an $\text{SrRuO}_3$ film annealed at 550$^\circ$C with a field...
Section 1.3. Physical Properties of Sr Ruthenates $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$

Figure 1.10: Temperature dependence of the magnetization of $\text{SrRuO}_3$ where the field is (a) parallel and (b) perpendicular to the sample surface. The solid line represents fitting by the scaling law of $M \propto (T_C - T)^\alpha$. (c) Magnetic field dependence of the magnetization hysteresis loop with the magnetic field perpendicular to the sample surface. Figure adapted from [103].

of 100 G applied parallel and perpendicular to the sample surface respectively. The anisotropic nature of the epitaxial $\text{SrRuO}_3$ film is indicated by the different magnetizations values along the parallel and perpendicular directions (see Figures 1.10(a) and 1.10(b)). The spontaneous magnetization close to $T_C$ follows the scaling law $M \propto (T_C - T)^\alpha$, with $\alpha = 0.51$ and 0.65 for the magnetic field parallel and perpendicular to the sample surface, respectively (see Figures 1.10(a) and 1.10(b)). The magnetization versus magnetic field loops of an $\text{SrRuO}_3$ film with the magnetic field applied perpendicular to the sample surface measured at 5 and 100 K, respectively is shown in Figure 1.10(c). This Figure shows typical ferromagnetic M-H hysteresis characteristics with well-saturated behaviour [103]. For more information about the magnetic and electronic properties of $\text{SrRuO}_3$ the reader can consulted references [107, 108, 109, 115, 103].
1.4 The Bilayer Ruthenate \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) (\( n = 2 \))

This section is focused on the details of the literature review on the physical properties and crystallographic structure of the \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) compound. After presenting the results of the previous research done on this compound relevant to this study, the motivation and the aim of the present study will be presented in section 1.5.

1.4.1 Crystal Structure

The double layered \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) is the second member of the strontium R-P series and possesses two layers of \( \text{RuO}_6 \) octahedra in the unit cell. The crystal structure of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) is shown in Figure 1.11. Early work on \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) reported that this compound has the same space group as \( \text{Sr}_2\text{RuO}_4 \) [116]. Later on it was found, using neutron diffraction, that this symmetry is broken by 7° counter rotation of the \( \text{RuO}_6 \) octahedra inside the unit cell [115, 117]. Thus, its resulting space group is \( \text{Bbcb} \), corresponding to a single face centred orthorhombic structure with a square base of sides \( \sqrt{2} \) larger than those of the undistorted crystal and rotated by 45° with respect to the original orientation (as shown in Figure 1.11(a)). In this new space group the crystal structure no longer has strictly fourfold rotational symmetry.
The $a$ and $b$ lattice parameters values are approximately equal after the rotation, since $a = 5.4979\ \text{Å}$ and $b = 5.5008\ \text{Å}$ \cite{117, 118} and impossible to distinguish in a Laue experiment. Figure 1.11(b) and 1.11(c) present the crystallographic axes before and after rotation \cite{93}. The lattice parameter $c$ remains unchanged, i.e., $c = 20.7327\ \text{Å}$ since no rotation is observed along the $c$-axis \cite{118}. Figure 1.11 shows the rotation of the octahedra. Its effect on the basal plane is presented in the bottom part of Figure 1.11(a), where blue squares represent the new unit cell. Figure 1.11(b) shows the crystal structure of $\text{Sr}_3\text{Ru}_2\text{O}_7$ before rotation with space group $I\text{4}mmm$. Figure 1.11(c) presents the effect of the distortion on the crystal structure where each neighbouring octahedron is rotated in the opposite direction, i.e., the green octahedra are rotated clockwise in the $ab$ plane while the red ones are rotated counter-clockwise. The primitive unit cell holds twice the number of atoms compared to the undistorted cell. Therefore, the undistorted primitive unit cell contains two octahedra, while the distorted possesses four \cite{93}.

$\text{Sr}_3\text{Ru}_2\text{O}_7$ is a quasi-two dimensional metal, with electron hopping between the layers much less than within the layers. This can be observed in transport measurements where the out-of-plane resistivity is $\sim 300$ times greater than the in-plane resistivity at $0.3\ \text{K}$ \cite{119}. In $\text{Sr}_3\text{Ru}_2\text{O}_7$ the angular dependence of de HVA measurements only reflects two dimensionality on the low-field side of the metamagnetic transition while on the high-field side of the transition the angular dependence is complex and not completely understood \cite{93}. Therefore, two-dimensionality is supported by the distinctive angular of HVA measurements in $\text{Sr}_3\text{Ru}_2\text{O}_7$ \cite{85, 93}.

### 1.4.2 Physical Properties

It is important to know that stacking faults in the ruthenate family can transform a part of a crystal of one member into another member. For example duplicating planes in $\text{Sr}_3\text{Ru}_2\text{O}_7$ will produce $\text{Sr}_4\text{Ru}_3\text{O}_{10}$, and suppressing RuO planes from $\text{Sr}_3\text{Ru}_2\text{O}_7$ can lead to inclusions of $\text{Sr}_2\text{RuO}_4$. The first single crystal samples of $\text{Sr}_3\text{Ru}_2\text{O}_7$ compound were grown by Cao and coworkers \cite{107} with the flux growth method and these samples were found to be ferromagnetic below $100\ \text{K}$. Afterwards, Ikeda and coworkers \cite{120} synthesized $\text{Sr}_3\text{Ru}_2\text{O}_7$ single crystals by using infrared image furnace growth and they found that this compound is paramagnetic at low temperatures. The previous observation of the ferromagnetic state in this compound was due to inclusions of impurities of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ which has a ferromagnetic transition at $\sim 105\ \text{K}$ (see section 1.3.2 for more details). Thus, one cannot underestimate the importance of working with the highest purity samples.

More recently, experimental work performed on high quality single crystals of $\text{Sr}_3\text{Ru}_2\text{O}_7$ have revealed the presence of fascinating properties. The next section presents some important properties observed in this compound.

#### 1.4.2.1 Metamagnetism in $\text{Sr}_3\text{Ru}_2\text{O}_7$

In 2001 magnetisation measurements on $\text{Sr}_3\text{Ru}_2\text{O}_7$ were performed down to $2.8\ \text{K}$ by Perry and coworkers in a commercial vibrating sample magnetometer \cite{43}. They concluded that the properties of $\text{Sr}_3\text{Ru}_2\text{O}_7$ are strongly influenced by magnetic fluctuations. They discovered metamagnetism in $\text{Sr}_3\text{Ru}_2\text{O}_7$, shown in Figure 1.12. A superlinear rise in magnetisation as a function of magnetic field was observed at $T = 2.8\ \text{K}$ around fields of $B_M = 5.5\ \text{T}$ ($||ab\ \text{plane}$) and $7.7\ \text{T}$ ($||c\ \text{axis}$). In 2003 Ohmichi et al., \cite{121} reported a double metamagnetic transition in high quality single crystals of $\text{Sr}_3\text{Ru}_2\text{O}_7$ detected by magnetisation and magnetic torque measurements. They have shown that in addition to the reported metamagnetic transition by Perry and coworkers \cite{43}, an unexpected second transition starts to appear...
in the higher field region below 2 K (for $H \parallel ab$), presenting stronger anisotropy between inter and intra plane field directions.

Figure 1.13 presents magnetisation curves of high quality single crystals of Sr$_3$Ru$_2$O$_7$ for a magnetic field applied along the $ab$ plane, together with $\frac{dM}{dH}$ curves as a function of magnetic field. No hysteresis was observed down to the lowest temperature of 0.47 K. A superlinear rise in magnetisation as a function of magnetic field was observed upon lower temperature for fields of $B_M \sim 5.1$ T ($H \parallel ab$ plane) and this present result is in agreement with the results show by Perry and coworkers [43]. An additional transition was found at $B_M \sim 5.8$ T at temperatures below 1.7 K, which were more clearly seen as a peak in $\frac{dM}{dH}$ curves (see Figure 1.13). The transition becomes sharper with decreasing temperature, and presents a steplike structure attributable to the second metamagnetic transition [121]. This second metamagnetism transition was not recognised in the magnetisation measurements done by Perry and coworkers [43], probably due to the rather high temperature of 2.8 K but was clearly seen in the low temperature resistivity data. Ohmichi et al., have also observed that the magnetisation jump associated with the second transition was evaluated to be about one-third of the first magnetisation jump [121]. Their magnetic measurements in pulsed fields along $H \parallel c$ are in agreement with the one observed by Perry and coworkers [43].

In 2005 Perry et al. [122], reinvestigated the metamagnetism in a high single crystal of Sr$_3$Ru$_2$O$_7$ at low temperature for a magnetic field parallel to the $ab$ plane. They clearly demonstrated the effect of
Section 1.4. The Bilayer Ruthenate Sr\(_3\)Ru\(_2\)O\(_7\) (n = 2)

Figure 1.14: (a) The effect of impurities on the metamagnetism in Sr\(_3\)Ru\(_2\)O\(_7\) for the magnetic field applied in the \(ab\) plane. The plotting of the magnetisation as a function of magnetic field for a high quality and low crystal at temperature 0.06 and 0.07 K respectively. (b) The \(\frac{dM}{dH}\) curves as a function of magnetic field and temperature in the high quality single crystal of Sr\(_3\)Ru\(_2\)O\(_7\). These curves were obtained with the measurement temperatures of 0.06, 0.2 and 0.4 K. The magnetic fields were applied parallel to the \(ab\) plane. Figure reproduced from [122].

Impurities on the metamagnetism by showing the static magnetisation curves across \(B_M\) for two crystals of different quality at low temperature (see Figure 1.14(a)). The magnetisation jump at 5 T is present in the two curves but is far sharper in the high quality crystal and there are also extra features resolved in the high quality crystal around \(\sim 6\) T (see Figure 1.14(a)).

An additional transition was found at \(B_M \approx 5.8\) T in agreement with the results presented by Ohmichi et al., and was more clearly seen as a peak in \(\frac{dM}{dH}\) curves as a function of magnetic field and temperature (see Figure 1.14(b)). Focusing in the range of 5.8 T and 6.4 T, there is the emergence of a rich structure of peaks which is the most striking feature of their results. The second peak at 5.8 T has become a double peak structure, another transition is observed around 6 T and the third transition is resolved at 6.3 T which also has a double peak. Since the split peaks of the 5.8 and 6.3 T features are unlikely to be due to mis-aligned single crystal domains, this is evidence that high quality single crystals of Sr\(_3\)Ru\(_2\)O\(_7\) presents a multiple metamagnetic transitions between 5.8 T and 6.3 T. These metamagnetic transitions appear to be qualitatively different from the peak observed at 5 T (see Figure 1.14(b)). It has been proposed that these multiple metamagnetism transitions observed in Sr\(_3\)Ru\(_2\)O\(_7\) are due to multiple sharp peaks in the density of states with different orbital character [122].

This phenomenon of metamagnetism could have different origins depending on the mechanism of electrons giving rise to it. Appendix A presents more details about the theory of metamagnetism. It has been proved by many authors [43, 123, 124] that the metamagnetism observed in Sr\(_3\)Ru\(_2\)O\(_7\) is associated with quantum criticality. The next paragraph gives more details about the relationship between the metamagnetism and quantum criticality observed in this compound.

1.4.2.2 Quantum Criticality in Sr\(_3\)Ru\(_2\)O\(_7\)

The k-space spectroscopic measurements performed by Lee and coworkers [125] have showed that Sr\(_3\)Ru\(_2\)O\(_7\) possess a very strongly renormalised 'heavy' d-electrons within the Fermi liquid framework,
Section 1.4. The Bilayer Ruthenate Sr$_3$Ru$_2$O$_7$ ($n = 2$)

Figure 1.15: (a) High temperature and field evolution of the exponent $\alpha$ derived from the expression of the resistivity, $\rho = \rho_{\text{res}} + AT^\alpha$, close to the metamagnetic transition in Sr$_3$Ru$_2$O$_7$ for magnetic field applied along the $c$ axis. Below 10 K and at low field, the quadratic temperature dependence expected in a Fermi liquid is observed. Close to the metamagnetic field 7.8 T, the exponent $\alpha$ decreases to 1 indicating a strong deviation from the Fermi liquid behaviour, before rising again as the field is increased. Figure reproduced from [123]. (b) Illustration of the phase diagram of the metamagnetism of Sr$_3$Ru$_2$O$_7$ showing a quantum critical endpoint (QCEP). The first study of Sr$_3$Ru$_2$O$_7$ have revealed a metamagnetic transition, the QCEP which is tuned by varying the angle of the external applied magnetic field with respect to the crystalline axis. Figure reproduced from [124].

and presents a field induced transition to an electric liquid crystalline phase. Therefore, the electronic ground state of Sr$_3$Ru$_2$O$_7$ is heavily renormalised by electron-electron correlations and also by magnetic exchange interactions. The possibility of quantum critical metamagnetic behaviour was indicated by Perry and co-workers [43] and was then proven by experiments. The concept of quantum criticality is explained in more details in Appendix B.

Figure 1.15(a) presents a summary of the high temperature resistivity $\rho = \rho_{\text{res}} + AT^\alpha$ (where $\rho_{\text{res}}$ denotes the resistivity due to elastic scattering at $T = 0$ K, $A$ denotes the temperature independent coefficient related to a quasiparticle effective mass and the exponent $\alpha$ holds information about the nature of the metallic state [123]), in the vicinity of the metamagnetic transition in Sr$_3$Ru$_2$O$_7$, for magnetic field applied along the $c$ axis. The values of $\alpha$ are represented by different colours as indicated by the color scale. The blue colour represents $\alpha = 2$, indicating a normal Fermi liquid behaviour, while the yellow area is a region of anomalous behaviour, $\rho \propto T$, which appears to have a quantum critical point (QCP) around 8 T (see Figure 1.15(a)). This figure shows that an indication of the existence of a QCP in Sr$_3$Ru$_2$O$_7$ originates from analysis of the high temperature data. It also shows that the Fermi liquid behaviour is suppressed near the metamagnetic field (see the caption of Figure 1.15(a)), and the metamagnetic transition ends in a QCP at low temperature.

Ohmichi et al., [121] have found that the primary metamagnetic field evolves smoothly with angle $\theta$ from 5.1 T (for $H \parallel ab$) to 7.7 T (when $H \parallel c$). The secondary metamagnetic feature also varies smoothly with $\theta$ from 5.8 T (for $H \parallel ab$) to 13.2 T (when $H \parallel c$). Grigera and coworkers [124] studied the differential magnetic susceptibility of Sr$_3$Ru$_2$O$_7$ as a function of magnetic field, field angle and temperature (see Figure 1.15(b)). Figure 1.15(b) shows the variation with $\theta$ of the critical endpoint $(H_M, T^*)$ of the
primary metamagnetism. When $H \parallel ab$, the metamagnetic critical endpoint is located at $H_M = 5.1$ T and $T^* = 1.25$ K. The metamagnetic critical endpoint was $H_M = 7.8$ T and $T^* \leq 50$ mK, when the external magnetic field was aligned within a few degrees of the crystalline c axis with the upper limit of $T^*$ equal to the base temperature of the dilution refrigerator used in their experiment. Grigera and co-workers have noted that, $T^* = 0$ K corresponds to a QCEP of the metamagnetism (see Figure 1.15(b)). Therefore Figure 1.15(b) can be compared directly with Figure B.1(b) (see Appendix B), with the angle ($\theta$) playing the role of $u$ ($u$ is one of the three axes of the Figure B.1(b)).

### 1.4.2.3 Nematicity in Sr$_3$Ru$_2$O$_7$

Improvements in sample purity of Sr$_3$Ru$_2$O$_7$ have enabled the observation of a novel ordered quantum phase known as a “nematic phase” [126, 127]. Nematicity in Sr$_3$Ru$_2$O$_7$ is beyond the scope of this dissertation, so it will not be dealt with in depth here.

The origin of this novel ordered quantum phase remains mysterious, but many experimental and theoretical works have been done in order to find its provenance. For example,

- references [18, 20] have shown that the integration of $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals in the second class of tight binding model indicates the possibility that this nematicity might originate from the 1D character of the $d_{xz}$ and $d_{yz}$ bands and the physics of 1D van Hove singularities;
- C. M. Puetter et al, [128] have demonstrated that orbital degrees of freedom play a main role in revealing the nematicity observed in Sr$_3$Ru$_2$O$_7$.

Figure 1.16(a) shows a magnetic phase diagram of an ultra-pure single crystal Sr$_3$Ru$_2$O$_7$ as a function of temperature, magnetic field and orientation of the field position. The green colour represents the first order metamagnetic transitions as a function of temperature, magnetic field magnitude and orientation of the field position. The black lines are the lines of critical endpoints (explained in more detail in appendix B).

The blue dome shaped area are electronic nematic phases bounded by two consecutive metamagnetic transitions (see Figure 1.16(a)). The evolution of the phase diagram of Sr$_3$Ru$_2$O$_7$ with different tilt angles ($\theta$) is presented in Figure 1.16(b). This figure shows how at low temperature and at $\theta = 0$, the nematic phase is bounded by two lines of first order metamagnetic transitions at $B_{c1} \approx 7.85$ T and $B_{c2} \approx 8.07$ T [130] ending at critical endpoints (see full black stars in Figure 1.16(b)) that are connected by a line of second order phase transitions shown by the dashed dotted black line [132] (see the black curve in Figure 1.16(b)). This dashed line was proved to be a second order phase transitions thanks to the temperature dependent specific heat studies [123] that provide evidence consistent with that from the thermal expansion measurements [131]. It has been proved that in such a phase the rotational symmetry is broken [133, 131]. The black phase boundary of the nematic phase presented in Figure 1.16(b) is in perfect agreement with the one observed by Grigera et al, [130]. Recent thermal expansion and transitions in magnetostriction data exhibit that the phase boundaries of the nematic phase can be also seen at higher tilt angles $\theta$ (see Figure 1.16(b)). This figure also shows how the density domain of the boundaries of the nematic phase at higher $\theta$ is inferred from the one obtained at $\theta = 0$. With this new observation, the electronic nematic phase is characterized by an extension of the symmetry breaking lattice distortion area in Sr$_3$Ru$_2$O$_7$. More comprehensive reviews of the theory of electronic nematic phase can be found in [129, 131].
Figure 1.16: Magnetic phase diagram of ultra-pure single crystal Sr$_3$Ru$_2$O$_7$: (a) The first order metamagnetic transition sheets as a function of temperature, magnetic field magnitude and orientation of the field position are shown in green. The lines of critical endpoints of these sheets are presented by the black lines. Moreover, the anomalous phase is in blue and it is accompanied by the formation of a novel ordered quantum phase known as a ‘nematic phase’. On the angular scale $90^\circ$ corresponds to the magnetic field being applied parallel to the $c$ axis and $0^\circ$ to the magnetic field being applied in the $ab$ plane. Figure reproduced from [129]. (b) Cuts through the phase diagram at different tilt angles (see different curve colours) derived from a variety of experimental probes namely, transitions in magnetostriction and thermal expansion (squares and circles respectively). The black full lines denote first order transitions ending at tricritical points (see black filled stars), connected by a dash dotted line of second order transitions [130]. The presumed critical points positions are shown by the coloured open stars connected by crossover lines. Figure from [131].

1.4.3 Electronic Structure of Sr$_3$Ru$_2$O$_7$

The rotation of the octahedra in Sr$_3$Ru$_2$O$_7$ has profound consequences on the electronic system. Due to the change of its lattice type, the first modification is the reconstruction of the first Brillouin zone (BZ). This zone has the same symmetry as the crystalline structure plus inversion through the center [93]. Thus, the new BZ possesses a lower symmetry than the initial one without distortions. The BZ for space group $I4mmm$ and $Bbcb$ are presented in the left and right parts of Figure 1.17 respectively, when the lattice parameter $a$ and $b$ are all lower than the $c$ lattice parameter. The left part of Figure 1.17

<table>
<thead>
<tr>
<th></th>
<th>BZ Area ($\text{Å}^{-2}$)</th>
<th>BZ Area (KT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_2$RuO$_4$</td>
<td>2.61</td>
<td>27.74</td>
</tr>
<tr>
<td>Sr$_3$Ru$_2$O$_7$</td>
<td>1.31</td>
<td>13.69</td>
</tr>
</tbody>
</table>

Table 1.2: The in-plane area value of Sr$_2$RuO$_4$ showing that it is twice that of Sr$_3$Ru$_2$O$_7$ value [93].
Section 1.4. The Bilayer Ruthenate Sr$_3$Ru$_2$O$_7$ (n = 2)

1.2), that presents these area values for Sr$_2$RuO$_4$ and Sr$_2$RuO$_4$ in units of k space and HVA frequencies determined by Mercure [93].

Another effect of this rotation is the deep modification of the band structure with a reconstruction of the Fermi surface (FS) of Sr$_3$Ru$_2$O$_7$. Electronic structure calculations and previous ARPES experiments [21] have resolved the FS. It was found to be more complex than the FS of Sr$_2$RuO$_4$ presented in Figure 1.6. Bands present in this FS do not only originate from $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals as expected from the crystal field splitting, as one band originating from the $d_{x^2-y^2}$ orbital was observed in this FS. More details and information about the FS of Sr$_3$Ru$_2$O$_7$ will be presented in chapter 4.

In the next paragraph we introduce the model on the origin of metamagnetism in Sr$_3$Ru$_2$O$_7$ due to van Hove singularities (i.e sharp peaks observed in the DOS), in the proximity ($\sim$ meV) of the Fermi energy. The mechanism which produces metamagnetism in an itinerant system is the presence of a peak in the electronic density of states (DOS). As explained in appendix A.2 this makes it favourable for a magnetic transition to occur when the Fermi energy level is split such that the Fermi energy level of one spin species approaches the peak. The phase diagram of Sr$_3$Ru$_2$O$_7$ fits qualitatively in this model. The natural origin of a peak in the DOS is a saddle point in the electronic band dispersion [134]. Tamai and coworkers [21] have investigated the low-energy electronic structure by angle resolved photoemission by evaluating the DOS near the Fermi level of $\gamma_1$ and $\gamma_2$ sheets with significant $d_{xy}$ contributions. The band topology along the $\Gamma X \Gamma$ line is presented in Figure 1.18(a). They have observed a very narrow dispersion with local minima and maxima separated by less than 3 meV over an extended k-space range. This dispersion indicates a very high DOS just below the Fermi energy level (see Figure 1.18(a)). The top band gives rise to the $\gamma_2$ Fermi surface sheet situated at $-1 \pm 1$ meV with the second local maxima at the X point near to $-4$ meV. They attribute the saddle points in the dispersion correspond to Van Hove singularities (vHS) in the DOS. These points were found symmetrically around the X point at an energy of 4 meV below the Fermi energy level. The $\gamma_2$ presents two sharp peaks in its DOS (see Figure 1.18(b)). In this Figure, a smaller peak corresponds to the top of the band while the saddle point represents the large peak. The saddle point is $\sim 3$ meV below the Fermi energy level. These sharp peaks in the DOS on the energy scale of the Zeeman splitting are similar to the context considered by Binz and Sigrist, [16] in their microscopic model of the metamagnetism transition. Tamai and coworkers have proposed that the pocket that is most likely to be strongly affected is the $\gamma_2$, which could become completely spin polarised in a field of $\sim 10$ T. This present situation is favourable to the electronic

Figure 1.17: Illustration of the Brillouin zone for I4mmm, (left) and Bbcb, (right) for the case where the lattice parameters $a \approx b < c$ [93].
Section 1.4. The Bilayer Ruthenate Sr$_3$Ru$_2$O$_7$ ($n = 2$)

Figure 1.18: Density of states: (a) Photoemission intensity in the vicinity of the $X$ point along the direction marked in the inset. This Figure presents the dispersion of the $\gamma_2$ band that constitutes the saddle point and the band top. This saddle point and the top band have been determined by the peak positions obtained by a fit of the energy distribution curves after normalization with the Fermi function. (b) Histogram of states near the Fermi surface from ARPES measurements from the band contours shown in (a). The blue curve represents the $\gamma_2$ band with two peaks. The green curve represents the $\gamma_1$ band that has no such features. The vertical line represents the Fermi surface with an error bar representing the uncertainty in its position. (c) The location of the saddle points is indicated by the red dots in the band structure of Sr$_3$Ru$_2$O$_7$ (presenting its six different Fermi surface sheets). Figure from Ref. [21, 93]

Lee et al., [125] have constructed the $\alpha_2$ band topology and dispersion primarily to model the quasiparticle data of Sr$_3$Ru$_2$O$_7$. Given that the steps of the model that they have used are very long, the reader can consulted Ref. [125] for more details. They found that the $\alpha_2$ size and shape closely resemble the cross shaped experimental Fermi surface contour of the $\alpha_2$ band derived from the out-of-plane $d_{xz}$, $d_{yz}$ orbitals [135] (see Figure 1.19(a)).

Figure 1.19(b) shows a perfect agreement (see red curve and image from photoemission data plotted in white and black colours) between the shape of the band dispersion of $\alpha_2$ obtained from ARPES experiments and the model used by Lee et al., [125].

Recently, Allan and co-workers [19, 136] have shown that the $\alpha_2$ band hybridizes with the $\gamma_2$ band and disperses very weakly until the $X$ point (see Figure 1.20). The most striking observation in this figure is the extremely flat bands confined to a narrow energy range of $\sim 5$ meV below the Fermi energy $E_F$ which is mostly present along the $\Gamma X$ high symmetry direction. The dispersion present in Figure 1.20 spans more that the first Brillouin zone and includes two van Hove singularities.
Section 1.5. Scope of This Study

In this study we focus on the investigation of the coupling between metamagnetism and electronic structure in Sr$_3$Ru$_2$O$_7$. In fact, according to theoretical predictions [16, 21], metamagnetic behaviour in itinerant systems, such as this bilayered ruthenate, can be explained by the existence of sharp peaks in the density of states (called van Hove singularities, vHS) located within the relevant energy scale of metamagnetism, i.e., a few meV around $E_F$ [137]. Such peaks may be the origin of magnetic fluctuations in this system. In particular, calculations suggest that the symmetry of the vHS could be the key question for the comprehension of the metamagnetism. More recently, an analysis by density-functional theory of the low-energy electronic structure of the $d_{xy}$ band dispersion of Sr$_3$Ru$_2$O$_7$ has predicted a complex
density of states (DOS) with sharp features resembling vHSS near the Fermi level \cite{18}. These complex DOS with vHSS near the Fermi level are favourable for magnetic instabilities by applying an external magnetic field, i.e., they favour the presence of metamagnetism due to peaks near the Fermi level when an external magnetic field is applied. Angle resolved photoemission spectroscopy (ARPES) will be used in this work because it is the only experimental technique able to probe directly the near-Fermi-level electronic structure of solids in the relevant energy scale needed for our purpose.

During the analysis of Sr$_3$Ru$_2$O$_7$ data presented in this dissertation (in chapters 4 and 5), Allan’s et al. paper \cite{136} was published. In this paper, they have exhibited over a large k space volume, the strong band renormalization of Sr$_3$Ru$_2$O$_7$, combined with marked multi band effects spanned by the hybridized $\alpha_2$-$\gamma_2$ sheet (see Figure 1.20). Their results are confirmed the presence of vHSS associated to the $\gamma_2$ pocket as demonstrated Tamai et al. \cite{21}. Moreover, the most remarkable observation in their results is the extremely flat band confined to a narrow energy range of $\sim 5$ meV around the Fermi energy (see Figure 1.20) indicated a vHSS associated to the FS sheet with $d_{xz,yz}$ orbital character \cite{18, 20} as predicted Refs. \cite{18, 20}. Furthermore, Allan \cite{19} had investigated the FS map of Sr$_3$Ru$_2$O$_7$ by using the local density approximation + spin orbit coupling (LDA+SO) calculations (see Figure 4.6 and more details about this FS map can be found at the end of section 4.5). From this result, we still remark different reconstruction of the FS map of Sr$_3$Ru$_2$O$_7$, and peculiar features in the band dispersion.

The presence of flat bands associated to different pockets at the low energy scale in the density of states is much more important to explain the vHSS’s in Sr$_3$Ru$_2$O$_7$. Thus, we expect to also find vHSS’s with $d_{xy}$ and $d_{xz,yz}$ \cite{18, 20} orbital characters in order to confirm works done by Tamai et al. \cite{21} and Allan \cite{19}. Moreover, the $d_{x^2-y^2}$ band around the $\Gamma$ point has also been found to give rise to high density of states near $E_F$. The presence of $d_{x^2-y^2}$ orbital character in the near $E_F$ region can be justified by the fact that both lattice distortions and the interlayer coupling in Sr$_3$Ru$_2$O$_7$ cause a strong reorganization of the electronic charge in the RuO$_6$ octahedra by allowing $t_{2g}$-$e_g$ hybridization.

In summary the aim of this work is to give a detailed study of the FS and band dispersion mapping of Sr$_3$Ru$_2$O$_7$ by analyzing data taken from ARPES measurements in order to determine the symmetry and locations of vHSS on the $d_{xz,yz}$ \cite{18, 20} and $d_{x^2-y^2}$ bands, and thus establish a link between electronic structure and metamagnetism in this compound. We will compare our results with theoretical studies that have been already done on this compound.
2. Theoretical Description of Angle Resolved Photoemission Spectroscopy

2.1 Introduction

Photoemission Spectroscopy (PES) is the most direct and the most convenient tool to investigate the electronic structure of a material. PES is based on the photoelectric effect, initially discovered in 1887 by Hertz [138], and later on explained by Einstein [139] in 1905 as a manifestation of the quantum nature of light. PES has practical applications in various areas such as material science and surface chemistry, and gives a better understanding of the fundamental principles of solid-state physics. The characteristics of the observed spectra and the properties of the photoemission process depend essentially on the solid angle seen by the electron spectrometer and the incident photon energy $\hbar \nu$. Therefore, various subfields of PES can be defined: the definitions of X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) are used for photoemission spectroscopy with X-ray light sources and ultraviolet (UV) respectively. XPS is used to study the energy levels of electrons in core levels (electrons in the inner levels of higher binding energy) while UPS is used to study energy levels of electrons in the valence band. Angle resolved photoemission spectroscopy (ARPES) uses UV and soft X-rays ($\hbar \nu \lesssim 100$ eV) as incident photon energies and it measures the momentum of the electrons as well as their kinetic energy. The reason for such low photon energies and also higher resolution in photon energy is that it is possible to reach higher momentum resolution [140] and see equation 2.5.

Furthermore, one can fully neglect the photon momentum $k = \frac{2\pi}{\lambda}$ at low photon energy, since the contribution of the wavelength of the photon $\lambda = \frac{hc}{E}$ is smaller compared to a typical Brillouin zone size of the probed crystal [141, 142].

The macroscopic properties of solid materials are ruled by their microscopic electronic structure. Therefore, it is important to study its electronic structure in order to understand and make use of the novel physics in various advanced materials. Electron energy ($E$), momentum ($k$) and spin ($s$) reveal the electronic states in materials. ARPES is the only technique that could probe all these physical quantities in solid materials, by supplying for instance, a detailed understanding of the connection between electronic and magnetic properties of solid state materials and other properties. This powerful experimental tool has played an irreplaceable role in the study for example of cuprate high-temperature superconductors [143].

Many important theoretical studies have been performed in order to understand the photoemission process, and to describe and analyse the spectral characteristics of the data [21, 144, 145]. This chapter gives a theoretical background of ARPES that will allow readers to understand the work presented in this dissertation. It also shows how the photoemission effect gives us a thorough overview into the quantum description of the solid state of matter.

This chapter begins with an introduction in section 2.1, followed by section 2.2 that gives a detailed description of the principles of ARPES. Section 2.3 describes the three-step model, known as the most commonly used model for the interpretation of photoemission spectra in solids. Section 2.4 introduces the photoemission intensity within the sudden approximation. Section 2.5 gives a brief discussion on the Green’s function, which describes the propagation of an electron in a many-body system and the spectral function $A(k, E)$. Section 2.6 presents a detailed discussion on the self-energy and the lifetime
Section 2.2. Principles of ARPES

Since the explanation of the photoelectric effect by Einstein in 1905 [139], there has been a large amount of theoretical and experimental research work that has been performed in order to understand this concept more thoroughly. Instrumental improvements in electrostatic electron energy analysers, improving vacuum pressures and various monochromatic light sources aided in the precision with which photoelectron energies could be measured. This experimental work was accommodated by a rapid progression in the theoretical understanding of molecular, atomic and solid state structure with quantum theory. These progresses allowed photoelectric experiments to develop into a technique for studying the arrangement of electrons in these structures.

The geometry of a typical PES experiment is shown in Figure 2.1(a). In a PES experiment, a beam of monochromatic photons with energy $h\nu$ strikes on the sample surface, and atoms which have absorbed those incident photons can be excited from an initial state with energy $E_i$ to a final state with energy $E_f$. If the frequency of light is sufficiently high, an electron gains the energy that is sufficient to make
it escape from the solid towards the vacuum. Such an electron is called a photoelectron \[139\]. Due to the conservation of the energy in the photoemission process, it was realized that, by measuring the kinetic energy \(E_K\) of a photoelectron in vacuum, knowing the work function of the analyser \(\Phi_A\) and the photon energy of the incident radiation \(h\nu\), one can compute the binding energy \(E_B\) of the electrons inside the solid. This is expressed as

\[
|E_B| = h\nu - E_K - \Phi_A.
\]

Note that \(E_K\) is measured with respect to the vacuum level and the negative values of \(E_B\) are measured with respect to the Fermi energy \(E_F\). If electrons emitted at all energies are collected, then the distribution of photoelectrons in kinetic energy \(E_K\) can be effectively mapped into the density of states (DOS) of the sample’s electronic structure. This idea is shown by the energetics of PES, which is sketched in Figure 2.1(b). The energy level diagram of the electrons inside the solid (sample) is represented on the left part of Figure 2.1(b), while the drawing of the associated PES spectrum measured by the analyser is represented on the right. It should be noted that the DOS inside the sample is reflected by what is measured outside of the solid (spectrum) due to the conservation of the energy given in equation 2.1.\(^2\) PES does not give the DOS straightforwardly, the DOS is convoluted with matrix elements. A more detailed about photoemission matrix elements is presented in section 2.7. We are interested in the valence electrons, which are close to the Fermi level and are responsible for various electronic properties of solids. A sample (see the left part of Figure 2.1(b)) possesses a valence band close to \(E_F\) dictated by the energy bands formed by the delocalized valence electrons. In Figure 2.1(b), an incident photon can excite an electron above the sample’s vacuum level, which can physically escape the sample and can be detected by the electron energy analyser.

Figure 2.1(b) holds a number of interesting details, although it seems to be a relatively simple diagram. Firstly, photoemission does not occur from states which are not actually occupied, this means that PES cannot access information about the electronic structure above \(E_F\). In other words, the electron occupation of the available DOS goes to zero above \(E_F\) following Fermi-Dirac statistics, and this will occur as a sharp cut-off in the measured spectrum, as seen in the top right part of Figure 2.1(b). Experimentally this cut-off is referred to as the Fermi edge and provides a good reference to set the energy scale. The width of the edge may also be used as a measure of the total energy resolution achieved in the experiment \[146\].

Secondly, the photoelectrons have a short mean free path (to be explained in more detail in section 2.3) while in the sample and may suffer inelastic collisions before leaving the sample surface. This may occur multiple times with a random amount of lost energy every time before an electron escapes into vacuum to be measured. Every collision can entrain other excited electrons in the process and these excited electrons may suffer inelastic collisions before exiting the sample. This effect establishes a cascade of ‘secondary’ electrons, building in intensity towards lower kinetic energy in the spectrum \[146\]. This common process causes the exponentially increasing secondary background in the measured spectrum as shown in Figure 2.1(b). A high enough photon energy can be used so that the parts of the spectrum of interest are not clouded by this background. In particular, the valence band is relatively free of this background as there are few secondary electrons with lower binding energy.

\(^1\)The Fermi energy of a metal is an expression used to describe the top of the electron energy levels at absolute zero temperature. For more information about the Fermi energy, the reader can consult section 4.3 which presents a detailed explanation of how the Fermi energy is determined from the data.

\(^2\)A sample has a certain DOS (see \(N(E)\) in the left part of Figure 2.1(b)) which includes both the valence band and the core levels of distinct inner-shell electron energy states which give rise to sharp peaks in the photoemission spectrum. The explanations concerning them are beyond the scope of this dissertation (The reader can consult the excellent book written by Schattke \[140\]).
Figure 2.2: (a) Geometry of a typical ARPES experiment; the emission direction of the photoelectrons is specified by the polar ($\theta$) and azimuthal ($\varphi$) angles. (b) Schematic representation of the momentum $k$ of the electron inside the solid and the momentum $K$ in vacuum. Because of the translational symmetry in going from inside to outside the solid, the component of the momentum parallel to the surface is conserved (i.e., vectors $k_{||}$ and $K_{||}$ have the same magnitude). To the contrary, the perpendicular component of the momentum is not conserved while moving out from the solid.

Finally, the kinetic energy $E_K$ is measured with respect to the analyser, thus the work function of the analyser $\Phi_A$ appears in the correct application of equation 2.1 (not the sample work function $\Phi_s$). The Fermi levels of the sample and the analyser are forced to be equal when the sample and analyser are electrically connected, and so the vacuum levels are not necessarily the same\(^3\). Useful information can be extracted from the PES experiment represented in Figure 2.1(b) only if it is performed with a total energy resolution which allows the critical features to be observed. It must also be done with a high enough count rate such that the data can be recorded in a reasonable amount of time with a good signal to noise ratio [146] (For more information about PES the reader can consult Ref. [146]).

Despite the useful details of a PES experiment given above, this technique has some limitations. In a conventional PES experiment it is only possible to measure the kinetic energy of the electrons integrated over momentum space. With the recent technological progress in the development of electron analysers, it has become possible to also obtain information about the momentum $k$ of the electrons. Hence, to obtain the dispersion of the electronic valence bands in the reciprocal lattice of the solid (by measuring the angle at which the electrons are emitted from the sample). In addition to their kinetic energy this refinement of the PES technique, called ARPES, constitutes nowadays the leading technique as far as the experimental determination of single particle excitations in solids is concerned [147].

Figure 2.2(a) shows the geometry of an ARPES experiment: the analyser collects the photoelectrons and measures both their kinetic energy $E_K$ and their momentum $K$ in vacuum. From these values one can obtain information respectively on the binding energy and the momentum $k$ of the electrons inside the solid. The binding energy can be obtained by the conservation of energy [equation (2.1)] as in a conventional PES experiment. The magnitude of $K$ in vacuum is given by $K = \frac{P}{\hbar} = \sqrt{\frac{2mE_K}{\hbar}}$ where

\(^3\)Nevertheless, $\Phi_s$ determines the 'low-energy cut-off' where electrons can no longer escape the sample, coinciding with the vacuum level of the sample, $V_s$. Since $\Phi_s > \Phi_A$, the analyser can directly measure this low-energy cut-off at a finite kinetic energy $E_K$ with respect to $V_A$. The final 'peak' in the measured spectrum is simply the low energy cut-off of secondary electrons.
the momentum $P = \sqrt{2mE_K}$ and $m$ is the mass of photoelectrons. The magnitude of its components $K_x$, $K_y$ and $K_z$ are determined in terms of the polar ($\theta$) and azimuthal ($\varphi$) angles defined in Figure 2.2(a), as follows:

$$K_x = \frac{1}{\hbar} \sqrt{2mE_K} \sin \theta \cos \varphi \quad (2.2)$$

$$K_y = \frac{1}{\hbar} \sqrt{2mE_K} \sin \theta \sin \varphi \quad (2.3)$$

$$K_z = \frac{1}{\hbar} \sqrt{2mE_K} \cos \theta \quad (2.4)$$

The magnitude of its components $K_x$, $K_y$ and $K_z$ are determined in terms of the polar ($\theta$) and azimuthal ($\varphi$) angles defined in Figure 2.2(a), as follows:

The momentum $K$ in vacuum is then completely determined and given by $K = K_x + K_y + K_z$. The momentum $k$ of an electron inside the solid is determined by measuring the momentum $K$ of the electron in vacuum. The $K$ component lying in the plane of the surface of the sample is given by $K_\parallel = K_x + K_y$, where the magnitude of $K_x$ and $K_y$ is given by equations (2.2) and (2.3) respectively. The component of $K$ perpendicular to the surface is $K_\perp = K_z$, where the magnitude of $K_z$ is given by equation (2.4). A schematic representation of the momentum $k$ of the electrons inside the solid and the momentum $K$ of photoelectrons in vacuum is shown in Figure 2.2(b). The component of the electron momentum parallel to the surface is conserved going from inside the solid into vacuum, since the surface does not break translational symmetry while moving across the surface normal direction of the crystal, i.e., $k_\parallel = K_\parallel$ [147] (see Figure 2.2(b)). Thus

$$|k_\parallel| = |K_\parallel| = |K_x + K_y| = \frac{1}{\hbar} \sqrt{2mE_K \sin \theta} \quad (2.5)$$

From equation 2.5, we can see that the parallel component of the momentum inside the solid $k_\parallel$ is fully determined by measuring the emission angle of the photoelectron and its kinetic energy in vacuum.

Because of the sudden change of the electric potential along the $z$ axis, the perpendicular component of the momentum is not conserved across the sample surface ($k_\perp$ is a good quantum number only in the depth of the solid), which means that $k_\perp \neq K_\perp$ (see Figure 2.2(b)). Therefore it is not possible to extract the value of $k_\perp$ directly from the measurements [141]. However, the perpendicular component $k_\perp$ is determined only if some prior assumptions are made for the dispersion of the electron final states $E_f(k)$ participating in the photoemission process. To determine $k_\perp$, one can either use the results of band structure calculations, or adopt a nearly free-electron description for the final bulk states, i.e., a parabolic dispersion (as proposed by Damascelli in Ref. [141]). Therefore, by using these approximations, the perpendicular component of the electron inside the solid $k_\perp$ can be written as

$$k_\perp = \frac{1}{\hbar} \sqrt{2m(E_K \cos^2 \theta + V_0)}$$

where $V_0$ and $E_K$ are the inner potential and the kinetic energy of a photoelectron in vacuum respectively, and $\theta$ is the polar angle. $V_0$ can be determined experimentally from the periodicity of the Fermi surface in 3D, but the determination of $V_0$ is beyond the scope of this work\footnote{The reader can consult Chapter 3 of Ref. [148].}

Luckily, there are special classes of materials for which the uncertainty in $k_\perp$ is less relevant. In particular this is true for low-dimensional systems where the band dispersion along the $z$ axis is considered to be negligible, and it is predominantly determined by $k_\parallel$ [149]. In the process of the data analysis presented in this thesis, the compound Sr$_3$Ru$_2$O$_7$ is considered as an almost two dimensional system, so that the dispersion along the $z$ axis can be neglected (see subsection 1.4.1).
2.3 The Three-Step Model

A rigorous theoretical description of a photoemission event necessitates a quantum mechanical treatment of the full process during which an electron is removed from an occupied state within a solid and arrives at the detector. Theoretical approaches of this type treat the photoemission process as a one-step event in which photon absorption, electron removal, and electron detection are treated as a single coherent process [150, 151]. Nevertheless, due to the complexity of the one-step model, a simpler approach, i.e., the three-step model (TSM) has often proven to be successful [151, 152]. The TSM was developed almost fifty years ago by C.N. Berglund and W.E. Spicer [152], and it is one of the earliest hypotheses used to describe experimentally measured photoemission intensity. The hypothesis at the base of this model is that the photoemission intensity can be decomposed as a product of three independent contributions which do not interfere with each other (see Figure 2.3). These three independent and sequential steps are the following:

- **Step 1:** Optical excitation of the electron from the initial bulk eigenstate \(|\Psi_{\text{init}}\rangle\) into the final excited bulk eigenstate \(|\Psi_{\text{fin}}\rangle\).
- **Step 2:** Propagation of the excited electron to the surface.
- **Step 3:** Escape of the photoelectron into vacuum after transmission through the surface potential.

A schematic representation of the TSM is given in Figure 2.3. To clarify the physical interpretation of the measured photoemission intensity, each step will be explained in more detail in the following paragraphs.

- **Step 1: Optical excitation**

  This step refers to the photon excitation process during which an electron absorbs one photon and enters an unoccupied state. Thus, the photoemission process starts with a system of \(N\) electrons and removes one of them, leaving an excited \((N-1)\) system and a free electron within the solid. This step contains the information about the intrinsic electronic structure of solids. In fact, a more rigorous investigation of this first step shows that there is a wealth of details about the many-body response of the \((N-1)\) system in an ARPES experiment. To develop a formal...
description of the photoemission process, one has to calculate the transition probability \( W_{\text{fin,in}} \) for an optical excitation between the \( N \)-electron ground state |\( \Psi_N^0 \rangle \) and one of the possible final states wave functions with \((N - 1) \) electrons |\( \Psi_N^\text{fin} \rangle \) [154]. This can be approximated by Fermi’s golden rule\(^5\) [141, 142, 154] as a result of perturbation theory\(^6\) to first order, in the following way:

\[
W_{\text{fin,in}} = \frac{2\pi}{\hbar} |\langle \Psi_N^\text{fin}|H_{\text{PE}}|\Psi_N^0 \rangle|^2 \delta(E_{\text{fin}}^N - E_{\text{in}}^N - \hbar\nu); \]

where \( H_{\text{PE}} \) is a perturbation Hamiltonian operator (the derivation of this Hamiltonian will be given below), \( E_{\text{in}}^N = E_{\text{in}}^{N-1} - E_B^k \) and \( E_{\text{fin}}^N = E_{\text{fin}}^{N-1} + E_K \) are respectively the initial and final state energies of the \( N \)-particle system. \( E_B^k \) is the binding energy of the photoelectron in the ground state with kinetic energy \( E_K \) and momentum \( k \).

The interaction of an electron in the system with the electromagnetic vector potential \( \mathbf{A} \) of the incoming photon is described by the perturbation operator \( H_{\text{PE}} \). \( H_{\text{PE}} \) is given by the transformation \( \mathbf{P} \rightarrow \mathbf{P} - e\mathbf{A} \) of the electronic momentum operator \( \mathbf{P} = -i\hbar\nabla \) in the unperturbed Hamiltonian \( H_0 = \frac{\mathbf{P}^2}{2m} + eV(\mathbf{r}) \), where \( m \) is the electron mass. One can omit the scalar potential \( \Phi \) of the incoming photon by choosing an appropriate gauge for the electromagnetic field [157]. Thus the total Hamiltonian is then given by [141, 157, 158]:

\[
H = \frac{1}{2m} \left( \mathbf{P} - \frac{e}{c}\mathbf{A} \right)^2 + eV(\mathbf{r}) = \frac{\mathbf{P}^2}{2m} - \frac{e^2}{2mc}(\mathbf{A} \cdot \mathbf{P} + \mathbf{P} \cdot \mathbf{A}) + \frac{e^2}{2mc^2}\mathbf{A}^2 + eV(\mathbf{r})
\]

\[
= \mathbf{P}^2 + eV(\mathbf{r}) - \frac{e}{2mc}(\mathbf{A} \cdot \mathbf{P} + \mathbf{P} \cdot \mathbf{A}) + \frac{e^2}{2mc^2}\mathbf{A}^2
\]

\[
= H_0 + H_{\text{PE}};
\]

where the photoemission perturbation operator \( H_{\text{PE}} \) is defined as:

\[
H_{\text{PE}} = -\frac{e}{2mc}(\mathbf{A} \cdot \mathbf{P} + \mathbf{P} \cdot \mathbf{A}) + \frac{e^2}{2mc^2}\mathbf{A}^2. \quad (2.7)
\]

In the linear optical regime, the quadratic term of the electromagnetic vector potential \( \mathbf{A} \) is generally negligible with respect to the linear term. Moreover, it becomes pertinent only for extremely high photon intensities which are not usually produced by standard light sources in the laboratory [141, 142].

By making use of the commutation relation \([\mathbf{P}, \mathbf{A}] = -i\hbar\nabla \cdot \mathbf{A} \) and the dipole approximation (i.e., \( \mathbf{A} \) is considered to be constant over atomic dimensions, and consequently, \( \nabla \cdot \mathbf{A} = 0 \)) it can be derived that \( \mathbf{P} \cdot \mathbf{A} = \mathbf{A} \cdot \mathbf{P} \). This approximation holds for photon energies in the ultraviolet region of the electromagnetic spectrum, which constitutes the typical energy of the incident radiation for an ARPES experiment. The expression \( \nabla \cdot \mathbf{A} \) becomes important at the surface where the

---

\(^5\)In quantum physics, Fermi’s golden rule is defined as an equation used in order to calculate the transition probability per unit time from one energy eigenstate of a quantum system into another of the energy eigenstates, due to a perturbation [155].

\(^6\)In quantum physics, perturbation theory is defined as a set of approximation schemes useful in describing real quantum systems since it is very difficult to find exact solutions to the Schrödinger equation for Hamiltonians of complex systems. The idea of this theory is to start with a simple system as for instance the hydrogen atom or the quantum harmonic oscillator for which a mathematical solution is known and add an additional ‘perturbing’ Hamiltonian representing a weak disturbance to the system in order to obtain the solutions of more complicated systems [155, 156].
electromagnetic fields may have a strong partial dependence \[141, 142\]. Therefore, by taking into account these previous approximations, the expression for the perturbed Hamiltonian operator given in equation 2.7 becomes

$$H_{PE} = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{P}. \quad (2.8)$$

Equation 2.8 is an appropriate basis for the theoretical description of most photoemission studies. There are some issues that still need to be addressed in this step, i.e., that of the need to simplify equation 2.6. The problem that makes the procedure difficult is that once the system is perturbed, it changes from an \(N\) electron state to a system of \((N-1)\) electrons and then it will relax by changing the electromagnetic vector potential \(\mathbf{A}\). The consideration in the three step model of a free-electron system in a periodic potential is not always true. The systems studied in practice behave like a many-body system so that the non-interacting picture does not take into account all the observed phenomena in a photoemission process \[159\]. Therefore, another useful approximation is often used in order to simplify equation 2.6. This approximation is called the sudden approximation, and will be explained in more detail in section 2.4.

- **Step 2: Propagation of the excited electron to the surface**

  In general, the propagation of the excited electron to the surface (transport to the surface) is described in terms of the electron mean free path \(\lambda\), describing the probability of the excited electron arriving at the surface of the sample without undergoing any inelastic scattering and so without suffering any change in its kinetic energy or momentum. During this transport process, electrons may be scattered and lose energy, becoming secondary electrons (see Figure 2.3).

  The mean free path \(\lambda\) is defined as follows \[160\]:

  $$\lambda = \frac{k}{2|\Im m \Sigma|}. \quad (2.9)$$

  where \(k\) is the total wave-vector inside the solid and \(\Im m \Sigma\) is the imaginary part of the self-energy. The self-energy concept will be explained later in more detail in section 2.6.
In a photoemission experiment, inelastic electron scattering is the major factor that limits the electron escape depth $\lambda$ [141, 142]. This inelastic scattering of electrons is principally due to electron-electron and electron-phonon interactions. The inelastically scattered electrons have a kinetic energy which is lower than that expected from their initial energy $E_{in}$. Thus, this gives an inelastic background present in photoemission experiments which generally decreases with the kinetic energy $E_K$. Figure 2.4 presents the universal curve of the electron mean free path at different photon energies. This curve has a universal trend because the experimental data for the inelastic mean free path collected in different materials have proved that its values follow more or less the same behaviour with a minimum of about $5 - 20 \, \text{Å}$ at the kinetic energy region of $20 - 200 \, \text{eV}$, which are the typical energies for most ARPES experiment.

This rather small electron escape depth implies that the majority of the photoemission intensity comes from the topmost surface layer. This is the reason why photoemission is considered as a surface sensitive technique [147]. This implies that clean and flat surfaces have to be prepared immediately before the experiment in ultra high vacuum conditions. Depending on the sample, this can be by cleaving, scraping or similar and annealing.

- **Step 3: Escape of the photoelectron into vacuum after transmission through the surface potential**

Usually this step is described by a transmission probability through the surface, depending on the material work function $\Phi$ and the energy of the excited electron. The work function $\Phi$ is defined as the minimum energy needed for an electron at the Fermi level to escape into the vacuum. Thus, this means that only those electrons with a kinetic energy higher than the work function can escape into vacuum [140]. The condition $\frac{\hbar^2 k_{\perp}^2}{2m} \geq |E_0| + \Phi$ on the momentum of the electron must be satisfied in order to have any finite escape probability [141]. For the optical excitation transition case, the crystal is frequently regarded as a three-dimensional transitional symmetry system. But due to the surface involvement, there is no translational symmetry at the surface when electrons move from solid to the vacuum. In section 2.2 it was seen that generally ARPES data are treated without considering the perpendicular component $k_{\perp}$ of the wave-vector.

Despite the success of the TSM during the past years [152, 151], it appears to be a rather general approximation of the photoemission process. It does however present a good starting point in getting a better understanding of the process [141, 142]. At present there are well advanced numerical methods to compute the photocurrent in the so-called one-step model. It is evident from the discussion on the TSM given above that the steps do not always describe the whole photoemission process. Photoemission is not described in terms of several independent events from a quantum mechanical point of view, but is rather described as a one-step process: an optical transition between initial and final states consisting of many-body wave functions that obey appropriate boundary conditions at the surface of the solid [150, 162].

## 2.4 The Sudden Approximation

Equation 2.6 is simplified within an assumption known as the sudden approximation, which is widely used in many-body calculations of the photoemission spectra from an interacting electron system, and is in principle applicable only to high kinetic energy electrons [141, 142]. This approximation was briefly introduced in the last paragraph of step 1 in section 2.3 on page 35. In this limit, the photoemission process has no post-collisional interaction between the photoelectron and the system left behind (i.e., the
electron is instantaneously removed from the system and the reaction is instantaneous and discontinuous at the time of interaction), and there is no relaxation during the photoemission process itself [159, 163]. This limit was supposed to be invalid at lower photon energies where the relaxation time approaches the escape time. It has been proved that at low kinetic energy the emitted electron may use a longer time than the system response time to escape into vacuum [141, 163]. However, recent laser research that used a laser source of energy (~7 eV) did not detect any crucial deviations from this approximation at low kinetic energies [164]. Thus, this implies that the sudden approximation may also be applicable at low kinetic energy. This situation has been shown to exist in cuprates [164].

In this approximation, i.e., if the photoemission process is assumed to be instantaneous, it is useful to factorize the wavefunctions of equation 2.6 into two parts, one describing the photoelectron \( \Psi^{N-1}_{\text{fin}} \) and the other one the \((N-1)\)-electron system. Regarding the initial state, we suppose for simplicity that \( \Psi^N_{\text{in}} \) is a single Slater determinant so that we can write it as the product of a one-electron orbital \( \Phi^k_{\text{in}} \) and the \((N-1)\)-particle term [141]. Therefore the initial state \( \Psi^N_{\text{in}} \) can be written as follows:

\[
\Psi^N_{\text{in}} = \hat{A}\Phi^k_{\text{in}}\Psi^{N-1}_{\text{in}}, \tag{2.10}
\]

where \( \hat{A} \) is an antisymmetric operator which correctly antisymmetrizes the \((N)\)-electron wave function so that the Pauli principle is satisfied. The final state wave function \( \Psi^N_{\text{fin}} \) is written as:

\[
\Psi^N_{\text{fin}} = \hat{A}\Phi^k_{\text{fin}}\Psi^{N-1}_{\text{fin}}, \tag{2.11}
\]

where \( \Phi^k_{\text{fin}} \) is the wave function of the photoelectron with momentum \( k \), and \( \Psi^{N-1}_{\text{fin}} \) is the final state wave function of the \((N-1)\)-electron system left behind, which can be chosen as an excited state with eigenfunction \( \Psi^{N-1}_{\text{in}} \) and energy \( E^{N-1}_{\text{in}} \) [141]. By substituting equations 2.10 and 2.11 into the matrix element \( \langle \Psi^N_{\text{fin}}|H_{\text{PE}}|\Psi^N_{\text{in}} \rangle \) from equation 2.6 we have:

\[
\langle \Psi^N_{\text{fin}}|H_{\text{PE}}|\Psi^N_{\text{in}} \rangle = \langle \Phi^k_{\text{fin}}|H_{\text{PE}}|\Phi^k_{\text{in}} \rangle \langle \Psi^{N-1}_{\text{fin}}|\Psi^{N-1}_{\text{in}} \rangle;
\]

where

\[
\langle \Phi^k_{\text{fin}}|H_{\text{PE}}|\Phi^k_{\text{in}} \rangle \equiv M^k_{\text{fin, in}};
\]

is the one-electron dipole matrix element that describes the transition probability of a single electron with momentum \( k \) from initial state \( \Phi^k_{\text{in}} \) into the final state \( \Phi^k_{\text{fin}} \). More details about the matrix elements will be given later in section 2.7. \( \langle \Psi^{N-1}_{\text{fin}}|\Psi^{N-1}_{\text{in}} \rangle \) is the \((N-1)\) electron overlap integral\(^7\) between an initial state wave function \( \Psi^{N-1}_{\text{in}} \) and the \( m \) state wave function \( \Psi^{N-1}_{\text{in}} \). This kind of integral depends strongly on the details of the initial state wave function such as the peak position of its radial part, and on the wavelength of the outgoing plane wave [141]. The total photoemission intensity, measured as a function of \( E_K \) and the momentum \( k \), is given by the sum over all possible transitions \( W_{\text{fin, in}} \) [141, 142]:

\[
I(k, E_K) = \sum_{\text{fin, in}} W_{\text{fin, in}}
\]

\[
= \frac{2\pi}{\hbar} \sum_{\text{fin, in}} |M^k_{\text{fin, in}}|^2 \sum_m |c_{m, in}|^2 \delta(E_K + E^{N-1}_{m} - E^{N}_{in} - h\nu); \tag{2.12}
\]

\(^7\)The overlap integral is defined in quantum mechanics as an integral over space of the product of the wave function of a particle and the complex conjugate of the wave function of another particle [28].
where $|C_{m,in}|^2 = |\langle \Psi_{in}^{N-1} | \Psi_{in}^{N-1} \rangle|^2$ is the probability that the removal of an electron from the initial state will leave the $(N-1)$ particle system in the excited state $m$. It should be noted that the binding energy $E_B$ is the difference in energy of the $(N-1)$ and $(N)$-electron system, i.e., $|E_B| = E_{N-1}^m - E_{in}^N$. Thus, the Dirac delta function in equation 2.12 is an explanation of the energy conservation (see equation 2.1) presented in section 2.2 (as this analysis only involves the first step of the TSM, the work function is not written here).

If $\psi_{in}^{N-1} = \psi_{m_0}^{N-1}$ for one particular $m = m_0$ and $M_{fin,in}^k \neq 0$, then the probability $|C_{m,in}|^2$ is one and zero elsewhere and in this case the ARPES spectrum is presented by a delta function located at the Hartree-Fock\(^8\) orbital energy $E_B^k = \epsilon_k$, as shown in Figure 2.5(a).

Many values of the probability $|C_{m,in}|^2$ (in the case where $m \neq m_0$) will be different from zero in strongly correlated systems, because the removal of the photoelectron results in a strong change of the effective potential of the system [141]. Thus, $\psi_{in}^{N-1}$ will have an overlap with many eigenstates $\Psi_{in}^{N-1}$ and consequently, the ARPES spectra will not consist of single delta functions but will show a main line and several satellites according to the number of excited states $m$ created in the process [142], as shown in Figure 2.5(b).

2.5 Representation of the Spectral Function $A(k, E)$ Through Green’s Functions

A common approach used in order to investigate the physics of interacting many-body problems is the use of the Green’s function formalism [166], where the one-electron spectral function $A(k, E)$ can be

---

\(^8\)The method used in order to determine the ground-state wave function and ground-state energy of a quantum many-body system is called the Hartree-Fock approximation. The Hartree-Fock approximation usually assumes that the exact $N$-body wave function of the system can be approximated by a single Slater determinant in the case where the particles are fermions [24, 165].
described by the time-ordered Green’s function. The sudden approximation described in section 2.4, is central to the interpretation of ARPES data, allowing a straight connection between the ARPES spectrum and the single electron spectral function \( A(k, E) \), which contains all of the electronic physics of the solid. Subsections 2.5.1 and 2.5.2 give more details about the spectral function \( A(k, E) \) and the Green’s function, respectively.

### 2.5.1 The Spectral Function \( A(k, E) \)

In the process of evaluating theoretically the experimental photoemission intensity within the TSM (see section 2.3) and the sudden approximation (see section 2.4), one ends up with the equation 2.12. From this equation, the one-electron spectral function is defined as:

\[
A(k, E_K) = \sum_m |\langle \Psi_m^{N-1} | \Psi_m^{N-1} \rangle|^2 \delta(E_K + E_m^{N-1} - E_m^{N} - \hbar \nu).
\]

The explanation of this type of equation was given in more detail at the beginning of page 38. The interaction between a photon and an electron in an interacting electro-magnetic field of bands can be written as the total spectral function as follows:

\[
A^\pm(k, E) = \mp \frac{1}{\pi} Im G^\pm(k, \pm E)
\]

where \( A^-(k, E) \) and \( A^+(k, E) \) define the one-electron removal and addition spectra which one can investigate with direct and inverse photoemission, respectively [141]. Equation 2.13 is often used in literature in order to connect the Green’s function and one-electron spectral function. Equation 2.13 also shows that the spectral function is proportional to the imaginary part of the Green function \( G(k, E) \) of the electron system. There are various types of Green’s functions used in the literature [167], but we are only interested on those that have immediate relation to the interpretation of inverse and direct photoemission experiments. The expression for this Green’s functions is demonstrated in more detail in the following subsection.

### 2.5.2 Green’s Function Representation

To demonstrate the expression of Green’s function \( G(k, E) \) related to the excitation spectrum of the full Hamiltonian, we start by defining the retarded and advanced one-particle many-body time ordered Green’s functions \( G^+(k_1, t_1, k_2, t_2) \) and \( G^-(k_1, t_1, k_2, t_2) \) respectively as follows [140]:

\[
G^+(k_1, t_1, k_2, t_2) = -i \theta(t_1 - t_2) \langle \psi_0^N | c_{k_1}(t_1) c_{k_2}(t_2) | \psi_0^N \rangle; \tag{2.14}
\]

\[
G^-(k_1, t_1, k_2, t_2) = +i \theta(t_2 - t_1) \langle \psi_0^N | c_{k_2}(t_2) c_{k_1}(t_1) | \psi_0^N \rangle; \tag{2.15}
\]

where \( k_1 \) and \( k_2 \) denote a set of momenta which are quantum numbers, \( t_1 \) and \( t_2 \) define the times of a single particle state \( k_1 \) and \( k_2 \) respectively, and \( \theta \) is the Heaviside function which is defined on page 40. It should be noted that the imaginary unit \( i \) is only introduced in formulas 2.14 and 2.15 for standard convention. The operators \( c_{k}^\dagger(t) \) and \( c_{k}(t) \) in the Heisenberg picture given by [140]:

\[
c_{k}^\dagger(t) = \exp \left( \frac{i}{\hbar} \hat{H} t \right) c_{k}(0) \exp \left( -\frac{i}{\hbar} \hat{H} t \right); \text{ and } \tag{2.16}
\]

\[
c_{k}(t) = \exp \left( -\frac{i}{\hbar} \hat{H} t \right) c_{k}(0) \exp \left( \frac{i}{\hbar} \hat{H} t \right),
\]

\[
\hat{H} = \sum_{k} \varepsilon_{k} c_{k}^\dagger c_{k}.
\]
are respectively the creation and destruction operators of an electron at time \( t \) with energy \( E \) and momentum \( \mathbf{k} \). \( \hat{H} \) is the Hamiltonian operator. The following lines show how the Green’s functions \( G^\pm \) can be related to the excitation spectrum of the full Hamiltonian (not just the interaction part of it).

By inserting the unit operator \( I = \sum_{n,M} |\psi_n^M\rangle \langle \psi_n^M| \) in equation (2.14), where \( n \) denotes the excited states of an \( M \)-particle system, and by applying the following changes: \( k_1 = k_2 = k \), \( t_1 = t \) and \( t_2 = 0 \), equation (2.14) becomes:

\[
G^+(\mathbf{k}, t) = -i\theta(t) \sum_{n,M} \langle \psi_0^N | c_{\mathbf{k}}(t) | \psi_n^M \rangle \langle \psi_n^M | c_{\mathbf{k}}^\dagger(0) | \psi_0^N \rangle. \tag{2.17}
\]

By substituting equation 2.16 into equation 2.17 and by changing the symbol \( M \) for \( M = N + 1 \), appropriate only for the addition of one-electron, then \( G^+(\mathbf{k}, t) \) becomes after some simplification:

\[
G^+(\mathbf{k}, t) = -i\theta(t) \sum_{n,N} \langle \psi_{n+1}^N | c_{\mathbf{k}}^\dagger(0) | \psi_0^N \rangle^2 \exp \left( -\frac{i\eta}{\hbar} \left( E_n^N + 1 - E_0^N \right) \right). \tag{2.18}
\]

By taking into account the fact that the Heaviside function \( \theta(t) \) is defined as:

\[
\theta(t) = \begin{cases} 
1 & \text{for } t \geq 0, \\
0 & \text{for } t < 0,
\end{cases}
\]

the calculation of the Fourier transform \( G^+(\mathbf{k}, E) \) of the retarded many-body time ordered Greens function \( G^+ \) (by using equation (2.18)) is given by:

\[
G^+(\mathbf{k}, E) = -i \sum_n \langle \psi_{n+1}^N | c_{\mathbf{k}}^\dagger(0) | \psi_0^N \rangle^2 \int_0^{+\infty} \left( \exp \left( -\frac{i\eta}{\hbar} \left( -E + \frac{E_n^N + 1 - i\eta}{\hbar} - E_0^N \right) \right) \right) dt. \tag{2.19}
\]

This eigenfunction expansion of the Green’s function \( G \) for an added particle \([168]\) (i.e., equation 2.19) was obtained by replacing \( E_0^N+1 \) by \( E_0^N+1 - i\eta \), where \( \eta \) is a positive infinitesimal number (which is expressed in terms of energy units), furthermore the integral is not sensitive to whether \(+i\eta\) or \(-i\eta\) sits in the nominator \([169]\). Let’s consider the energy in units of frequency, so that \( \hbar \) can be dropped out of equation 2.19 \((\hbar = 1)\) [i.e., take \( \frac{E_n^N+1}{\hbar} \rightarrow E_n^N+1, \frac{E_0^N}{\hbar} \rightarrow E_0^N, \frac{\eta}{\hbar} \rightarrow \eta, \frac{E}{\hbar} \rightarrow E \)], equation 2.19 becomes:

\[
G^+(\mathbf{k}, E) = \sum_n \frac{\langle \psi_{n+1}^N | c_{\mathbf{k}}^\dagger(0) | \psi_0^N \rangle^2}{E_n^N + 1 + E_0^N + i\eta}. \tag{2.20}
\]

Equation 2.20 is called the retarded Green’s function. By using the same procedure as above we can calculate the expression for the advanced Green’s function \( G^- (\mathbf{k}, E) \):

\[
G^- (\mathbf{k}, E) = \sum_n \frac{\langle \psi_{n-1}^N | c_{\mathbf{k}}(0) | \psi_0^N \rangle^2}{E_n^N - E_0^N - i\eta}. \tag{2.21}
\]

The total Green’s function \( G(\mathbf{k}, E) \) at \( T = 0 \) is defined as:

\[
G(\mathbf{k}, E) = G^+(\mathbf{k}, E) + G^-(\mathbf{k}, E), \tag{2.22}
\]

where \( G^+(\mathbf{k}, E) \) and \( G^-(\mathbf{k}, E) \) are defined respectively by equations (2.20) and (2.21).
The poles of advanced Green’s function \( G^- (k, E) \) occur at \( E = -(E_n^{N+1} - E_0^N) + i\eta \), i.e., above the real axis in the complex plane, while the poles of the retarded Green’s function \( G^+ (k, E) \) occur at \( E = E_n^{N+1} - E_0^N - i\eta \), i.e., below the real axis in the complex plane. This shows that the energy eigenstates \( E \) are actually poles of the Green’s function \[170\]. Thus, this turns out to be the general structure for any one-particle Hamiltonian \[170\]. These poles of the Green’s function represent also the excitation energies of the whole system, i.e., the energy due to an excitation from adding a particle to or subtracting a particle from the excited quantum state \( n \) of the \((N + 1)\)-particle system \[171\] (either \(-(E_n^{N+1} - E_0^N) + i\eta \) for particle excitations or \(E_n^{N+1} - E_0^N - i\eta \) for hole excitations, where \(E_n\) denotes the system has an excitation at \( n \)). By introducing the \((N \pm 1)\) ground state energy \( E_n^{N\pm 1} \) and by referring the total excitation energies to them, we have:

\[
\varepsilon_n^{N+1} = E_n^{N+1} - E_0^N, \quad \text{and} \quad \varepsilon_n^{N-1} = E_n^{N-1} - E_0^N.
\] (2.23)

The chemical potential \( \mu^{N\pm 1} \) of the \( N \pm 1 \)-particle systems, are given respectively by:

\[
\mu_n^{N+1} = E_n^{N+1} - E_0^N, \quad \text{and} \quad \mu_n^{N-1} = E_n^{N-1} - E_0^N.
\] (2.24)

The different formulas of chemical potentials (see equation 2.24) are assumed to be independent of the particle number when \( N \) is large. By substituting equations (2.23) and (2.24) into equation (2.22) and by making some simplifications, equation 2.22 becomes:

\[
G(k, E) = \sum_n \frac{|\langle \psi_n^{N+1} | \psi_{k}^{N} \rangle|^2}{E - (\varepsilon_n^{N+1} + \mu) + i\eta} + \sum_n \frac{|\langle \psi_n^{N-1} | \psi_{k}^{N} \rangle|^2}{E - (\varepsilon_n^{N-1} - \mu) - i\eta}.
\] (2.25)

The structure of the denominators of equation 2.25 accounts for the generalized application of the Green’s function formalism in spectroscopy. The poles of the retarded and advanced Green’s functions (shown above) give the affinity potentials\(^9\) and the ionization potential\(^10\) of the \( N \)-particle system, respectively. \( \varepsilon_n^{N\pm 1} = 0 \) corresponds to the lowest affinity and ionization potential in a conduction band of a metal. The conservation of energy for the photoemission process at this level, is given by:

\[
h\nu + E_0^N = E_K + E_n^{N-1};
\] (2.26)

where \( h\nu \) is the photon energy and \( E_K \) is the kinetic energy of the photoemission outside the solid. Equation (2.26) is generally applicable for solids, atoms and molecules. It is important to take the effect of the solid-vacuum barrier into account, so that the work function \( \Phi \) can be added to a certain kinetic energy \( E_{K1} \) to obtain the binding energy \( E_B \) from the difference to the photon energy \[140\]. By adding \( \mu \) on both sides of the equation 2.26 and rewriting it, the binding energy for the photoelectron is given by

\[
E_B = \mu + E_n^{N-1} - E_0^N = h\omega - E_K + \mu.
\] (2.27)

By assuming that, the work function \( \Phi = -\mu \), equation (2.27) becomes

\[
E_B = \Phi + E_{K1} = E_n^{N-1} - E_0^N + \mu = h\omega - E_K - \Phi = \varepsilon_n^{N-1}.
\]

Note that binding energies are always referred to the Fermi level and the spectrometer measures the kinetic energy \( E_{K1} \) with a specific work function.

\(^9\)The affinity potential is defined as the energy required to add in the \( N \)-particle ground state a particle in a single-particle state \[140\].

\(^10\)The ionization potential is defined as the energy required to remove from the \( N \)-particle ground state a particle occupying a single-particle state \[140\].
During the process of adding to or subtracting a particle from the $N$-particle ground state, the remaining single particle states remain unchanged [140]. Therefore the final states of the $(N+1)$- and $(N-1)$-particle systems can be written as: $|\psi_{n+1}^\uparrow\rangle = c_n|\psi_n^\uparrow\rangle$ and $|\psi_{n-1}^\downarrow\rangle = c_n|\psi_0^\downarrow\rangle$, respectively. Let $\varepsilon_{n+1}^\uparrow = \varepsilon_k$, and $\varepsilon_{n}^\downarrow = -\varepsilon_k$ be positive energies for the Hartree-Fock energies $\varepsilon_k$ for particles and holes respectively [172], and $\varepsilon = \varepsilon - \mu$ (i.e., the energy $E$ is referred to the chemical potential). By taking into account these changes equation (2.25) becomes:

$$
G(k, \varepsilon) = \frac{\theta(k - k_F)}{\varepsilon - \varepsilon_k + i\eta} + \frac{\theta(k_F - k)}{\varepsilon - \varepsilon_k - i\eta}
$$

(2.28)

where $\sum_n |\langle \psi_n^\uparrow | c_n^\dagger c_k(0)|\psi_0^\uparrow\rangle|^2 = \theta(k_F - k)$, while $\sum_n |\langle \psi_n^\downarrow | c_n c_k^\dagger(0)|\psi_0^\downarrow\rangle|^2 = \theta(k - k_F)$. The values of $\pm(\varepsilon_k + \mu)$ are the affinity and the binding energies of the system for $k > k_F$ and $k < k_F$ respectively, where $k_F$ is a Fermi level state.

It is important to note that in the photoemission process, equation (2.28) is based on the assumption that $|\psi_{n-1}^\downarrow\rangle = c_n|\psi_0^\downarrow\rangle$, i.e., in the process of subtracting from the $N$-particle ground state a particle in the $sps$ state $k$ where the momentum is $k$, the remaining single particle states remain unchanged, i.e., only the $sps$ state $k$ is an active state [140].

Equation (2.28) shows that single-particle states in the system are not represented by a delta function but by a function with a certain width centred around the peak position. At this point we can assume that the peak is represented by a Lorentzian line shape [140].

### 2.6 Self-Energy Function and Lifetime of the Quasiparticles

This section is strongly based on the discussion reported in references [147, 160, 154, 173]. In this work we will concentrate only on the function $A^-(k, E)$ (whose its expression is given by equation 2.13) since it is used to describe the one-electron removal that can be probed by a direct photoemission process. At this point it is natural to ask how a single-particle Green’s function can be described when considering the many-body interactions which are present in a system of particles. A useful aspect of the one-particle many-body Green’s function is that it allows conserving a one-particle picture while considering many-body systems. Therefore, to describe the many-body interaction of a single-particle Green’s function, it is possible to introduce an energy dependent effective function, called the self-energy $\Sigma$. The self energy $\Sigma$ holds all information due to the particle interaction effects. The derivation of the self-energy expression is beyond the scope of this dissertation and would need an introduction of more topics. The expression of the self-energy can be expressed more explicitly in terms of its real and imaginary parts by

$$
\Sigma(k, E) = Re \Sigma(k, E) + i Im \Sigma(k, E).
$$

(2.29)

The real part of the self-energy $Re \Sigma(k, E)$, describes the correction to the energy value of the non-interacting particle, while the imaginary part $Im \Sigma(k, E)$ take into account the lifetime of the particle state (see Figure 2.6). All interaction effects will then be expressed by just considering a particle with renormalized energy $\varepsilon_k = \varepsilon_k + Re \Sigma(k, E) + i Im \Sigma(k, E)$, where $\varepsilon_k$ is the energy of the non-interacting particle with momentum $k$. The Green’s function can be written in terms of the self-energy of the system in the following way

$$
G^-(k, E) = \frac{1}{E - \varepsilon_k - \Sigma(k, E)}.
$$

(2.30)
By taking into account the imaginary part of this Green’s function, the expression of one-electron spectral function is given by

\[
A^{-}(\mathbf{k}, E) = -\frac{1}{\pi} \frac{\text{Im} \Sigma(\mathbf{k}, E)}{[E - \varepsilon_{\mathbf{k}} - \text{Re} \Sigma(\mathbf{k}, E)]^2 + [\text{Im} \Sigma(\mathbf{k}, E)]^2}.
\]

The one-electron spectral function given by equation 2.31 is frequently used in literature to describe theoretically the measured photoemission intensity in an ARPES experiment. By taking into account the assumption that the self-energy depends weakly on energy and its imaginary part is small compared to the binding energy, then the spectral function 2.31 becomes a Lorentzian (see Figure 5.2). The complex self-energy contains all information about contributions from many-body processes like electron-electron, electron-phonon, or electron-impurity interaction. Therefore the self-energy function can also be written as follows

\[
\Sigma_{\mathbf{k}}(E) = \Sigma^{\text{el-el}}_{\mathbf{k}}(E) + \Sigma^{\text{el-ph}}_{\mathbf{k}}(E) + \Sigma^{\text{el-imp}}_{\mathbf{k}}(E) + \cdots.
\]

It is important to know the contributions of electron-electron (el-el), electron-phonon (el-ph) and electron-impurity (el-imp) interactions to the electron self-energy, in order to describe a non-magnetic metal. The dominant contribution at higher binding energies is the \(\Sigma^{\text{el-el}}\) contribution, which is described by the 3D Fermi-liquid and depends on the energy and temperature. The electron-phonon (el-ph) contribution allows the energy dependence close to the Fermi level to be determined. This increases rapidly on the scale of the Debye energy \(\hbar \omega_{D}\) even if the electron-phonon coupling is small [160]. Finally, the electron-impurity (el-imp) contribution is usually considered as independent of temperature and energy and has not been studied in detail by theory up to now. Thus, the experimentalists try to keep their samples (and consequently their data) as free as possible from the influence of contaminations [160].

Given that, the spectral function (see equation 2.31) is a Lorentzian, as explained above, its peak is centred at \(E = \varepsilon_{\mathbf{k}} + \text{Re} \Sigma(\mathbf{k}, E)\) and its width (Full Width Half Maximum: FWHM) is given by
Section 2.6. Self-Energy Function and Lifetime of the Quasiparticles

\[ \Gamma = 2 \Im \Sigma(k, E). \] By considering the expression \( \Im \Sigma(k, E) = \frac{\hbar}{2\tau} \), where \( \tau \) is the lifetime of the photoelectron, then the FWHM is proportional to the inverse lifetime \( \tau \), i.e.,

\[ \Gamma = \frac{\hbar}{\tau}. \] (2.33)

Usually the result of the photoemission intensity is a convolution of the spectral function of the photoemitted electron and the spectral function of a photohole given by equation 2.31 [154]. The linewidth of the quasiparticle peak contains contributions from both the photohole (initial state) and the photoelectron (final state) lifetimes. These contributions are represented by Lorentzians, where \( \Gamma_i \) is the linewidth (or inverse lifetime) of the photohole in the initial state, and \( \Gamma_f \) is the linewidth of the photoelectron in the final state. It can be shown that, the resulting linewidth \( \Gamma \) is a linear combination of \( \Gamma_i \) and \( \Gamma_f \), given by the following formula [173]:

\[ \Gamma = \frac{\Gamma_i v_{i \perp}}{v_{i \perp}^2 \left(1 - \frac{m v_{i \parallel} \sin^2 \theta}{\hbar k_{\parallel}}\right)} + \frac{\Gamma_f v_{f \perp}}{v_{f \perp}^2 \left(1 - \frac{m v_{f \parallel} \sin^2 \theta}{\hbar k_{\parallel}}\right)}. \] (2.34)

where \( v_i \) and \( v_f \) are the group velocities for the initial and the final states respectively. The symbols \( \parallel \) or \( \perp \) indicate if the velocities are considered as parallel or perpendicular to the surface of solid, i.e.,

\[ h v_{i \perp} = \frac{\partial E_i}{\partial k_{\perp}}. \] Equation 2.34 can be simplified by means of several approximations such as the following:

- If the initial states are very close to \( E_F \) (i.e., \( \Gamma_i \to 0 \)), then the linewidth \( \Gamma \) is proportional only to the linewidth of the final state \( \Gamma_f \).
- For the case where a material is characterized by a two dimensional crystal structure, reflected in a 2D electronic structure (i.e., \( v_{i \perp} \approx 0 \)), the linewidth \( \Gamma \) is given as follows [154]:

\[ \Gamma = \frac{\Gamma_i}{\left|1 - \frac{m v_{i \parallel} \sin^2 \theta}{\hbar k_{\parallel}}\right|}. \] (2.35)

This expression shows us that the final state lifetime has disappeared and this is the reason why often in experiment surface states are sharper than bulk states. For a normal emission (i.e., \( \theta = 0 \)) and if \( v_{i \parallel} = 0 \) (at a symmetry point), the measured lifetime is equal to the inverse lifetime of the photohole in the initial state, i.e., \( \Gamma = \Gamma_i \). This relation shows that the surface states are of great interest in extracting hole state lifetimes from the experimental linewidth.

- For a normal emission situation (i.e., \( \theta = 0 \)) and if \( v_{i \perp} \ll v_{f \perp} \), then the linewidth \( \Gamma \) is defined as [154]:

\[ \Gamma \simeq \Gamma_i + \left|\frac{v_{i \perp}}{v_{f \perp}}\right| \Gamma_f. \] (2.36)

In the limit case where \( v_{f \perp} \to 0 \), the measured linewidth is proportional to the inverse lifetime of the photohole in the initial state [173], i.e., \( \Gamma \simeq \Gamma_i \). In ARPES studies of quasi-2D systems, this approximation is often used. Therefore, this approximation is taken into account in the process of analysis of ARPES data present in this work, since the system investigated is a quasi-2D system.
2.7 Matrix Elements

The relevant information presented in this section is mainly based on references [141, 142, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183]. The expression for the measured ARPES photoemission intensity \( I(k, E) \) given by equation 2.12 holds the matrix elements and is only valid at \( T = 0 \) K. To acquire a complete expression for the photoemission intensity at finite temperatures, one can write the equation 2.12 as a product of functions as follows:

\[
I(k, E, T) = \sum_{f_{in},m} |M^k_{f_{in},m}|^2 f(E, T) A(k, E);
\]

where \( |M^k_{f_{in},m}|^2 \) is the square of the single-electron dipole matrix elements, which depend on electron momentum, photon energy, the geometry of the experiment and the light polarization of the incoming photon energy. The effect of matrix elements can be so severe as to even result in the complete suppression of the photoemission intensity [174, 175].

\[ f(E, T) = \frac{1}{\text{exp} \left( \frac{E}{K_B T} \right) + 1}; \]

which takes into account the fact that direct photoemission only probes the occupied states [141]. \( A(k, E) \) is the single particle spectral function given by equation 2.31. \( k \) is the component of the electron momentum and \( E \) is the electron energy with respect to the Fermi-level. In this section, the implications of the matrix-elements on the photoemission process are discussed in detail.

Let us now illustrate the effect of the matrix element term in the photoemission process. We saw in section 2.4 that the matrix element can be defined as:

\[
M^k_{f_{in},m} = \langle \Phi^k_{f_{in}} | H_{PE} | \Phi^k_{in} \rangle;
\]

where the Hamiltonian \( H_{PE} \) is given by equation 2.8. By substituting equation 2.8 into 2.39 we get,

\[
M^k_{f_{in},m} \propto \langle \Phi^k_{f_{in}} | \hat{\epsilon} \cdot \hat{\mathbf{x}} | \Phi^k_{in} \rangle.
\]

This expression can be further simplified by expressing the electromagnetic vector potential \( \mathbf{A} \) as a plane wave, i.e.,

\[
\mathbf{A} \sim A_0 \hat{\epsilon} \exp \left\{ i \left( \frac{E}{C} \right) \hat{\mathbf{n}} \cdot \mathbf{x} \right\},
\]

where \( \hat{\epsilon} \) is a unit vector along the polarization direction of the vector potential \( \mathbf{A} \), while \( \hat{\mathbf{n}} \) is the unit vector along the light propagation direction [142]. The exponential term can be expanded in a power series in the standard electric dipole \( (E) \), i.e.,

\[
\exp \left\{ i \left( \frac{E}{C} \right) \hat{\mathbf{n}} \cdot \mathbf{x} \right\} \approx 1 + i \left( \frac{E}{C} \right) \hat{\mathbf{n}} \cdot \mathbf{x} + \cdots
\]

and by approximation, only the first term is kept, thus the electromagnetic vector potential \( \mathbf{A} \) becomes \( \mathbf{A} \sim A_0 \hat{\epsilon} \). By making use of this approximation to \( \mathbf{A} \) and the commutation relation of the full Hamiltonian \( [\mathbf{x}, H] = \frac{i\hbar}{m_e} \) (where \( m_e \) is the mass of the electron and \( \mathbf{x} \) is a spherical tensor of rank 1), equation 2.40 becomes:

\[
M^k_{f_{in},m} \propto \langle \Phi^k_{f_{in}} | \hat{\epsilon} \cdot \mathbf{x} | \Phi^k_{in} \rangle.
\]
This is the standard dipole transition which gives the highest contribution within the photoemission process, therefore $M_{fin,in}^k$ becomes subject to the standard dipole selection rules. At this point, we can see that with ARPES one can make use of specific selection rules because there are symmetry forbidden and symmetry allowed transitions.

Here we report an example of such behaviour as discussed in Ref. [141]. Figure 2.7 shows photoemission from a $d_{x^2-y^2}$ orbital, with the detector located in the mirror plane. Note that, when the detector is out of the mirror plane, the problem becomes more complicated because of the lack of an overall well defined even/odd symmetry [141]. In order to have a non-vanishing photoemission intensity, the total integrand in the overlap integral must be an even function under reflection with respect to the mirror plane. For high kinetic energy photoelectrons, the final state wavefunction $\Phi_{fin}^k$ can be approximated by a plane wave state $\exp\{ik \cdot r\}$ with momentum $k$ located in the mirror plane for the electron analyser slit in Figure 2.7. As a result, the final state $\Phi_{fin}^k$ is even with respect to the mirror plane (it should be noted that odd parity final states are zero everywhere on the mirror plane and also at the detector). Therefore, for the photoemission process to be symmetry allowed, $\langle \hat{\varepsilon} \cdot x | \Phi_{fin}^k \rangle$ must be even [176]. The initial state wave function $\Phi_{in}^k$ must be even (or odd) symmetry with respect to the mirror plane in the $\pi$ (or $\sigma$) experimental geometry [177].

Figure 2.7 represents the case where $\Phi_{in}^k$ is also even and the photoemission process is symmetry allowed for $A$: even or in-plane, i.e., $\hat{\varepsilon}_p \cdot x$ depends only on the in-plane coordinates and is therefore even under reflection with respect to the plane [141]. The photoemission process is forbidden for $A$ either odd or normal to the mirror plane, i.e., $\hat{\varepsilon}_a \cdot x$ is odd as it depends on normal to the plane coordinates. For an initial state of either even or odd symmetry with respect to the mirror plane, the polarization conditions result in an overall even matrix element and can be summarised as:

$$\langle \Phi_{fin}^k | \hat{\varepsilon} \cdot x | \Phi_{in}^k \rangle :$$

- $\Phi_{in}^k$ : even \quad $\langle + | + \rangle \Rightarrow \hat{\varepsilon}(A) :$ even
- $\Phi_{in}^k$ : odd \quad $\langle + | - \rangle \Rightarrow \hat{\varepsilon}(A) :$ odd

"+
" and "-" signs described even and odd symmetries, respectively. By considering a plane wave $\exp\{ik \cdot r\}$ for the photoelectron at the detector and the photon energy dependence from equation 2.8, the matrix element can conveniently also be written as $|M_{fin,in}^k| \propto |\langle \varepsilon k | \Phi_{fin}^k | \exp\{ik \cdot r\} \rangle|^2$. From this expression one can see that the overlap integral strongly depends on the details of the initial state wavefunction $\Phi_{in}^k$ (i.e., the peak position of its radial part and its oscillating character) and the wavelength of the outgoing plane wave [141]. If both kinetic energy $E_K$ and momentum $k$ increase, the photon energy also increases. $|M_{fin,in}^k|$ then changes in a fashion that is not necessary monotonic (see
Figure 7(c) in Ref. [141], which shows that the cross section of the Cu 3d and the O 2p are photon energy dependent.

As a result a powerful tool to identify the orbital character within the band structure is the polarization sensitivity of the orbitals in ARPES. The polarisation of the light in combination with the experimental geometry supplies an opportunity to study the orbital symmetry of the initial states (see Figure 2.7). We refer to A: odd or $E_s$ (A: even or $E_p$) as $\sigma - (\pi -)$ geometry$^{11}$ (see Figure 2.7 which shows two different polarisation geometries). The $d_{yz}$ and $d_{xy}$ orbitals are odd with respect to the $xz$ plane, while the $d_{xz}$, $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are even as shown in Figure 2.8 [177]. Thus, by taking the $xz$ plane as the mirror plane, the condition in which ARPES intensity is forbidden is summarised in Table 2.1.

<table>
<thead>
<tr>
<th>Orbitals</th>
<th>$\pi$-geometry</th>
<th>$\sigma$-geometry</th>
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<tbody>
<tr>
<td>$d_{xy}$</td>
<td>forbidden</td>
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<tr>
<td>$d_{yz}$</td>
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<tr>
<td>$d_{zx}$</td>
<td>forbidden</td>
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<tr>
<td>$d_{x^2-y^2}$</td>
<td>forbidden</td>
<td>forbidden</td>
</tr>
<tr>
<td>$d_{z^2}$</td>
<td>forbidden</td>
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</tr>
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</table>

Table 2.1: Representation of the forbidden orbital symmetries by assuming $xz$ plane as a mirror plane. Table taken from [177].

Table 2.1 can be explained in the following way: consider the high symmetry cut along the $x$ direction which defines a mirror plane as shown in Figure 2.7. We saw above that the final state $\Phi_{k_{\text{fin}}}$ is even with respect to the mirror plane. For a polarisation that is odd with respect to the mirror plane, only $d_{yz}$ and $d_{xy}$ orbitals in the initial state $\Phi_{k_{\text{ini}}}$ with odd parity with respect to this mirror plane will have a non-zero contribution to the measured signal, i.e., the photoemission intensity, while $d_{x^2-y^2}$, $d_{xz}$ and $d_{z^2}$ orbitals with even parity will be suppressed along this high symmetry cut.

Matrix element effects also allow the signal from some bands to be enhanced with respect to others due to different matrix element dependencies on photon energy [178, 179], photon polarization [180, 181], or polarisation geometry [182]. Therefore, this may also give us some information about the electronic structure of solids. Matrix element effects may also be used for aiding in identifying initial state characteristics such as orbital symmetry character [183]. When the system is symmetry forbidden then the matrix element causes the intensity to be zero (or almost zero). In this dissertation, the effect of matrix elements was investigated and ARPES results on this effect will be presented later in section 5.2.

$^{11}$It should be noted that, for the $\sigma$ (or $\pi$) experimental geometry, the electric field direction of the incident photons is out of (or in) the mirror plane [177].
Electron correlation effects are not only important in atomic physics, but also for phenomena in condensed matter physics such as high temperature superconductivity [1] and itinerant magnetism [21]. The photoelectrons in an ARPES experiment do not only carry important information about the electronic structure of a metal, but also about any electron correlation effects present in it. In general, the challenge in the physics of correlated electron metals is to distinguish between different contributions to the quasiparticle mass enhancement. Band renormalization can arise because of electron-electron correlations and/or coupling of the electrons to collective modes, such as modes of lattice vibrations [184], and produce a strong deviation from the simple band-like picture [154]. Details on the band renormalization effects will be given in subsection 2.8.1, followed by a detailed explanation on the electron-phonon interactions in subsection 2.8.2.

### 2.8.1 Band Renormalization Effects

The interactions between electrons which are responsible for the unusual properties of metals can be deciphered from several approaches. To take into account these interactions, one has to consider electronic excitations as quasiparticles which, compared to the non-interacting electrons, are characterized by an additional complex self-energy given by expression 2.29 [185]. The imaginary part of the self-energy is related to the quasiparticle lifetime, while the real part is related to the renormalization of the quasiparticle dispersion in the momentum space [186]. Thus, the extraction of the self-energy from experiment is of great importance to check the validity of the quasiparticle concept and to understand the nature of the associated interactions. However, the extraction of the self-energy can be difficult since the underlying band structure of the bare electrons is a priori unknown. In order to extract band renormalization parameters such as the lifetime of the particle, reliable and precise knowledge of the bare band dispersion (i.e., band dispersion of a non-interacting system) is needed. The sensitivity of ARPES to correlation effects is deeply connected to the one-particle spectral function previously discussed in subsection 2.5.1, whose expression in term of self-energy is given by equation 2.31. In equation 2.31, $\varepsilon_k$ is the bare band dispersion and within such a definition of the spectral function, $Im \Sigma(k, E) < 0$ and $Re \Sigma(k, E) > 0$ for $E < 0$. In the literature, most approaches used in order to determine the bare band dispersion in a small (or wider) energy range near to the Fermi energy level are based on the consideration of the dispersion as linear or quadratic.

### Linear dispersion

In the case where there is no interaction the spectral function (equation 2.31) is a Delta function (see Figure 2.5(a)) with the pole of $E - \varepsilon_k = 0$, and the bare band dispersion can be represented as shown by the solid line (black) in Figure 2.9(a). Let $\varepsilon_k$ be $\varepsilon(k)$, and $\omega = E$ in the rest of this section. When the interactions are switched on, the self energy leads to a shifting and broadening of the noninteraction spectral function [186]. The resulting picture is illustrated by the measured band dispersion with the red momentum distribution curve (MDC) in Figure 2.9(a).

The analysis of the MDC provides a method of extracting the electron self energy that holds information about interactions as it is illustrated in Figure 2.9(a). By neglecting the momentum dependence of the self energy, then the MDCs have maxima at $k_m(E)$ determined by $E - \varepsilon(k_m) - \Sigma'(E) = 0$ for a given energy $E$. Thus, the real part of the self energy, which is illustrated in Figure 2.9(a) by the blue
Figure 2.9: Representation of the real ($\Sigma'(\omega)$ or $R_e\Sigma(E)$) and imaginary ($\Sigma''(\omega)$ or $Im\Sigma(E)$) parts of the self energy from ARPES spectra. (a) Bare band dispersion (black solid line) along a given direction of the high $T_c$ superconductor Bi$_2$Sr$_2$CaCu$_2$O$_8$ and renormalized dispersion (red points) on top of the spectral weight of interacting electrons. The red solid line (red curve) represents a single MDC taken at a certain energy $\omega (E)$. $k_m$ is the momentum of the position corresponding to the maximum MDC, while $k_1$ and $k_2$ are momenta of the half maximum level of the MDC. (b) Bare band dispersion (black solid parabola) along a given direction of the high $T_c$ superconductor (Bi, Pb)$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ and renormalized dispersion points (red line) on top of the spectral weight of interacting electrons. Figures reproduced from [186, 187]. Please see text for more details.

The quadratic band dispersion takes into account the fact that, in the wider energy range, the bare band dispersion deviates from being a line and the band in the occupied part can be well approximated.
by a simple parabola (see the black solid parabola representative of the \( \varepsilon(k) \) function in Figure 2.9(b)) defined as:

\[
\varepsilon(k) = \omega_0 \left( \frac{k^2}{k_F^2} - 1 \right);
\]  
(2.46)

where \( \omega_0 \) is the bottom of the bare band and the bare Fermi velocity \( v_F = \frac{-2\omega_0}{k_F} \). By substituting equation 2.46 and the expression of \( v_F \) given in the previous line into equation 2.43, the real part of the self energy is this case is given by:

\[
\Sigma'(E) = \frac{v_F}{2k_F} \left[ k_m^2(E) - k_F^2 \right] + E.
\]  
(2.47)

By using equation 2.31 for each fixed energy \( E \), the three momenta \( k_m(E), k_2(E) \) and \( k_1(E) \) are defined as (see details of the photoemission spectra analysis in Ref. [186]):

\[
A(k_m) = \text{max}[A(k)],
\]
\[
A(k_{1,2}) = \frac{\text{max}[A(k)]}{2}.
\]  
(2.48)

By taking \( k_2 > k_1 \), the half full width maximum \( W \) is defined as \( 2W = k_2 - k_1 \). By solving equation 2.48 one obtains,

\[
E - \varepsilon(k_m) - \Sigma' = 0,
\]
\[
E - \varepsilon(k_{1,2}) - \Sigma' = \pm|\Sigma''|.
\]  
(2.49)

From equation 2.49 three expressions for \( \Sigma'' \) are derived and given by:

\[
|\Sigma''| = \frac{\varepsilon(k_m) - \varepsilon(k_{1,2})}{2},
\]
\[
= \frac{\varepsilon(k_2) - \varepsilon(k_m)}{2},
\]
\[
= \frac{\varepsilon(k_2) - \varepsilon(k_{1,2})}{2}.
\]  
(2.50)

These general equation are exact and it is possible to use any of them depending on what one determines in the experiment [186]. The two experimental quantities the renormalized dispersion \( k_m(E) \) and FWHM equal to \( 2W(E) \) are preferable, so one can focus on the last equation from 2.50. By substituting equation 2.46 and \( 2W = k_2 - k_1 \) into the last expression of equation 2.50, we get:

\[
|\Sigma''| = -\frac{\omega_0 W}{k_F^2} (k_2 + k_1) \quad \text{with} \quad & \omega_0 > 0.
\]  
(2.51)

By substituting the property of a parabolic function \( \varepsilon_k \), i.e., if \( 2\varepsilon(k_m) = \varepsilon(k_2) + \varepsilon(k_1) \), then \( 4k_m^2 = (k_2 + k_1)^2 + (k_2 - k_1)^2 \) [186] into equation 2.51 the imaginary part of the self energy is given by:

\[
|\Sigma''| = -\frac{2W}{k_F} W(E) \sqrt{k_m^2(E) - W^2(E)}.
\]  
(2.52)

Figure 2.9(b) shows the real part of the self energy \( \Sigma' \) which is represented by the vertical blue double headed arrows and its expression in the case of the quadratic dispersion is given by equation 2.47. This figure also shows the imaginary part of the self energy \( \Sigma'' \) which is delimited by the two horizontal blue arrows and its expression is given by equation 2.52. It should be noted that the expression of \( 2Im\Sigma(E)/V_{oF} \) (see Figure 2.9(b)) can be deduced from equation 2.52.

It has been pointed out that a linear \( k \) dependence of the real part of the self energy \( \Sigma' \) is a more general case which leads to the perfect Lorentzian lineshape of the momentum distribution curves (MDCs) [190]. Therefore, in the process of ARPES data analysis, the linear dispersion is a good approach used in order to determine the bare band dispersion and the real and imaginary part of the self energy.
2.8.2 Electron-Phonon Interactions

The relevant information presented in this section is mostly based on references [147, 191, 192, 193].

The abrupt change of the group velocity, frequently called a “kink”, of the dispersing peak in ARPES spectra is widely reported in the high temperature superconducting cuprates [191, 192]. The kink in the dispersion is due to the electronic coupling to a bosonic mode such as phonons [191, 194] or magnetic excitations [195, 196]. Its size is related to the phonon energies and the electron-phonon mode coupling strength [38, 197]. Consequently, kinks contain interesting informations about the electron-phonon interactions present in a system. In the following paragraph a basic mechanism for the appearance of kinks in the spectra is presented.

Engelsberg and Schrieffer [198], by using the perturbation theory in the normal state, have proved that there are notable effects in the electronic self-energy \( \Sigma(k, E) \) when electrons are coupled to a sharp bosonic mode characterised by frequency \( \Omega \). By modelling the collective mode as an undamped oscillator with a propagator \( D(k, E) \) given by [147]:

\[
D(k, E) = \frac{1}{E^2 - \Omega^2 + i\delta};
\]

where \( E \) and \( k \) are energy and momentum respectively, \( \Omega \) is the frequency and \( \delta \) is a Delta function, the electronic self-energy can be written as [147]:

\[
\Sigma(k, E) = ig^2 \int \frac{dk'}{(2\pi)^4} D(k - k', E - E') G_0(k', E');
\]

where \( G_0(k', E') \) is the Green’s function of the uncoupled electronic system given by equation 2.30. By substituting equations 2.53 and 2.30 into 2.54, the electronic self-energy becomes:

\[
\Sigma(k, E) = ig^2 \int \frac{dk'}{(2\pi)^4} \frac{1}{(E - E')^2 - \Omega^2 + i\delta} \left( E - E' - \varepsilon_k - \Sigma(k', E') \right);
\]

where \( g \) is the coupling constant which is taken as energy and momentum independent. By assuming a constant density of states in the normal state, by evaluating the integral (equation 2.55) over \( \varepsilon_k \) and by separating the real and imaginary part of the self-energy, expressions of the real and imaginary part of the self-energy at \( T = 0 \) are given by [147]:

\[
Re\Sigma(E) = -\frac{g^2 N}{2\Omega} \ln \left| \frac{E + \Omega}{E - \Omega} \right|;
\]

\[
Im\Sigma(E) = -\frac{g^2 N\pi}{2\Omega} \theta(|E| - \Omega);
\]

where \( N \) denotes the number of undamped oscillators. Equation 2.56 presents an onset of the scattering rate in the imaginary part of the self-energy at \( |E| > \Omega \) and a logarithmic divergence in the real part. In reality the singularities in the self-energy are effectively removed when the mode must have a finite width. For moderate coupling strength the self-energy given by equation 2.56 leads to the appearance of a “kink” in the band dispersion at energy equal to the mode energy \( \Omega \) [147], which has in fact been detected experimentally in the photoemission spectra of some cuprates [191, 192, 199], as stated above.

The self-energy for the superconducting (SC) state is still given by equation 2.55 but the appropriate Green’s function of this state has the following form [147]:

\[
G_{SC}^0(k, E) = \frac{E + \varepsilon_k}{E^2 - \varepsilon_k^2 - \Delta_k^2};
\]
where $\Delta$ is the superconducting gap. By substituting equation 2.57 into equation 2.55, by evaluating the integral over $\varepsilon_k$ and by separating real and imaginary parts of the self-energy, the imaginary part of the self-energy is given for $E < 0$ by [147]:

$$
Im \Sigma(E) = -\frac{g^2 N \pi}{2\Omega} Re \frac{E + \Omega}{\sqrt{(E + \Omega)^2 - \Delta^2}}.
$$

(2.58)

The significant difference between the imaginary part of self-energy obtained from the normal state (equation 2.56) and the superconducting state (equation 2.58) is the appearance of the superconducting gap ($\Delta$), the shift of the scattering onset and the shift of the “kink” position from $E = -\Delta$ to $E = -(\Delta + \Omega)$.

Recently, kinks have been found in the layered strontium ruthenates by Aiura et al. [193] (see Figure 2.10). The experimental band dispersions along the high symmetry line $\Gamma X$ of $\text{Sr}_2\text{RuO}_4$ and $\text{Sr}_3\text{Ru}_2\text{O}_7$ are shown in Figures 2.10(a) and 2.10(b) respectively. Figure 2.10(a) shows three bands indicated by the greek letters $\beta$, $\alpha$ and $\gamma$, while Figure 2.10(b) shows three spectral features indicated by the letters A, B and C. Experimental band dispersions of $\text{Sr}_2\text{RuO}_4$ and $\text{Sr}_3\text{Ru}_2\text{O}_7$ plotted along the high symmetry line $\Gamma X$ extracted by fitting MDCs with a Lorentzian function together with the calculated band structure (red, blue lines and the black dotted lines) are shown in Figures 2.10(c) and 2.10(d) respectively. The prominent features $\alpha$ and $\gamma$ in Figure 2.10(c) and $\alpha$ and $\gamma$ of $\text{Sr}_2\text{RuO}_4$ (solid circles) indicate a kink in the dispersion around 40 meV. The behaviour of these kinks were found to be similar to the one reported in ARPES of the cuprate superconductors by Lanzara et al. [191]. To compare the behaviour of the kink between the single and double layered strontium ruthenates in detail, the authors, i.e., Aiura et al., have plotted the experimental dispersion of spectral feature A of $\text{Sr}_3\text{Ru}_2\text{O}_7$ (open circles) and $\alpha$ and $\gamma$ of $\text{Sr}_2\text{RuO}_4$ (solid circles) together see Figure 2.10(c). This figure also shows how the energy position of the kink are the same (at about 40 meV) and the slope in the low energy part near the Fermi energy $E_F$ is almost the same between the single and double layered strontium ruthenates, while the dispersion in the high energy varies between them. The slope of these kinks show the universality of the slope in dispersion [192].

In the literature, there exist only a few reported works that treat kinks in the strontium ruthenates family [193]. In this dissertation, kinks associated to different Fermi surface sheets were determined from the
band dispersion of $\text{Sr}_3\text{Ru}_2\text{O}_7$. Section 5.5 will presents results and discussion about kinks observed in the double layered ruthenates $\text{Sr}_3\text{Ru}_2\text{O}_7$. 
3. Experimental Description

3.1 Introduction

Before the 1960’s the majority of photoemission data were angle-integrated. Gobeli and co-workers in 1964 showed that momentum is conserved during the photoemission process and then proved that it could be possible to map out the complete band structure \[200\]. Initially, angle resolved photoemission detectors were single point energy detectors and could only find the energy dependence of outgoing electrons. At that time, the aperture of detectors allowed only electrons emitted from a small angle to enter the entrance slit of the analyser and, by moving samples through different angles, it was possible to probe different momenta and to map the complete band structure. However, there were limitations on the intensity and the resolution of the radiation sources, and also on the energy resolution of analysers. The early ARPES studies, like those on cuprates, were mapped in this way \[201\]. Before the 2D detectors there were also hemispherical electron energy analysers located completely inside the vacuum chamber \[202\]. These were moved inside the chamber so that they can detect the electrons emitted from the sample surface at different polar and azimuthal angles in order to perform angle resolved measurements \[202\]. Nowadays, in some laboratories this type of ARPES facility is still used in order to perform experiments \[203\]. In the last ten years, with the improvement of the experimental aspects of ARPES, the data sets are usually collected with a 2D detector which allows the detection of a wide angular range. The improvements achieved in the light sources (i.e., synchrotron sources) and the electron energy analysers have allowed scientists to perform ARPES experiments with good momentum and energy resolution, allowing to also measure band dispersion and map Fermi surfaces in a short time. Recently, A. S. Tremsin and co-workers have developed a new time of flight detector which is capable of recording both $X$ and $Y$ positions, (converted into 2-D momentum) and timing, $T$ (used to calculate the energy), of photoelectrons arriving at the detection plane simultaneously \[204\].

This chapter begins with an introduction section 3.1, followed by section 3.2, which gives a short description of the characteristics of synchrotron radiation (see subsection 3.2.1), and the state-of-the-art electron energy analyser Scienta R4000 (see subsection 3.2.2) used to acquire the data presented in this work. Subsection 3.3.1 presents how a typical 2D color map of $\text{Sr}_3\text{Ru}_2\text{O}_7$ is acquired with a Scienta R4000 spectrometer. Finally subsection 3.3.2 illustrates how the energy and momentum distribution curves (used in ARPES data analysis) are obtained from the 2D colour map. Section 3.4 describes in some details the floating zone method used in order to grow pure single crystals of $\text{Sr}_3\text{Ru}_2\text{O}_7$ used in this study. This section also describes the cleavage procedure of the samples in the experimental chamber.

3.2 Experimental Apparatus

An ARPES system is constituted by several components namely:

1. a complete vacuum system equipped with a manipulator, cryostat and a transfer arm;
2. an electron energy analyser;
3. a source of incident radiation which can be a standard laboratory source or synchrotron radiation.

In the following, we will review some of the fundamental aspects of synchrotron radiation and the state-of-the-art electron energy analyser, the Scienta R4000.
Figure 3.1: The electron storage ring of the national synchrotron radiation research centre BESSY II in Berlin, Germany. (a) Aerial view. (b) Model of the storage ring showing the inside view of Figure 3.1(a). High energy electrons (accelerated in a linear accelerator and a booster synchrotron) travel along a closed orbit in the storage ring, experience acceleration and emit light. (c) Schematic of an insertion device beamline. Before the light beam is focused and delivered to the sample for experiments, electrons undergo a complex monochromatization and focusing process which takes place inside each beamline by passing through several optical elements such as mirrors and diffraction gratings. Figure adapted from [205].

3.2.1 Synchrotron Radiation

The term synchrotron radiation designates the electromagnetic radiation that is produced when charged particles (usually electrons, but also positrons, protons, etc.) are forced by magnetic fields to move in a closed circular path at a speed close to the speed of light.

The movement of the electrons in the ring causes the emission of a continuous spectrum of light with different wavelengths and intensities. This allows scientists to select the wavelengths they require for their experiments, ranging from infrared to X-rays [206, 207]. Modern ARPES experiments are typically performed using synchrotron light sources [142].

The principal characteristics of synchrotron radiation are:

- high brilliance of the photon flux;
- full control of the polarisation of the radiation;
These characteristics make synchrotron radiation highly preferable with respect to conventional laboratory sources e.g. photon tunability plays a big role in the photoemission matrix elements, and also in the polarisation dependence of the measured photoemission intensity.

Figure 3.1(a) shows the aerial view of the BESSY II synchrotron facility located in Berlin, Germany. The synchrotron consists of many technical components such as the booster, the injection system, the storage ring, the beamlines where the light gets focused, monochromatised and delivered to the sample for experiments and many other components (see Figures 3.1(b) and 3.1(c)). Some functionalities of the main storage ring components will be explained in detail in the following.

1. **Injection system**

   From the electron source (electron gun), electrons are introduced into the injector system. Afterwards, these electrons from the low linear accelerator (principally a linear accelerator) are accelerated in a booster synchrotron to the operating energy of the storage ring (some GeV). These electrons are then transferred to the storage ring. Various electron bunches are injected to achieve the operational high beam intensity in the storage ring.

2. **Ultra high vacuum tube**

   The term ultra high vacuum (UHV) refers to any pressure below $1 \times 10^{-9}$ Torr. To attain such a low pressure, a vacuum chamber must be thoroughly closed from the outside and several pumps must be placed along the storage ring. This is usually realised by using all stainless steel parts closed together by soft copper gaskets cut with knife edges in both sides of the gasket and pumped down with several pumps [148]. Vacuum is necessary in order to avoid electron losses due to scattering on residual gas atoms. Electrons inside the storage ring are expected to circulate for many hours and produce synchrotron radiation with a minimum rate of loss once injected into a storage ring. For more information about the ultra high vacuum tube, the reader can consult Ref. [208].

3. **Magnets**

   The circular path of the storage ring consists of several types of magnets such as bending magnets, quadrupole magnets and sextupole magnets.

   - **Bending magnets** are generally used in order to deviate the electron beam so that it follows a closed circular path in the accelerator [209]. Therefore, electrons that are situated inside this region experience acceleration due to the Lorentz force and emit light [207]. This force is produced by the presence of a dipolar magnetic field perpendicular to the direction of motion of the electrons. During this process, energy is lost because of light emission and this loss is balanced by the use of radio frequency cavities that are located around the storage ring [206]. Therefore, bending magnets are also used as sources of synchrotron radiation and the radiation that they produce is polarised in the plane of the orbit and its emission spectrum ranges from the infrared to X-rays as a continuum. The location of the bending magnets defines the geometry of the storage ring.

   - **Quadrupole magnets** are used in analogy with optical systems in order to focus the electron beam in the synchrotron ring.
• **Sextupole magnets** are constituted of six magnets arranged around a common axis. They are necessary in order to correct chromatic aberrations caused by focusing errors for electrons with different energies [209].

4. **Insertion devices**

Insertion devices are situated in the straight line sections between two consecutive bending magnets in the storage ring. They consist of several magnets with opposing polarities, which force the electrons inside their region to wiggle (see Figure 3.2). It should be noted that each curve in the electron path results in the production of synchrotron radiation. There are three types of insertion devices:

- The **wigglers**, producing high intensity radiation, with a broad band of emission frequencies.
- The **undulators**, producing a quasi monochromatic radiation with high brightness.
- The **wavelength shifters** containing magnets capable to produce a very high magnetic field in the central pole for the production of hard X-rays.

The most common choice as radiation source in the photon energy range required by ARPES (i.e., soft X-rays) is undulators, because of their access to the full control of the photon polarization. This can range from linear horizontal and vertical to circularly left and right polarised light. This is achieved by changing the configuration of the magnets inside the undulator. The radiation directly enters the beamline (that guides the radiation to the experimental endstation) when it leaves the undulator.

5. **Beamline**

The beamline is situated after a radiation source (that could be either a bending magnet or an insertion device) and it is constituted of several components such as slits, mirrors, a monochromator (see Figure 3.1(c)), which makes the radiation monochromatic and focuses it on the sample in the experimental chamber for the data acquisition. Every beamline situated on the storage ring has its own special characteristics that are preferable for a particular kind of experiment [211]. A typical ARPES beamline is optimized to work in the $10 - 150$ eV photon energy range, and with a photon energy resolution $\lesssim 5$ meV. The most essential part of an ARPES end station is naturally the electron analyser, which will be explained in more detail in section 3.2.2.

All the ARPES data presented in this dissertation were taken at the $1^3$ end-station installed at the beamline UE112-lowE-PM-b of the synchrotron BESSY II in Berlin, Germany [205] (see Figures 3.1 and 3.3(c)). This instrument enables access to the very low temperatures that were needed for these studies, as well as possessing very high energy and angular resolutions (1 meV and $0.15^\circ$ respectively). The ARPES end-station is equipped with a Scienta R4000 hemispherical electron energy analyser.
Figure 3.3: (a) Schematic diagram of the Scienta hemispherical electron energy analyser. This setup is used to measure emitted photoelectrons from the sample surface. The two hemispheres (the inner and outer hemispherical plates with radius $R_1$ and $R_2$) deflect the electrons to produce a 2D image observed on the detector. (Figure from Ref. [212]) (b) Representation of the interior of the Scienta R4000 hemispherical electron energy analyser in 3D (note that for clarity the outer hemisphere in the picture is partially cut away). Electrons from the sample surface penetrate into an electrostatic lens system that focuses them onto an entrance slit. The electron paths are shown by the red, green, blue and yellow colors. The 2D detector located on the opposite side to the entrance slit consists of a camera which produces a 2D energy and momentum map. (Figure reproduced from Ref. [213]) (c) A picture showing a part of the 1$^3$ARPES endstation at BESSY.

3.2.2 The Scienta R4000 Electron Energy Analyzer

The hemispherical electron energy analyser is the most important instrument in all state-of-the-art ARPES experiments, and it must be able to provide high efficiency in the data acquisition over a wide angular range [214]. The Scienta R4000 electron energy analyser is doubly shielded by $\mu$-metal$^1$ in order to shield the inside from any magnetic field including that of the Earth. The sample is located in front of the lens (see Figure 3.3(a)) with a beam of monochromatic light which strikes the sample from the side. The acceptance angle depends on the distance from the sample to the entrance slit, the diameter of the opening of the lens and the lens voltages. It should be noted that the farther the sample is located from the opening, the smaller the acceptance angle.

Figure 3.3(b) shows a schematic drawing of a Scienta R4000, which consists of three important parts: the electron lens, which selects the electrons according to their ejection angle; the hemispherical energy

$^1\mu$-metal is a nickel-iron alloy (i.e., \( \approx 75\% \) nickel and \( 15\% \) iron, plus copper and molybdenum) that possesses a very high magnetic permeability [219].
analyser, which selects the electron according to their kinetic energy; and a 2D detector, which records the two quantities (kinetic energy and angle or momentum) for each photoelectron. More details of these three important parts of the Scienta analyser are given in the next paragraphs.

**Electron lens**

Once electrons are expelled from the sample, they move in a straight line through the vacuum until they attain the entrance slit of the lens. μ-metal shielding ensures that their trajectories are straight lines [148]. Once the emitted electrons enter the lens, they are directed towards the entrance slit of the hemispherical capacitor. Inside the electrostatic lens metal plates are kept a constant potential creating a static lens. Thus, electrons from the sample are focused by electrostatic fields. The emitted electrons are decelerated by the retarding voltage $V_r$ (see Figure 3.3(a)) which causes the speed of the moving electrons to be reduced before entering the hemispherical energy analyser through the aperture of the entrance slit. This retarding voltage is applied at the lens to decelerate the electrons to the pass energy (will be explained in the next paragraph), in order to scan various energies. Figure 3.4 shows the schematic path of the electrons inside the lens.

**Hemispherical energy analyser**

Electrons enter directly inside the two concentric hemispheres of the analyser, after leaving the lens. Figure 3.3(a) shows how this hemispherical analyser is made up of two metal hemispheres. The two half spheres are disposed in such a way that their centres of curvature are situated at the same point. An electric field is produced between the two half spheres (i.e., the inner and outer hemispheres) by applying differential voltages to each hemisphere. The application of differential voltages to each hemisphere allows to alter the electron’s trajectory depending on their incoming energy. Once electrons are inside the two hemispheres, the ones which possess a high energy will move faster and will end up closer to the outer sphere, while the other with the lower energy will end up closer to the inner sphere. But if the energy of the electrons is too low or too high, they will strike the walls of the two hemispheres before reaching the end of the two half spheres. Therefore, only electrons which possess the right kinetic energy can go through the hemispherical part of the analyser and pass through the exit slit. By adjusting the biasing voltage between the inner and outer hemispheres, $V$, the kinetic energy of the electron moving on the central path $R_0 = (R_1 + R_2)/2$ is given by the following formula:

$$E_P = \frac{eV}{R_2 \frac{R_1}{R_1 - R_2}}; \quad (3.1)$$
where, $e$ is the charge of an electron. This kinetic energy $E_P$ (3.1) is also called the pass energy $E_P$ of the analyser and it is determined by the radii $R_1$ and $R_2$ and the voltage applied between them. Electrons with different entrance angles and the same kinetic energy can still attain the exit aperture, despite the fact that they undergo slight different trajectories. The relation between the retarding voltage $V_r$ and the pass energy $E_P$ is expressed as [216]:

$$E_P = E_{kin} - eV_r - \Phi_A; \quad (3.2)$$

where $\Phi_A$ denotes the work function of the analyser as shown in Figure 2.1(b), $E_{kin}$ is the kinetic energy of the electron moving on paths different to the central path ($R_0 = (R_1 + R_2)/2$). Equation 3.2 shows how one can sweep $E_{kin}$ by sweeping $V_r$ or $E_P$. Then the energy resolution $\Delta E$ (defined as the full width at half maximum of the peak (FWHM)) is expected to be proportional to $E_P$. The energy resolution $\Delta E$ of the incident electrons into a hemisphere analyser is given by the following expression [216]:

$$\Delta E = E_P \left( \frac{W}{2R_0} + \frac{\alpha^2}{4} \right); \quad (3.3)$$

where $R_0$ is the average of the two concentric inner and outer hemispheres radii, $R_1$ and $R_2$ (i.e., $R_0 = (R_1 + R_2)/2$), $W$ is the mean slit width (i.e., $W = (W_1 + W_2)/2$ where $W_1$ and $W_2$ are the widths of entrance and exit slit respectively), and $\alpha$ is the angular half aperture of the electron beam at the entrance aperture. $\alpha$ is determined by the electrostatic lens system. The pass energy is usually fixed during an energy distribution curve (EDC) scan (for a constant energy resolution). Equation 3.3 shows that it is highly favourable to use a large hemisphere for a better resolution. In other words, the resolution is improved (smaller $\Delta E$) by decreasing the pass energy $E_P$ or by increasing the mean radius $R_0$ (see equation 3.3). In fact, the pass energy and the aperture sizes are usually set to achieve a good agreement between signal intensity and energy resolution.

The energy resolution of the analyser can also be written as:

$$\Delta E_\alpha = \sqrt{(\Delta E_0)^2 + (\Delta E_P)^2};$$

where $\Delta E_0$ is an intrinsic constant due to the stability of the electronics and precision of the mechanical parts and $\Delta E_P$ is proportional to the pass energy. With the Scienta R4000 electron energy analyser it is possible to reach a resolution better than 2 meV, which is a suitable energy scale for most phenomena in condensed matter physics. The entire energy resolution ($\Delta E_T$) of the experiment is determined as a function of both the contribution of the energy resolution from the synchrotron radiation monochromator light source with a photon energy $h\nu$ and the electron energy resolution of the analyser ($\Delta E_\alpha$) by the expression [217]:

$$\Delta E_T = \sqrt{(\Delta E_{h\nu})^2 + (\Delta E_\alpha)^2}.$$ 

Thus, the maximum signal is achieved by matching the photon energy and analyser resolutions for a fixed resolution. For the case of the parallel momentum resolution $\Delta k_\parallel$ (a parallel momentum resolution is the only one present because in this dissertation we are dealing with a two quasi-dimensional system), one should also take into account the angular resolution in an ARPES experiment for the influence of the lineshape of the observed peaks. By neglecting the contribution due to the finite energy resolution, the parallel momentum resolution is written as [141]:

$$\Delta k_\parallel \approx \sqrt{\frac{2mE_{kin}}{\hbar^2}} \cdot \cos \varphi \cdot \Delta \varphi; \quad (3.4)$$
where $\Delta \varphi$ is defined as the finite acceptance angle of the electron analyser. Equation 5.6 shows how the parallel momentum resolution is better at lower kinetic energy $E_{\text{kin}}$, i.e., at lower photon energy, and larger polar angular $\varphi$. Most of the ARPES experiments are performed in the ultraviolet (generally for $h\nu < 100$ eV) because if $\frac{\Delta V_r}{V_r}$ fixed, then $\Delta V_r$ is smaller at low $V_r$ and therefore at low $E_{\text{kin}}$, i.e., low photon energy. Similarly holds for $\Delta E_{h\nu}$ if $\Delta E_{h\nu}$ is fixed.

In Figure 3.3(b), the apertures are replaced by slits, which allows electrons with a large range of emission angles to enter the electron energy analyser simultaneously. Figure 3.3(b) shows paths of electrons inside the two concentric hemispheres of the analyser. In this figure, green and red electron paths have the same momentum and different energies, while blue and yellow electron paths possess the same energy, but different momenta. We also see that electrons with different momenta enter the slit at different locations, enabling the electron’s momentum to be measured along the slit direction, while the electrons with different energies and same momenta enter the slit at the same position.

2D detector

After passing through the hemispheres of the analyser, electrons hit the 2D detector. The location where an electron hits the 2D detector is now determined by the electron kinetic energy and the emission angle. The electron lens focuses parallel electron beams at different parts of the entrance slit situated in the focal plane of the lens, so that, after passing through the electric field between the two hemispheres, the electrons will be separated according to their emission angle and their kinetic energy at the same time forming a two dimensional image on the detector. The Scienta software takes into account the correct conversion between the position on the detector and the electron kinetic energy/emission angle. The detector is constituted of an electron micro channel plates (MCP) coupled to a phosphorus screen positioned in front of a high sensitivity charge-couple-device (CCD) camera [148]. A single incident electron converted into million of electrons through secondary emission by the electron multiplier plate [148]. Thus, this package of electrons strike the screen and creates a flash of light. A 2D energy momentum map is then produced as shown in Figure 3.3(b).

It should be noted that the energy window on the 2D detector is relatively small. Thus, if a wide energy range is needed, the retarding voltage has to be scanned (swept mode). After one scan, the resulting data is a 2D matrix where one axis is represented by the emission angle and another one by the electron kinetic energy. The acceptance angle of the Scienta is 40° given that the angular resolution on the detector is about 0.05°, this means that approximately 800 spectra can be measured simultaneously. In addition to the fast data acquisition rate, the advantage of this new electron energy analyser is the direct visualisation of the features in the raw photoemission data, as depicted in Figure 3.3(b). This invention has brought great efficiency in the rate of data acquisition during ARPES experiments.

3.3 Energy-Momentum 2D Images and Data Visualization

In an ARPES experiment, the representation of the dataset consists of a multi-dimensional map of photoemission intensity as a function of $k$ ($k_x$, $k_y$ and/or $k_z$) and binding energy $E_B$, in order to map the band dispersion along that direction in the reciprocal space. In this section, a detailed description of how a 2D colour photoemission intensity image of $\text{Sr}_3\text{Ru}_2\text{O}_7$ is visualized after being measured with the Scienta R4000 (see subsection 3.3.1) is presented. Subsection 3.3.2 presents ways to analyse such 2D images.
Figure 3.5: A basic schematic representation of how 2D image colour map (acquired in the case on Sr$_3$Ru$_2$O$_7$ at the photon energy $h\nu = 25$ eV and temperature $T = 1.03$ K) is acquired with a Scienta R4000 spectrometer. The red and blue regions denote the maximum and minimum photoemission intensity respectively. The high intensity colour corresponds to the quasi-particle peak dispersion approaching the Fermi level. The vector $n$ is the normal vector to the sample surface while $\varphi$, $\theta$ and $\alpha$ are azimuthal, polar and tilt angles respectively. Figure modified from Ref. [142].

3.3.1 2D Colour Maps

With the Scienta R4000 electron energy analyser described in subsection 3.2.2, it is possible to acquire a two-dimensional (2D) matrix of the photoelectrons intensity $I(E_{\text{kin}}, \theta, \varphi)$ where the kinetic energy $E_{\text{kin}}$ of electrons is given as a function of the emission angle $\theta$ along a particular direction given by $\varphi$. Usually 2D colour maps are used because they represent data more conveniently [141], as colours encode the intensity as a function of energy and angle (momentum). Figure 3.5 illustrates the arrangement of the experimental geometry of ARPES together with the electron energy analyser. Also shown is an example of a 2D image of Sr$_3$Ru$_2$O$_7$ (obtained at the photon energy $h\nu = 25$ eV and temperature $T = 1.03$ K) collected by a Scienta R4000 in the near Fermi level region, where the red regions represent the maximum of the photoemission intensity, corresponding to a dispersing peak approaching the Fermi level. This figure also shows the direction of the incident monochromatic light (see the the violet light beam), the vector normal to the surface $n$, the outgoing photoelectrons and the $\pm 15^\circ$ analyser acceptance angle of the outgoing photoelectrons in momentum space. A series of intensity images can be collected when the polar ($\theta$) and azimuthal ($\varphi$) angles of the sample are moved with respect to the entrance slit while the tilt angle ($\alpha$) is implicitly scanned through the acquisition process, i.e., the fact that the acceptance angle of the Scienta is $30^\circ$. This allows to map the entire 1st Brillouin zone in the reciprocal space.
3.3.2 Momentum Distribution Curves (MDCs) and Energy Distribution Curves (EDCs)

In modern ARPES approximately 800 spectra can be measured simultaneously in both energy and momentum-space (see Figure 3.6), so that one can slice the two-dimensional image into different one-dimensional strips. A slice showing the photoelectron intensity at a fixed values of \(|k|\) (actually, fixed angle) as a function of binding energy \(E_B\) is the traditional EDC (see Figure 3.6). To the contrary, the photoelectron intensity plotted at a fixed binding energy \(E_B\) as a function of momentum was recently introduced \([218, 219]\) and it is called a momentum distribution curve (MDC) (see Figure 3.6). Thus, MDC and EDC are the two standard curves which are used frequently in order to analyse the type of 2D image from ARPES data present in Figure 3.6.

The expression of the EDC function is given by the following formula \([220]\):

\[
I_{EDC}(\omega) = I_0(k_{\text{const}}, \hbar\nu, A) \frac{1}{\pi} \frac{Im\Sigma(k, \omega)}{[\omega - \epsilon_k - Re\Sigma(k, \omega)]^2 + [Im\Sigma(k, \omega)]^2} f(\omega); \tag{3.5}
\]

where \(f(\omega)\) is the Fermi Dirac distribution function which signifies that ARPES measures only the occupied states and \(I_0(k_{\text{const}}, \hbar\nu, A)\) is the magnitude of the matrix element at a constant electron momentum \(k\) and polarization of the incoming photon \([220]\). \(Re\Sigma(k, \omega)\) and \(Im\Sigma(k, \omega)\) are real and imaginary parts of the self-energy respectively. \(\omega\) denotes the energy. We can see from equation 3.5 that the EDC function has a constant matrix element for a constant momentum, which represents the advantage of using EDCs in the data analysis process. Nevertheless, the EDC function given by equation 3.5 has a non-trivial \(\omega\)-dependence, i.e.,:

- An EDC function is neither a Lorentzian function, nor any simple function.
- The EDC function (3.5) possesses the Fermi function term, that makes the EDC function asymmetric in such a way that its peak position is not given by the pole condition.
- Finally, the EDC width does not only depend on the imaginary part of the self-energy \((Im\Sigma(k, \omega))\), but on both the imaginary and real \((Re\Sigma(k, \omega))\) parts of the self-energy.

All these above restrictions make the data analysis of the EDC function more complicated.
With the development of the Scienta electron energy analyser, that can measure simultaneously the 2D map with better resolution, the MDC analysis becomes available for ARPES data analysis. The MDC function can be written in the form [220]:

\[
I_{MDC}(\omega) = I_0(k, \hbar \nu, A) \frac{1}{\pi} \frac{\text{Im} \Sigma(k, \omega)}{[\omega - \epsilon_k - \text{Re} \Sigma(k, \omega)]^2 + [\text{Im} \Sigma(k, \omega)]^2} f(\omega_0).
\]

Since the MDC is obtained at constant energies, its function has a simpler lineshape, as the inelastic background and the Fermi function depend weakly on the momentum and strongly on the energy. This suggests that the MDC analysis presents some advantages such as:

- The MDC lineshape is a symmetric Lorentzian in the vicinity of the Fermi energy, and it is not affected by the Fermi function.
- The position of renormalized and non-renormalized bands are given by the Lorentzian peak positions.

Thus, this makes the MDC analysis very useful to follow band dispersion and extract the real part of the self-energy function \( \text{Re} \Sigma(k, \omega) \). The extraction of the imaginary part of the self-energy \( \text{Im} \Sigma(k, \omega) \) through the MDC analysis is however very complicated, since the knowledge of the non-interacting (bare band dispersion) velocity is required and it is not measured experimentally [186]. From the above discussion, we can see that the quantities derived from EDCs and MDCs are different. Extracting the band dispersion from an MDC analysis is generally not difficult when one considers the bare dispersion as a linear line (see Figure 2.9(a) in subsection 2.8.1); the resulting dispersion \( \omega(k) \) can be compared to a non-interacting bare band \( \epsilon_k \) to extract the real part of the self-energy \( \text{Re} \Sigma(k, \omega) \) as well as the lifetime information. A standard model to investigate many-body interactions in detail is the use of MDC analysis [179, 191].

In conclusion, Figure 3.6 summarised the relationship between the obtained ARPES spectra, the energy distribution curve (EDC) and the momentum distribution curve (MDC). This relationship will be used for the analysis of ARPES spectra of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) in chapter 5. The use of the MDCs and EDCs for the ARPES spectra analysis, allows to extract the dispersion and scattering rate of quasiparticles and to observe phonon effects in the electronic structure of various materials. It also allow to study different features of bands crossing the Fermi level and the renormalized bands that present kink behaviour in electronic band dispersion. More detailed reviews about the EDCs and MDCs methods and their relations to the single particle spectral function, are given in Refs. [186, 187, 189].

### 3.4 Sample Preparation for ARPES

The starting point of all experimental research in condensed matter physics is to get good samples to investigate. Therefore, to resolve the intrinsic properties of some samples, high quality single crystals are required since the ground state properties of ruthenates are very sensitive to the quantity of impurities in the samples [221, 222, 223]. For instance, the thermodynamic properties of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \), especially in a magnetic field, were found to depend significantly on the sample quality after a detailed growth study by Perry and coworkers [221]. Additionally, multiple metamagnetic transitions [122] and nematic phase [129] have been discovered in \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) thanks to the high purity of the crystals. The method best suited for the synthesis of high quality samples with almost no impurities is the floating zone technique (FZT). Generally, strontium ruthenate crystals are grown using this technique. All the single crystals...
3.4.1 The Floating Zone Technique (FZT)

The important information presented in this section are mainly based on references [4, 225]. FZT is a popular method for single crystal growth because it is performed without a container, for the precursor materials so that the contamination from the container (for instance sample holders or crucibles) can be avoided.

A sketch of the floating zone furnace with double ellipsoidal mirrors is presented in Figure 3.7(a). This floating zone furnace contains a sealed quartz chamber, which enables the growth of single crystals to be conducted in a large range of carefully controlled atmospheres and pressures [225]. Before starting the growth process, it is necessary to put the proper amounts of precursors (in powder form) that will constitute the eventual sample. The mix of this powder is then packed into rubber sheaths and pressed into the shape of a rod. Once the powder is pressed, the casing can be removed and the rod (mixed powder with the rod shape) is sintered (see the black rod which represents the crystal in Figure 3.7(a)), ready for use in the FZ furnace. A small hole pierced through the upper part of the feed rod is used to hang it from the upper drive shaft of the furnace using platinum wire. A seed rod, which is part of a crystalline rod of identical composition, was fixed to the sample holder on the top of the lower

---

The dimension of rods used in the FZT are about $4 - 6$ mm in diameter and $4 - 5$ cm in length [4].
Figure 3.8: Illustration of sample cleaving procedure: (a) firstly the metal rod is glued to the top of the sample after the sample has been glued to the sample holder and then it is introduced in ultra high vacuum (UHV). (b) The metal rod is hit using a screwdriver in order to get a cleaved sample in UHV.

 Shaft. A narrow floating zone of molten material adjoining the rods is produced, when the heat from halogen bulbs is focused by ellipsoidal reflecting mirrors. These two mirrors allow the infra-red radiation to focus into a narrow band around the rod. The rods are rotated in contrary directions in order to favour uniform mixing of the sample and reduce gradient concentration at the solid/liquid interface. Crystalline layers are gradually deposited onto the seed crystal by simultaneously reducing the rotating drive shafts, when the floating zone has stabilized. The growth takes place at the boundary between the molten zone and the seed rod, where the microscopic preference of the cooling melt is to grow with the symmetry identical to the seed crystal. The growth of the crystal and the control of the stability of the FZT can be controlled using a video camera located inside the image furnace and monitored by computer.

Figure 3.7(a) also shows how the molten zone is formed and maintained between two solid rods by its own surface tension. When a small section of the rod is melted, the molten zone is then translated along the sample length by displacing the material with respect to the radiation focus. Therefore, the crystal material is grown on the solidifying end of the float zone.

An example of the single crystal of Sr$_3$Ru$_2$O$_7$ grown by FZT is presented in Figure 3.7(b). More information concerning this technique can be found in references [4, 225, 227].

3.4.2 Sample Cleaving

Since photoemission is a surface sensitive technique [147], before performing any ARPES experiment the surface of the sample should be cleaned and stay free of contamination during the experiment. One of the methods used in order to obtain such a clean surface is to cleave the sample in situ inside the ultra high vacuum (UHV) chamber where the measurements are going to take place. The following expands in more detail the cleaving procedure.
The steps of the cleavage method are as follows:

- a ceramic post or a metal rod (see Figure 3.8(a)) is glued to the top of the sample surface with a conducting silver epoxy\(^3\);
- the bottom surface of the sample is also glued in the same way as the metal rod to the sample holder (see Figure 3.8(a));
- to create contrast in the signal coming from the sample during the experiment, so that it can be noticed when the photon beam is not well focused on the measured sample, graphite is sprayed on the sample and the sample holder;
- after doing the three steps above, the sample is then inserted into the preparation chamber on a carousel before transferring it into the UHV chamber, onto the manipulator (which is the measuring chamber);
- the metal rod is then in situ pushed by a screwdriver and it is removed with some part of the sample. The rest of the sample which is fixed to the sample holder is a cleaved (broken) sample with a clean and fresh surface ready to be measured (see Figure 3.8(b)).

To perform a successful experiment and to preserve the cleave sample free from contamination, during the whole ARPES experiment, the chamber must be kept in UHV conditions at a pressure of \(\approx 2 \times 10^{-10}\) mbar.

\(^3\)The conductive silver epoxy is used because during the cleaving process, the exposed surfaces have to be conductive in order to avoid charging during the photoemission. Additionally, if the silver epoxy is used during the cleaving, the holder has to be heated to 120\(^\circ\)C for 20 minutes in order to harden it \([228]\).
4. The Fermi Surface of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \)

4.1 Introduction

The surface of constant energy \( E = E_F \) in the reciprocal space (or \( k \)-space) is called the Fermi surface (FS). This surface separates the unfilled states/bands from the filled states/bands in non-interacting systems\(^1\), whereas for interacting systems, a sharp discontinuity in the momentum distribution at absolute zero temperature \( (T = 0 \text{ K}) \) is frequently used as the definition of the Fermi level \([38, 229]\). The FS shape determines the electrical properties of the metal, which depend on the occupancy of states near the Fermi surface \([38]\). The FS also plays an important role in developing and understanding the physics of a material by predicting the thermal, magnetic and optical properties of metals, doped semiconductors, and semi-metals. Its shape is determined by the periodicity and symmetry of the crystalline lattice and from the occupation of electronic energy bands. Thus, we can simply say that understanding the properties of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) depends on a knowledge of its FS.

In this chapter, the experimental Fermi surface maps of the bilayered strontium ruthenate \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) are presented. This chapter begins with an introductory section 4.1 followed by section 4.2 that gives the experimental details for the FS mapping for this work. This section is followed by section 4.3 that clarifies the procedure used to determine the Fermi-level of the experimental band dispersions together with the overall experimental energy resolution used during the whole experiment. It continues with section 4.4 that explains how the first Brillouin zone of the compound \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) was determined. Section 4.5 focuses on the explanation of the construction of the FS maps of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) starting from the FS of the parent compound \( \text{Sr}_2\text{RuO}_4 \). Section 4.6 shows the technical details of the procedure used to reconstruct the FS maps seen in this work. Section 4.7 presents the analysis of the four experimental maps for \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) obtained in this study. Section 4.8 focuses on the details of distortions observed in such maps. A summary of the chapter is presented in section 4.9.

4.2 Experimental Details for Fermi Surface Mapping

All ARPES data presented in this dissertation were taken at the \( ^1 \) 3\(^2 \) ARPES endstation installed at the beamline of the \( 3^{\text{rd}} \) generation high-brilliance synchrotron radiation source BESSY II in Berlin (Germany), using a Scienta R4000 electron energy analyser and a \( ^3 \)He cryostat \([205]\). \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) single crystals of dimensions of approximately \( 1 \times 1 \times 0.5 \text{ mm}^3 \) were measured. Photon energies of 60 eV, 65 eV, 85 eV and 95 eV with a linear horizontal polarization were used to acquire these FS maps. During the whole experiment, the sample temperature ranged from 5 K to 1 K, and the temperature will be specified for every map. The Fermi surface maps shown in this chapter were acquired using combined energy resolutions\(^2\) of 6.7 meV, 10.2 meV, 18.9 meV, and 12.4 meV corresponding to each photon energy given above while keeping the same angular resolution of 0.15°.

\(^1\)The concept of non-interacting systems is defined as a system with no interactions among the constituents of the system.

\(^2\)The total width of the Fermi edge is expressed by the Fermi-Dirac distribution function, convoluted with a Gaussian whose the full width at half maximum (FWHM) equals the overall experimental resolution (photon + electron analyser) (see section 3.2.2). The individual energy distribution curve (EDC) with a Fermi-Dirac distribution shape taken at each particular momentum was fitted with these two convolved functions in order to get the experimental energy resolutions (FWHM) given in this study.
Section 4.3. Determination of the Fermi Energy $E_F$

PES and ARPES spectra are generally displayed in binding energies relative to the Fermi edge of the sample. Therefore, it is important to determine the kinetic energy corresponding to the Fermi energy $E_F$ for a given set of data acquired in the same experimental conditions, in such a way that the conversion of energy can be done from the kinetic energy scale to the binding energy scale. The binding energy is measured relative to the Fermi energy. To determine $E_F$ for every sample measured and for every incoming photon energy used, it is necessary to fit the energy distribution curves (EDCs) taken at a particular momentum with a Fermi-Dirac distribution function given by:

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - \mu}{k_B T}\right)}, \quad (4.1)$$

where $E$ is the energy of the single photoelectrons, $\mu$ is the chemical potential, $k_B$ is the Boltzmann constant and $T$ is the temperature of the sample. In order to take into account the electrons produced by higher order light coming from optics of the beamline and the undulator of the synchrotron ring, a linear background was also introduced in the fitting when necessary. Figure 4.1(a) presents a set of equally spaced energy distribution curves taken at different momenta for an ARPES band dispersion collected at a photon energy of 60 eV along the direction tilted 20° clockwise with respect to the ΓX direction of the first Brillouin zone. To get the Fermi energy $E_F$, a single EDC with a Fermi-Dirac distribution line-shape was taken out of the equally spaced EDCs (the pink one). This particular EDC was selected since it does not present a quasi-particle peak which complicates the determination of the Fermi energy.

**Figure 4.1:** (a) ARPES energy distribution curves (EDCs) measured along the high-symmetry direction parallel to the line tilted 20° clockwise with respect to the ΓX line of the first Brillouin zone as indicated by the black line drawing on top of the diamond located in the bottom left side of Figure 4.1(a). The pink curve represents the EDC fitted in (b). (b) EDC fitting with a Fermi-Dirac distribution function represented by the blue curve.

---

3Note that the Fermi energy is equal to the chemical potential $\mu$ (which usually depends on temperature) at $T = 0$ K and it is always called chemical potential $\mu$ even at higher temperatures, but they are all different at $T \neq 0$ K [230]
Table 4.1: Different Fermi energies ($E_F$) obtained from EDCs fitting of the five samples measured. For every photon energy used in the experiment, FWHM values, pass energy of the analyser and the type of polarization used to construct the Fermi surface maps are also shown.

4In order to verified the precision of the obtained value of $E_F$, 10 different EDCs have been fitted in every case, and the change in $E_F$ value was found to be $\sim \pm 0.7$ meV.
In this section we will first explain how atoms can be packed together in order to form simple crystal structures. We will continue by giving a clear definition of the first Brillouin zone (BZ) followed by how to construct it. Finally we will present a discussion on how the first BZ of Sr$_3$Ru$_2$O$_7$ was determined.

A crystal is made up by an infinite repetition of identical structural units named unit cells. The unit cell is the smallest structural unit that can be used as the building block of a crystal [232]. The smallest structural unit needed in order to reproduce a particular crystal structure may include one or many atoms. All crystals are described in terms of a Bravais lattice, with a group of atoms attached to each lattice point [38]. This group of atoms is called a “basis” and when it is repeated in space it forms the crystal structure (see Figure 4.2(b)). In the structure of the crystal, each atom in a unit cell is related to every other equivalent atom in other unit cells (even at an infinite distance) by translational symmetry. Primitive unit cells hold lattice points and form the entire lattice by translation, without coinciding and without space missing between unit cells.

There are diverse methods to select the primitive unit cell. For simplicity, it is suitable to select a primitive unit cell that is centred about a lattice point [229] (see Figure 4.2(a)). The Wigner-Seitz cell about a lattice point is defined as a region of space that is closer to that lattice point than to any other lattice point [38, 197] (see Figure 4.2(b)). Each Bravais lattice in real space has a corresponding reciprocal space.

---

**Figure 4.2:** (a) Two dimensional square Bravais lattice where primitive vectors $b_1$ and $b_2$ form the atomic basis. This crystal structure is constructed by the unit cell containing one lattice point translated by vector $R = cb_1 + db_2$ (where $c$ and $d$ are non-zero integer numbers). The sketch shows how atoms are arranged after translation. (b) Construction of the Wigner-Seitz cell in real space. (c) The first Brillouin zone is the Wigner-Seitz cell of the reciprocal space.
reciprocal lattice in the reciprocal $k$-space. The reciprocal lattice does not depend on the atomic basis, it depends only on the Bravais lattice. The reciprocal lattice is described as the set of all vectors $G$ that satisfy the equation $e^{iG \cdot R} = 1$ for all lattice point position vectors $R$. The real space vector $R$ is defined by $R = n_1 b_1 + n_2 b_2 + n_3 b_3$, with $n \in \mathbb{N}$ and $b_1, b_2, b_3$ are a set of primitive vectors for the direct lattice. The reciprocal lattice $(b_1^*, b_2^*, b_3^*)$ can then be determined by generating the three primitive vectors through the formulæ

\[
\begin{align*}
    b_1^* &= 2\pi \frac{b_2 \times b_3}{|b_1 \cdot (b_2 \times b_3)|}; \\
    b_2^* &= 2\pi \frac{b_3 \times b_1}{|b_1 \cdot (b_2 \times b_3)|}; \\
    b_3^* &= 2\pi \frac{b_1 \times b_2}{|b_1 \cdot (b_2 \times b_3)|}
\end{align*}
\]

where the scalar triple product $|b_1 \cdot (b_2 \times b_3)|$ is the volume of the unit cell in real space. The reciprocal primitive vectors satisfy the relation $b_i^* \cdot b_j = 2\pi \delta_{ij}$, $(i,j = 1,2,3)$ where $\delta_{ij}$ is the Kronecker delta symbol defined by $\delta_{ij} = 0$ if $i \neq j$ or $\delta_{ij} = 1$ if $i = j$. By analogy to the translation vectors of the regular lattice (direct lattice), we can also define the general translation reciprocal lattice vector $G$ by $G = m_1 b_1^* + m_2 b_2^* + m_3 b_3^*$, where $m_1, m_2$ and $m_3$ are integers. Since the crystal structure of Sr$_3$Ru$_2$O$_7$ is a quasi-two dimensional tetragonal structure (see subsection 1.4.1 for more details), its lattice unit cell in the $ab$ plane is a square in two dimensions, i.e., $b_1 = b_2$, the third dimension can be neglected as we are dealing with a 2D structure, so of course $b_3 = 0$. Thus, by considering a 2D square lattice unit cell, equations 4.2 become: \[38\]

\[
\begin{align*}
    b_1 = \frac{2\pi}{\sqrt{2}}; \\
    b_2 = \frac{2\pi}{\sqrt{2}}.
\end{align*}
\]

The first Brillouin zone (BZ) is obtained by constructing the perpendicular bisectors on the shortest lattice vectors. The area that is surrounded by these perpendicular bisectors is called the first BZ. An example of the construction of the first BZ for the two dimension reciprocal space is shown in Figure 4.2(c). The Wigner-Seitz cell of the reciprocal space is the first BZ, and it is also defined as an area of the reciprocal space that can be reached from the origin by crossing no Bragg planes\footnote{Bragg planes are all planes that bisect lines joining the origin to points of the reciprocal lattice \[38\].}. It should be noted that the Wigner-Seitz cell of the real lattice is constructed in exactly the same way as the first BZ.

After giving an explanation on the constitution of the crystal and the definition of the first BZ above, let us now deal with the determination of the BZ of Sr$_3$Ru$_2$O$_7$. The crystal structure of layered Sr$_3$Ru$_2$O$_7$ has been analysed by neutron powder diffraction by Shaked and Huang \[115, 117\]. The experimental ARPES and electronic structure studies of the Fermi surface of this compound by Tamai et al. \[21\] have presented the consequence of this rotation, i.e., an elongation by $\sqrt{2}$. Figure 4.3 shows the unit cell in the reciprocal space and the positions of the high symmetry points ($\Gamma$, $X$ and $M$). As the $\Gamma$ point is the center of the first BZ, it is also the center of the rotated square BZ (see the black diamond in Figure...
4.5 Construction of the Fermi Surface from Basic Arguments

The Fermi surface (FS) plot of Sr$_2$RuO$_4$ was discussed in some detail in section 1.3.1 of Chapter 1. It actually constitutes a good starting point for understanding the rather more complex Fermi surface topology of Sr$_3$Ru$_2$O$_7$. In fact, the Fermi surface of Sr$_3$Ru$_2$O$_7$ can be constructed from the FS of Sr$_2$RuO$_4$ by using the argument of:

1. band folding$^7$ presented in Refs [71, 83, 93].
2. the bilayer splitting due to the interaction of the two adjacent RuO$_2$ octahedra in the unit cell.

In both materials, the energy bands largely originate from the Ru 4d orbitals which cross the Fermi energy. In the following we first consider the single RuO$_2$ layer, then we incorporate the effects of bringing two of these layers together into a bilayer structure. Finally we take into account the effect of the rotation of octahedra in the ab plane that causes a $\sqrt{2} \times \sqrt{2}$ reconstruction of the unit cell by back-folding the Fermi surface sheets and the energy bands. By these back-folding arguments an understanding of the structure and orbital nature of this complex Fermi surface is presented.

$^7$This argument of band folding does not implicate any band structure calculation, but only the simple law that bands cannot cross one another, and hybridise instead.
We start by an explanation of the origin of bands in the Fermi surface of Sr$_2$RuO$_4$. At the Fermi surface, the electronic states are composed of Ru $4d$ orbitals as mentioned above. Given that the Ru $d_{xz}$ orbitals hybridise strongly through the oxygen $2p$ orbitals along the $x$ direction and only weakly in $y$, this strongly directional hybridisation forms quasi one-dimensional bands as shown by the two red lines in Figure 4.4(a). Along the opposite directions the $d_{yz}$ orbital does the same (see the two blue lines in Figure 4.4(a)). The $d_{xz}$ and $d_{yz}$ give rise to almost no dispersion in the $z$ direction. Therefore, the Fermi surface corresponding to these bands should be close to two dimensional in the $k_x k_z$ and $k_y k_z$ directions [93]. Ru $d_{xy}$ orbitals hybridise equally in all directions through the oxygen $2p_x$ and $2p_y$ orbitals to form a quasi two-dimensional band. This band is close to a perfect circular Fermi surface sheet in the $k_x k_y$ plane as shown by the green circle in Figure 4.4(a). These one-dimensional bands (the red and blue one) and the two dimensional band (the green one) present in Figure 4.4(a) then cross with each other in certain regions of the BZ (see Figure 4.4(a)), where hybridisation gaps arise and the sheets reconnect into closed surfaces (see Figure 4.4(b)). These closed surfaces form the FS of Sr$_2$RuO$_4$. The resulting FS of Sr$_2$RuO$_4$ possesses three bands labelled $\alpha$, $\beta$ and $\gamma$ originating from the hybridization of the $d_{xy}$, $d_{xz}$ and $d_{yz}$ orbitals of the Ru atoms with O $2p_x$ and $2p_y$ orbitals [88, 233], as shown in Figure 4.4(b). This construction is appropriate to the fourfold rotational symmetry of the 14 mmm space group. $\alpha$ is a hole-like pocket centred at the $X$ point, while the $\beta$ and $\gamma$ bands are electron-like pockets centred at the $\Gamma$ point [73].
The change from a single layer to a double layer unit cell in Sr$_2$RuO$_4$ causes a bilayer splitting, i.e., the doubling of the number of bands, but it does not affect the quasi-two dimensionality of the Fermi surface. We now take into account the effects of this bilayer splitting. Due to such splitting, one expects each band to duplicate. Therefore the result is different from that of Sr$_2$RuO$_4$. One begins with six surfaces (see Figure 4.4(c)), with four that originate from the $d_{xy}$, $d_{yz}$ orbitals, which are connected at the crossing points. One should obtain a result analogous to that shown in Figure 4.4(d).

Without the $\sqrt{2} \times \sqrt{2}$ reconstruction due to the octahedral rotation, the FS of Sr$_3$Ru$_2$O$_7$ should look like Figure 4.4(d). Since the BZ reconstructs into a square half of its original size and rotated by 45° due to the in-plane rotation of the octahedra, back-folding of the bands takes place into the reduced zone as shown in Figure 4.4(e). The new BZ is shown by the violet diamond in Figure 4.4(e) and 4.4(f). Many band crossings are visible in Figure 4.4(e) and the method by which the surfaces reconnect is very complicated. The FS of Sr$_3$Ru$_2$O$_7$ with rotations is obtained by anti crossing these bands. In this complicated arrangement there are several possible results and it is not a priori certain which one will occur. Nevertheless, one can acquire hints from recent ARPES measurements [21] and the reconnection (this reconnection is not accepted by proposed in a couple of references because of the importance difference observed on the FS shape) which is accepted by a couple of references is shown in Figure 4.4(f). This argument, but by no means strict, presents good agreement with ARPES and Density Functional Theory (DFT) results, see Figure 4.4(f) and 4.5(b). Figure 4.5(b) shows the Fermi surface in the $k_x k_y$ plane as extracted from an ARPES measurements (Figure 4.5(a)) by Tamai et al. [21]. Though different in detail, some geometrical similarities between the prediction and the measurements based on a very simple model is almost remarkable.

For an understanding of the band structure of Sr$_3$Ru$_2$O$_7$, one can assume that the above assumptions are a good starting point [238]. From Figure 4.5(b), six FS sheets have been identified by using ARPES measurement on Sr$_3$Ru$_2$O$_7$ and labelled $\alpha_1$, $\alpha_2$, $\gamma_1$, $\gamma_2$, $\beta$ and $\delta$ [21]. These sheets are thus labelled in conformity to their relation to the Fermi surface and band structure in Sr$_2$RuO$_4$. For instance the $\alpha_1$ and $\alpha_2$ sheets are mostly derived from the $\alpha$ FS sheet of Sr$_2$RuO$_4$ which possesses $d_{xz}$ and $d_{yz}$ orbital character respectively (see section 1.2 and Figure 1.4). The two sheets $\gamma_1$ and $\gamma_2$ are labelled like this for their relation with the $\gamma$ sheet of Sr$_2$RuO$_4$, or the $d_{xy}$ orbital, although they are also hybridised partly.

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8Sr$_3$Ru$_2$O$_7$ possesses four instead of two non-equivalent Ru atoms in the unit cell after rotation of RuO$_6$ octahedra. After this rotation the number of $d$ bands crossing the Fermi level changes from three to six [93]. The same scenario, i.e., the bilayer band splitting observed in this system, was also observed in both normal and superconducting states in the high-$T_c$ superconductors cuprates [234, 235].

9The anti crossing rule was formulated in 1929 by Von Neumann and Wigner [236]. Thus they were proving the theorem that was already put forward earlier by Hund [237]. The anti crossing in this section is defined as the fact that two bands in the reciprocal space cannot cross each other.
Section 4.5. Construction of the Fermi Surface from Basic Arguments

Figure 4.6: Fermi surface of Sr$_3$Ru$_2$O$_7$ obtained by a local-density approximation + spin-orbit coupling (LDA+SO) calculation with different orbital contributions namely, $d_{xz,yz}$ (blue color), $d_{xy}$ (red color) and $d_{x^2-y^2}$ (with a yellow color) orbitals. This figure shows more than the first Brillouin zone and it has been rotated by $45^\circ$ in order to compare features observed around the high symmetry points $X$, $M$ and $\Gamma$ with Figure 4.5. Figure reproduced from Ref. [19].

with a band parent to the $\beta$ sheet of Sr$_2$RuO$_4$. It is not actually known for certain whether $\gamma_2$ actually crosses the Fermi energy ($E_F$) or exists below $E_F$ [93]. Finally, the $\delta$ FS sheet does not appear in Figure 4.4(f) as specified by the DFT calculations in [71, 144]. It originates from the $d_{x^2-y^2}$ band stepped down from the $e_g$ manifold above the Fermi energy, as deduced from Local-Density Approximation (LDA) calculations by Singh and Mazin [144].

The shape and character of these FS sheets are as follows: the circle ($\delta$) shaped electron pocket, the square ($\alpha_1$) and cross ($\alpha_2$) shaped hole pockets are centred at the $\Gamma$ point. Two lens shaped ($\beta$ and $\gamma_1$) electron pockets are centred at the $M$ point and the small lens shaped ($\gamma_2$) hole pockets are centred at the $X$ point. Figure 4.5(d) presents two dimension FS centred around $\Gamma$ point at $k_z = 0$ obtained in the first calculation of the band structure of Sr$_3$Ru$_2$O$_7$ by Singh and Mazin [144], using the general potential linearised augmented plane wave method on the distorted unit cell [93]. One can see from this FS that identifying all the different FS sheets can be a difficult task without ARPES data. Figure 4.5(c) presents LDA calculations performed by Singh [21], for an octahedral rotation of 6.8o. The black lines represent the FS at the plane $k_z = \pi/2$ showing the extent of the $k_z$ dispersion and the blue lines represent the FS at the basal plane $k_z = 0$ [21, 93]. From the FS obtained by Singh (Figure 4.5(c)) [21] it is straightforward to identify the FS sheets centred at the $\Gamma$ point since they are in agreement with the FS obtained from basics arguments in section 4.5, the FS obtained by ARPES measurements, and the one presented by Singh in Figure 4.5(d). To the contrary, there is not agreement on the FS sheets present at the $X$ and $M$ points, neither amongst those shown in Figures 4.5 and 4.6, nor with those when compared to this work.

Figure 4.6 presents the FS map of Sr$_3$Ru$_2$O$_7$ calculated by LDA+SO with the different $d$-orbital contributions, i.e., the $d_{xy,yz}$, $d_{xy}$ and $d_{x^2-y^2}$ orbitals coloured in blue, red and yellow, respectively. More than the first Brillouin zone of the FS map is exhibited and the map has been rotated about $45^\circ$ in order to compare easily features observed around the high symmetry points $X$, $M$ and $\Gamma$ with FS display in Figure 4.5. The first thing we have to notice from Figures 4.5 and 4.6 is that all the proposed FS map of Sr$_3$Ru$_2$O$_7$ present $\delta$, $\alpha_1$ and $\alpha_2$ FS sheets centred around the $\Gamma$ point. The theoretical FS map (see Figures 4.5(c), 4.5(d) and 4.6) present the splitting of the $\delta$ FS sheet, while the experimental FS maps do not present any splitting (see Figure 4.5(a)). The FS sheets $\beta$ and $\gamma_1$ are also identified in Figures 4.5 and 4.6, but maps obtained by calculations presents a complex shape located inside the $\beta$ FS sheet.
Section 4.6. Fermi Surface Mapping Method

ARPES enables the direct measurement of the zero field FS via measuring the momentum of photoelectrons emitted from the surface [21, 88, 239]. In the mid-1990s, de Haas-Van Alphen experiments were used for the bulk studies of the Fermi surface [240], but nowadays ARPES is dominating. As we said at the beginning of this chapter, to understand transport and correlated properties of magnetic materials it is very important to map the FS since often electrons near the Fermi level are coupled to other lower energy excitations [38]. In this work the FS maps of Sr$_3$Ru$_2$O$_7$ have been investigated and the acquired results are discussed in detail in section 4.7. The intensity of the energy-momentum space map taken at the Fermi level represent the FS. Figure 4.7 demonstrates how FS maps are made in the laboratory frame of reference. In this section we are going to explain the technical aspects of how FS maps are built up from experimental ARPES data. Figure 4.7(a) presents the experimental geometry of the experiment. The manipulator allows for the sample movement along three independent axes ($x$, $y$, $z$) plus the rotation about the vertical axis measured by the \( \phi \) angle (polar angle) [147]. By changing such angle in a small increment one can have the coordinates of \( k \). It is necessary to find the projections of the electron momentum on the sample surface, as this would be the parallel component of quasi-momentum ($k_{\parallel}$) for the state from which the electron has been excited [147].

In the laboratory coordinate system, the coordinates of the electron momentum \( k \) depend only on the analyser angle \( \alpha \) and its expression or formula is given by \( k = |k|(0, \sin \alpha, \cos \alpha) \) see Figure 4.7(a). By performing translation of coordinates from the laboratory system of coordinates to a system of coordinates that is bound to the sample surface, i.e., move from \((x, y, z)\) coordinates to \((x_1, y_1, z_1)\) (as seen in Figure 4.7(a)), one can get the projection of coordinates \((k_x, k_y, k_z)\) of the electron momentum \( k \) on the sample surface by the following expression:

\[
\begin{pmatrix}
  k_x \\
  k_y \\
  k_z
\end{pmatrix} =
\begin{pmatrix}
  \cos \varphi & 0 & -\sin \varphi \\
  0 & 1 & 0 \\
  \sin \varphi & 0 & \cos \varphi
\end{pmatrix}
\begin{pmatrix}
  0 \\
  |k| \sin \alpha \\
  |k| \cos \alpha
\end{pmatrix}, \tag{4.4}
\]

where the above matrix is a three dimensional basic rotation matrix around the $y$ axis. To make a map covering the whole first BZ, one needs first to investigate different cuts in reciprocal space and to change the sample orientation [147, 141, 149]. This is realised by just modifying the manipulator angle \( \varphi \) in small increments (see pink arrows in Figure 4.7(a)) and taking a 2D image at every manipulator angle. An example of a 2D image taken at a specific manipulator angle is shown in Figure 4.7(a). After taking all 2D images for different values of \( \varphi \) (i.e., \( \varphi_1, \varphi_2, \cdots, \varphi_n \)), the cut of a small slice (few meV) of the obtained 2D image around the Fermi level (see the violet line in Figure 4.7(a)) in a small energy window (see the green rectangle around the Fermi level of Figure 4.7(a)) is necessary. Finally, these slices are plotted in \( k \)-space with coordinates \((k_x, k_y)\), resulting in a FS map. An example of the Fermi surface map obtained by following this above procedure is shown in Figure 4.7(b).
Section 4.7. Experimental Fermi Surface Maps of Sr$_3$Ru$_2$O$_7$

All experimental FS maps presented in this section were reconstructed from the raw data by using the parameters shown in Table 4.2. A serious and detailed analysis was performed on the four FS maps in

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10During this work the Igor Pro procedure (computer program) for building this kind of FS map written by a student of the group was modified according to our data and then used.
Section 4.7. Experimental Fermi Surface Maps of Sr$_3$Ru$_2$O$_7$

Figure 4.8: Schematic illustrating how the FS maps of Sr$_3$Ru$_2$O$_7$ presented in this section were acquired by taking several cuts in the tilt direction $\theta$ in the clockwise ($+20^\circ$) and counter clockwise ($-15^\circ$) with respect to the high symmetry direction $\Gamma'X$ of the first BZ.

Table 4.2: A summary of the different sample names, photon energies, polarization, temperatures, resolutions, integrating ranges (integrating range is defined as an interval of energy around the Fermi energy $E_F$, i.e., for example that an integration range of $\pm 10$ meV, is simply the energy range from $E_F - 10$ meV up to $E_F + 10$ meV with respect to the Fermi level.) and Fermi energies used in order to acquire the four FS maps presented in this dissertation.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>C001BA1</th>
<th>C001BA1</th>
<th>C679C9</th>
<th>C679C9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photon Energy (eV)</td>
<td>95</td>
<td>60</td>
<td>85</td>
<td>65</td>
</tr>
<tr>
<td>Polarization</td>
<td>Horizontal</td>
<td>Horizontal</td>
<td>Horizontal</td>
<td>Horizontal</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>1.15</td>
<td>1.15</td>
<td>3.75</td>
<td>30.40</td>
</tr>
<tr>
<td>Resolution (meV)</td>
<td>12.4</td>
<td>6.7</td>
<td>18.9</td>
<td>10.2</td>
</tr>
<tr>
<td>Integration range (meV)</td>
<td>$\pm 10$</td>
<td>$\pm 16$</td>
<td>$\pm 6.5$</td>
<td>$\pm 20$</td>
</tr>
<tr>
<td>$E_F$ (eV)</td>
<td>91.171</td>
<td>55.873</td>
<td>81.045</td>
<td>60.972</td>
</tr>
</tbody>
</table>

$\theta$ ($^\circ$) (see the caption of Figure 4.8 for more details) $+20^\circ$ $+20^\circ$ $-15^\circ$ $-15^\circ$

order to compare them with FS maps of Sr$_3$Ru$_2$O$_7$ existing in the literature. We start with common descriptions observed in all experimental FS maps present in this work.

Since the method used in order to analyse all FS maps exhibited in this work is the same, we first focus on the explanation of one FS (Figure 4.9 for example), it is means that all the other FS maps presented in this section, i.e., Figures 4.10, 4.11, 4.12, 4.13, 4.14 are analysed in the same way.

On these experimental FS maps, yellow and black colours represent the high and low intensity respectively. $\Gamma$, $X$ and $M$ denote the high symmetry points in the first Brillouin zone. All these maps cover more than the first BZ. From section 4.5 we know that after introducing a small electron-electron correlation, bands and FS sheets do not cross each other, and the degeneracy is removed by the opening of gaps. This allows to go from the FS represented in Figure 4.4(e) to the one represented in Figure 4.4(f), where the FS sheets are separated from one another. By looking at our four experimental maps, it will be evident that some FS sheets still cross each other, evidence that the just mentioned gap opening did not occur. Therefore, the shape of some bands (bands located around $M$ points) in our maps are different from those observed in Figures 4.4(f) and 4.5(b), also from the FS map obtained by LDA+SO calculations [19] (see Figure 4.6). However, there are some similarities between our four experimental FS maps with the theoretical FS exhibits in Figure 4.4(e). More details about these similarities are presented in the next paragraph.
Section 4.7. Experimental Fermi Surface Maps of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \)

Figure 4.9: (a) Experimental ARPES FS map of the single crystal of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) labelled C001BA1 taking at photon energy \( h\nu = 95 \text{ eV} \). \( \Gamma \), \( X \), and \( M \) represent high symmetry points. (b) FS contours extracted from the same data plotting on top of the experimental FS map. (c) FS contours extracted from data shown in (a) and plotting on top of the theoretical Fermi map from simple argument when many bands crossing the FS map.

Visible bands observed in Figure 4.9(a) for instance were redrawn by dashed lines over the bands in order to emphasize and present all bands observed in these experimental FS maps (see the dashed white lines presented by Figures 4.9(b)). The identification of the FS sheets with respect to the literature is also given here.

We are now going to explain how we obtained the blue bands plotted on top of the theoretical FS map (see Figure 4.4(e): in this particular FS map, bands are crossing each other, i.e., no gap openings is observed) presented by Figure 4.9(c) for example in order to compare them.

We have measured the different position of bands (the ones redrawn with dashed lines) observed in Figure 4.9(b) with respect to the positions of high symmetry points, and then we have redrawn the same bands by blue lines on top of the theoretical prediction of the FS map of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) (see Figures 4.4(f) and 4.9(c)). From these last plots, we see that some bands are perfectly superimposed, while
Section 4.7. Experimental Fermi Surface Maps of Sr$_3$Ru$_2$O$_7$

Figure 4.10: (a) FS contours extracted from data shown in (b) and plotting on top of the theoretical Fermi map from simple argument when many bands cross the FS map. (b) Experimental ARPES FS map of the single crystal of Sr$_3$Ru$_2$O$_7$ labelled C001BA1 taking at photon energy $h\nu = 95$ eV. This map was obtained from the white rectangle shown in Figure 4.9(a) and symmetrized with respect to the Ru-Ru nearest neighbour direction and it presents more than the first BZ. $\Gamma$, $X$ and $M$ denote high symmetry points. FS contours extracted from the same data plotting on top of the experimental FS map.

other are not predicted by the theory (like the $\delta$ pocket, which is however predicted by Allan et al. [136]).

We have also noted the displacement of some high symmetry points from their right positions (see blue and turquoise lines that intersect in a green point present in Figure 4.9(b) for instance). The details of these displacements, sizes and shapes of the FS sheets, i.e., $\delta$ and $\alpha_1$ observed in these experimental FS maps are presented in section 4.8. We have noted the presence of new bands in the FS map presented by Figure 4.9(b) which were not predicted by the calculations. These bands are better seen in Figure 4.10(a) by dashed blue lines.

We now continue our analysis with the description of the individual experimental FS map:

- Figures 4.9(b) and 4.13(b). In these two maps we see two complete shapes of the FS sheets, labelled $\delta$, $\alpha_1$ centred at the $\Gamma$ point. The incomplete shape of $\alpha_2$ FS sheet centred around $\Gamma$ point was also observed in these two experimental FS maps. Shapes of the two FS sheets ($\delta$ and $\alpha_1$) which are experimentally resolved on these FS maps of Sr$_3$Ru$_2$O$_7$ are similar to those present by Tamai and co-workers in Ref. [21] (see Figures 4.5(a) and 4.5(c)), by Singh et al., in Ref. [144] (see Figure 4.5(d)), and by Allan et al., in Ref. [19] (see Figure 4.6). The inner FS sheet $\delta$ around the $\Gamma$ point is circular, surrounded by $\alpha_1$ which takes a form of a square rounded on edges. The contours of some of these sheets are clearly resolved (those of $\delta$, $\alpha_1$) from the experimental FS maps while the precise contours of $\alpha_2$ is not clearly resolved. It should be noted that the theoretical FS maps present a double $\delta$ pocket (see Figures 4.5(c), 4.5(d) and 4.6) while, the experimental FS maps exhibit only a single $\delta$ pocket (see Figures 4.5(a), 4.9(a), 4.13(a) and 4.11(a)). This is probably due to a problem of momentum resolution which are not sensitive
Section 4.7. Experimental Fermi Surface Maps of Sr$_3$Ru$_2$O$_7$

Figure 4.11: (a) Experimental ARPES FS map of the single crystal of Sr$_3$Ru$_2$O$_7$ labelled C679C9 taking at photon energy $h\nu = 85$ eV. $\Gamma$, $X$, and $M$ are high symmetry points. (b) FS contours extracted from the same data plotting on top of the experimental FS map. (c) This Figure clarify the existing bands and bands position observed in Figure (a). the Background FS map with many bands crossing was taken from Ref. [145].

The white quadrant of the larger tetragonal BZ (see white dashed rectangle in Figure 4.9(a)) was taken and symmetrized with respect to the Ru-Ru nearest neighbour direction in order to suppress directions dependent matrix element effects (see Figure 4.10(b)). The fact to take a quadrant of the larger tetragonal Brillouin zone from the FS map and then symmetrized it, is not an orthodox procedure, it is a common procedure in literature done by many authors in references [19, 21, 97]. We symmetrized our FS map because we observed distortions of the lattice and also to get a periodicity in our FS map in order to better understand what is going on on our FS maps. Figure 4.10(b) shows a region of the reciprocal space extending beyond the first BZ. The same procedure as mentioned above was done in this FS, i.e., the plotting of the dashed lines on top of bands observed in the experimental map (see Figure 4.10(b)) and then compare with the
Section 4.7. Experimental Fermi Surface Maps of Sr$_3$Ru$_2$O$_7$

Figure 4.12: (a) Experimental ARPES FS map of the single crystal of Sr$_3$Ru$_2$O$_7$ labelled C679C9 taking at photon energy $h\nu = 85$ eV. By taking the part of the experimental FS map delimited by the white dashed rectangle shown in Figure 4.11(a) and by symmetrising it, we reconstruct this map. $\Gamma$, $X$ and $M$ are high symmetry points. (b) FS contours extracted from the same data plotting on top of the experimental FS map. (c) This Figure clarify the existing bands and bands position observed in Figure (a). the Background FS map with many bands crossing was taken from Ref. [145].

Theoretical FS from simple argument (see Figure 4.10(a)). There exist also a good agreement between features observed in Figure 4.10(a) with features observed in 4.10(b). The only similarity between Figure 4.10(b) and Figures 4.5 (from Tamai et al., [21] and Singh et al., [144]) and 4.6 (from Allan et al., [144]) is the presence of the circular $\delta$ pocket in all these FS maps.

• Figure 4.11(b). In this figure three FS sheets are resolved, i.e., $\delta$, $\alpha_1$ and $\alpha_2$. The shapes of all these three FS sheets are in perfect agreement with those observed in the previous experimental FS maps presented in this section, by Tamai et al., [21], Singh et al., [144] and by Allan et al., [144] (see Figures 4.5 and 4.6).

The part of the experimental FS map delimited by the white dashed rectangle drawn in Figure 4.11(a) was taken and symmetrised by folding this image in order to reconstruct the entire FS map presents in Figure 4.12(a). This figure shows less than the first BZ. The same method as mention at the beginning of this section, i.e., the drawing of the blue dashed lines over bands observed in the experimental FS map (see Figure 4.12(b)) and then compare with the theoretical FS from simple argument (4.12(c)) was also done here. As results, the perfect agreement between Figures 4.12(a) and 4.12(c) is observed. The three FS sheets as state in the previous paragraph are also well resolved.

• Figure 4.14(b). In this figure two incomplete FS sheets namely $\delta$ and $\alpha_1$ were observed in this map but are not well resolved. Since the FS sheets in this particular FS map are not resolved, we can compare anything.

In summary, by looking at our experimental FS maps, the first thought that may come to our mind is to simply think that the electrons are weakly correlated in this system (Sr$_3$Ru$_2$O$_7$) due to the non-opening gaps present in these FS maps. But it has been proved by many authors [19, 21] that in Sr$_3$Ru$_2$O$_7$ electron correlations are very strong due to the fact that its electronic specific heat is 110 mJ/molRuK$^2$ which is among the highest in any oxide. The fact that we are not observing some openings of the gap (energy gap at the zone boundaries causes by the interaction of electron with the periodic potential of the crystal [38]) in our four experimental FS maps is probably due to the strong effect of the matrix element. We have also noted the displacement of some high symmetry points from their right positions. These unusual phenomenon present in the FS map of Sr$_3$Ru$_2$O$_7$ could be probably due to the fact that
Section 4.7. Experimental Fermi Surface Maps of $\text{Sr}_3\text{Ru}_2\text{O}_7$

Figure 4.13: Experimental ARPES FS map of the single crystal of $\text{Sr}_3\text{Ru}_2\text{O}_7$ labelled C001BA1 taking at photon energy $\hbar\nu = 60$ eV. $\Gamma$, $X$ and $M$ are high symmetry points. (b) FS contours extracted from the same data plotting on top of the experimental FS map. (c) This Figure clarify the existing bands and bands position observed in Figure (a). the Background FS map with many bands crossing was taken from Ref. [145].

the experiment was not done in a perfect $ab$ plane with $k_z = 0$, i.e., may be during the experiment, we were mapping different plans with different $k_z$ due to the fact that the use of different kinetic energy $E_{\text{kin}}$ imply the probing of different $k_z$. Despite all this, the four FS maps acquired in this work have presented some FS sheets namely $\delta$, $\alpha_1$ and $\alpha_2$ in agreement with the ones present in the literature. We have also noticed that the three FS sheets ($\delta$, $\alpha_1$ and $\alpha_2$) have different sizes compared to those presented in the literature, this might be probably due to the strong effect of matrix element and the fact that we were mapping different $k_z$. Figure 4.4e) in section 4.5 is very complex and they can exist divers possible arrangement in order to reconstruct the FS map of $\text{Sr}_3\text{Ru}_2\text{O}_7$. Due to the fact that we are observing some bands crossing our four FS maps like bands present in Figure 4.4e), it can be possible that the real FS map of $\text{Sr}_3\text{Ru}_2\text{O}_7$ is even more complicated than the ones present in the literature.
Figure 4.14: (a) Experimental ARPES FS map of the single crystal of Sr$_3$Ru$_2$O$_7$ labelled C679C9 taking at photon energy $\hbar\nu = 65$ eV. $\Gamma$, $X$ and $M$ are high symmetry points. (b) FS contours extracted from the same data plotting on top of the experimental FS map. (c) This Figure clarify the existing bands and bands position observed in Figure (a). the Background FS map with many bands crossing was taken from Ref. [145].

All FS maps exhibit in this work present high intensity (yellow colour) around $X$ points (see Figures 4.9(a), 4.13(a), 4.11(a) and 4.14(a)) indicating positions of the van Hove singularities as predicted by Mercure and co-workers [145]. The presence of these high intensities shown in these FS maps can be also refer to lens shapes observed in the theoretical FS map obtained by calculations by Allan et al., [19] (see Figure 4.6 around the $X$ point).
4.8 Analysis of the Distortions in the Fermi Surface Maps of Sr$_3$Ru$_2$O$_7$

The FS maps presented in section 4.7 come from two different samples (C001BA1 and C679C9) and have been acquired with different photon energies and linear horizontal polarization as we saw previously. By looking these FS maps it can be noted that some high symmetry points (Γ, M and X) are not situated in their right positions. Therefore, we have undertaken a serious analysis of the distortions of the FS sheets comparing each of them to the position and size/shape they are supposed to have. Sizes of the three FS sheets observed on the four FS sheets acquired in this work were calculated and the difference between these sizes was observed. Sizes and shapes of all FS sheets are compared with respect to those of the FS sheets calculated by Tamai and co-workers [21]. I have been searching quite extensively in literature for places where the analysis of similar distortions was shown, but I could not find any. Table 4.7 taken as table reference, summarizes the six FS sheets sizes and shapes, distortion observed in the FS sheets, the displacement observed on the real position of the sheets. Table 4.3 shows details on sizes and shapes of the two FS sheets from the sample labelled C001BA1 taking at photon energy $h\nu = 95$ eV. It also shows if distortions have been observed in the FS sheets and the displacement observed on the real position of the FS sheets.

Table 4.4 shows the same details as above from the sample labelled C001BA1 taking at photon energy $h\nu = 60$ eV. Table 4.5 shows the same details as above from the sample labelled C679C9 taking at photon energy $h\nu = 85$ eV. Table 4.6 also shows the same details as above from the sample labelled C679C9 taking a $h\nu = 65$ eV photon energy. From these four tables below we can see that there are some similarities between the FS sheets sizes calculated in this work with the one calculated by Tamai and co-workers see Table 4.7 from [21] and the FS sheets sizes acquired in this work.

<table>
<thead>
<tr>
<th>FS sheets</th>
<th>FS size sheet (% of BZ)</th>
<th>Distortions</th>
<th>Displacement observed on the real position of FS sheets ($k_x, k_y$)(Å$^{-1}$)</th>
<th>Shape of FS sheets</th>
</tr>
</thead>
<tbody>
<tr>
<td>α$_1[3]$</td>
<td>14.8 ± 2</td>
<td>No</td>
<td>$(−0.08, −0.02)$</td>
<td>rectangle rounded edges</td>
</tr>
<tr>
<td>α$_2[3]$</td>
<td>—</td>
<td>—</td>
<td>$(−0.08, −0.02)$</td>
<td>—</td>
</tr>
<tr>
<td>γ1</td>
<td>3.0 ± 1</td>
<td>No</td>
<td>$(0, 0)$</td>
<td>circle.</td>
</tr>
<tr>
<td>γ2</td>
<td>2.0 ± 1</td>
<td>No</td>
<td>$(0, 0)$</td>
<td>/</td>
</tr>
<tr>
<td>γ3</td>
<td>3.0 ± 1</td>
<td>No</td>
<td>$(−0.08, −0.02)$</td>
<td>/</td>
</tr>
<tr>
<td>γ4</td>
<td>2.0 ± 1</td>
<td>No</td>
<td>$(0.03, −0.01)$</td>
<td>/</td>
</tr>
</tbody>
</table>

Table 4.3: FS sheets, size in % of BZ of FS sheets from the experimental ARPES resolved FS sheets of the single crystals of Sr$_3$Ru$_2$O$_7$ labelled C001BA1 taking at photon energies $h\nu = 95$ eV. Distortions observed on the FS sheets, displacement observed on the real position of the FS sheets. Shape of FS sheets.
### Table 4.4: FS sheets, size in % of BZ of FS sheets from the experimental ARPES resolved FS sheets of the single crystals of Sr$_3$Ru$_2$O$_7$ labelled C001BA1 taking at photon energies $h\nu = 60$ eV. Distortions observed on the FS sheets, displacement observed on the real position of the FS sheets. Shape of FS sheets.

<table>
<thead>
<tr>
<th>FS sheets</th>
<th>FS size sheet (% of BZ)</th>
<th>Distortions</th>
<th>Displacement observed on the real position of FS sheets $(k_x, k_y) (\text{Å}^{-1})$</th>
<th>Shape of FS sheets</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1[1]$</td>
<td>—</td>
<td>—</td>
<td>$(0.1, -0.05)$</td>
<td>—</td>
</tr>
<tr>
<td>$\alpha_1[2]$</td>
<td>—</td>
<td>—</td>
<td>$(0.2, -0.07)$</td>
<td>—</td>
</tr>
<tr>
<td>$\alpha_1[3]$</td>
<td>—</td>
<td>–</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$\alpha_1[4]$</td>
<td>$15.2 \pm 2$</td>
<td>Yes since 15.2 &gt; 14.1</td>
<td>$(0, 0)$</td>
<td>square rounded edges</td>
</tr>
<tr>
<td>$\alpha_2[1]$</td>
<td>—</td>
<td>—</td>
<td>$(0.1, -0.05)$</td>
<td>—</td>
</tr>
<tr>
<td>$\alpha_2[2]$</td>
<td>—</td>
<td>—</td>
<td>$(0.2, -0.07)$</td>
<td>—</td>
</tr>
<tr>
<td>$\alpha_2[3]$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$\delta[1]$</td>
<td>$2.5 \pm 1$</td>
<td>No</td>
<td>$(0.1, -0.05)$</td>
<td>—</td>
</tr>
<tr>
<td>$\delta[4]$</td>
<td>$2.5 \pm 1$</td>
<td>No</td>
<td>$(0, 0)$</td>
<td>—</td>
</tr>
</tbody>
</table>

### Table 4.5: FS sheets, size in % of BZ of FS sheets from the experimental ARPES resolved FS sheets of the single crystals of Sr$_3$Ru$_2$O$_7$ labelled C679C9 taking at photon energies $h\nu = 85$ eV. Distortions observed on the FS sheets, displacement observed on the real position of the FS sheets. Shape of FS sheets.

<table>
<thead>
<tr>
<th>FS sheets</th>
<th>FS size sheet (% of BZ)</th>
<th>Distortions</th>
<th>Displacement observed on the real position of FS sheets $(k_x, k_y) (\text{Å}^{-1})$</th>
<th>Shape of FS sheets</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1[1]$</td>
<td>—</td>
<td>—</td>
<td>$(0, 0)$</td>
<td>square rounded edges</td>
</tr>
<tr>
<td>$\alpha_2[2]$</td>
<td>$14.5 \pm 3$</td>
<td>—</td>
<td>$(0.02, 0.15)$</td>
<td>—</td>
</tr>
<tr>
<td>$\delta[1]$</td>
<td>$2.6 \pm 1$</td>
<td>No</td>
<td>$(0, 0)$</td>
<td>circle</td>
</tr>
<tr>
<td>$\delta[3]$</td>
<td>$2.6 \pm 1$</td>
<td>No</td>
<td>$(0.02, 0.15)$</td>
<td>/</td>
</tr>
</tbody>
</table>

The displacement of $M[1]$ point have been observed and is equal to $(0.02, 0.1)$.
Section 4.9. Summary

In this chapter we have presented a complete ARPES FS maps of Sr₃Ru₂O₇. These maps have presented some similarities with the one obtained from ARPES measurements, published by Tamai and co-workers [21]. The three FS sheets labelled α₁, α₂ and δ are clearly visible in our FS maps. Some bands observed on FS maps obtained in this work resemble to some bands present in Figure 4.4(e), which is one of the map presented in section 4.5 when many band crossings arise in the plot taken from [145]. The fact that the FS maps presented here posses a combination of some FS sheets (α₁, α₂ and δ) and some band present in Figure 4.4(e) is probably due to strong effect of the matrix elements. Additional to these above observations on the four FS maps acquired in this work, distortions on the FS sheets and the displacements on the real position of certain high symmetry points (Γ, M and X) have been also observed. In this chapter a complete analysis of this distortions have also been presented. The four tables above have shown some similarities with table 4.7. these similarities are situated on the shape of FS sheet, some FS size and the not displacement of the FS sheets. At the end of this FS map analysis, the peculiar remark observed is that the reconstruction of the FS of Sr₃Ru₂O₇ from the literature differ from each other, this allow us to conclude that the real FS of Sr₃Ru₂O₇ at the edges of the first Brillouin zone can be more complex than expected.

### Table 4.6: FS sheets, size in % of BZ of FS sheets from the experimental ARPES resolved FS sheets of the single crystals of Sr₃Ru₂O₇ labelled C679C9 taking at photon energies hν = 65 eV. Distortions observed on the FS sheets, displacement observed on the real position of the FS sheets. Shape of FS sheets.

<table>
<thead>
<tr>
<th>FS sheets</th>
<th>FS size sheet (% of BZ)</th>
<th>Distortions</th>
<th>Displacement observed on the real position of FS sheets $(k_x, k_y)(\text{Å}^{-1})$</th>
<th>Shape of FS sheets</th>
</tr>
</thead>
<tbody>
<tr>
<td>α₁[1]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>α₁[2]</td>
<td>—</td>
<td>—</td>
<td>(0.05, −0.05)</td>
<td>—</td>
</tr>
<tr>
<td>α₁[3]</td>
<td>—</td>
<td>—</td>
<td>(0.0)</td>
<td>—</td>
</tr>
<tr>
<td>δ[2]</td>
<td>—</td>
<td>—</td>
<td>(0.05, −0.05)</td>
<td>—</td>
</tr>
</tbody>
</table>

### Table 4.7: Fermi surface volumes of Sr₃Ru₂O₇ FS sheets obtained from ARPES and dHVA. The dominant orbital character is indicated in brackets. Error are estimated from the statistical accuracy of the analysis and the reproducibility of the experiments. This table is reproduced from [21]. No distortion is observed, no displacement is observed on the real position of the FS sheets. Shape of FS sheets.

<table>
<thead>
<tr>
<th>ARPES FS-volume A (% BZ)</th>
<th>dHVA FS-volume A (% BZ)</th>
<th>Distortions</th>
<th>Displacement observed on a real position of FS sheets $(k_x, k_y)(\text{Å}^{-1})$</th>
<th>Shape of FS sheets</th>
</tr>
</thead>
<tbody>
<tr>
<td>α₁($d_{xz}, d_{yz}$)</td>
<td>α₂($d_{xz}, d_{yz}$)</td>
<td>β($d_{xz}, d_{yz}$)</td>
<td>γ₁($d_{xy}/d_{xz}, d_{yz}$)</td>
<td>γ₂($d_{xy}$)</td>
</tr>
<tr>
<td>14.1 ± 2</td>
<td>31.5 ± 3</td>
<td>2.6 ± 1</td>
<td>8.0 ± 2</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>13.0 ± 1.0</td>
<td>30.1 ± 1.1</td>
<td>1.1 ± 0.2</td>
<td>6.6 ± 0.9</td>
<td>–</td>
</tr>
<tr>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>(0,0)</td>
<td>(0,0)</td>
<td>(0,0)</td>
<td>(0,0)</td>
<td>(0,0)</td>
</tr>
<tr>
<td>Square rounded on edges</td>
<td>Cross</td>
<td>Lens</td>
<td>Lens</td>
<td>Lens</td>
</tr>
<tr>
<td>shaped</td>
<td>shaped</td>
<td>shaped</td>
<td>shaped</td>
<td>shaped</td>
</tr>
<tr>
<td>Circle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5. Analysis of the Band Dispersion in \( \text{Sr}_3\text{Ru}_2\text{O}_7 \)

5.1 Introduction

The study of the band structure of solids is one of the most important tasks in condensed matter physics. It constitutes the heart of all modern understanding of physical properties of solids, as it describes the energy and momentum ranges that an electron in the solid may have (energy bands), and may not have (band gaps). Therefore, based on their electronic properties all materials fall into one of these three classes, namely: insulating, metallic and semiconducting, which are described by band theory. This theory has been effectively used in order to explain many physical properties of solids, such as electrical, optical, and some magnetic properties as well. It also constitutes the foundation of the understanding of all solid state apparatus such as transistors. ARPES is the most suitable tool to probe the electronic structure and the band dispersion of solids directly.

Along one \( k \) direction, band structure can be displayed in several zone schemes, but most often the reduced zone scheme is used \([38]\). In three dimensions, the band structure is generally shown along particular paths in the BZ. The most important bands relevant for electronic properties of solid are, within the valence band, those with energy close to the Fermi level. Bands can be either electron-like or hole-like (this will be explained later in section 5.3).

This chapter begins with an introduction section 5.1, followed by section 5.2 that exhibits the effect of the matrix elements observed in our data, which are due to the polarization, the photon energy and polar angles. Section 5.3 shows the analysis of different bands that cross the Fermi level of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \). The line shape analysis of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) spectra is presented in section 5.4. Section 5.5 focuses on the investigation of the kinks present in band dispersion of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \), followed by the effect of renormalisation of the \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) bands shown in section 5.6. Finally, the possible locations of the vHS in the band structure are presented in section 5.7.

5.2 Matrix Element Effects

Before going too deep into this section, I would firstly like to highlight the difference between LHP and LVP experimental geometries. Before performing any ARPES experiment, samples can be oriented with respect to the light polarization of the beam. This is done in order to take advantage of different matrix elements for the photoemission intensity.

As mentioned earlier in section 2.7, the expression \((2.37)\) of the measured ARPES photoemission intensity \( I(k, E) \) is given as follows:

\[
I(k, E, T) = \sum_{fin,in} |M^k_{fin,in}|^2 f(E, T) A(k, E);
\]

where \( |M^k_{fin,in}|^2 \) is the square of the single-electron dipole matrix elements, \( f(E, T) \) is the Fermi Dirac distribution function and \( A(k, E) \) is the single particle spectral function. The matrix element \( M^k_{fin,in} \) modifies the intrinsic intensities according to electron momentum, geometric settings, light polarization and photon energy \([141, 214]\). To obtain information on the electronic structure of the investigated materials, it is possible to take advantage of one of these matrix elements in order to
enhance some bands while suppressing others. Nevertheless, matrix elements can sometimes suppress the photoemission intensity which is disadvantageous to the measurement of the spectral function [141].

The data used in order to map the Fermi surface topology were acquired for samples whose axes were not aligned with respect to the light polarization, while samples used for the high resolution cuts were aligned with respect to the light polarization. This was done with the intention, by taking advantage of different matrix elements, to determine the symmetry and character of dispersing bands close to the Fermi level [141].

The horizontal and vertical light polarization configurations used here are presented in Figure 5.1. To probe the in-plane and out-of-plane bands, one needs to change the sample orientation by altering the manipulator angle $\varphi$ within a specific incoming light polarization (see Figure 5.1). It should be noted that not all samples were aligned in the $ab$ plane like in this case. The electric field $E$ of the incoming photon oscillates in the same plane as the orbit of the electrons in the ring only if the incoming light is in LHP and stays in the plane determined by the $a$ and $c$ axes of the sample. The electric field $E$ oscillates in the perpendicular plane to the orbit of the electrons only when the incoming light is LVP and it is always parallel to the $ab$ plane. Thus, this signifies that when light is in LHP the electric field $E$ possesses two components, i.e., an in-plane component ($E_\parallel$) parallel to the $ab$ plane and an out-of-plane component ($E_\perp$) parallel to the $c$ axis, while when the light is in LVP the electric field $E$ is always in the $ab$ plane. To summarise this paragraph we can see that when the incoming light is LHP, it is possible by rotating the sample with an angle $\varphi$ around the vertical axis, to probe both out-of-plane (for biggest values of $\varphi$) and in-plane ($\varphi \approx 0$) bands (see Figure 5.1). However, when the incoming light is LVP it is only possible to probe the in-plane bands (see Figure 5.1).

Here, we have investigated the effect of matrix elements using different polar angles, light polarizations (LHP, LVP, circular polarizations left and right) and photon energies, all combined with the experimental geometry. This was done in the interest of extracting the symmetry properties of the electronic states and investigating different features located close to the Fermi level in Sr$_3$Ru$_2$O$_7$. For the remainder of this section, the effect of matrix elements observed on bands dispersions of Sr$_3$Ru$_2$O$_7$ measured at different polarizations, photon energies and polar angles (electron momentum) is presented.
Figure 5.2: ARPES band dispersions taken at a photon energy of 20 eV for the sample C679D2. Cuts in (a) and (b) were measured in LHP and LVP respectively. In these cuts the blue colour represents the low photoemission intensity while the white colour denotes the high photoemission intensity. The black diamond situated on the left side of the figure represents the first Brillouin zone. $\Gamma$, $M$ and $X$ are the high symmetry points. The red line drawn on the left corner of the first Brillouin zone indicates the place where these two cuts have been taken. These two cuts have been blown up in order to illustrate the difference between the two polarizations (see blue arrows). (c) and (d) show the comparison between LHP and LVP EDCs extracted from (a) and (b) respectively at the $X$ point and at $K_{\parallel} = 0.65$ Å$^{-1}$ indicated by pink arrows in (a) and (b). The black curves represent the difference between LHP and LVP spectra.

The Effect of Polarization

Figure 5.2 shows an example of how matrix elements can affect the photoemission intensity. It exhibits two band dispersions taken with $h \nu = 20$ eV for sample C679D2 (see Figure 5.2(a) and (b)). These two cuts were taken in the same region of the reciprocal space with the same experimental conditions, the only difference being the polarization of the incident light. The cut presented in Figure 5.2(a) was taken with LHP while the one shown by 5.2(b) was taken with LVP. In these two cuts, there is a band crossing the high symmetry point $X$ whose central part is more visible in LVP (see the blue arrow in Figure 5.2(b)) while the intensity of its outer part - symmetric with respect to the $X$ point is more pronounced in LHP (see the blue arrow in Figure 5.2(a)).

Additionally, according to what has been discussed at the beginning of this section, we can say that the LVP enhances the in-plane states, while LHP enhances the out-of-plane states. This is also indicated in Figures 5.2(c) and (b) by the difference between the EDCs in LHP and LVP that shows how LVP enhances the intensity close to the Fermi level $E_F$ around the $X$ point while the intensity is suppressed away from $X$ point. The in-plane character of this band close to the $X$ point is in agreement with the
The Effect of Photon Energy

Figures 5.3(a) and (b) shows two cuts taken at the high symmetry point $\Gamma$ in the direction $\Gamma X$ of the first BZ (see the blue line inside the black rotated square located at the right side of Figure 5.3(b)). These two cuts were acquired with LHP of the incoming light, using different photon energies of 25 eV (see Figure 5.3(a)) and 19 eV (see Figure 5.3(b)). By comparing the bands indicated by violet arrows in the two cuts, we can see that the intensity at 25 eV is more enhanced than the intensity at 19 eV. This is also reflected in Figure 5.3(c) that shows MDC 1 with four peaks while MDC 2 exhibits only two peaks and the two other ones (those two peaks are indicated by black arrows in Figure 5.3(c)) are noisy. This is an example of how the photon energy can be used to enhanced the contribution of certain bands.

The Effect of Polar Angles

The Fermi surface (FS) map of $\text{Sr}_3\text{Ru}_2\text{O}_7$ (see Figure 4.9(a)) shows the effect of matrix elements due to polar angles. This map presented by this figure was taken at photon energy $\hbar\nu = 95$ eV in LHP for sample C001BA1 covering an area more than the first Brillouin zone. The photoemission intensity in this map is more enhanced for FS sheets located in the negative part of $k_x$ (see the left hand side of the $X$ point) while it is low for sheets located in the positive part of $k_x$ (see the right hand side of the $X$ point). This above explanation shows that it is possible to take advantage of some matrix elements that enhance the photoemission intensity of some FS pockets while suppressing the intensity of others.
5.3 Fermi Surface Sheet Analysis

In this section we focus on the formation of the heavy \( d \) electron quasiparticles in \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) by analysing the dispersion of the bands in the proximity of the Fermi level. Figure 5.4(a) shows a summary of the quasiparticle band dispersions along the high symmetry direction \( \Gamma X \Gamma \) extracted from several ARPES measurements (19 cuts in which 50 bands were visible) with different photon energies (15, 20, 25 and 65 eV) and polarizations (LHP, LVP, circular polarization +, circular polarization -). In order to quantitatively investigate the behaviour of the quasiparticle band dispersions in \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) several MDCs and EDCs extracted from several cuts were fitted with Lorentzian and Gaussian functions and their peak positions were plotted in the energy-momentum domain in order to trace them in the experimental dispersion. Figure 5.4(a) shows the summary of all these peak positions (see open circles, full triangles and other shapes) from the MDC and EDC fitting. The band names were given relative to those present in the literature, except the unknown band called “u band” which will be discussed in the following.

These experimental bands were plotted together with the theoretical bands from Ref. [136] published by Allan et al. (see theoretical bands exhibited in Figure 5.4(a)), in order to compare our results with those calculations existing in the literature. These theoretical data were obtained by converting the theoretical bands (see blue and green curves in Figure 5.4(b)) into numbers using a digitizing software. First of all, I would like to briefly explain Figure 5.4(b) taken from Ref. [136] before going back to our results in Figure 5.4(a). Figure 5.4(b) exhibits a resulting low energy band dispersion along the \( \Gamma X \Gamma \) direction extracted from ARPES measurements with various photon energies and polarizations. It should be noted that the figure obtained by Allan and co-workers in Ref. [136] have been symmetrized and shown in Figure 5.4(b) in order to compare it with our results. In this figure the parallel momentum is given in units of \( \frac{\pi}{a} = \frac{\pi}{3.88} \approx 0.81 \text{ Å} \), where the parameter \( a \) is the lattice constant in the undistorted tetragonal structure of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \). In order to describe their experimental dispersions with a minimal model, they have approximate within the tight binding method the peak positions by eight cosine bands that track the dispersions of the fundamental bilayer splitting for the \( xy, xz/yz \) orbitals and their backfolded copies \( xy', xz'/yz' \) [136]. This backfolding occurs from a rotation of the RuO\(_6\) octahedra by 7\(^\circ\) as discussed earlier in section 1.4.1. The reader can consult Ref. [136] for more information about the backfolding.

By comparing the cosine bands of their simple model with the experimental bands, we see that all bands (theoretical and experimental) disperse in the same way (see Figure 5.4(b)).

Figure 5.4(a) shows a general good agreement with the band dispersion of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) obtained by Allan et al. (see Figure 5.4(b)), but there are some differences which I am going to highlight in the following. Due to the distortions analysed in Chapter 4 (see sections 4.7 and 4.8), the \( \Gamma \) point located at the adjacent first BZ (see the right side of Figure 5.4(a)) is not well centred at the exact position (\( \sim 1.6 \text{ Å} \)) where it is supposed to be. Therefore, the \( \alpha_1 \) and \( \gamma_2 \) bands located around the \( \Gamma \) point on the right hand side of Figure 5.4(a) are a little bit off-centred. The green parabolic band centred at the \( X \) point predicted by Allan et al. [136] (see Figure 5.4(b) around the \( X \) point) was not observed in our experimental bands. This might be due to the effect of matrix elements, and so more data might be needed in order to measured it.

Another major difference with respect to Figure 5.4(b) is the presence of the most inner parabolic band centred around the two \( \Gamma \) points, i.e. the unknown band called “u band” which was not predicted by the theory. One possibility would be that this \( u \) band is a replica of the \( xy \) band centred at the \( X \) point, translated by the reciprocal vector \( \Gamma X \) and due to a reconstruction of the surface that alters the symmetry (as it occurs in \( \text{Sr}_2\text{RuO}_4 \) [96]). In order to investigate the origin of this band, we have translated the \( xy \) band by \( -\Gamma X \) vector and we have potted in a separate graph the \( u \) bands together.
Figure 5.4: (a) Band dispersions along the high symmetry direction $\Gamma X \Gamma$ extracted from ARPES measurements with different photon energies and polarizations. These experimental bands were plotted together with the eight cosine bands and their backfolded counterparts taken from (b) in order to compare our bands with those existing in the literature. Please see text for more details. (b) ARPES band dispersions (look at the curves plotted by the full circles and triangles) extracted from measurements with different photon energies and polarizations. These experimental bands were plotted along the high symmetry line $\Gamma X$ together with the eight cosine dispersions that track the fundamental bilayer split orbitals $xz/yz$ and $xy$ and their backfolded copied ($xz'/yz'$, $xy'$) (see blue and green lines). The thick blue line indicated the low energy contour that arise from the hybridization of these bands. It should be noted that experimentally, the bilayer splitting in the $xy$ band (see parabolic green curves) is not resolved and these split observed in $xy$ is only there for illustrative purpose. Figure reproduced from Ref. [136].
with the \( xy \) bands translated in Figure 5.5. By looking at Figure 5.5 we can see that the \( u \) and \( xy \) bands do not superimpose, therefore we can suggest that the \( u \) band can be simply a new band observed in the band dispersion of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \). Another hypothesis could be that the \( u \) band is just the \( \alpha_1 \) band that occupies a different \( k \) position because of the distortions observed in our FS maps (see section see sections 4.7 and 4.8). For the remainder of this section we focus on the analysis of FS sheets which give rise to the hole and electron pockets.

The complicated experimental FS of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) presented in section 4.7 consists of several pieces, namely electron and hole FS sheets. These FS sheets are essentially different because the transport phenomena occurring in an electron and hole FS sheet are considered as coming from electrons and holes respectively. Before analysing the electron and hole characters of the FS sheets, it is necessary to introduce the energy band dispersion curve of a free electron theory of solids, since the fact to know if the curve is convex or concave is essential to define the electron and hole character of the FS sheets.

Consider a certain number of free electrons with mass \( m \) each, moving within a crystal where the details of the periodic potential due to the ionic cores are ignored in order to replace this effect by the mean potential \(-U_0\) [229]. The time-independent Schrödinger equation for conduction electrons inside the crystal in the free electron approximation is then given as follows [29, 38]:

\[
H\psi(r) = \left( \frac{\hbar^2}{2m} - U_0 \right) \frac{d^2\psi(r)}{dr^2} = E\psi(r); \tag{5.1}
\]

where \( H \) is the Hamiltonian of the system and \( \psi(r) \) is the free electron wave function. The eigenfunctions of equation (5.1) are of the form [38]:

\[
\psi(r, k) = e^{ik \cdot r};
\]

and the eigenvalues are given by:

\[
E(k) = -U_0 + \frac{\hbar^2|k|^2}{2m}. \tag{5.2}
\]

The free electron approximation is defined as a simple model that describes the behaviour of valence electrons in a crystal, by taking into account that interactions between free electrons and ions are neglected and the lattice potential is considered constant. This approximation was developed by Sommerfeld [242] and it is used to describe many properties of simple metals, i.e., the alkali metals (K, Na, Li), the noble metals (Rh, Pd, Ag) and Al.
Figure 5.6: Energy dispersion curve in (a) one dimension (parabola) and (b) two dimension (paraboloid).

By choosing the origin of energy in such a way that \( U_0 = 0 \), the energy wave vector (5.2) becomes [38]:

\[
E(k) = \frac{\hbar^2 k^2}{2m}; \tag{5.3}
\]

which is a parabolic dispersion in reciprocal lattice space. The energy dispersion (5.3) can be written in one and two dimensions as follows:

\[
E(k) = \frac{\hbar^2 k^2}{2m} \quad (1D); \tag{5.3}
\]

\[
E(k) = \frac{\hbar^2 (k_x^2 + k_y^2)}{2m} \quad (2D); \tag{5.4}
\]

represented in Figures 5.6(a) and 5.6(b), respectively, where the periodic boundary conditions are given by: \( k_x = \frac{2\pi}{a} n_x \) and \( k_y = \frac{2\pi}{a} n_y \), with \( n_x \) and \( n_y \) being positive integers \( (1, 2, 3 \ldots) \), such that the wavevector \( k \) is quantised in the reciprocal space [243]. If the free electrons are confined in a line, \( a \) is the length of the crystal. On the other hand, if the free electrons are confined in a square, the size of the crystal will be \( a \times a \). At zero temperature and by taking into account the Pauli exclusion principle, one can fill the energy levels \( \frac{\hbar^2 k^2}{2m} \) adding one electron at a time until all electrons are considered; there will then be a maximum state of occupied energy known as the Fermi energy \( E_F \) [197, 243]. In reciprocal space, the occupied states of energy \( (E(k) < E_F) \) are separated from unoccupied states \( (E(k) > E_F) \) by the FS [38, 229].

In the process of analysing the electron and hole character of the ARPES resolved FS sheets of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \), the free electron approximation is considered, giving use to a parabolic energy band dispersion (5.3). To determine the character, i.e., electron or hole character, of a particular FS sheet, it is necessary to follow the band dispersion that gives rise to that particular FS sheet. The sketch of the upright paraboloid band dispersion that is occupied inside together with the closed FS sheet pattern that is occupied in the interior are presented by Figure 5.7(a). If a particular FS sheet gives rise to a similar band dispersion exhibited by Figure 5.7(a), i.e., paraboloid (2D) or parabola (1D) shape, then the FS sheet has an electron character. Figure 5.7(b) shows the inverse paraboloid band dispersion with its corresponding
closed FS sheet which is unoccupied in the interior. If an individual FS sheet gives rise to the band dispersion with the inverted paraboloid (2D) (or parabola (1D)) shape as the one depicted by Figure 5.7(b), then the FS sheet has a hole character.

Several band dispersions taken at different positions of the first and second BZ, in the direction parallel to the high symmetry line Γ–X (see Figures 5.8(c) and 5.8(e)), and the one taken in the direction tilted 15° counter-clockwise (see Figure 5.8(a)) were analysed. This analysis was done in order to determine electron and hole characters of the three FS sheets resolved in the ARPES FS maps presented in section 4.7.

An ARPES cut measured with a photon energy of $h\nu = 65$ eV in LHP for the sample C679C9 is shown in Figure 5.8(a). The red open circles plotted on top of this ARPES cut are several MDC peak positions obtained by fitting many MDCs with Lorentzian line shapes. MDCs were fitted from the Fermi energy level $E_F$ down to $-0.4$ eV binding energy. Below this specific binding energy ($-0.4$ eV) the spectra were too noisy to give a meaningful fit (see Figure 5.8(a)). These MDCs have been generated by integrating the intensity of the ARPES cut over a binding energy range of $1.6$ meV in $1.6$ meV steps. One can see that the $\alpha_1$ and u band from the MDC derived dispersion have an inverted parabolic dispersion as illustrated by the black inverted parabolae$^2$. By comparing the dispersion of the $\alpha_1$ and u bands with the dispersion shown in Figure 5.7(b), one can conclude that $\alpha_1$ and u band give rise to hole FS sheets.

The same scenario as explained above in the case of Figure 5.8(a) was observed in the sample C679D2 measured with photon energy of $h\nu = 25$ eV. The only difference is that the fitting was interrupted at the binding energy of $-0.37$ eV due to the same reason of noise mentioned above (see Figure 5.8(c)). Figure 5.8(e) exhibits an ARPES energy momentum distribution measured with a photon energy of $h\nu = 15$ eV for the sample C679D5. The red open circles plotted on top of the $\delta$ pocket are the EDC derived dispersions of this band obtained by fitting many EDCs with a Gaussian function. We have fitted this dispersion with EDC functions due to the thinness of the band. Thus, EDCs were fitted from $-0.12$ Å$^{-1}$ up to $0.12$ Å$^{-1}$, by integrating the intensity of the ARPES cut over a momentum range of $9.1$ mÅ$^{-1}$ in $4.55$ mÅ$^{-1}$ steps. From the EDC derived dispersions, one can see that the $\delta$ pocket

\hspace{1cm}$^2$Black parabolae observed in Figures 5.8(a), 5.8(c) and 5.8(e) were obtained by fitting MDCs with a set of parabolic functions.
Figure 5.8: Study of the electron and hole character of the ARPES resolved FS sheets of Sr$_3$Ru$_2$O$_7$. (a), (c) and (e) represent cuts measured with $h\nu = 65$ eV, 25 eV, and 15 eV, respectively, along the direction shown by the blue lines located in the first and second BZ (black diamonds) together with different peak positions from several MDCs and EDCs plotted on top of the bands (see red open circles). Black parabola (convex and concave) were obtained by fitting the red open circle curves with a parabola function. These figures show that the $\alpha_1$ pocket and $u$ band give rise to a hole FS sheet, while the $\delta$ FS sheet gives rise to an electron FS sheet. $M$, $X$ and $\Gamma$ denote the high symmetry points. The blue and white colours indicate the low and high photoemission intensity respectively. (b) and (d) show examples of MDCs taken at $E_F$ and fitted with Lorentzian functions. (f) exhibits an example of an EDC spectrum fitted with a Gaussian function. this EDC was taken at the position indicated by the black arrow in (e).
has an upward parabola dispersion as illustrated by the black parabola plotted on top of the band. By comparing Figure 5.8(e) and 5.7(a), one can conclude that $\delta$ FS sheet gives rise to an electron pocket since it has the shape of an upward parabola occupied below $E_F$.

Figures 5.8(b) and 5.8(d) present examples of MDC curve taken at $E = E_F$ that have been fitted using Lorentzian line shapes. These plots demonstrate the good agreement between fit and experimental data.

### 5.4 Line Shape Analysis

In this section we investigate the line shape of Sr$_3$Ru$_2$O$_7$ spectra taken from a 2D image around the $\Gamma$ point (see Figure 5.9). Figure 5.9(b) shows evidence for signature of strongly correlated effects in the line shape of the quasiparticle peak of Sr$_3$Ru$_2$O$_7$ from the EDC taken at the position indicated by the white arrow in Figure 5.9(a). Figure 5.9(b) shows how the spectral weight of the coherent quasiparticle peak has been reduced and pushed to higher binding energies to form the characteristic “peak-dip-hump” line shape of strongly correlated systems [136]. This kind of line shape was observed for the first time in high-$T_c$ superconductors [244, 245] and then in other correlated systems such as Bi misfit cobaltates [246]. The origin of this kind of line shape in high $T_c$ superconductor was suggested by the fact that it comes naturally by the interaction between electrons and a sharp collective mode [244], which modifies the shape of the self energy resulting in the appearance of an incoherent peak (the hump). The position of the hump is situated where the spectrum changes the slope as highlighted by the black arrow in Figure 5.9(b) [245]. This hump position is the value corresponding to the intersection point of two red dashed lines presented in Figure 5.9(b). The hump for this particular EDC was found to be located at 38 meV below the Fermi level. The origin of the hump in Sr$_3$Ru$_2$O$_7$ and further investigation on the dispersion are beyond the scope of this dissertation.

Figures 5.10(a) and (b) show the plotting of the full width half maximum (FWHM) versus binding energy of the quasiparticle peak for the momentum energy-cut acquired in Figure 5.2(a) and in the same cut taken with different light polarization (CP+) with the same experimental conditions. These
FWHMs values were obtained by fitting several EDCs from the cuts mentioned in the previous sentence. These experimental FWHMs were then fitted with a parabolic function (see black dashed lines in Figure 5.10) indicated fingerprint of Fermi liquid behaviour of this heavy quasiparticle in Sr$_3$Ru$_2$O$_7$ [247].

### 5.5 Kinks in the MDC-Derived Band Dispersion

An introduction on kinks in ARPES spectra was given earlier in section 2.8.2. This section reports a detailed analysis of kinks observed in the electronic band dispersion of Sr$_3$Ru$_2$O$_7$. Figures 5.11(a)-(e) and 5.11(k)-(p) show raw ARPES intensity cuts for selected positions in the first and adjacent first BZs in a direction indicated by the lines on the BZ shapes (see white and blue diamonds on top of cuts). The ARPES cuts shown in these figures were measured with a photon energies of 25 and 65 eV in LHP and LVP. These kinks belong to $\alpha_1$, $\gamma_2$ and u band FS sheets as indicated in these figures. Our analysis focuses on the spectral features indicated by red arrows.

The method used was to extract the MDCs from different ARPES cuts from Figures 5.11(a)-(e) and 5.11(k)-(p) and to fit the peak positions, in order to find the dispersion of these spectral features. Figure 5.12(a) shows, as an example of the MDC fitting procedure, for the series of MDCs extracted from the purple boxes highlighted in Figures 5.11(m) and 5.11(n). Each of these MDCs has been generated with an energy widows of 1.6 meV in 1.6 meV steps and was fitted with a combination of Lorentzian functions (see an example of fitting in Figure 5.12(b)). For the particular band of interest several MDCs was fitted from $E_F$ down to the binding energy where that spectrum became noisy to be fitted reasonably, in order to get the peak positions of each MDC. The peak positions extracted in such way are plotted as a function of momentum in Figures 5.11(f)-(j) and 5.11(q)-(v) for a comparison with the raw data. On these figures we notice a change in the slope often called “kink” in the dispersion of these bands. In order to obtain the energy of nine kinks presented in this work, the low energy parts of the experimental dispersions near to the Fermi energy level were fitted with two straight lines passing through the Fermi momentum $k_F$ (see blue and black straight lines in Figure 5.11). These two lines intersect at the kink energy (pointed out by black arrows). The values of kink energies of approximately 21, 15, 16.8 and 10 meV were extracted after a careful analysis of each experimental dispersion. The summary of kink energies determined in this dissertation together with their corresponding FS sheets is exhibited in Table 5.1.

As reported earlier in section 2.8.2, the behaviour of kinks observed in Sr$_3$Ru$_2$O$_7$ was found to be similar to the one reported in ARPES of the cuprate superconductors by Lanzara et al. [191]. As for high $T_c$ superconductors there has been a debate for whether the presence of kinks had to be assigned
Section 5.5. Kinks in the MDC-Derived Band Dispersion

Figure 5.11: Panels (a)-(e) and (k)-(p): ARPES intensity measured at different positions in the first and adjacent first BZ. The band of interest is indicated by the red arrow in each cut. The black and white diamonds at the top (bottom) of each cut represent the drawing of the first and adjacent first BZ of Sr$_3$Ru$_2$O$_7$. $X$, $\Gamma$, $M$ indicate the positions of the high symmetry points in the first and adjacent first BZ. The position and the direction in which the corresponding cut was acquired are shown by the red vertical and oblique lines on the BZ. The low and high intensity are presented by blue and white colours respectively. Panels (f)-(j) and (q)-(v): The red circles account for the experimental dispersion extracted from the fitting of MDCs extrapolated from the corresponding cuts in the top panels for the band of interest. Black arrows indicate where kinks are observed. The linear fit to the low energy data is presented by the blue lines.
to electron-phonon coupling [191, 248], or to magnetic fluctuations [249, 250, 251]. Therefore, it is very useful to understand if the kinks observed in this work are due to the presence of electron-phonon coupling or spin fluctuations.

To understand the microscopic origin of the kinks in low energy band structure of Sr$_3$Ru$_2$O$_7$, we compare in Table 5.2 the kink energies obtained in this work to the energy of the phonon modes observed in a previous Raman study on Sr$_3$Ru$_2$O$_7$ and lattice dynamic calculations from Ref. [15]). We have also indicated in the table the symmetry of the Raman modes, i.e., the observed Raman lines $A_g$ or $B_{1g}$ that are attributed to particular atomic vibrations in the Raman study and lattice dynamic calculations. It should be noted that the $A_g$ phonon mode corresponds to the in-plane rotations of the middle RuO$_6$ octahedra and to the out-of-plane vibrations of Ru, Sr and O, while the $B_{1g}$ phonon mode is associated with the internal vibrations of the RuO$_6$ octahedra [15]. Table 5.2 shows that all kink energies resolved in our ARPES data are in very good agreement with the phonon energies derived in Ref. [15], indicating a compatibility between their energy scales. Therefore, one can deduced that the observed kinks in the electronic band dispersion of Sr$_3$Ru$_2$O$_7$ are due to the presence of strong electron phonon couplings. This tells us that in this system kinks are a manifestation of a coupling between structural and magnetic properties.

The spin-phonon coupling plays a significant role in the unusual properties observed in Sr based layered ruthenates [252]. Both Sr$_3$Ru$_2$O$_7$ and Sr$_4$Ru$_3$O$_{10}$ are particularly good materials from the perspective of spin lattice coupling since the presence of a large spin phonon coupling leads to tunable phase transitions in which structural properties are manipulated using the external parameters such as applied magnetic field, pressure or strain [100]. For instance, Sr$_3$Ru$_2$O$_7$ was found to be an enhanced Pauli paramagnet [98, 119] that presents induced ferromagnetism upon application of hydrostatic pressure [119] or magnetic field [43, 123]. It was suggested by density functional calculations that the induced ferromagnetism in Sr$_3$Ru$_2$O$_7$ compound results from rotations of the RuO$_6$ octahedra that leads to an orthorhombically distorted unit cell [144]. Thus, this was not supported by a previous Raman spectroscopy study, but only by a previous lattice dynamic calculations in which the frequency of 108 cm$^{-1}$ ($\approx 13.40$ meV) $B_{1g}$ phonon mode contributes strongly to magnetic order in Sr$_3$Ru$_2$O$_7$ [15]. This frequency demonstrates a sensitive structural contribution to magnetic order in Sr$_3$Ru$_2$O$_7$ which corresponds to the ARPES kink of $\approx 10$ meV.
Section 5.6. Renormalisation of the Band Dispersion

5.6 Renormalisation of the Band Dispersion

We saw earlier in section 2.8.1 that band renormalisation can occur because of electron-electron correlations and/or coupling of the electrons to collective modes, such as lattice vibrations [184]. In this section we discuss the renormalisation effects in the band dispersion of Sr$_3$Ru$_2$O$_7$.

Figures 5.13(a) and (b) exhibit ARPES intensity plots measured with a photon energy of 65 and 25 eV in LHP for the samples C679C9 and C679D2, respectively. The $\gamma_2$ and u bands are analysed in these cuts. In order to study the behaviour of these bands (indicates by black arrows) up to the Fermi level, the binding energy of the MDCs maxima for the two bands have been followed down to a binding energy of 0.08 and 0.025 eV, respectively. These maxima MDCs were plotted as a function of momentum in Figures 5.13(c) and (d) (see red open circles which are the MDCs peak maxima derived dispersion of $\gamma_2$ and u band). We also saw earlier in section 2.8.1 that in the case where there are no interaction in the system, the spectral function (2.31) is a Delta function with the pole at $\omega = \varepsilon_k$ and the dispersion would be depicted by a straight line near to the Fermi level. Therefore, due to the presence of interactions in the system, one obtains a renormalised quasiparticle dispersion caused by the self energy that leads to a shifting and broadening of the non interacting spectral function [186]. This is reflected in Figures 5.13(c) and (d) by red open circles that deviate from straight lines (see black lines in these two figures).

The previous investigation on band dispersion analysis of high temperature superconductors have reported band renormalisation in these systems. Therefore, it is known that the presence of electron phonon interactions in cuprate superconductors are responsible of leading to 1) a renormalised quasiparticle dispersion, 2) the quasiparticle lifetime near the phonon energy and 3) mass enhancement of the low energy excitations immediately below the Fermi level [253]. It could also be possible that the renormalised bands observed in the electronic band dispersions of Sr$_3$Ru$_2$O$_7$ is due to the presence of the electron phonon coupling. This is sustained by the fact that all ARPES kink energies acquired in this
work are the same energy scale as the phonon mode obtained by Raman spectroscopy investigations, as reported in the previous section.

At the end of this section, one can conclude from the above explanations that the presence of kinks and bands renormalisation in the low energy electronic structure of Sr$_3$Ru$_2$O$_7$ is the proof of a coupling between electrons and phonons. To conclude therefore, it is important to 1) perform more ARPES measurements studies in order to examine the possibility of spin lattice coupling in this compound; and 2) perform temperature dependent ARPES experiments in order to know if the resolved kinks are magnetically coupled, i.e., to know if they are not strengthened or weakened above the transition temperature because these studies will yield to a more quantitative analysis on the presence of renormalised bands and kinks mechanism such as characteristic energy scale, lifetime and coupling strength.

### 5.7 Van Hove Singularities: Origin of Metamagnetism in Sr$_3$Ru$_2$O$_7$

The mechanism and the microscopic origin of the metamagnetic transition in the bilayer ruthenate Sr$_3$Ru$_2$O$_7$ are presented in this section. A careful discussion on the itinerant metamagnetism was presented in sections 1.5 and A.2. Here, we only present electronic bands of Sr$_3$Ru$_2$O$_7$ that are susceptible
Section 5.7. Van Hove Singularities: Origin of Metamagnetism in Sr$_3$Ru$_2$O$_7$

Figure 5.14: (a, b) ARPES two dimensional cuts obtained in the proximity of Fermi energy $E_F$ around the $X$ point. These cut were acquired at a temperature of 1 K with a photon energy of 20 eV with linear horizontal (LHP) and vertical (LVP) polarization. They were taken along the direction parallel to the high symmetry line $\Gamma X$ as shown the red line in the sketch of the first BZ. White and blue colours represent the high and low intensity, respectively. The red and blue curves plotted on top of the band correspond to the momentum dependence of the quasiparticle peak binding energy obtained by fitting with a Gaussian function a binding energy versus momentum curves with several EDCs. On these figure the $d_{xy}$ orbital character of the band is mentioned. The left side of (a) and the right side of (b) present very sharp peaks in DOS located below a few meV obtained by integrating a momentum over a full range of figure (a) and (b). (c) Momentum dependence of peak binding energy fitted from momentum-energy cuts at different polarisations. These peak positions were found by fitting EDCs taken from (a) and (b) with a Gaussian function (the ARPES momentum-energy cuts for circular polarisations are not presented in this work). (d) ARPES spectrum that shows an example of EDC fitting. This peak is one of the sharpest peak in the raw data with a FWHM of $\sim 6$ meV.

Recent work done by Tamai et al. has reported the presence of vHS associated to $\gamma_2$ FS sheet with a significant $d_{xy}$ contributions in Sr$_3$Ru$_2$O$_7$ (see Figures 1.18(a) and (b) and section 1.4.3 for more details). More recently, Allan and coworkers [19, 136] have reported the presence of extremely flat bands along the high symmetry direction $\Gamma X$ that is confined to a narrow energy range of $\sim 5$ meV below the Fermi energy $E_F$ (see Figure 1.20). Their results for the band dispersion around $X$ point shows two vHS, one of which is in agreement with that reported by Tamai et al. [21] and another one is a new one. They observed a vHS associated to $\gamma_2$ FS sheet with a significant $d_{xy}$ orbital contributions, while another one is associated to $\alpha_2$ FS sheet with a significant $d_{x^2-y^2}$ contributions. According to their findings the $\gamma_2$ and $\alpha_2$ bands will be strongly affected by the application of a suitable external magnetic field. Thus, this means that resolved peaks in the DOS will jump discontinuously over the Fermi level and give rise to the metamagnetic behaviour seen in Sr$_3$Ru$_2$O$_7$ compound, as proposed by Binz et al. [16].

Our data also report direct evidence of flat Ru 4$d$ bands in the proximity of the Fermi energy that give rise to vHS located within a few meV below $E_F$ which is the energy scale relevant for metamagnetism. Figures 5.14(a) and (b) show two cuts measured around the $X$ point with photon energy of 20 eV with horizontal and vertical polarization respectively, in the vertical direction parallel to the $\Gamma X$ line. The
Figure 5.15: (a, b) ARPES band dispersions taken close to $E_F$ around the $\Gamma$ point acquired at different polarizations (LHP and LVP) along the direction indicated in the first BZ (see black rotated square) and at temperature of 1 K with a photon energy of 20 eV. Blue and white colours denote the low and high intensity respectively. The red and blue markers plotted on top of the cuts indicated the fitted binding energy versus momentum curves. (c) Momentum dependence of peak binding energy fitted from momentum-energy cuts at different polarisations. These peak positions were obtained by fitting several EDCs taken from (a) and (b) with a Gaussian line shape (the momentum-energy cuts for circular polarisations are not exhibited in this dissertation). (d) An example of the narrow peak in the raw data with a FWHM of approximately 6 meV.

blue and red curves plotted on top of each cut respectively, represent the position of the dispersing quasiparticle peak as a function of momentum $(k_{||})$ which have been determined by fitting several EDCs with a Gaussian function. Figure 5.14(c) exhibits the plotting of peak positions for four different light polarizations. We can see from these plots that the dispersion of the quasiparticle peak is very narrow and confined within a bandwidth of approximately 2.5 meV for all polarizations since the binding energy range is located between 3 to 6.8 meV. It should also note that the central part of the bands, i.e., the

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We have fitted many EDCs with a Gaussian function instead of MDCs with Lorentzian line shape due to the fact that the two bands presented by Figures 5.14(a)-(b) are too thin.
Section 5.7. Van Hove Singularities: Origin of Metamagnetism in Sr$_3$Ru$_2$O$_7$

Figure 5.16: Band dispersion of Sr$_3$Ru$_2$O$_7$ along the high symmetry direction ΓX as indicated the red (a) and green (b) lines plotted on top of white diamonds. (a) and (b) also show the positions of $\alpha_1$, $\alpha_2$, $\gamma_2$ FS sheets and two vHS. Moreover these 2D cuts were acquired with photon energy of 20 eV (a) and 21 eV (b) respectively, with horizontal polarization. (a) This cut was acquired with a temperature of 1 K. (b) presents δ pocket and the peak-dip-hump shape of the spectra (see the left inset), which is a characteristic of the strong correlation system. white colour represents the high intensity while the blue represents the low intensity. Figure reproduced from [19].

one centred at $X$ point does not show any dispersion and it is centred at binding energy of $\sim 5$ meV. Such flat band have a complex DOS just below the Fermi level and give rise to vHS in the near Fermi level. This vHS is associated to the $\gamma_2$ FS sheet with $d_{xy}$ orbital character.

The same scenario and analysis as mentioned in the previous paragraph was also done in the cuts measured around the Γ point with the same photon energy and polarizations (see Figures 5.15(a)-(c)). Here, the dispersion of the quasiparticle peak is even narrower with a bandwidth of $\sim 2.2$ meV for all polarizations, since the binding energy range goes from 1.2 to 3.4 meV. This band does not show any dispersion in the central part of the band and it is centred at an average binding energy of $\sim 3$ meV. This kind of band gives rise to a very high DOS below the Fermi level $E_F$ and vHS located within a few meV from $E_F$. This vHS is associated to the FS sheet δ with a significant $4d_{x^2-y^2}$ orbital contributions.

Figure 5.16 shows a comparison between 2D cuts acquired along the high symmetry direction ΓX with photon energy of 20 eV (in this work) and 21 eV (with the one from Allan thesis [19]) respectively (see Figures 5.16(a) and (b)). These two figures show how a flat band associated to $\alpha_2$ (with a significant $d_{xz/yz}$ orbital contribution) is confirmed to a narrow energy range of $\sim 5$ meV below the Fermi energy. Such flat band is also among potential candidates that give rise to vHS in the near Fermi level of Sr$_3$Ru$_2$O$_7$. 
In order to resolve vHS in the near Fermi level DOS, it is important to emphasize the effect of resolution. In the work of Tamai et al., they manage to achieve an experimental resolution of 5.5 meV in order to resolved flat bands. In our experiment in Sr$_3$Ru$_2$O$_7$, it was noticed through EDC fitting that the FWHM of the sharpest peak is approximately $\sim$ 6 meV (see Figures 5.14(d) and 5.15(d)). The resolutions are therefore comparable.

One noticed at the end of this section that the low energy electronic structure of Sr$_3$Ru$_2$O$_7$, reveals the presence of heavy quasiparticles associated to three very flat bands centred around X and $\Gamma$ points in the first BZ with different orbital character namely $d_{xy}$, $d_{xz,yz}$ (confirmed works done by Tamai et al. [21] and Allan [19]) and $d_{x^2-y^2}$ (observed for the first time in this work). These types of bands give rise to vHS closed to the Fermi level, which are responsible for the appearance of multiple metamagnetic transitions observed in this compound, as proposed Perry and co-workers [122].
6. Summary

The aim of this dissertation was to analyse the near Fermi level electronic structure of Sr$_3$Ru$_2$O$_7$. This analysis was done in order to give a detailed study of the FS maps and band dispersions of Sr$_3$Ru$_2$O$_7$ by analysing data from angle resolved photoemission spectroscopy (ARPES) measurements, to find the location and symmetry of the vHS within the BZ and thus establish a link between electronic structure and metamagnetism in this compound. The experimental results exhibited in chapters 4 and 5 are the basis of a number of conclusions related to this aim. Moreover, a number of suggestions for future research are also shown in this summary.

6.1 Conclusions

Chapter 1 of this dissertation is dedicated in general to the previously reported magnetic and electronic properties of Sr ruthenates Sr$_{n+1}$Ru$_n$O$_{3n+1}$, focusing specifically on the bilayer compound Sr$_3$Ru$_2$O$_7$.

Chapter 2 exhibits some main features of the theoretical aspects of ARPES, such as self energy, since it is very important to know the electron self energy in order to get insights into the physical properties of a solid.

Chapter 3 presents some important features of the experimental aspects of ARPES. It also describes the main characteristics of synchrotron radiation and electron energy analyser, the Scienta R4000, and examines the functionalities of the main components of a synchrotron storage ring and analyser. The same chapter presents how to acquire a 2D images with a Scienta R4000 spectrometer and the common method used in order to analyse these 2D images.

The experiment was performed at the 1$^{\text{st}}$ ARPES endstation installed at the beamline of the 3$^{\text{rd}}$ generation high-brilliance synchrotron radiation source BESSY II in Berlin (Germany), using a Scienta R4000 electron energy analyser and a He$^3$ cryostat [205].

Chapter 4 deals in particular with the four experimental FS maps of Sr$_3$Ru$_2$O$_7$ acquired in this work. From the careful analysis of these maps we identified three FS sheets namely $\delta$, $\alpha_1$, $\alpha_2$ with the same shape as those observed in the literature, while their sizes differ slightly from the sizes calculated by Tamai et al. [21]. We know from section 4.5 that two bands cannot cross each other in the reciprocal space, but this situation was not observed in our four FS maps and therefore the shape of some bands (bands located around the $M$ points) are similar to those presented by Mercure [71] in Figure 4.4(e). We also observed distortions and displacements of some high symmetry points from their correct positions in our four FS maps which is explained in more detail in section 4.8. In order to understand what is going on in detail in our FS maps, we symmetrized two FS maps to obtain the periodicity of our FS maps (see Figures 4.10(b) and 4.12(a)). We also observed in one FS map, exhibited by Figure 4.9 bands which have not been predicted by the theory. These bands are well elucidated in Figure 4.10(a) by dashed curves.

Chapter 5 deals particularly with the band dispersions of Sr$_3$Ru$_2$O$_7$. It was possible to distinguish some features in band dispersions and FS maps of Sr$_3$Ru$_2$O$_7$ by changing light polarization and also by using different photon energies. For instance, we can see in Figure 5.3 how the bands indicated by pink arrows are better resolved in the cut acquired with higher photon energy. We observed that band dispersions along the high symmetry direction $\Gamma'X\Gamma$ extracted from ARPES measurements with different photon energies and polarizations presented by Figure 5.4(a) is in perfect agreement with the one exhibited by
Allan et al. [136] in Figure 5.4(a). After a careful analysis of the inner most bands centred at the \( \Gamma \) points (see the inner most parabolic bands in Figure 5.4(a) centred at the \( \Gamma \) points), we interpreted the presence of these bands as replica bands of the theoretical \( xy \) band (see green parabolic bands in Figure 5.4(b)) presented by Allan et al. [136], shifted by the vector \( \pm \Gamma X \).

The values of the kink energies of 21, 15, 16.8 and 10 meV were extracted from the electronic band dispersions. These kink energies were found to be very close to the energies of the vibrational states detected by the previous Raman spectroscopy measurements [15] and lattice dynamic calculations (LDC) [15]. Thus, the presence of these resolved kinks was explained as evidence for the presence of strong electron phonon coupling in this system. Additionally, the 108 cm\(^{-1}\) \( B_{1y} \) phonon mode found by LDC in Ref. [15] corresponds to the ARPES kink of 10 meV. This demonstrates evidence of a structural contribution to the magnetic order in \( \text{Sr}_3\text{Ru}_2\text{O}_7 \). This suggests that there exists a possible spin lattice coupling in this system.

ARPES data presented in this dissertation exhibit flat bands, \( \gamma_2 \), \( \delta \) and \( \alpha_2 \), that show a complex DOS closer to the Fermi level \( E_F \) which give rise to sharp peaks in the DOS a few meV from \( E_F \) in \( \text{Sr}_3\text{Ru}_2\text{O}_7 \). The flat band \( \gamma_2 \) confirmed the presence of this vHSS observed in this compound by Tamai et al. [21] with a \( d_{xy} \) orbital character, while the flat band \( \alpha_2 \) also confirmed the presence of vHSS seen in this system by Allan et al. [19] with \( d_{xz}, d_{yz} \) orbital characters. Finally the vHSS associated to the \( \delta \) pocket is a new flat band observed in this system with \( d_{x^2-y^2} \) orbital character. We can conclude at this level that the flat bands observed in this compound with different symmetry are responsible for the multiple metamagnetism observed in this compound.

6.2 Suggestions for Future Work

Given that the Fermi surface maps of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) in the literature and those acquired in this work present different features around the \( M \) and \( X \) points and different sizes and similar shapes of FS sheets centred at the \( \Gamma \) point, i.e., the shape and size of FS sheets of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) resolved in literature around the \( M \) and \( X \) points are not 100\% the same and those centred at the \( \Gamma \) point present the same shape with different sizes, it is highly recommend to perform momentum dependent measurements around the high symmetry points in order to investigate if all the FS sheets centred at these points possess the same size and shape.

With the presence of the new features on the FS of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) shown by dashed lines in Figure 4.10(a), it is also highly recommended to perform another ARPES experiment on the near Fermi level band structure of this compound in order to reconstruct another FS and to confirm the presence of these bands.

Damascelli et al. [88], by investigating the surface and bulk electronic structure of the unconventional superconductor \( \text{Sr}_2\text{RuO}_4 \) which is the parent compound of \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) have realised that the FS map of \( \text{Sr}_2\text{RuO}_4 \) is composed of the FS from the bulk and the one from the surface. Moreover, the reconstruction results in the appearance of replica bands, shifted by the vector \( \Gamma X \). The same situation can also occur in the \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) compound.

New bands centred at \( \Gamma \) points that we observed and which had been predicted by the theoretical work of Allan et al. in Ref. [136] seem to be reproduced periodically in the Brillouin zones, therefore, motivating further ARPES studies. It should be noted that the bands that they observed are centred around the \( X \) point and those that we resolved experimentally in this work are centred at the \( \Gamma \) points, but by shifting the band that they observed by \( \pm \Gamma X \), it corresponds to the experimental band that we have resolved.
The 108 cm$^{-1}$ $B_{1g}$ phonon mode found by LDC in Ref. [15] as stated above, indicates that the possible spin lattice coupling in this system still needs to be investigated. This investigation can be done by performing electronic calculations and more ARPES experiments on the near Fermi level band dispersion of Sr$_3$Ru$_2$O$_7$. Furthermore, it is necessary to perform more quantitative analysis of kink energies in Sr$_3$Ru$_2$O$_7$ in order to extract relevant parameter such as the coupling strength, characteristic energy and lifetime. In order to see if the resolved kink energies are magnetically coupled, i.e., to see whether they behave the same below and above the magnetic transition temperature, it is highly recommend to perform temperature dependent ARPES experiments on Sr$_3$Ru$_2$O$_7$. 

Appendix A. Theory of Metamagnetism

Metamagnetism is often defined in literature as a sudden superlinear rise in magnetisation as a small change of an external magnetic field is applied. Such phenomenon may have a different origin depending on the character of the electrons giving rise to it:

- Metamagnetism in localised systems is seen with an antiferromagnetic transition and it is attributed to spins-flop or spins-flip reorientation \[254\]. This type of metamagnetism was first treated theoretically using mean field theory by Stryjewski and Giordano \[255\]. Such metamagnetism is observed for example in the insulating antiferromagnet double layered calcium ruthenate Ca$_3$Ru$_2$O$_7$ \[256\].

- Metamagnetism observed in an itinerant system is associated to a rise in magnetisation. The peculiar explanation of this kind of metamagnetism is associated to the presence of sharp peaks in the density of states located a few meV around the Fermi level \[137\]. This phenomenon is well explained in section A.2. This type of metamagnetism was first treated theoretically by Wohlfarth and Rhodes \[241\] and referred to an itinerant metamagnetism. Similar metamagnetism is observed in many heavy fermion systems such as CeRu$_2$Si$_2$ \[257\] and in some strongly correlated electron systems such as Sr$_3$Ru$_2$O$_7$ \[123\].

The following sections will deal with the theory behind these two types of metamagnetism.

A.1 Metamagnetism in Localised Systems

Figure A.1 from Ref. \[258\] shows how in an antiferromagnet compound with uniaxial symmetry, the perpendicular susceptibility $\chi_\perp$ is larger than the parallel susceptibility $\chi_\parallel$ below the Néel temperature $T_N$. In order to provide more explanation on the previous sentence, i.e., on the fact that $\chi_\perp > \chi_\parallel$ below $T_N$, we will assume two different directions of the applied magnetic field with respect to the antiferromagnetic direction (D).

Let consider an antiferromagnetic compound which is constituted by two sublattices $A$ and $B$ with opposite orientations in magnetisation ($M$) and with an uniaxial symmetry for the two cases.

When a small field is applied perpendicular to the antiferromagnetic direction (D) below $T_N$, the magnetisation of each sublattice (A and B) rotates by a small angle $\alpha$ (see Figure A.1). This rotation minimises the total energy densities, namely the exchange energy $E_{ex}$, the Zeeman energy $E_Z$ due to the field applied and the anisotropy energy $E_a$. By setting the magnetisation of each sublattice as $|M_A| = |M_B| = M'$ and by considering a uniaxial anisotropy, these densities (per unit volume) can be expressed by limiting the expression to the second order in $\alpha$ as: $E_Z = -2\mu_0 M' H \alpha$, $E_{ex} = \mu_0 [-w M'^2 - w M'^2 (1 - 2\alpha^2)]$ (with $w > 0$ and $w' > 0$), and $E_a = k_1 \alpha^2$ where, $w$ and $w'$ denote the molecular field coefficients between the two sublattices and within each sublattice respectively. $\mu_0$ is the vacuum permeability, $H$ is the field apply along or perpendicular to the antiferromagnetic direction (D). $k_1$ often represented as $k_u$ is defined as a magnetocrystalline anisotropy constants, it

\[\text{The susceptibility of a material describes how this material responds to an applied magnetic field at a certain temperature.}\]

\[\text{Magnetocrystalline anisotropy is defined as a variation of magnetic properties with crystallographic orientation and its magnitude depends on the ratio of spin orbit coupling and crystal field energy \[259\].}\]
has units of energy density and depends on the composition of the compound and temperature. The effect of the field and the thermal agitation on moments is shown in the insets of Figure A.1. The total energy minimises with respect to $\alpha$ leads to the equilibrium value $\alpha = \frac{\mu_0 M' H}{(2\mu_0 w M'^2 + k_1)}$, and to the perpendicular susceptibility:

$$\chi_\perp = \frac{2M'\alpha}{H} = \left[w\left(1 + \frac{k_1}{2\mu_0 M'^2}\right)\right]^{-1}. \quad (A.1)$$

Since the coefficient $w$ is practically temperature independent, and the expression $\frac{k_1}{2\mu_0 M'^2}$ usually remains very small compared to the unity, moreover, it varies weakly with temperature. Thus, by applying all these approximations above on equation A.1, the expression of the susceptibility (A.1) becomes $\frac{1}{w}$ which is approximately constant below $T_N$, as illustrated Figure A.1.

Let consider now the case where the field is applied along the antiferromagnetism direction (D) (see Figure A.1). With this application of the magnetic field ($H$), the magnetisation of parallel and antiparallel sublattice are clearly modified (if $T \neq 0$) and according to the Brillouin law, this modification is based on the shift in magnetisation of the parallel and antiparallel sublattices as $M' + \Delta M$ and $M' + \Delta M$ respectively. When a small field is applied, the expansion to first order of the susceptibility is given by [258, 260]:

$$\chi_\parallel = \frac{2\Delta M}{H} = \frac{2C' \left[\frac{3J}{(J+1)}\right] B'_J(x_0)}{[T + wC' \left(\frac{3J}{J+1}\right) B'_J(x_0)]}; \quad (A.2)$$

with $C' = \frac{\mu_0 m_{eff}^2 (n/2)}{3K_B}$, where $n/2$ is the number of magnetic atoms of each sublattice per unit volume, $\mu_0$ and $K_B$ are permeability of vacuum and Boltzmann constant respectively. $B'_J(x)$ denotes the derivative of the Brillouin function $B_J(x)$ with respect to $x$ where $J$ represents the total angular momentum quantum number and $x_0 = \frac{\mu_0 m_w M_\alpha}{K_B T}$, where $\alpha = A, B$, the coefficient $w$ denotes the intersublattice molecular field coupling. The magnetisation of each sublattice is maximum at $T = 0K$ and the small change in magnetisation $\Delta M = 0$. Thus, the parallel susceptibility ($\chi_\parallel$) is zero at $T = 0K$. At $T_N$, $x_0 = 0$, $T_N = wC'$ and $B'_J(x_0) = (J + 1)\frac{3J}{3J}$ and by substituting these into equation A.2, one can then shows that $\chi_\parallel = \frac{1}{w}$ which is the same expression or value as $\chi_\perp$ and the paramagnetic susceptibility.
The parallel susceptibility ($\chi_\|$) continuously increases between 0 to $T_N$ (see Figure A.1). Figure A.1 shows how both the parallel and antiparallel susceptibility change their slope at $T_N$ and above $T_N$ they are practically the same (provided only if the anisotropy is not too large). In conclusion Figure A.1 is an agreement with the results obtained from experiments on of a large number of antiferromagnetic substances, in particular those where the only important interaction are those in the model. For other materials, the model is qualitatively considered for the observed properties.

The energy density in a given field being $E = -\chi\mu_0 H^2$ (where $\chi$ is the susceptibility of the antiferromagnet compound, $\mu_0$ is the constant permeability and $H$ is the magnetic field), the state with the magnetic field $H$ perpendicular (or almost) to the magnetisation is more stable (i.e., energetically favourable) than the state with the magnetic field $H$ parallel (or antiparallel) to the magnetisation. When applying a low magnetic field parallel to the magnetisation direction, it tends to make a sudden change toward the former position. Nevertheless, this effect works against the magnetocrystalline anisotropy\(^3\) which favours the configuration stable in zero magnetic field. Thus in order to investigate the magnetic field effect on an antiferromagnet in the above simple model, two situations have to be considered, i.e., the cases of large and weak anisotropy energy. An antiferromagnet is constituted by two sublattices $A$ and $B$ with opposite orientation in magnetisation $M$.

If an increasing magnetic field is applied along the antiferromagnetic direction (D) and if the anisotropy energy is weak (small enough), the magnetisation of each sublattice, i.e., $M_A$ and $M_B$ suddenly switches for a critical value of the field into the perpendicular configuration sketched in the Figure A.2(a), so that the total magnetisation ($M = M_A + M_B$) suddenly increases. Figure A.2(a) (see the arrow that connects Figure A.2(b) and A.2(a)) also shows how in large fields, the magnetisation of each sublattice progressively turns and tend to align along the field direction. The curve (b) of Figure A.2(a) represents the associated variation of the total magnetisation. Such a transition is called a spin-flop metamagnetic transition [258].

If the field is apply parallel to the antiferromagnetism direction (D) and if the uniaxial anisotropy is

---

\(^3\)The term magnetocrystalline anisotropy just describes the fact that some material takes more energy to be magnetised in a certain directions more than others.
large, the magnetisation of each sublattice stays parallel to this direction. By increasing the magnetic field, the magnetisation of the sublattice antiparallel to the field suddenly rotates to a critical value of the field and becomes parallel to the field. In this case the total magnetisation switches from a smaller value to a larger value close to saturation (see curve (b) in Figure A.2(b)). Such a transition is called a spin-flip metamagnetic transition [258].

Note that, when a magnetic field is applied perpendicular to (D) in both cases, the magnetisation increases approximately linearly up to saturation (see curve (a) of Figure A.2(a) and A.2(b)). This variation corresponds to the progressive rotation of moments toward the applied magnetic field. The model predicts an agreement with experimental results whatever the magnitude of the anisotropy on a transition in the magnetisation process of a single crystal when the magnetic field is applied along the antiferromagnetism direction. This suggests that the metamagnetic transition must also be observed on a polycrystalline sample [258].

It has been proved that, multi-step metamagnetic processes are observed in a large number of collinear antiferromagnetic compounds with a strong uniaxial anisotropy. In this case, each transition is associated with the partial reversal of the moments of the sublattice originally antiparallel to the field. Therefore the magnetic arrangement of the different intermediate states can be determined by neutron diffraction experiments [258].

A.2 Metamagnetism in Itinerant Systems

Most of microscopic approaches used in order to describe an itinerant electron system are based on the Stoner model. This model is defined as a mean-field approximation of the Hubbard model that summarises the basic competition between kinetic energy and Coulomb interactions [24]. This competition is at the origin of a metamagnetic transition in itinerant electron systems. This theoretical description of itinerant metamagnetism is discussed in the band picture.

The orbital degeneracy for d electrons is five-fold, but for simplicity the one band model is considered since the d orbitals in the transition metals are much localized than those of the s electrons and also because the overlap of d wavefunctions (between d orbitals) is much less than the s wavefunctions (between s orbitals) [24]. Thus, a conduction electron system is treated in one band with short range interaction, i.e., an electron system is described by the Hubbard Hamiltonian [24]:

$$ H = \sum_{lj} T_{lj} c_{l\sigma}^\dagger c_{l\sigma} + \frac{1}{2} U \sum_{l\sigma} n_{l\sigma} n_{l\bar{\sigma}}; \quad (A.3) $$

where l and j are the atomic positions, \( \sigma \) represents the spin, \( T_{lj} \) denotes a matrix element between the two sites l and j. \( c_{l\sigma}^\dagger \) and \( c_{l\sigma} \) are creation and annihilation operators of an electron localised at site l with spin \( \sigma \) respectively. \( U \) represents the exchange interaction constant, \( n_{l\sigma} \) (\( n_{l\bar{\sigma}} \)) is the density operator for electrons at site l with spin \( \sigma \) (\( \bar{\sigma} \)) and it is given by the expression \( n_{l\sigma} = c_{l\sigma}^\dagger c_{l\sigma} \) (\( n_{l\bar{\sigma}} = c_{l\bar{\sigma}}^\dagger c_{l\bar{\sigma}} \)).

This Hamiltonian (A.3) under the mean field approximation is given in the form:

$$ H = \sum_{lj} T_{lj} c_{l\sigma}^\dagger c_{l\sigma} + U \sum_{l\sigma} n_{l\sigma} \langle n_{l\bar{\sigma}} \rangle. \quad (A.4) $$

\( \langle n_{l\bar{\sigma}} \rangle \) has no dependence on position in an homogeneous system, thus \( \langle n_{l\bar{\sigma}} \rangle = \langle n_{\bar{\sigma}} \rangle \) and the equation
\[ H = \sum_{l,j} T_{lj} c_{l\sigma}^{\dagger} c_{l\sigma} + U \sum_{l\sigma} \langle n_{\sigma} \rangle c_{l\sigma}^{\dagger} c_{l\sigma}. \] (A.5)

In the reciprocal space, \( c_{l\sigma}^{\dagger} \) and \( c_{l\sigma} \) are given by the following formulas:

\[
\begin{align*}
    c_{l\sigma}^{\dagger} &= \frac{1}{\sqrt{N}} \sum_{k} c_{k\sigma}^{\dagger} e^{-ikl}; \\
    c_{l\sigma} &= \frac{1}{\sqrt{N}} \sum_{k} c_{k\sigma} e^{ikl};
\end{align*}
\] (A.6) (A.7)

where \( N \) and \( k \) denote the number of site and the momentum, respectively. By substituting equations A.6 and A.7 into A.5 and by making some simplifying, the Hubbard Hamiltonian (in the momentum space) becomes [24]:

\[
H = \sum_{k\sigma} \epsilon_{k\sigma} c_{k\sigma}^{\dagger} c_{k\sigma} + \sum_{k\sigma} U \langle n_{\sigma} \rangle c_{k\sigma}^{\dagger} c_{k\sigma};
\] (A.8)

where the first term of the equation represents the total energy of band electrons (its minimum value is obtained when \( n_{\sigma} = \bar{n}_{\sigma} \)), while the second term is the Coulomb energy for anti-parallel electrons (when the difference of electron numbers with anti-parallel spins increases, this value of the Coulomb energy is lower). \( \epsilon_{k\sigma} \left( \propto \frac{1}{N} \sum_{l,j} T_{lj} e^{-ik(l-j)} \right) \) represents the electronic dispersion with momentum \( k \) and spin \( \sigma \). \( c_{k\sigma}^{\dagger} \) and \( c_{k\sigma} \) represent the creation and annihilation operators of an electron of momentum \( k \) and spin \( \sigma \) respectively. \( U \) represents the exchange interaction constant and \( n_{\sigma} \) is the number of electrons with spin \( \sigma \) [24].

Equation A.8 can be rewritten as:

\[
H = \sum_{k\sigma} (\epsilon_{k\sigma} + U \langle n_{\sigma} \rangle) c_{k\sigma}^{\dagger} c_{k\sigma};
\] (A.9)

where \( E_{k\sigma} = \epsilon_{k\sigma} + U \langle n_{\sigma} \rangle \) represents the energy of an itinerant electron of momentum \( k \) and spin \( \sigma \) and is correlated to the number of anti-parallel electrons. The equation A.9 is similar to a Hamiltonian describing noninteracting electrons. The competition of the two terms of equation A.9, i.e., the term \( \epsilon_{k\sigma} \) and the term \( U \langle n_{\sigma} \rangle \), leads to the splitting of the energy bands. This is the Stoner model [24]. The splitting of energy bands implies the splitting of the density of states (DOS) into two subbands with spin up and spin down electrons (see Figure A.3). Thus, the magnetisation \( M \) can be written by a relation between the number of electrons of spin up and spin down in the following form:

\[
M = \mu_B (n_{\uparrow} - n_{\downarrow})
\] (A.10)

where \( \mu_B \) represents the Bohr magneton and \( n_{\uparrow} \) is the number of electrons in the spin up band and \( n_{\downarrow} \) is the number of electrons in the spin down band. The \( n_{\uparrow\downarrow} \) number of electrons derives from the DOS and it is given by the formula:

\[
n_{\uparrow\downarrow} = \int_{E_F}^{E} g_{\uparrow\downarrow}(e) f_{\uparrow\downarrow}(e) de;
\]
Figure A.3: Representation of band splitting of ferromagnetic phases in transition metals. $g(E)^{↑}$ and $g(E)^{↓}$ are density of states with spin up and spin down respectively. (a) shows a paramagnetic state where no splitting of the density of state is observed. (b) shows half-metallic ferromagnet with full spin polarisation. (c) shows ordinary ferromagnet with partial spin polarisation. [24]

where $g^{↑}(\epsilon)$ is the DOS of each subband, and $f^{↑}(\epsilon)$ is the Fermi Dirac distribution function for each subband and finally $\epsilon_F$ is the Fermi energy level [197].

The term $U$ provides a molecular field for the energy band electron. Thus, the number of itinerant electrons for each atom $n$ and the number of the relative magnetisation per atom $m$ are given by:

$$n = \langle n^↑ \rangle + \langle n^↓ \rangle \quad \text{and} \quad m = \langle n^↑ \rangle - \langle n^↓ \rangle$$

(A.11)

Taking into account equations A.10 and A.11, $\langle n^\sigma \rangle$ can be written in the following way:

$$\langle n^\sigma \rangle = \frac{1}{2}(n + \sigma m) \quad \text{with} \quad \sigma = \pm 1.$$  

(A.12)

By taking into account equation A.12, the energy of an itinerant electron found in equation A.9 becomes:

$$E_{k^\sigma} = (\epsilon_{k^\sigma} + \frac{1}{2}nU) - \sigma\mu_B\left(\frac{U}{2\mu_B^2}M\right);$$

(A.13)

where the second term is a molecular field. The energy band splitting is given by the following formula

$$E_{k^↓} - E_{k^↑} = U(\langle n^↑ \rangle - \langle n^↓ \rangle) \quad \text{if} \quad \langle n^↑ \rangle = \langle n^↓ \rangle.$$  

(A.14)

Figure A.3 shows an illustration of the spontaneous magnetisation in the system when the bands are splitting and the energy band splitting is given by equation A.14. Equation A.13 can be rewritten as equation A.15, if there is an apply field $H$ in the system and if the term $\frac{1}{2}nU$ is lefted out.

$$E_{k^\sigma} = \epsilon_{k^\sigma} - \sigma\mu_B\left(H + \frac{U}{2\mu_B^2}M\right).$$

(A.15)

For itinerant electron, the magnetisation $M$ as a function of temperature can also be written as follows:

$$M(T) = \frac{\chi_P(T)}{1 - 2(U/N)\left[\chi_P(T)/4\mu_B^2\right]}H \equiv \chi(T)H;$$

(A.16)

where $\chi_P(T)$ and $\chi(T)$ are the paramagnetic and magnetic susceptibility of itinerant electrons respectively. $N$ is the number of atoms per unit volume. The spontaneous magnetisation appears and the paramagnetic phase is unstable only when the denominator of equation A.16 is equal to zero, i.e.,
Figure A.4: Schematic representation of the formation of the metamagnetism in an itinerant system. $g_\uparrow(e)$ and $g_\downarrow(e)$ are spin up (blue color) and spin down (red color) density of states respectively. $\epsilon_F^\uparrow$ and $\epsilon_F^\downarrow$ are Fermi energy levels of spin up and spin down respectively. (a) This Figure shows that when no external magnetic field is applied, the Fermi energy levels of both spin species are in the same position. The Fermi energy levels of the two species are split due to the application of an external magnetic field. (b) and (c) show that, by applying successively larger external magnetic fields, i.e., $H_1$ and $H_2$, one of the spin species Fermi energy level is pushed more closer to the peak in the DOS. (d) Possibility that one of the Fermi energy level of spin species split further and cross over the sharp peak in the DOS [241]. (e) This Figure results in a discontinuous jump in magnetisation.

\[ 2(U/N) \left( \chi_P(T)/4\mu_B^2 \right) = 1. \]

Therefore the condition of stability for the ferromagnetic phase is given by [24]:

\[ 2(U/N) \left( \chi_P(T)/4\mu_B^2 \right) > 1. \] (A.17)

By assuming that $\chi_P(T = 0)/4\mu_B^2 = g(\epsilon_F)/2$, equation A.17 can be rewritten in terms of DOS at the Fermi energy level at $T = 0$ as follows:

\[ U \frac{N}{Ng(\epsilon_F)} > 1. \] (A.18)

The condition shown in equation A.18 is called the Stoner criterion. Equation A.18 shows that the ferromagnetism from the itinerant electrons depends on the product of the DOS at the Fermi energy level and the exchange interaction constant $U$. The Stoner criterion (A.18) is a good theoretical starting point to explain the presence of ferromagnetic fluctuations in transition metals. The following paragraph will allow us to understand how the Stoner criterion (A.18) is related to the formation of itinerant metamagnetism seen in transition metals such as Sr$_3$Ru$_2$O$_7$.

The condition for spontaneous magnetisation is known as the Stoner criterion (A.18). Therefore, the system is magnetised if the DOS at the Fermi energy level is high enough. If the Fermi energy level is tuned by some external parameter such that it moves through the peak in the density of states, then the system shows a ferromagnetic phase when the Fermi surface is close to the peak [71]. We now study how the presence of the peak can favour the metamagnetism and not just ferromagnetism. For a system to be paramagnetic, the Fermi energy level should be slightly away from the peak in the DOS such that the Stoner criterion (A.18) is not satisfied. If an external magnetic field is not applied, then the spin up and spin down Fermi levels are not split (see Figure A.4(a)). However, an external magnetic...
field is applied, then the spin up and spin down Fermi energy levels are split, and one of these is brought closer to the peak in the DOS so that the Stoner criterion \((A.18)\) is satisfied. Note that, the two spin species are shown in red (spin down) and in blue (spin up). Figure A.4(b) and A.4(c) show that, by applying successively larger external magnetic fields, i.e., \(H_1\) and \(H_2\), one of the spin species Fermi level is pushed closer to the peak in the DOS. In conclusion we can say that, when one of the spin species Fermi energy level is getting closer enough to the peak in the DOS, it is favourable for the system to rapidly increase its magnetisation, and then metamagnetic transition is obtained [71].

A second order transition between the paramagnetic and ferromagnetic phase is predicted by the Stoner criterion. In other words, the Stoner criterion predicts a continuous phase transition between the paramagnetic and ferromagnetic phase. But Wohlfarth and Rhodes [241] have shown that if the peak in the density of states is sharp enough, it is possible that the two Fermi energy level of the two species can split further and then it becomes energetically favourable for one of the Fermi energy level of the two species to jump over the peak discontinuously (see Fig A.4(d)). Therefore, this produces a first order transition in magnetisation or a discontinuous transition in magnetisation (see Figure A.4(e)). Note that these sharp peaks in DOS are usually called van Hove singularities. Wohlfarth and Rhodes [241] have also given the condition for the discontinuous transition in magnetisation that can take place at low temperature, and this condition is given by:

\[
g(\epsilon_F)g''(\epsilon_F) > 3 \left( g'(\epsilon_F) \right)^2; \quad (A.19)
\]

where \(g'(\epsilon_F)(g''(\epsilon_F))\) is the first (second) energy derivative of the DOS at the Fermi energy [16]. The condition \(A.19\) takes place for example when there is a large DOS closer to the Fermi energy level. The magnetic instabilities observed in \(\text{Sr}_3\text{Ru}_2\text{O}_7\) and \(\text{Sr}_4\text{Ru}_3\text{O}_{10}\) have been described theoretically by this condition [16].
Appendix B. Quantum Criticality

It has been largely proved that the metamagnetism observed in Sr$_3$Ru$_2$O$_7$ compound is associated with a quantum critical endpoint (QCEP) [43, 71, 123, 130]. In these paragraphs a qualitative discussion of the general features of quantum criticality in the itinerant metamagnet Sr$_3$Ru$_2$O$_7$ will be given, in order to show the similarities and the differences between the traditional quantum critical points (QCP) and QCEP.

Quantum Criticality

The thermal fluctuations\(^1\) of the thermodynamic order parameter are not observed at $T = 0$ K, but the quantum fluctuations\(^2\) (in both space and time) arise from zero point motion. These quantum fluctuations compete with internal ordering interactions and give rise to a quantum phase transition (QPT) [227]. A QPT between two ordered phases at $T = 0$ is driven by an application of a non-thermal control variables such as the magnetic field $H$ [227]. The critical value $H_c$ of the external variable at which the QPT occurs is known as a quantum critical point (QCP) (see Figure B.1(a)).

Figure B.1(a) shows how the QCP arises when a continuous second order phase transition approaches absolute zero ($T = 0$) in any phase diagram by the application of an external parameter (magnetic field in this case). For instance, if the critical temperature of a second order transition can be varied using a non thermal control parameter like magnetic field such that it is depressed to absolute zero, the end point constitutes a QCP. The graphs of the evolution of the temperature dependence of the resistivity of Sr$_3$Ru$_2$O$_7$ as a function of magnetic field applied parallel to the $ab$ plane and along the $c$ axis present a QCP at $\sim 5.5$ T (see Figure 3 in Ref. [43]) and $\sim 7.8$ T (see Figure 1 in Ref. [123]) respectively. The classical critical part of the phase diagram is suppressed as $H \rightarrow H_c$. At finite temperatures above the QCP, the thermal population of the modes of the quantum fluctuations occur, leading to a quantum critical fan region of the phase diagram [227] (see Figure B.1(a)).

Critical Endpoints

A new type of QCP was found in the Sr$_3$Ru$_2$O$_7$ compound. This type of QCP is associated with a first order metamagnetic phase transition, in which no symmetry is broken [123]. The next paragraph will

\(^1\)Thermal fluctuations denote random deviations of a physical system from equilibrium. Thermodynamic variables such as pressure and entropy experience thermal fluctuations. For instance, a system has an equilibrium pressure, but its actual pressure changes to some extent about the equilibrium.

\(^2\)Quantum fluctuation is the temporary change in the amount of energy in a point in space and time, arising from Heisenberg’s uncertainty principle.
The magnetisation rises linearly with the field in a paramagnetic material, while in a metamagnet the magnetisation rises much more sharply at a certain critical field. The metamagnetism observed in \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) refers to an itinerant metamagnetism that have been explained in more details in subsection A.2. Therefore, the metamagnetism can be defined as a discontinuous jump in the magnetisation as a function of the applied external magnetic field. The drawing of the metamagnetic transition as a function of magnetic field and temperature plane is presented in Figure B.2. This Figure shows how a metamagnetic transition is revealed in a magnetic field dependence of magnetisation. Figure B.2 shows also how, at a low temperature \( T_3 \), the size of the jump in magnetisation is bigger. While, this size of the jump in magnetisation decreases as the temperature is increased until the magnetisation becomes continuous at a critical endpoint (see red point in Figure B.2) at \( T_2 \). The continuous transition is observed for example a \( T_1 \). From this previous explanation of Figure B.2, we can just conclude that a critical endpoint terminates a line of first order metamagnetic transitions.

**Quantum Critical Endpoints**

From the previous paragraph we saw that the signatures of quantum criticality are not only limited to system with \( 2^{nd} \) order classical transition. Figure B.1(b) presents a representation of how a critical endpoint \( (H_{c1}, T^*) \) of a line of first order transition may be depressed towards \( T = 0 \) by the application of an external magnetic field. A first order transition (as function of \( H \)) when \( T < T^* \) becomes a crossover (as a function of \( H \)) at temperatures above \( T^* \). The value of both \( T^* \) and \( H_{c1} \) depend on the \( u \) (\( u \) is one of the three axes presented in Figure B.1(b)) values. A quantum critical endpoint (QCEP) at \( (H_{c2}, T^* = 0) \) occurs at some critical value of \( u \) see Figure B.1(b). The free energy landscape of such a system would be flattened on approach to the QCEP, thus it is making the system susceptible to novel phase formation, with quantum fluctuations that also plays a crucial role in the physics of the system \([227]\).
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