Emergent electronic matter: Fermi surfaces, quasiparticles and magnetism in manganites and pnictides

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Emergent electronic matter: Fermi surfaces, quasiparticles and magnetism in manganites and pnictides

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Cover: Photoemission spectra collected on the bilayered manganite LSMO.

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Achtung, Achtung: das Injektion System wird in betrieb genommen... 

(Waring message upon the start of the electron injection into BESSYII, the storage ring of the Helmholtz Zentrum Berlin (Germany). Often an annoying interference of the synchrotron based measurements, but at the same time, often a welcome end of a long night shift.)
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1 Introduction

1.1 Manganites and colossal magnetoresistance

Amongst the most intensively investigated materials in contemporary solid state physics of strongly correlated electronic systems, the colossal magnetoresistant manganese oxides probably need only take second place to the high temperature cuprate superconductors. This large group of materials displays many interesting properties, most notably the colossal magnetoresistant effect. This effect manifests itself as a huge change in conductivity under the application of a magnetic field.

It is worth mentioning that in principle this effect is related to the giant magnetoresistance (GMR) displayed by special multilayer materials. In the GMR systems, ferromagnetic layers, separated by a thin non-magnetic spacer (typically $\approx 1$ nm thick) can have an anti-parallel spin alignment with respect to each other. Application of a small magnetic field can align the spins of the different layers ferromagnetically, causing a considerably lower resistance (a decrease in the order of several tens of %) across the layers. This effect has been exploited commercially in for instance hard disks, and the discoverers, Peter Grünberg and Albert Fert, have received the Nobel Price in Physics in 2007 for their discovery.

Despite the well earned interest for the GMR materials, the colossal magnetoresistant (CMR) effect in the perovskite and related manganese oxides is even more dramatic than the GMR effect: the change in resistivity can in some cases be orders of magnitude. However, the nature of the colossal magnetoresistant effect is still poorly understood. The effect has its roots in the electronic structure of the manganites or, more specifically, the connection of the electronic structure to the lattice degrees of freedom, such as phonons or coupled versions thereof such as polarons. As angle resolved photoemission is capable of directly probing the electronic structure of a compound, including the electron-electron and electron-phonon interactions, this technique would seem an ideal tool to investigate the origin of the colossal magnetoresistant effect.

This is what we set out to do during the PhD trajectory described in this thesis: to get a thorough description of the electronic structure of the manganites, in order to gain insight in the mechanism behind the CMR effect. During the experimental work conducted by our group in the past years, several other photoemission groups shared their world view on the CMR effect and the manganites through the literature. These world views did not all point in the same direction and are in some cases even contradicting
each other. In this thesis we give, amongst others, our view on the electronic structure of the manganites and we try to reconcile the results obtained from photoemission with those from other electronic structure probes such as transport, optical conductivity and scanning tunneling spectroscopy.

During our work on the manganites, a small revolution occurred in the field of the high temperature superconductors. A completely new family of superconductors was discovered, the iron pnictides. As our work on the manganites was already very much leading us to the ‘story’ that finds its first full publication in this thesis, we decided to shift the focus of the later period of the PhD trajectory to the quickly developing field of the iron pnictides. These materials are briefly introduced in the coming section.

1.2 Pnictides and high temperature superconductivity

One of the holy grails of contemporary condensed matter physics is the unravelling of the mechanism behind unconventional and (more specifically) high temperature superconductivity. Finding a way to engineer materials that are superconducting at room temperature would surely lead to a revolutionary change in technology of great relevance to the current debate as regards energy efficiency and sustainability.

No wonder that ever since their discovery in 1986, the high temperature superconducting cuprates (with a record $T_c$ above 135 K) have been in the spotlight of physical research. Yet, despite an unprecedented body of experimental and theoretical work, the mechanism behind high temperature superconductivity remains to date elusive.

In the beginning of 2008, very unexpectedly, superconductivity at temperatures in the range of 55 K was found in a compound based on iron. Transition temperatures that high were previously only known from copper oxides. Even more so, iron is usually associated with ferromagnetic ordering, that is all but mutually exclusive with superconductivity.\footnote{Some material show unconventional superconductivity coexisting with ferromagnetism, but they have transition temperature that are typically (far) below 1 K.}

It appeared that the particular compound, Sm(O$_{1-x}$F$_x$)FeAs, is a member of an entire family of compounds, called iron pnictides, that all show superconductivity.

In light of the enormous research effort on unconventional superconductivity since the mid-eighties of the last century, the discovery of high temperature superconductivity for an entirely new class of materials, \footnote{Ironically enough, the transition metal pnictide compounds as a class of materials are not per se new, but no-one had thought to investigate possible superconductivity in the ‘right’ representatives of these systems.} is a truly remarkable fact.

Our research group, up to that point mainly focused on cuprates and manganites, recognized that this was a rare chance to enter into a young and very dynamic research field. This is the reason that this thesis has somewhat of a dual character. The manganites were intended to be the main and sole topic of the research related in this PhD thesis. However, neither the PhD sponsor, nor the PhD student could resist the temptation to dive into the pnictide field. Thus, although the manganites are not really closely
connected to the pnictides (their physical properties are very different: the physics of the former is rooted in strongly correlated electrons and localized lattice dynamics, while the physics of the pnictides seems to be governed by itinerant magnetism), the chance to work in the newly developing field of the pnictides and the excitement and sense of urgency associated with it was just too good to let it pass. Therefore, a major part of the experimental work discussed in this thesis is on the iron pnictides.

As the pnictide high $T_c$ superconductors form such a young research field, many of the fundamental issues concerning their electronic structure and the mechanism underlying the superconductivity in these systems are not settled. Even seemingly ‘simple’ questions such as the local iron moment in the anti-ferromagnetic phase and the value of the Hubbard U are still not clear. Only time will show whether the discovery of this family of compounds will help us to understand the mechanism behind unconventional superconductivity, or if it will just lead to more open issues concerning the nature of this extraordinary physical phenomenon.

1.3 This thesis

This thesis is organized in the following way: in Chapter 2 the experimental methods and theoretical background are treated. We begin with an introduction into the crystal structure and the physical properties of the colossal magnetoresistant (CMR) manganites, in particular $\text{La}_{2-x}\text{Sr}_x\text{Mn}_2\text{O}_7$, and the iron pnictide high temperature superconductors, in particular $M\text{Fe}_2\text{As}_2$ ($M$ is Ba and Eu). Due to limitations in space, and the fact that two completely different systems are to be discussed, we have chosen to give only a brief overview of the physical properties and focus more on the subjects that are of relevance to the four experimental chapters, rather than giving an in depth overview of the entire fields of colossal magnetoresistance and high temperature superconductivity (although one can wonder whether it is even possible to give a full overview of either of the two fields without at least tripling the number of pages contained in this thesis).

After the systems of interest are introduced, the main experimental techniques will be discussed: angle resolved (vacuum ultra-violet) photoemission (ARPES) and hard x-ray core level photoemission spectroscopy (HaXPES). After a short theoretical treatment of these techniques, some of the more practical aspects of photoemission spectroscopy will be treated. As the work described in this thesis has (almost) without exception been conducted at large-scale, international synchrotron facilities, the basic physics of synchrotron photon sources gets a brief mention, followed by an overview of two representative beamlines that were the most often used in the line of the research reported here. Lastly, an overview of the experimental details per chapter is given for the readers interested in the reproduction of the experiments described here.

Chapter 3 is the first experimental chapter, dealing with ARPES measurements on the bilayered CMR manganite $\text{La}_{1.28}\text{Sr}_{1.72}\text{Mn}_2\text{O}_7$ (LSMO). Previously, somewhat contradictory studies had appeared in the literature (see Chapter 1.1.4), showing different Fermi surfaces for very similar doping levels of LSMO. Sharply peaked features [quasi particle (QP) peaks] were reported at the Fermi level, but different groups had observed them in different regions of $k$-space. We show that these QP peaks form a closed Fermi
surface and thus that a pseudo gap-less Fermi surface can be observed for this particular manganite. Additionally, we show that the temperature dependent behavior of the QP peaks is rather anomalous.

Having published these results in Ref. [1], and continuing APRES measurements on other doping levels of the same manganite, we noticed that the spread in results obtained from different cleaves of a single doping level was larger than the difference between various doping levels. Also, the behavior of the QP peaks did not seem to correspond to many bulk physical properties of bilayered LSMO. We have therefore conducted a detailed HaXPES study on this compound, described in Chapter 4. From this study we can infer that: (i) the surface and bulk of bilayered LSMO are similar in terms of doping and charge transfer (at temperatures far below or far above $T_C$), (ii) the electronic signature of the cleavage surfaces of the studied doping levels is in line with their nominal doping, and (iii) electronic phase separation does not occur far above or below $T_C$. These results have been published in Ref. [2].

The last conclusion is an important one, in the sense that it disqualifies the anomalous temperature behavior of the QP peaks as resulting from intrinsic electronic phase separation, as was suggested in prior reports. Based on these observations, we give a compelling explanation in the final section of Chapter 4 for the observed anomalous behavior of the QP peaks. We interpret them as a minority phase resulting from the (inevitable) presence of stacking faults in the multilayer quasi-perovskite LSMO crystal structure. Thus the QP peaked data are not representative of the physical properties of bilayered LSMO. This implies that the real spectral signature of bilayered LSMO is that of a pseudo-gapped ‘bad metal’ without a real Fermi surface. This conclusion is in line with the observations made by many earlier optical spectroscopy and transport studies, and (ironically enough) with early ARPES work on bilayered LSMO.

From the end of 2008 onwards, our research shifted focus, so as to cover the newly discovered iron pnictide high temperature superconductors. In Chapter 5, angle integrated valence band photoemission results obtained from some of our first BaFe$_2$As$_2$ (Ba122) single crystals are presented. We show experimentally that the near Fermi level ($E_F$) electronic states are (almost) exclusively of Fe 3d character and thus that the Fe 3d and As 4p valence band states are barely hybridized close to the Fermi level. Additionally, we show, using HaXPES measurements, that the surface and bulk electronic structure of Ba122 are, at most, only slightly different. This is due to the formation of a partially ordered, residual, half-closed Ba layer on top of the top-most, fully closed As layer upon cleavage. However, we predict that the influence of the surface is mainly restricted to the first As and Ba layers at the crystal surface and will not much influence the electronic structure as probed by for instance angle resolved photoemission or scanning tunneling experiments involving the near $E_F$ electronic states. These results have been published in Ref. [3].

The final chapter (Chapter 6) of this thesis deals with angle resolved photoemission measurements on Eu122 in the low temperature orthorhombic and anti-ferromagnetically (AFM) ordered phase. The nature of the AFM ordering for these compounds is still under debate. Moreover, ARPES studies clearly demonstrating the AFM band structure are mostly incomplete. By making use of variable light polarization and different
photon energies, we show, with unprecedented clarity, that the large Fermi surfaces of the pnictide parent compounds observed in the tetragonal phase, break up into small droplet-like Fermi surfaces in the AFM phase.
Chapter 1. Introduction
Experimental methods and background

2.1 Bilayered manganites

In this section an introduction into the physics of (bilayered) manganites will be given. First, the crystal structure and the magnetic and electronic phase diagram are discussed. From there, we proceed with an introduction to their most striking physical property, the colossal magnetoresistant effect, something which is intimately connected with the strong electron lattice coupling seen for these compounds. Currently, the origin of the CMR effect is still under debate. We will focus primarily on the bilayered manganite $\text{La}_{(2-2x)}\text{Sr}_{(1+2x)}\text{Mn}_2\text{O}_7$ (LSMO327, or LSMO for short). We then proceed by introducing the reader to the predicted band structure of this bilayered manganite and we conclude with a short (and far from complete) overview of the photoemission literature on this compound, intended to sketch a context for the experimental work on $\text{La}_{(2-2x)}\text{Sr}_{(1+2x)}\text{Mn}_2\text{O}_7$ discussed in the following chapters.

2.1.1 Crystal structure: the Ruddledson-Popper series

The manganite family contains a very large number of compounds (that have rather similar physical properties), but their unit cells all share one common ingredient: a central Mn ion that is octahedrally surrounded by six oxygen ligands. The simplest possible structure is the perovskite one, where each oxygen is shared between two MnO$_3$ octahedra, and the interstitial sites in between the oxygens are occupied by a di- or trivalent alkaline earth or Lanthanide metal-ion $A$, see Fig. 2.1. Typical $A$ metals are: La, Sr, Ca, Pr, Nd,...

Formally, the charge on the manganese cation at the center of the octahadra is 3+ or 4+, depending on the valency of the $A$ site metal-ion, for each oxygen ligand has a formal charge of 2−. By partial substitution of a di- for a trivalent $A$ site cation, one is adding holes to the Mn sites, leading to a formal Mn charge in between 3+ and 4+. Thus, a mixed valence compound is obtained, whose physical properties subtly depend on the $A$ site species and the cationic doping level at hand.

---

1This crystal structure is even far more common in nature: Mn can be exchanged by many other (transition) metals, such as Ti, Ru, Al or Cu, leading to materials with a wide variety of physical properties, ranging from plain insulators, to multi-ferroic materials and superconductors, depending on a subtle, often illusive, balance between the lattice, the relevant orbitals near the Fermi level and the strength and type of electronic and orbital correlations.
Alternatively, one can view the perovskite crystal structure as a stacking of alternating MnO$_2$ and AO planes. Other compounds can be added to the manganite family by changing the stacking sequence of the alternating MnO$_2$ and AO planes. Addition of AO rock-salt planes to the perovskite crystal structure leads to a decrease in dimensionality and a lower stacking number $N$ of the MnO octahedra along the crystallographic c-axis. A general structure formula in terms of the number of consecutive octahedra stacked along c is given by: $(A,B)_{N+1}Mn_{N}O_{3N+1}$, where the ratio between $A$ and $B$ determines the doping level. This is the so-called Ruddlesden-Popper series. The $N = 2$ and $N = 1$ members of the series are also displayed in Fig. 2.1. Note that the perovskite analogue corresponds to $N = \infty$. The $N = 2$ analogue is the so-called bilayered system and is the subject of study in this thesis.

### 2.1.2 The magnetic phase diagram and transport properties

#### The phase digram

In Fig. 2.2 three phase diagrams (hole doping $x$, versus temperature) are depicted for perovskite manganites involving different $A$ cation species. It is clear that in all cases the low temperature part of the phase diagram features several magnetically ordered phases, the details of which depend strongly on doping. Although the phase diagrams bear a lot of resemblance to one another, it is clear that the transition temperatures and nature of the magnetic order is influenced by the identity of the $A$ site species. The main cause of this difference between the three phase diagrams is the (average) size of the $A$ site cation, as this determines the levels of distortion of the MnO$_2$ octahedra. The degree of distortion is expressed by the tolerance factor $f$, that is a function of the ionic radii $r_i$:

\[
f = \frac{r_{Mn} + r_O}{\sqrt{2}(\langle r_A \rangle + r_O)}.
\]  

(2.1)
2.1 Bilayered manganites

Figure 2.2: Magnetic phase diagrams for three perovskite manganites: $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, taken from Ref. [4]. PI, PM and CI denote the paramagnetic insulating, paramagnetic metallic and spin-canted insulating states, respectively. FI, FM and AFM denote the ferromagnetic insulating and ferromagnetic metallic and anti-ferromagnetic (A-type) metallic states, respectively. At $x = 0.5$ in $\text{Nd}_{1-x}\text{Sr}_x\text{MnO}_3$, the charge-orbital ordered insulating (CO/I) phase with CE-type spin ordering is present. For $0.3 < x < 0.5$ in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, the anti-ferromagnetic insulating (AFI) state exists within the charge-orbital ordered insulating (CO/OOI) phase. The canted anti-ferromagnetic insulating (CAFI) state also shows up below the AFI state in the CO/OOI phase for $0.2 < x < 0.4$ for PCMO. The tolerance factors of the three compounds at half-doping ($x = 0.5$) are $f = 1.00$, 0.98 and 0.96 for LSMO, NSMO and PCMO, respectively.

The closer $f$ is to unity, the closer the crystal structure is to a simple cubic perovskite lattice. The crystal structure has lower symmetry (orthorhombic or monoclinic) for smaller $f$ values, leading to a canting the MnO$_3$ octahedra. As this canting means that the in-plane Mn–O–Mn bond angles deviate from 180°, the hopping between neighboring Mn sites becomes less effective, leading to a narrowing of the band width $W$. This is the reason that $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, with the smallest $f$ value of the compounds shown in Fig. 2.2, has the least amount of metallic character of the three manganites shown.

Also hole doping via $A$ site cation substitution has a rather dramatic effect on the presence of metallic behavior and the magnetic ordering of the manganites. If we zoom in on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO113 for short), where the Sr doping barely changes the $f$-factor, yet, as a function of $x$, addition of holes leads to the appearance of a ferromagnetic insulating, a ferromagnetic metallic, an anti-ferromagnetic metallic and anti-ferromagnetic insulating state (at $x > 0.7$), consecutively. How can one explain this multitude of electronic and magnetic phases?

One of the defining interactions in the strongly correlated manganites is the electron-lattice coupling (as also illustrated above by the sensitivity of the phase diagram to the $A$ site species), that is intimately connected to the fact the electrons on the Mn sites
Figure 2.3: Lattice and electron interactions in LSMO. (a) Energy level diagram for the 3d atomic orbitals. From left to right: the 5-fold degenerate state for the free atom, a large ligand field energy splitting between the \( e_g \) and \( t_{2g} \) orbital sets (with an energy of \( 10Dq \)) for an isotropic octahedral ligand configuration (i.e. the case for a \( 3d^3 \) occupancy), and a Jahn-Teller (JT) distorted crystal field for a \( 3d^3 \) electron configuration, with two elongated Mn–O bonds, taken from Ref. [4]. (b) Top: illustration of super exchange interaction leading to an anti-ferromagnetic coupling between the two Mn sites. Bottom: orbital ordering in LaMnO\(_3\). Alternating Mn sites are JT distorted along the crystallographic \( a \)- or \( b \)-axes, respectively. Super exchange interaction leads to an A-type AFM ordering: in the \((a,b)\) plane the ordering is ferromagnetic, but along the \( c \)-direction the coupling is of AFM nature, similar to the picture described in the top panel. (c) Illustration of double exchange interactions in a mixed valence compound leading to ferromagnetic ordering due to Hund’s rule coupling.

have orbital, spin and charge degrees of freedom. In an (over-) simplified, molecular frame work, the Mn electronic configuration in the undoped case of LSMO113 is \( 3d^4 \). For this electron configuration, distortion of the MnO\(_3\) octahedra along one axis leads to a lowering of the total energy of the system. This so-called Jahn-Teller distortion effect is illustrated in Fig. 2.3a. For a crystal with macroscopic dimensions, JT distortion would lead to a tremendous increase in strain energy. By alternating the elongation of the octahedra at neighboring Mn sites along the ‘\( 3d_{x^2-r^2} \)’ and ‘\( 3d_{y^2-r^2} \)’ orbital, the elastic strain energy of the crystal is minimized. In turn, this orbital ordering leads to a super-exchange interaction that is of A-type anti-ferromagnetic nature, see Fig. 2.3b. This simplified example illustrates the complex interplay between the lattice and the magnetic ordering in manganites. It must be noted that the fact that the lattice plays such a crucial role in the physics of the mangnites, was realized already many years ago, see for instance Ref. [6].

Around half doping, the amount of Mn\(^{3+}\) and Mn\(^{4+}\) are roughly equal and there is again the possibility for orbital ordering to reduce crystal strain. This is because
for Mn$^{4+}$ ($3d^3$), there is no energy to be gained from JT distortion, thus half of the Mn lattice sites will have regular octahedra, while the other half is JT distorted. In this case, charge ordering (CO) is established, such that at alternating sites the MnO$_3$ octahedra are non-distorted and JT distorted in the (a,b) plane. This again gives rise to an A-type AFM ordering governed by a super exchange mechanism, much like the case depicted in Fig. 2.3b for the parent compound.

At intermediate doping levels ($x < 0.5$), less than half of the Mn sites will have a formal $3d^9$ electron configuration. The static orbital and AFM ordering becomes more short-ranged and eventually breaks down. The electron interactions then become dominated by a double exchange mechanism. In this case the Hund’s rule coupling favors ferromagnetic alignment of the spins on neighboring Mn sites with a different valence. The hopping from site $i$ to $j$ ($t_{ij}$) in this case is directly depending on the angle between the spins on the neighboring sites: $t_{ij} = \cos \theta_{ij}$, as illustrated in Fig. 2.3c [7, 8]. The manganite now shows metallic behavior below the Curie temperature ($T_{\text{Curie}}$), provided that the band width $W$ is large enough and the sizable on-site coulomb repulsion $U$ and residual electron-lattice interactions can be overcome.

One can view the super-exchange driven charge/orbital ordered AFM phases and the double exchange mediated FM metallic electronic states as two competing phases.
What tips the balance between the two and causes bulk metallic or insulating behavior is a complicated interplay between band-width, band-filling and electron-electron and electron-lattice coupling. It is worth mentioning that recent transport measurements on thin manganite films underline the crucial role the lattice plays. The films are grown under anisotropic substrate induced strain conditions in the (a,b) plane. The resistivity versus temperature is affected strongly, but very differently in the low and high strain direction [9].

As temperature is raised above the Curie temperature for the metallic compositions, the spin alignment at neighboring Mn sites is lost and thus an increase in resistivity is expected from double exchange theory (as $\theta_{ij}$ becomes larger). Indeed, the high temperature regimes of the phase diagrams shown in Fig. 2.2 (and Fig. 2.4) consist predominantly of the paramagnetic insulating phase.

Let us now change our focus to another member of the Ruddlesden-Popper series (one that is more suitable for photoemission experiments)\(^2\). The phase diagram of bilayered LSMO, $\text{La}_{(2-2x)}\text{Sr}_{(1+2x)}\text{Mn}_2\text{O}_7$ (LSMO in the following) is very similar to that of the perovskite analogue, see Fig. 2.4. Only the transition temperatures are much lower in the bilayered case.\(^3\) This is due to the more two dimensional nature of the bilayered compound, causing a larger susceptibility towards fluctuations and thus a much less robust magnetic ordering. Another reason that the magnetic order and metallic character in the bilayered case is weaker, is an increased distortion, compared to the perovskite, of the apical MnO bond of the octahedra at the outside of the bilayer for the $N = 2$ compound. As mentioned earlier, an increased distortion of the MnO$_3$ octahedra generally corresponds to a decrease in metallic character.

One could even say that the transport properties of the low temperature FM phase of bilayered LSMO are only barely metallic. In Fig. 2.5a the resistivity versus temperature is depicted for LMSO with a doping level of $x = 0.40$ [10]. The PM to FM transition with decreasing temperature coincides with the transition from the insulating to metallic state at roughly $T_C = 120$ K. Eye catching are the high values for the resistivity even at temperatures below 20 K. The $c$ axis resistivity is two orders of magnitude higher than the in-plane $(a,b)$ resistivity, owing to the two dimensional nature of the material, but also the in-plane resistivity is barely reaching a value consistent with Mott’s idea of a minimum conductivity for a metal being $10^{-3}\Omega\text{cm}$ (corresponding to a mean free carrier path length in the order of one unit cell). From resistivity alone, one could thus conclude that bilayered LSMO is a very poor metal at best.

This is further emphasized by optical conductivity measurements, depicted in Fig. 2.5b [11]. Metallic behavior is evident in optical spectroscopic data in the form of a sharp peak at zero frequency, the so-called Drude peak. Obviously, the depicted spectra lack such a sharp Drude feature. Instead, the $c$-axis optical conductivity approaches zero (not shown), down to the lowest temperatures, characteristic for insulating behavior. Though the $(a,b)$-plane optical conductivity is finite below the transition temperature,

\(^2\)The reason for the choice for the two dimensional manganite over the perovskite one will be elucidated during the introduction about (angle resolved) photoemission later on in this chapter

\(^3\)Note that in the bilayered case, single crystals with hole doping levels below 30% cannot be obtained, due to difficulties with single crystal growth.
2.1 Bilayered manganites

Figure 2.5: Transport properties of bilayered LSMO with $x = 0.40$. (a) Bulk resistivity and magnetization versus temperature. The magnetization data were recorded under application of a field of 5 kOe along the $(a, b)$ direction, taken from Ref. [10]. (b) The in-plane optical conductivity at different temperatures, taken from Ref. [11]. The inset shows the optical conductivity at 10 K down to an energy of 80 cm$^{-1}$ ($\approx 10$ meV). The sharply peaked features close to $\omega = 0$ are due to phonons and are not connected to the Drude weight, that should be a peak at $\omega = 0$.

there is no sign of Drude-like behavior, emphasizing the highly incoherent nature of the electronic states and ‘bad metallic’ nature of the low temperature phase of LSMO.

2.1.3 Colossal magnetoresistance

Despite (or maybe, in fact, thanks to) the ‘bad metal’ nature of the low temperature ferromagnetic phase of bilayered LSMO, it features one of the most interesting phenomena displayed by these compounds. For one, the nature of the metal-to-insulator transition is more complicated than explained before. The change in resistivity across the transition is more than two orders of magnitude, but the double exchange mechanism mentioned earlier can only account for a change in resistivity of about 30% [12]. Therefore, the metal-to-insulator transition in this compound must be quite unusual. Below, it will be explained that the charge carriers in these compounds are indeed of rather exotic nature.

A direct consequence of the special nature of the metal-to-insulator transition is the transport behavior of bilayered LSMO and other manganites in the presence of a magnetic field. In Fig. 2.6 the resistivity of perovskite LCMO is depicted as a function of temperature, for different applied external fields. Clearly, the metal-to-insulator transition shifts to higher temperatures with increasing field. Equivalently, the resistivity at $T = 250$ K drops by a factor 50. This phenomenon is called the colossal magnetoresistant (CMR) effect. The CMR effect in bilayered LSMO is among the largest known and
Figure 2.6: The colossal magnetoresistant effect: resistivity versus temperature of La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) for different applied external fields. The transition temperature is shifted by about 50 K under application of a magnetic field of 5 T, or equivalently, the resistivity (for example at $T = 250$ K) drops maximally by a factor 50 upon application of a modest magnetic field, taken from Ref. [4]

the change in resistivity can reach values as high as $2 \times 10^4$ % (i.e. a factor 200) for a doping level of $x = 0.40$. The nature of the CMR effect is still under debate, but it is clear that the origin of the effect must lie in the unusual metal-to-insulator transition and the strong coupling between the electrons and the lattice.

That the interplay between the lattice and electrons is still very important for doping levels in the parts of the phase diagram that support metallic behavior, has been shown with neutron and x-ray scattering studies. It is clear from these experiments on bilayered LSMO single crystals [13, 14], that the static charge and orbital order of the undoped and half-doped compounds, turns into a dynamical, short lived phenomenon for these intermediate doping levels. In the scattering experiments, diffuse scattering intensity around the Bragg peaks is observed above the Curie temperature. This diffuse or (Huang) scattering is typically caused by polaronic lattice deformations. Also in-plane incommensurate superstructure peaks [with a $\mathbf{q}$-vector of (0.3, 0, $\pm$1) in units of $2\pi/a_i$] are observed. These superstructure peaks are coming from correlated polarons, forming a strain field with a period of $\approx 3$ unit cells in the $(a,b)$ plane, with a correlation length of $26 \AA \approx 6$ unit cells and a life time in the picosecond range. Thus, the CMR manganites have a dense population of overlapping and interacting polarons in the paramagnetic state and it is the fact that the carriers are strongly dressed by the these lattice distortions that makes the PM phase insulating in nature. A representation of
2.1 Bilayered manganites

Figure 2.7: Polarons in the high temperature PM phase of bilayered LSMO with $x = 0.40$. Left: Schematic representation of a coherent polaron distortion field with a period of $3a_0$, taken from Ref. [14]. Right: x-ray scattering intensity of the diffuse (Huang) scattering (open symbols) and superstructure spots (closed symbols), associated with (coherent) polaronic behavior, as a function of temperature, taken from Ref. [13]. Note the abrupt collapse of intensity for temperatures $T < T_C$.

such a correlated polaron is given in Fig. 2.7, and can be easily recognized as incipient, fluctuating charge and orbital ordering due to dynamic JT distortions. These dynamic structural distortions have been associated with short range canted ferromagnetic ordering [15]. Resistivity measurements have also shown that -in the paramagnetic regime- both along the $c$ and the $(a, b)$ axes, the charge transport can be described within an activated hopping framework, one which fits the identity of the charge carriers as small polarons [16].

Returning to the x-ray and neutron scattering experiments, with decreasing temperature the intensity of the Huang and incommensurate scattering increases, indicating that the polaron correlations increase upon approaching $T_{\text{Curie}}$, see Fig. 2.7. However, at the transition temperature the scattering intensity drops rapidly to zero. Thus, a common view of the temperature dependence of bilayered LSMO is the following: for $T > T_C$ a ‘small polaronic liquid’ starts to freeze out with decreasing temperature, and becomes more and more correlated. Yet, before static polaron order sets in, the dynamic structural distortions are largely expelled by long range ferromagnetic order and metallic behavior governed by a double exchange mechanism. We must note that recent neutron scattering experiments have found that far below $T_C$ (10 K) polarons remain as fluctuations that strongly broaden and soften certain phonons near the wavevectors where the charge-order peaks appeared in the insulating phase. This study was done on bilayered LSMO with $x = 0.40$, indicating the even below the metal-to-insulator transition the signature of polaronic behavior is still clearly present in this material [17].

As the metal-to-insulator-transition seems to be linked to the competition between two phases (being the JT distorted orbitally ordered insulating phase and the ferromagnetic metallic phase), a much debated framework to explain the CMR effect is that of electronic phase separation [19, 20]. At temperatures around the transition temperature, the uniform electronic system starts to segregate into (nm sized) patches with two
distinct electronic properties: one being metallic and the other insulating. As the temperature is changed across the transition temperature, one of the two phases will start to gain in abundance with respect to the other phase. The CMR effect is then based on the fact that the externally applied field stabilizes the FM metallic phase and aligns the fluctuating and randomly aligned ferromagnetic ‘nano-patches’, enabling metallic-like transport via a percolative path at temperature above the zero field metal-to-insulator transition. According to theoretical predictions [19, 20], this type of behavior would lead to a pinning of the chemical potential as a function of doping, whereas one would normally expect a smooth shift of the chemical potential with doping, due to the addition of extra charge carriers (in the case of LSMO these are holes) in a rigid-band-like manner.

Though phase separation scenarios form a compelling model to explain the CMR effect, a large number of reports in the literature on phase separation in manganites cannot be due to the type of electronic phase inhomogeneity that drives the CMR effect. The presence of chemical or structural inhomogeneities is often hard to exclude from
bulk single crystals. Most reports on static phase separation in the metallic part of the phase diagram of bilayered LSMO, often reported at temperatures far above or below the bulk transition temperature, are probably due to such extrinsic effects, rather than being temperature driven electronic phase separation between competing phases.

**Band structure**

The band structure of bilayered LSMO is predicted to be rather reminiscent of that of the bilayer high $T_c$ cuprates. Different local density approximation (LDA) calculations have appeared over the years [18, 21], giving a consistent picture of the theoretically predicted band structure. As the formal charge at the Mn sites is $(3 + x)^+$, Mn has a $3d^{4−x}$ electron configuration. From this, in combination with a large octahedral crystal field splitting, one would expect the $d_{z^2−r^2}$ and $d_{x^2−y^2}$ atomic orbitals to be the relevant ones at the Fermi level, as was already suggested in Fig. 2.3a.

Indeed, the LDA calculations show that the near $E_F$ states are based on these atomic orbitals [18, 21]. For the doping levels in the metallic regime ($0.30 < x < 0.48$), three Fermi surface sheets comprise the Fermi surface, as indicated in Fig. 2.8. There is one electron-like Fermi pocket around the $(0, 0)$ point of $k$-space and two bands that form hole pockets around the $(\pi, \pi)$ point. The latter will exhibit a bilayer splitting if there is coherent hopping in the...... $c$-axis crystallographic direction between the MnO$_2$ planes within a single bilayer. The degree of hybridization between the $d_{z^2−r^2}$ and $d_{x^2−y^2}$ derived electronic states is predicted to be rather high close to $E_F$ [21], leading to a mixed character of the electron bands.

**2.1.4 Photoemission spectroscopy on bilayered LSMO**

Over the years, several (angle resolved) photoemission studies on bilayered LSMO have appeared in the literature in an attempt to shed light on the CMR effect and the metal-to-insulator transition from a $k$-space point of view. One of the earlier studies, on LSMO with a doping level $x = 0.40$, reported a pseudo-gapped Fermi surface, with finite, but very low spectral weight at the Fermi level ($E_F$), in keeping with the poor metallic properties evident from optical and transport studies [22].

Surprisingly, a more recent study on the same doping level, showed the existence of sharply peaked features at the Fermi level ($E_F$). Interestingly, these quasi particle (QP) peaks were only found in the $(0, 0) - (\pi, \pi)$ (zone diagonal) direction of $k$-space [23]. At the zone face, around the $(\pi, 0)$ point of $k$-space, the signature of the photoemission spectra was again that of a pseudo-gapped bad metal, like the data reported in Ref. [22].

Another study on bilayered LSMO with doping levels very close to the previous one, being $x = 0.38$ and $x = 0.36$, showed the existence of QP peaks, but now at the $(\pi, 0)$ point of $k$-space, and did not allude to their presence or absence at the $(\pi, \pi)$ direction of $k$-space [24]. The photoemission data presented in Chapter 3 confirmed this observation, but also showed that these QP peaks are simultaneously existing at both the zone face and zone diagonal direction of $k$-space for a doping level of $x = 0.36$, thus forming
a conventional, continuous and non-gapped Fermi surface. This data is presented in Chapter 3 and has been previously published in Ref. [1].

The temperature dependence of the QP peaks for $x = 0.36$ and $k$-space locations near $(\pi, 0)$ was found to be rather surprising: at temperatures far above $T_{\text{Curie}}$ their spectral weight at $E_F$ was still found to be significant, despite the crystal being nominally well into the insulating regime. One particular study has taken this observation as evidence for electronic phase separation as the root cause for the CMR effect [25]. However, the temperature dependence of the $x = 0.40$ QP peaks at the $(\pi, \pi)$ point of $k$-space reported in Ref. [26] was more conventional. These spectral features showed a vanishing spectral weight upon crossing the bulk $T_C$ of 120 K. This observation has in turn been interpreted as an evidence for polaron condensation as the cause of the CMR effect, rather than phase separation [26].

To complicate the picture even further, other studies on doping levels across the metallic phase diagram of bilayered LSMO with $x = 0.36, 0.40$ [27] and 0.45 [28], have shown again psuedo-gapped Fermi surfaces without any sharply peaked features at $E_F$.

All in all, the picture arising from photoemission experiments on the near $E_F$ electronic states of bilayered LSMO is not very consistent. In the next two experimental chapters, we present a thorough angle resolved and hard x-ray core level photoemission study on this system, to try to find an explanation for the seemingly contradictory photoemission data in the literature and to come to a consistent description of the near $E_F$ electronic states of bilayered LSMO from a spectroscopic point of view.

### 2.2 Pnictides

In this section a short introduction is given into the physics of the recently discovered iron pnictide superconductors. We will focus specifically on BaFe$_2$As$_2$, a compound typical for the $M122$ pnictide family. We will begin with a short section about unconventional superconductivity to place the iron pnictides into perspective. Next, the crystal structure, the phase diagram and the band structure of the pnictides will be discussed. We will conclude with a short overview of some of the important open issues with regards to the electronic structure and magnetism for these compounds. A nice overview of the recent status of research on the pnictide high $T_c$ superconductors can be found in a special issue of Physica C, volume 469 (issues 9–12) (2009).

#### 2.2.1 Unconventional Superconductivity

One of the biggest questions in contemporary condensed matter physics is: what mechanism lays at the heart of the electron pairing interaction in unconventional superconductors? Despite years of intensive research since the mid-eighties of the last century, the debate is still very much open towards either magnetic interactions or interactions of magnetic plus phonon origin. In Fig. 2.9 several phase diagrams of superconducting compounds are shown. From left to right they are: (i) UCoGe, a uranium intermetallic compound showing superconductivity coexisting with ferromagnetic order, (ii) La$_{2-x}$Sr$_x$CuO$_4$, a member of the well known cuprate high $T_c$ superconductor family and
2.2 Pnictides

Figure 2.9: Phase diagrams for several types of unconventional superconductors. From left to right: The temperature versus pressure phase diagram for UCoGe, taken from Ref. [29] and the temperature versus hole doping phase diagrams of a prototypical cuprate high $T_c$ superconductor La$_{2-x}$Sr$_x$CuO$_4$, taken from Ref. [30] and of CeFeAsO$_{1-x}$F$_x$, Ref. [31]. FM denotes ‘ferromagnetic’, SC/S is ‘superconducting’, AF means anti-ferromagnetic insulator and AFM is an anti-ferromagnetic metal.

(iii) CeFeAsO$_{1-x}$F$_x$, a member of the newly discovered pnictide high $T_c$ superconductor family. For the pnictides, the superconducting order parameter and even details of the general phase diagram are still under heavy debate.

The superconductivity in all of these systems behaves very differently. The $T_c$ in the U intermetallic case barely reaches above 0.5 K, and is discussed to have a $p$-type order parameter. For certain members of the cuprate family a $T_c$ in excess of 130 K has been reported, and the order parameter is $d$-wave. The pnictides to date have a record $T_c$ of 55 K and are believed the have an order parameter of the $s_{\pm}$ type, although also many studies also seem to point towards $d$-wave superconductivity. Nonetheless, the three phase diagrams, though belonging to completely different systems, bear a lot of resemblance. Most notably, they all show some sort of magnetic ordering close to or in the region of the phase diagram where superconductivity is observed. Unconventional superconductivity thus seems to be related to the presence of magnetically ordered phases in the vicinity in the phase diagram, although to date it is not yet settled whether the two are competing phases or not.

Secondly, the superconducting domes are centered in all cases around a point at which a zero-temperature phase transition would take place: thus seemingly, superconductivity appears to thrive where otherwise a quantum critical point could have been observed. This is the reason that the relation between superconductivity and quantum criticality is to date a point of lively debate.

The pnictides are the latest addition to the ongoing debate about the origin of high $T_c$ superconductivity. Their properties differ somewhat from the cuprates and U intermetallics, as the pnictide parent compounds are poor anti-ferromagnetic metals and certainly not Mott insulators displaying localized AFM ordering, like in the case of the cuprates. The uranium intermetallic compounds, in turn, show itinerant ferromag-
netism accompanied by truly metallic low temperature resistivity values (in the order of $10^{-5} \, \Omega \text{cm}$). It is not yet known to which degree the electrons in the pnictides are correlated, but it is evident that they are located in the mid-field, in between the strongly correlated cuprates and fully itinerant intermetallic U and other heavy fermion compounds. The coming years will show whether the pnictides will help to understand the mechanisms behind unconventional superconductivity, or whether they will remain as enigmatic themselves as the cuprates have been for already almost 25 years.

2.2.2 Crystal structure and phase diagram

Superconductivity has been found in several types of pnictide compounds. Although their crystal structure is rather different, their overall phase diagram is quite generic, albeit that the maximum superconducting transition temperature, and details of the crystal symmetry are rather dependent on the specific crystal structure (as well as on the cation species).

The four types of pnictide crystal structures that show superconductivity are depicted in Fig. 2.10. A common feature shared between all four different crystal structures is a quasi-two dimensional FeAs plane, where the Fe sites are tetrahedrally surrounded by pnictide ($Pn$) ligands, either As or (Te,Se). The interstitial planes in between the FePn layers are different for the four families. Additionally, within a single family, the interstitial planes can contain several different metal cations. The highest $T_c$ (up to 55 K [32]) is found in the so-called 1111 compounds, $RE$FeAsO, where $RE$ can be a number of rare earth or lanthanide metal ions such as La, Nd, Ce or Tb. Interestingly, the pnictide high $T_c$ superconductors can be both electron or hole doped. In the case of the 1111 compounds this is done by doping fluorine for oxygen, or by partial substitution of a divalent for a trivalent rare-earth metal ion, respectively.

The $M$122 compounds, $M$Fe$_2$As$_2$, with $M$ is a divalent alkaline or rare-earth metal ion (Sr, Ca, Ba or Eu), form an even more special case. Here, the FeAs layers are
2.2 Pnictides

Figure 2.11: Hole and electron doped phase diagrams of Ba122. The cobalt doped side has been adapted from Ref. [33]. The potassium doped side is taken from [34]. The anti-ferromagnetic state is indicated with SDW (‘spin density wave’). SC denotes ‘superconductivity’. The structural and magnetic transition is indicated with $T_s$ of the K doped side. In the case of Co doped $M122$, the structural ($\alpha$) and magnetic ($\beta$) phase transitions become decoupled. The inset to the right hand phase diagram shows the iron lattice for the paramagnetic case (left) and for the orthorhombic anti-ferromagnetically ordered case (right). In the latter case the moments on the Fe sites are indicated. The thick solid lines indicate the unit cell in the (a,b) plane. Though the $a$ and $b$-axes do not change much in length across the transition, mainly a change in the position of the iron metal ions causes orthorhombicity.

separated by a single $M$ layer. Doping for these compounds can be carried out by substituting $M$ for K (i.e. hole doping) or by substituting Fe for Co (electron doping). The latter is rather special, as the Fe electronic states are responsible for the superconductivity in these compounds. This means that the superconductivity is robust enough to overcome significant doping, hence chemical disorder, within the superconducting plane.

In the following, we will restrict the discussion to the $M122$ compounds, specifically Ba122. The physical properties of Ba122 however, are highly similar to those of the other $M122$ compounds and the pnictides in general.

We do want to note that the ‘11’ compounds are do not have an interstitial layer in between the Fe-pnictide crystal planes. The ‘undoped compound’, Fe$_{1+y}$Se also shows superconductivity (8 K at ambient pressure) [35], making it probably the simplest of all the superconducting pnictides in term of crystal structure. However, the role of the excess iron ($y$, typically a few percent only) often present in the (Te,Se) planes is still
Figure 2.12: Resistivity in the (a,b) plane normalized to the room temperature resistivity for various doping levels of BaCo$_2$Fe$_{2-x}$As$_2$ (off-set with respect to each other for clarity). The right panel shows a zoom of the low temperature range. The superconducting transition temperatures ($T_c$) (defined here as the mid-point of the resistive transitions) are indicated with round symbols. In the left hand panel, the structural transition and/or Neél temperatures (both denoted with $T_{Neel}$) are indicated with round symbols. Note that resistivity measurements cannot distinguish between the two transitions, that are maximally 10 K apart. Data measured on single crystals grown in Amsterdam, courtesy of Rein Huisman.

under debate. The AFM spin ordering for the iron telluride compounds also deviates from that of the other pnictides [36]. Note also that Se substitution for Te does not correspond to electronic doping, but rather to the application of chemical pressure.

One additional issue concerning the pnictides, especially relevant for surface sensitive measurement techniques such as photoemission, is that they lack a natural cleavage plane (except the ‘111’ and ‘11’compounds). The pnictides cleave in between the FeAs planes. This means that upon cleaving either a M1111 or M122 compound, half of the interstitial layer will remain behind on top of the terminating, fully closed As plane. This may lead to surface doping effects. Additionally, for the M122 compounds, the residual, half closed M layers has been shown to (partially) order upon cleavage at low temperatures [37, 38], leading, amongst other effects, to clearly observable surface diffraction patterns in low energy electron diffraction experiments (see Chapter 5).

In Fig. 2.11 the temperature versus hole and electron doping ($x$) phase diagrams are depicted for Ba122. The high temperature phase of undoped Ba122 is a paramagnetic metal. The crystal structure is tetragonal with $a = b = 3.96$ Å and $c = 12.96$ Å. At
\( T = 130 \text{ K} \), upon cooling down, there is a phase transition to an anti-ferromagnetic orthorhombic structure (with \( a \approx b \approx 5.6 \text{ Å} \)). The ordering is that of the Fe moments and is indicated in both Figs. 2.10 and 2.11. With increasing doping, both in terms of adding extra electrons or holes with respect to the parent compounds, the magnetic transition temperature decreases and eventually a part of the phase regime is entered where superconductivity is observed. Note that for the Co doped case, the magnetic and the structural transitions become decoupled upon doping [39]. Also, doping with cobalt is much more effective in suppressing the magnetic ordering and introducing superconductivity than K-doping, which might be due to the fact that the Co dopants go directly into the magnetically ordered plane. The maximum \( T_c \) reached in the Co case is around 24 K, while a maximum \( T_c \) of about 40 K is obtained by doping with potassium.

Resistivity versus temperature curves of Ba122 for a broad range of Co doping levels are depicted in Fig. 2.12. The magnetic transition is seen as a sudden decrease in resistivity for the parent compound, and an increase for the doped compounds. The origin of this difference between the undoped and doped compounds is not yet clear, but may be due to a subtle difference in the balance between the loss in charge carriers and a decrease in scattering rate across the transition [40].

In the superconducting state, the crystal structure remains tetragonal [41]. To date (like in case of the cuprate high \( T_C \) superconductors), a controversial point remains whether the superconductivity and the anti-ferromagnetic order are competing phases or not. Several studies have found a coexistence of the two phases at the low doping side of the superconducting dome [42, 43] of the \( M122 \) compounds. While a homogeneous mixing of the two phases was shown in the case of Co doping, in the case of K doping, there seems to be macroscopic phase separation into magnetically ordered and superconducting areas [43]. In the case of the \( M1111 \) family, some compounds do show an overlap of the superconducting and AFM dome, while others do not (see e.g. CeFeAsO\(_{1-x}\)F\(_x\) in Fig. 2.9), depending strongly on the \( M \) cation species. Also, some AFM to superconducting transitions haven been reported to be of first order nature with doping, while others have found to be second order (for an overview of several published phase diagrams, see for instance Ref. [44]). The extent to which this spread in phase diagrams can be ascribed to intrinsic differences between the different pnictide compounds, or to a varying sample quality is not fully clear to date.

Worth mentioning is the fact that some pnictide parent compounds, most notably Sr122, have been reported to become superconducting under the influence of water vapor. These reports have been interpreted as strain induced superconductivity (due to intercalation of water molecules into the bulk crystal), hinting at the fact that charge carrier doping is not a prerequisite for inducing superconductivity in the pnictides. Rather, a weakening of the anti-ferromagnetic ordering would suffice, as might also the case for the ‘11’ compounds. However, the exact mechanism behind the water induced superconductivity for undoped parent compounds is not yet resolved [45].
2.2.3 Band structure and magnetism

In the two years after the discovery of high $T_C$ superconductivity in pnictides, ample band structure calculations have appeared in the literature and on the preprint servers. The pnictide compounds from the different families have a rather generic band structure in the tetragonal phase. The Fe electron configuration, from simple crystal field considerations, is $d^6$, which, in combination with a weak tetrahedral crystal field should correspond to $S = 2$ and (at least) 4 unoccupied bands at the Fermi level.

Indeed, local density approximation (LDA) calculations find four to five bands at the Fermi surface, depending on the details of the calculations and the specific pnictide compound of interest. A striking discrepancy between theory and experiment is however that the predicted As positions from LDA calculations do not match the experimentally observed ones. The As positions are therefore usually constrained in the band structure calculations. At the same time, in spin resolved calculations on the orthorhombic phase, several ‘tricks’ are applied to reduce the calculated Fe local moment. The predicted moment would otherwise be much larger than experimentally observed one. One such trick is to apply a (fictive) negative value for the Hubbard U. Although the calculations are thus not perfect, and the results can in general not be mapped one-to-one onto the band structure observed in photoemission experiments, the predicted qualitative features correspond rather well.

Around the (0, 0) point of $k$-space four or three concentric, hole-like Fermi surface sheets are located. Additionally there are two electron-like Fermi surface sheets around the ($\pi$, $\pi$) point of $k$-space. As can be seen in Fig. 2.13, the calculated Fermi surface

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Figure 2.13: The electronic structure of M122. Left: Three dimensional Fermi surface in $(k_x, k_y, k_z)$ space depicted in the simple tetragonal Brillouin zone for Ba122 with 10% Co doping, taken from Ref. [46]. Right: calculated band dispersion for undoped Ba122 in the paramagnetic phase, taken from Ref. [47].
sheets do show significant ‘warping’ as a function of $k_z$ (or at least much more than is the case for the highly two dimensional manganites, see previous section), owing to the more three dimensional electronic nature of these compounds (despite their two dimensional crystal structure).

The three dimensional character of the Fermi surface has been reported to increase with doping, see Fig. 2.14a. Photoemission experiments have also shown the existence of a three dimensional Fermi surface [48, 49], but it must be noted that mainly the inner of the $\Gamma$ centered bands has been reported to show significant ‘warping’ [49], see Fig. 2.14b. In contrast: according to most calculations, mainly the outer of the hole bands and the electron pockets would show a high degree of three dimensionality.

A subject thought to be closely related to the shape of the Fermi surface is the origin of the magnetic order for the parent and low doped compounds. The shape of the Fermi surface, with (at least for the parent compounds) roughly equally sized hole and electron barrels, leads to a large nesting susceptibility with a nesting vector of $(\pi, \pi)$, as illustrated in Fig. 2.14c [50]. This nesting makes the Fermi surface unstable towards spin density wave ordering. Hence, the anti-ferromagnetic ordering of the pnictide parent compounds is thought to be (at least partly) driven by the shape of the Fermi surface, meaning that the AFM ordering has itinerant character. However, there are also reports in the literature that the AFM ordering may be of more localized nature [51].

Whatever the origin of the magnetic ordering, the spin density wave (SDW) transition and orthorhombic structural transition lead to a major depletion (roughly 90%) of the free charge carrier density across the transition temperature at the low doping side of the phase diagram, as has been observed in quantum oscillation and optical spectroscopy studies [52–55]. This is because the large Fermi surfaces of the tetragonal phase are suggested to break up into many little ’droplet-like’ FS sheets below $T_c$ [52, 53], see also Fig. 2.14c. The low temperature electronic structure of the pnictide parent compounds, must thus be very different from that of the tetragonal one. However, to date, no clear, uniform model for the band structure has been indentified that fits well enough with experiments.

As mentioned, many calculations describing the magnetically ordered phase have appeared, however, the predicted local iron moment for the AFM ordered (parent) compounds is close to $2\mu_B$. This is much higher then the actual measured staggered moment on the iron sites by for instance neutron scattering. While the $M122$ compounds show local moments of $\approx 1 \mu_B$, the $M1111$ compounds have local moments below $0.5 \mu_B$. The origin of the low measured magnetic iron moments is at present still under discussion. It has been suggested to be due to the presence of magnetic domains [56], or could be due to the influence of highly polarizable As ligands [57].

Finally, angle resolved photoemission experiments have not yet provided a clear-cut picture of the Fermi surface in the AFM phase. Although many reports have appeared in the literature of Fermi surfaces that are, in some manner or other reconstructed (amongst others, see Refs. [58–61]), the data are not yet clear enough to resolve all $k$-space features present and to make a one-to-one connection to theory. It is thus fair to say that the true nature of the anti-ferromagnetic ordering in the pnictides is still elusive. However, it is very important to unravel the mechanism at the root of the
spin ordering, as this may hold the key to the mechanism behind the high temperature superconductivity displayed by these compounds.

### 2.2.4 Superconductivity: the order parameter

Although the work described in this thesis does not include measurements on actual superconducting pnictide compounds, it is of course crucial to know the superconducting order parameter in order to learn something about the mechanism behind the superconductivity. Therefore a few words about this matter. Triplet superconductivity \((p\text{-type})\) can be excluded for the pnictides [46], leaving the following order parameters as a possibility: (i) \(s\) and (ii) \(s\pm\), having a node-less Fermi surface, or (iii) \(d\)-wave pairing [46]. As there are multiple bands at the Fermi surface, there is the possibility for multi-band superconductivity. Indeed, many angle-resolved photoemission studies have found the existence of two different node-less gaps on the concentric Fermi surface sheets, in favor of \(s\pm\) pairing. However, many reports in literature, including nuclear magnetic resonance (NMR), tunneling spectroscopy and specific heat studies, are mutually contradicting each other and find evidence in favor for any of the possible pairing symmetries [46]. To be short: this issue is far from resolved and the defining experimental result has yet to be produced.

Still, this is not surprising: many other fundamental issues concerning the pnictides are not answered yet. As mentioned above, the nature of the anti-ferromagnetic order and the size of the local moment of the low doped and parent compounds, as well as their band structure in the orthorhombic phase are still under debate. Even more fundamentally, the degree of electronic correlation in these compounds is not yet clear. Though the pnictides are evidently less correlated than the cuprates (as they have a metallic ground states and the cuprates originate from Mott-insulating materials) the exact value of \(U\) with respect to the bandwidth \(W\) is still not settled. Reported values of the Hubbard \(U\) range from maximally 2 eV [63] (weakly correlated) to 3–4 eV [64] (or moderately correlated [65]. The exact determination of the value for the Hubbard \(U\) will be very important to properly place the pnictides somewhere in the spectrum between Mott insulator and Fermi liquid.

In the last two experimental chapters, we present our photoemission spectroscopy measurements on two pnictide parent compounds (Ba122 and Eu122) and we attempt to answer some of the more fundamental questions concerning their electronic properties. In the first of the two chapters we present angle integrated VUV and hard x-ray photoemission measurements on Ba122 and we show that the surface electronic structure of this compound is comparable to the bulk structure in terms of charge transfer. Additionally, we show that the near \(E_F\) electronic states are mainly those of iron. In Chapter 5 we present angle resolved photoemission measurement taken in the anti-ferromagnetic low temperature phase of Eu122, in an attempt to clarify the band structure and the nature of the reconstructed Fermi surface for this compound.
2.3 Experimental techniques

This section gives an overview of the most important experimental techniques used during the work that embodies this thesis. The main part of this section deals with photoe-
mission spectroscopy. The basic principles, as well as the actual set-up and procedures of a core level spectroscopy and angle resolved photoemission spectroscopy experiment will be discussed. Next, some other frequently encountered experimental techniques such as low energy electron diffraction and magnetometry will be discussed in much less detail, as they have served primarily as an analytical tools to characterize the samples for our spectroscopy measurements. Also, very briefly, some methods of crystal growth will be discussed.

2.3.1 Photoelectron spectroscopy

The basic principles of photoemission

Photoemission spectroscopy (PES) is based on the photoelectric effect. Upon impinging light on matter, an electron, through interaction with a photon, is emitted from the atom, molecule or solid under investigation. The electron can be detected and its velocity (or rather kinetic energy) can be measured. Photoemission can be performed on atoms or molecules in the gas phase, or on polycrystalline solids (and under special conditions even on liquids), but in the following, we will deal exclusively with photoemission from single crystalline solids. The measured kinetic energy $E_{\text{kin}}$, of a photoelectron emitted from a solid, is given by the following formula:

$$E_{\text{kin}} = h\nu - |E_B| - \Phi$$

(2.2)

Where $h\nu$ is the energy of the incoming photon, $|E_B|$ is the binding energy of the electron in the solid and $\Phi$ the work function, or surface potential energy barrier the electron has to overcome to be emitted from the solid. In practice, $\Phi$ is the work function of the electron analyzer, rather than the solid under investigation and is a priori not known. This requires a calibration of the binding energy scale via the measurement of the Fermi edge of a metal, usually Au or Ag, as, by definition, the mid-point of the Fermi-edge has $BE = 0$.

Phenomenologically, one can view the photoemission process as consisting of three steps: (1) the actual excitation of an electron from an occupied into an empty electronic state of the solid, (2) the transport of the excited electron to the surface of the crystal and (3) the transmission of the electron across the surface of the solid. These steps are schematically depicted in Fig. 2.15a.

The excited photoelectron can interact with the solid during the transmission to the surface of the solid and can lose kinetic energy via inelastic scattering processes. This typically causes a secondary electron background in a photoemission experiment. At low

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5For more detailed and exhaustive overviews of the basic principles of photoemission, see Refs. [30, 66]

6The binding energy in a photoemission experiment on solid, electrically conducting compounds is given with respect to the Fermi level and not with respect to the vacuum level $E_{\text{vac}}$.

7A more realistic description of the photoemission process is given within the far more complicated one-step model, where the bulk, surface and vacuum are included in the Hamiltonian of the crystal [68]. The computational complexity of this model means that the more accessible three-step model is often used to describe the photoemission process.
kinetic energies, the collisions are mainly of electron-phonon nature, but in general, the important contribution comes from electron-electron collisions. This kinetic energy loss due to inelastic scattering processes leads to a finite escape depth of the electrons. The mean free path length $\lambda$, of the electrons is defined as the depth at which the probability of loss-free emission of the electron is decreased by a factor $e$:

$$I(z) = I_0 e^{-z/\lambda \cos \theta}$$  \hspace{1cm} (2.3)$$

Where $\theta$ is the emission angle of the electron from the surface, and $I(z)$ the effective photocurrent from depth $z$. In practice, the value for $\lambda$ is not very material dependent, leading to a 'universal' curve that gives an approximation of the mean free path length as a function of the kinetic energy of the photoelectrons for a wide range of materials. This universal curve is depicted in Fig. 2.15b. Notably, the values for $\lambda$ are very small in the energy range where conventional vacuum ultra-violet (VUV: $h\nu = 20 - 100$ eV) photoemission experiments are performed: only several Å. The consequences of the small electron escape depth will be explained later.

If, in addition to the number and kinetic energy of the photoelectrons also their emission angle is measured, one is performing an angle resolved photoemission (ARPES) experiment. During the transmission of the photoelectron across the sample surface (the third of the three steps), the momentum $p$, of the electron is conserved in the direction parallel to the surface. The following simple relations link the momentum of the outgoing electron to the crystal momentum $k$, and to the emission angle $\theta$:

$$p_\parallel = \hbar k_\parallel = \sqrt{2mE_{\text{kin}} \sin \theta_{\text{ext}}}$$, \hspace{1cm} with: $k_\parallel^2 = k_x^2 + k_y^2$$  \hspace{1cm} (2.4)$$

The geometry of a typical photoemission experiment is shown in Fig. 2.15c. Thus, by measuring simultaneously the kinetic energy and the emission angle of the photoelectron,
a complete mapping of the electron states of the solid under investigation can be realized. The consequence of only strict conservation of the in-plane momentum components during the transmission across the surface, is that \( k_z \) cannot be accessed easily during the photoemission experiment, other than by varying the excitation energy \( h\nu \). The \( k_z \) value of the outgoing electron is given by the following relation:

\[
k'_\parallel = \frac{1}{\hbar} \sqrt{2m(E_{\text{kin}} \cos^2 \theta + V_0)}
\]  

Where \( V_0 \) is the surface potential felt by the electron upon crossing the surface. As \( V_0 \) is generally unknown, an accurate determination of \( k_z \) is in general cumbersome. This is the reason that angle resolved photoemission is mainly performed on compounds with a highly two dimensional (2D) electronic structure, where \( k_z \) does not play a major role in the determination of the energies of the electronic states. Another problem with highly 3D solids, is that the line shapes in the photoemission spectrum are broadened due to a finite lifetime of the excited hole in the resulting \((N-1)\)-electron system, leading to an extra averaging over a portion of the Brillouin zone in the \( k_z \) direction of \( k \)-space. \(^8\)

In general, during an ARPES experiment, the photoelectron current (intensity, \( I \)) as a function of emission angle (\( k_\parallel \)) and kinetic energy (\( E_B \)) is measured. The transition probability \( w \), of an electron in initial state \( \Psi_i \) to a final state \( \Psi_f \) is given by Fermi’s golden rule:

\[
w = \frac{2\pi}{\hbar} |\langle \Psi_f | H^{\text{int}} | \Psi_i \rangle|^2 \delta(E_F - E_i - h\nu)
\]  

\(^8\)Another, more practical reason to consider two dimensional solids for ARPES, is that single crystals of these compounds in general cleave rather easily along the crystal plane spanned by the axes corresponding to the electronically highly dispersive directions of \( k \)-space. The necessity of cleavage will be explained later.
Where the delta functions enter the expression due to the fact that during the excitation process energy should be conserved. The $H^{\text{int}}$ term denotes the interaction operator between the electrons in the solid and the incoming photon. Under various approximations, $H^{\text{int}}$ can be expressed as:

$$H^{\text{int}} = -\frac{e}{mc}A \cdot p = -\frac{e\hbar}{mc}A \cdot \nabla \quad : w \propto |\langle \Psi_f | A \cdot p | \Psi_i \rangle|^2 \delta_E$$ (2.7)

Where $A$ is the vector potential of the photon field and $p$ the momentum operator. Within the sudden approximation, that states that the actual photoexcitation and the transport of the photoelectron to the surface are instantaneous (which is typically valid for electron kinetic energies above 20 eV in the case of cuprates [30]), hence ignoring interaction between the exited photoelectron and the excited system lacking one electron (the $(N-1)$ electron system), the final and initial state wave functions can be separated into wave functions for the $(N-1)$ electron system and the excited electronic state:

$$\Psi_i = A \psi^k_i \Psi_{N-1}^i = A \psi^k_i c_k \Psi_{N-1}^i \quad \text{and} \quad \Psi_f = A \psi^k_f \Psi_{N-1}^f$$ (2.8)

Where $\psi^k_{i(f)}$ are the initial (final) state wave function of the excited photoelectron with momentum $k$, $c_k$ is an annihilation operator to express that the initial state of the $(N-1)$ system is merely that of the $N$ electron system, without the excited electron and $A$ is the anti-symmetrization operator introduced to satisfy the Pauli exclusion principle. The final $(N-1)$ state can be expressed as an excited state with eigenstate $\Psi_{N-1}^m$ and energy $E_{M}^{N-1}$. The total transition probability is then given by the sum over all possible excited states $m$. We thus arrive, taking Eq. (2.6), at the following expression for the intensity measured at momentum $k$ in a photoemission experiment:

$$I(k, E_{\text{kin}}) \propto \sum_{f,i} w_{f,i} \propto \sum_{f,i} |\langle \Psi_f | H^{\text{int}} | \Psi_i \rangle|^2 \delta_E$$

$$\propto \sum_{f,i} |\langle \psi^k_f | H^{\text{int}} | \psi^k_i \rangle |\langle \Psi_{N-1}^m | \Psi_{N-1}^i \rangle|^2 \delta_E$$

$$\propto \sum_{f,i} |M_{f,i}^k|^2 \sum_m |c_{m,i}|^2 \delta_E$$ (2.9)

The probability that the $(N-1)$ electron system after removal of electron state $i$ is left in excited state $m$, is given by $|c_{m,i}|^2$. In case of non-interacting particles, if $\Psi_{N-1}^i = \Psi_{N-1}^{m_0}$ for a particular state $m = m_0$, $|c_{m_0,i}|^2$ is unity and all other $c_{m,i}$ yield zero. The ARPES spectrum for a certain $k$ value will thus be given by a delta function in the energy channel, at an energy corresponding to the binding energy of the excited electron in the ‘solid’, as shown in Fig. 2.16a. However, in the case of a many body system

---

9The most important approximation being that the divergence of $A$ is 0. This approximation typically does not hold at the surface of the material under investigation, where $\Delta \cdot A$ may have a strong spatial dependence.
in which there is significant interaction between the electrons and between the electron system and other degrees of freedom such as phonons, the electron removal results in a strongly altered effective potential of the system and the initial $(N-1)$ wave function will have significant overlap with several excited states $m$. This leads to a series of a series of possible final states, giving rise to so-called ‘shake up’ peaks at higher binding energies and a suppression and broadening of the non-interacting (coherent) pole, as is illustrated in Fig. 2.16b and c. The latter panel shows the photoemission spectra of gaseous and solid molecular hydrogen. In the case of $\text{H}_2\text{(g)}$ the shake-ups, due to vibrational modes of the $\text{H}_2^+$ ion, are discrete levels, while in the case of solid hydrogen, these modes have broadened into a continuum.

The first summation term of equation (2.9) is often called the ‘matrix element’ and contains the dependence of the measured intensity on the experimental geometry and the excitation energy used. The second summation term of the expression is directly related to the one particle spectral function $A(k,\omega)^\pm$, that describes the chance of removal (or addition) of an electron from the interacting system. Hand-wavingly stated, this part of the expression contains the energy vs. $k$ relation of the many-body, interacting system, including deviations from the single particle dispersion relation, linewidth and lineshape due to the ‘dressing’ of the electrons with the elementary excitations of the system in question.

Another important factor playing a role in the intensity of a real (non-zero temperature) photoemission experiment is the Fermi-Dirac distribution (FDD), $f(\omega)$. The excitation of electrons due to thermal excitations leads to a broadening of the near $E_F$
spectral features and the observation of the unoccupied states within the envelope of the FDD at higher temperatures. The ‘full’ expression of the photocurrent, as a function of excitation energy and momentum is therefore given by:

\[ I(k, \omega) \propto |M(k, \omega)|^2 A(k, \omega)^\pm f(\omega) \]  

(2.10)

Where \( \omega \) is the binding energy with respect to the Fermi level. The matrix element, \( |M(k, \omega)|^2 \), can even cause a complete suppression of the intensity of certain features in an experiment, given the right experimental conditions. Let us consider a high symmetry experimental ARPES set-up, as depicted in Fig. 2.17a, and an electronic state with d-like symmetry. The detector, the incoming photons and the surface normal all lie in the same plane, that also defines a mirror plane of the electronic state under consideration. The matrix element, also indicated as \( I_0 \), can be expressed in the following way:

\[ I_0(k, \omega, A) \propto |\langle \psi^f_k | A \cdot p | \psi^i_k \rangle|^2 \]  

(2.11)

Only if the entire matrix element is of even parity with respect to the mirror plane, can the electronic state be detected. The same also holds for the final state \( \psi^f_k \), itself, because odd-parity wave functions would be zero at the mirror plane and hence also at the detector. So, only if \( A \cdot p | \psi^i_k \rangle \) is of even parity, would the measured intensity be non-zero. This means that in the geometry depicted in Fig. 2.17a the d-like electronic state pictured can only be detected with p-polarized light (\( E_p \) in the figure). Under rotation of the sample with 45° around the surface normal, the state can only be detected with s-polarized light.

These selections rules apply only under strict geometrical conditions but for every value of \( h\nu \). A more general effect of the matrix element is a (strong) photon energy dependence of the measured intensity. This follows directly from Eq. (2.11), as the size of \( I_0(k, \omega, A) \) directly depends on the overlap between the initial and final one-electron state. The latter is directly related to the excitation energy, as the kinetic energy of the resulting excited, free electron depends on \( h\nu \), see Eq. (2.2). The overlap between the initial and final state does not necessarily show a monotonic behavior as a function of photon energy. In fact, in solids, this leads to an oscillatory behavior of the measured intensity as a function of \( h\nu \), see Fig. 2.17b [69].

To summarize: under several assumptions, that are valid at higher electron kinetic energies, APRES is capable of probing the spectral function of the electronic states of a solid. The intensity (spectral weight) probed in the experiment depends not only on the number of occupied states in the relevant \((E, k)\) region, but also on the matrix element. For the interpretation of an ARPES this has important consequences, amongst which: (1) If an electronic state is not detected in an ARPES experiment, this does not necessarily mean it does not exist: the experimental conditions may merely suppress its spectral weight. And (2), by changing the experimental geometry and photon energy, it is possible to selectively probe a particular state of interest or determine the character and/or symmetry of the electronic states under investigation.
Core level photoemission spectroscopy

Angle resolved photoemission with VUV light is very useful for obtaining information about the valance band (near $E_F$) electronic states. It provides a direct measurement of the interactions of the low lying electronic structure and can directly map the band structure of a solid. But kinds of photon energies generally used for such studies are too low to address the deeper lying core level lines. Although these, due to their localized nature, do not contain any $k$-space information, there is still a lot of physical information that can be extracted from the lineshapes of a core level photoemission spectrum. As a major part of the experimental chapters within this thesis deal with core level spectroscopy, we here take a moment here to briefly introduce the reader to some aspects of this technique.

Typically, core level photoemission is performed using x-rays as an excitation source. Lab based x-ray sources mostly produce Al $K_\alpha$ (1253.6) and Mg $K_\alpha$ radiation (1486.6 eV) radiation. As can be seen in Fig. 2.15, the mean free path length at these energies has more than doubled compared to excitation energies in the conventional VUV regime. Increasing the photon energy beyond that accessible to conventional monochromized lab sources, for instance by use of synchrotron radiation (see sections below), increases the escape depth of the electrons even further. This makes (hard) x-ray photoemission [(Ha)XP(E)S] extremely suitable to study the bulk versus surface properties of solids.

Note that also by varying the angle of the sample under investigation (rather than the excitation energy), with respect to the optical axis of a fixed electron analyzer, a different bulk-to-surface signal ratio can be obtained. Taking a fixed mean free path length, a more grazing angle of photoelectron emission will correspond to a smaller escape depth of the electrons, according to Eq. (2.3).

Although the (higher binding energy) core level lines of atoms within a solid are highly localized, they do feel the chemical surroundings of the photoemitter. From a more molecular point of view, the electronegativity $^{10}$ of the neighboring atoms causes a larger (in case of electropositive ligands) or smaller (in case of electronegative ligands) electron density on the atom under consideration. $^{11}$ This leads to a decrease or increase, respectively, in the Coulomb attraction between the core level electron and the nucleus of the atom. Because of the extra potential felt by the core electron it will escape the solid with greater or reduced kinetic energy, showing up as a reduced or increased binding energy. This is called a chemical shift and is illustrated in Fig. 2.18a, where several distinct C 1s lines are distinguished for the four inequivalent carbon sites of ethyl trifluoroacetate in the gas phase $^{[66]}$.

Besides chemical shifts, there are several other important mechanisms determining the binding energy and peak form of a core level line. The width of the spectral peak is determined by the life time of the excited state (as is the case for VUV-PES), leading to a Lorentzian line-shape. The lifetime for deeper lying core levels is usually much shorter than for the more shallow ones, leading to an increase of peak width with in-

$^{10}$The electronegativity is the ability of an atom to attract electrons towards itself. Electropositive atoms are electron donators.

$^{11}$The redistribution of electron density is mainly realized by the molecular orbitals close to the Fermi level (or within the valence band in the case of solids).
2.3 Experimental techniques

Figure 2.18: Core level spectroscopy, taken from Ref. [66]. (a) C 1s spectrum from Ethyl trifluoroacetate in the gas phase. (b) Cu 2p spectra from three different copper dihalides. The spin orbit splitting ($\Delta E_S$) is indicated for CuF$_2$ with the vertical arrows. The multiplet structure for CuCl$_2$ is indicated in the inset, taken from Ref. [71].

creasing binding energy. The Lorentzian line shape should be convolved with a Gaussian contribution from the electron analyzer and the line width of the excitation radiation (these are treated in the following sections), leading to a Voigt-like line shape. State of the art synchrotron XPS experiments are now capable of achieving about 200 meV resolution at excitation energies as high as 6 keV (non-monochromated x-ray lab sources typically produce line widths of about 1 eV. Monochromated Al $K_\alpha$ anodes are capable of producing a line width of 300–400 meV).

The interpretation of a core level spectrum can be rather complicated. This is nicely shown in the case of the Cu 2p line for the copper dihalides. In Fig. 2.18b an XPS spectrum for the Cu 2p line of CuF$_2$, CuCl$_2$ and CuBr$_2$ are shown. It is clear that the line shapes are far from a simple, symmetric Voigt function. First of all, for all compounds the 2p lines consists out of two sets of peaks, separated by about 20 eV in binding energy. This is the spin orbit splitting, arising from interaction of the electron with spin $S = 1/2$ with the angular momentum of the orbital it resides in. Note that lines from s orbital states do not display spin orbit splitting, as they do not posses any angular momentum ($l = 0$).$^{12}$

Still, in Fig. 2.18b, also the separate spin-orbit split features each form doublets. Moreover, the shape of the peaks comprising the Cu 2p lines is (slightly) dependent on the halide. Note that while the satellite peaks at the high BE side of the most intense (main) Cu 2p$_{1/2,3/2}$ peaks have roughly the same binding energy for the three halides, but the more intense main lines shift towards lower BE going from from CuF$_2$ to CuBr$_2$.

$^{12}$Although this does not mean that the spectral from of an s-orbital state always has a simple Voigt line shape. Final state effects can lead to slitting of the s line shape, along the lines discussed below.
The complicated line shape and compound dependent binding energies can be explained within a molecular orbital picture in terms of charge-excited final states.

Upon exciting the electron from the Cu 2p core level into the vacuum, the system (the copper and the surrounding halides) is left with one core electron missing, denoted as \(2p^{-1}3d^9H\), where \(3d^9\) is the ground state of the divalent copper and \(H\) denotes the ground state filled shell of the halide ligands. The system however, can react to the presence of the core hole by transferring an electron from the ligands into the open Cu 3d shell: \(2p^{-1}3d^{10}H^{-1}\), thus screening the positive charge of the core hole.

In Fig. 2.18b, the intense main line corresponds to the ligand-hole state (and not to the ground state electronic configuration). The difference in binding energy of the main line between the different dihalides is due to the change in electronegativity (or polarizibility) of the different ligands. The charge transfer is easiest for the large Br ions, hence the BE of the main line is the lowest for this compound.

The satellites of the Cu 2p\(_{1/2}\), 2p\(_{3/2}\) line themselves also consist of multiple peaks, indicated in the inset of Fig. 2.18b for CuCl\(_2\). As the satellite corresponds to the \(2p^{-1}3d^9H\) electron configuration, the holes in both the 2p and 3d shells give rise to different final states that differ slightly in energy and lead to multiplet splitting. The main line, corresponding to the \(3d^{10}\) electron configuration does not show multiplet splitting, due to the absence of an open shell on the Cu atom.

The discussion above shows that the line shape of a core level is sometimes not easy to interpret, but that there is important information to be gleaned if one is able to do so. It also shows that the exact binding energy or line shape is often only interpretable when compared to other substances. For instance, in Chapter 4 we compare the binding energy of several core level lines as a function of hole doping for the bilayered manganite \(La_{2−2x}Sr_{(1+2x)}Mn_2O_7\). In a simplified (ionic) model, the binding energy \(E_B\) of an electron in a solid is given by the following equation:

\[
E_B = L + K \cdot Q + V - E_R \tag{2.12}
\]

Where \(L\) is the bare atom electron binding energy of the electron on the atom under consideration, \(K \cdot Q\) is a term arising from the difference in (formal) charge between the atom in the solid and a free atom (hence a contribution that can be compared to the chemical shift mentioned earlier), \(V\) is the potential field created by the surrounding atoms and \(-E_R\) describes the relaxation of the electronic system upon creating the core hole due to screening by polarization or charge transfer. This last term thus decreases the binding energy of the electron in the solid. The binding energy shift of two different compounds (due to doping or otherwise), is then given by the following equation:

\[
\Delta E_B = \Delta \mu + K \cdot \Delta Q + \Delta V - \Delta E_R \tag{2.13}
\]

Where \(\Delta \mu\) expresses the shift in chemical potential due to the addition or removal of charge carriers in a rigid band-like manner as a result of the doping. The size of the contribution of the different terms to the total binding energy shift is in general not \textit{a priori} clear.

With this short overview of some of the aspects of core level photoemission, the reader is hopefully convinced that, though seemingly rather simple compared to ARPES,
x-ray core level spectroscopy can give a wealth of physical information concerning the physical properties of solids and the degree of electron correlation within a solid and has contributed significantly to our understanding of many physical phenomena.

**A typical photoemission setup**

In this section an overview of a typical photoemission setup is given. In Fig. 2.19a such a setup, the ‘FAMoS’\(^{13}\) lab system at the Van der Waals-Zeeman Institute, is depicted. The major parts are indicated: the experimental chambers, the pumps, the sample manipulator, the electron analyzer and the light source. Each of these elements is briefly described below.

As mentioned earlier, the mean free path length of an excited photoelectron inside a solid is small, typically a few Å. This means that, in order to obtain signal from the sample under investigation, an ARPES experiment has to be done under ultra high vacuum conditions (UHV: pressures smaller than \(10^{-10}\) mbar). Furthermore, a clean sample surface will have to be prepared in vacuum. Common surface preparation procedures are *in situ* sputtering and annealing for simple metallic compounds and evaporation in case of organic films and polycrystalline metallic films. ARPES experiments on more complex compounds require in vacuum cleavage of the single crystals. This is done in general by gluing a cleavage post onto a flat sample surface in air. The post is meant to create sufficient leverage and is removed in vacuum with a wobble stick, taking part of the single crystal with it and leaving behind a clean, single crystalline cleavage surface on the sample holder, see Fig. 2.19b. Of course, when doing (Ha)XPES measurements the need for UHV can be relaxed somewhat, due to the increased electron kinetic energies. Pressures up to \(1 \times 10^{-9}\) mbar are sufficient to perform these experiments.

UHV conditions are reached by taking several steps. First of all, the experimental chambers of a photoemission setup are made of welded stainless steel components. Different components are bolted together using a so-called *Conflat* connection, where two knife-edges are pressed into a copper gasket to obtain a connection that is sufficiently leak-tight (see Fig. 2.19c). Manipulation of the sample and other components inside the vacuum is done with magnetic transfer rods, multi-stage differentially pumped rotation mechanisms, and transfer mechanisms that move via welded bellows.

The pumping of the chambers themselves is continuously done by a number of different pumps, such as ion-getter pumps, cryopumps and/or turbo molecular pumps, the latter backed by oil-free pre-pumps (usually a scroll or membrane pump). The experimental setup is usually divided in different compartments, that are separately pumped: (1) In the analysis (main) chamber the actual photoemission experiment takes place. (2) In the preparation chamber, evaporation of organic films, sputtering, sample cleavage and surface characterization by means of electron diffraction is performed. (3) The load lock is a small compartment that can be quickly vented and pumped down to \(10^{-8}\) mbar to introduce samples from air into the preparation chamber.

Furthermore, to reach UHV, all in vacuum components must be clean and free of oil, fat or other (organic) contamination. Also materials with high vapor pressures,

\(^{13}\)FAMoS stands for FOM Amsterdam Momentum Space microscope
Figure 2.19: A modern photoemission setup. (a) Photo of the FAMoS ARPES setup in the basement of the University of Amsterdam (left). Right: a schematic of the photo with the most important parts of the setup indicated with different shaded areas. The sample position during measuring is indicated with an ‘S’. The impinging photons are indicated with a red arrow, and the electrons entering the analyzer with a black arrow. (b) Copper sample holders with samples and cleavage posts glued on top of them. Left: before cleavage, right: after cleavage. The glued crystal (S, black square) has split into two parts: one remaining on the sample holder and one part on the cleavage post. (c) Stainless steel Conflat UHV components. The Cu gasket is pressed between the two knife-edges and forms an air-tight seal. Photos courtesy of F. Massee.

such as most plastics and rubbers and some metals such as Sn, Pb, Zn, etc...should be avoided. Lastly, all in vacuum components, including the chamber walls, will have to be
heated to 140°C for several days to desorb adsorbed water vapor on the interior of the setup and allow for sufficient time to pump away the released adsorbates. If all these steps are followed, reaching and maintaining pressures in the 10^{-11} mbar range is rather straightforward.

Additionally, as PES experiments probe electrons with relatively low kinetic energies, it is of paramount importance to avoid stray magnetic fields (such as the earth magnetic field) from the measurement chamber and analyzer. In order to do so, these components are usually lined with an internal μ-metal shielding. Close to the sample and the analyzer entrance, no magnetizable materials, such as stainless steel, may be used. Acceptable materials for sample holders and sample manipulation stages are for instance Ta, Ti and Cu.

Having reached UHV conditions, one should think about sample manipulation. In order to do an ARPES experiment, one wants to have access to a large range of k-space. Although modern multiplexing electron analyzers can probe a one-dimensional strip of k-space simultaneously, it is important to have a large number of rotational degrees of freedom for the sample. In the ideal case, one access to a six-axis manipulator, as displayed in Fig. 2.20. A schematic of the AdamIII manipulator is shown, designed and
Figure 2.21: The electron analyzer. (a) Schematic of the working principles of a hemispherical analyzer. The important parts are labeled and the path of the photoelectrons passing through the analyzer is indicated with dotted lines (fast electrons follow the trajectory with the larger radius). An example of a recorded spectrum [an \( (I, E, k) \) image] shown as a false-color plot, is also depicted, together with a vertical and horizontal cut through the data. (b) Ray-tracing diagrams of the angular (A) and transmission (T, or ‘spatially resolved’) mode of a Scienta SES2002 hemispherical analyzer, showing the radial position of the electrons in the lens system as a function of distance traveled, as well as their kinetic energy. These particular traces are for electrons entering the lenses with \( E_{\text{kin}} = 20 \text{ eV} \) and being retarded to \( E_{\text{pass}} = 10 \text{ eV} \). Taken from Ref. [72].

constructed at the University of Amsterdam.\(^{14}\) This manipulator has three translational degrees of freedom and additionally can rotate the sample around three axes, with a precision in the 0.1° range, to have very accurate access to a large range of \( k \)-space. Furthermore, the sample manipulation stage is connected via a copper braid to a Janis Supertran liquid He (4 K) flow cryostat with internal heater, to enable cooling-down or warming-up of the sample to any temperature between 16 and 400 K.

The most important part of the photoemission setup is the electron analyzer, so, for the interested reader, a few more words will be dedicated to this part of the machine. The most common type of high resolution electron analyzer is the hemispherical one, where

\(^{14}\)The AdamIII manipulator is an adapted version of the Carving manipulator, designed by the University of Amsterdam as part of a collaboration between the UvA and the Paul Scherrer Institute (Swiss Light Source). The CARVING manipulator is commercially available from SPECS.
the electrons are separated with respect to their kinetic energy by a potential difference between two concentric half-spheres, see Fig. 2.21a. These analyzers are commercially available from a number of companies and are capable of achieving a resolution in the energy channel of about 1 meV (although under real experimental conditions, an energy resolution of 5-10 meV is typically achieved), and an angular resolution in the order of 0.2°.

Upon entering the analyzer, the emitted photoelectrons first pass a set of electrostatic lenses. By applying different potentials on the different tube-like lens elements, the electrons are retarded to a nominal kinetic energy, called the pass energy $E_{\text{Pass}} \pm \Delta$, at the end of the lens assembly. Simultaneously, in the lenses a radial separation on either emission angle (‘angular mode’ for doing ARPES) or emission position (‘transmission’ or ‘angle-integrated’ mode, suited for core level spectroscopy, for instance) is accomplished. Both modes are done with the same sets of lenses, but by applying different voltages. In Fig. 2.21b ray-tracing diagrams of both measurement modes are depicted, showing the electron trajectories and kinetic energies as the photoelectrons pass through the lens system.

At the end of the lens system the electron pass through a narrow slit and they enter the actual hemispherical part of the analyzer. Here the energy selection takes place parallel to the surface normal of the hemispheres (perpendicular to the slit direction). As the electron detection is done at the end of the hemispheres with a two dimensional phosphor screen and a CCD camera, angular multiplexing detection along the slit direction (perpendicular to the energy selection) is possible, as shown in Fig. 2.21a. State of the art spectrometers can simultaneously measure an angular range of about 30°, corresponding to the full width of the first Brillouin zone at an excitation energy of $h\nu = 50$ eV, with an angular resolution better than 0.5°.

The width of the slit $w$, can be varied and determines the resolution in energy, as well as the $k$-resolution perpendicular to the slit length. The more narrow the slit, the higher the resolution, but in turn, the lower the count-rate. Also choosing a lower pass energy increases the resolution of the instrument at the same cost of intensity. The theoretical resolution limit of a hemispherical analyzer is given by the following simple relation:

$$\Delta E = E_{\text{pass}} (w/R_0 + \alpha^2/4)$$  \hspace{1cm} (2.14)

Where $R_0$ is the mean radius of the inner and outer hemisphere and $\alpha$ the acceptance angle.\(^{15}\)

A field termination mesh with about 90% transmission separates the end of the analyzer from the electron multiplying multichannel plates (MCPs). After the MCPs, the electrons impinge on a phosphor screen at high voltage. The resulting light pulses are recorded by a regular CCD camera on the air-side of a vacuum viewport and collected by pulse-counting software to produce an $(I, E, k)$ image.

The kinetic energy range of the detector is approximately 8% of the pass energy, thus at $E_{\text{Pass}} = 10$ eV, the detector window is 800 meV wide. Spectra are usually recorded in ‘swept-mode’: the nominal pass energy through the detector is kept constant, while the lens voltages are changed in a step-wise fashion, such that the desired range of measured

\(^{15}\)Typical values are: $R_0 = 200$ mm, $w = 0.2$ mm, and $\alpha$ is a few mrad.
energies is moved stepwise over the entire detector. The dwell-time at each voltage step and the size of the energy range determine the time a single spectrum takes to accumulate. This way of measuring provides an averaging over the entire detector in the energy direction to account for efficiency differences of the MCP and CCD camera. Also, the shadow of the termination grid is thus averaged out. In the $k$-direction, sweeping is not possible. The efficiency of the detector in this direction has to be accounted for by normalizing the spectrum after recording. This can be done by measuring for instance an amorphous Au film and determining the intensity as a function of emission angle (that should in theory of course be uniform over the entire detector, as an amorphous gold film is expected to be an isotropic emitter). Simultaneously, the position of the Fermi edge can be determined as a function of emission angle from such a reference measurement, as to correct for slight differences across the detector due to stray fields and lens aberrations.\footnote{Typically, the energy scale is offset by not more than 3 meV across the entire detector. However, high precision measurements of for instance small superconducting gaps in the order of several meV, can necessitate such a binding energy correction across the detector.}

The excitation radiation in a lab environment is typically provided by a gas discharge lamp coupled to a monochromator. In the lamp a gas (usually He) is excited to produce light with wavelengths that correspond to the narrow emission lines of that particular gas (21.2 eV in the case of HeI $\alpha$ radiation). Nowadays, lasers are also used as excitation sources. The advantage of lasers is that they produce very high intensity and highly focused light and, additionally, they offer the possibility of producing polarized light. A disadvantage is that the energy of laser light is rather low, only a few electron volts, meaning that the kinetic energy of the excited electrons is maximally one or two eV. In this regime the sudden approximation is no longer valid and interpretation of the acquired spectra becomes much more complicated. Also, the amount of $k$-space accessible becomes very small, see Eq. (2.4). In turn, this does mean that the $k$-resolution of the experiment becomes very high. Another possibility is the use of (monochromized) x-ray radiation from x-ray anodes, to perform core level spectroscopy.

Yet, lab based excitation sources are rather limited in the sense that they restrict the user to one or two fixed excitation energies only. From the previous discussion about matrix elements, it is evident that a quantitative interpretation of (AR)PES spectra often requires the use of multiple excitation energies, so as to get sufficient knowledge of the effects of the matrix elements on the measured intensities. Sources of tunable light in the VUV and x-ray regime are available at large scale synchrotron facilities. For instance, the work described in this thesis has (almost) exclusively been measured at the synchrotron, using wavelengths generally unaccessible to lab photon sources. The next section of this thesis is devoted to the working and optical lay-out of a synchrotron source.

**Synchrotron radiation**

Electromagnetic radiation is produced whenever a charged particle is accelerated. In the case of third generation synchrotrons, specially dedicated to producing high intensity...
photon radiation, these are virtually always electrons that travel around in a quasi-
circular storage ring several 100 meters in circumference. The storage ring is basically
a narrow pipe under UHV conditions (in the range of $10^{-12}$ mbar) that has alternating
straight and bend sections. The electron orbit is very precisely controlled with di-
quadru-, and hexapole magnets. The dipoles account for the bending of the electron
trajectory, and the quadru- and hexapoles focus the electron beam. In Fig. 2.22a a
typical lay-out of a synchrotron is given. As the electrons lose energy whenever they
travel around the storage ring due to the emission of synchrotron light, radio frequency
cavities continuously accelerate the electrons. By matching the radio frequency with the
orbit of the electrons, the electrons are bunched.

Due to electron collisions with residual gas in the storage ring, the beam current in
the storage ring decreases slowly with time. This means that every now and then high
kinetic energy electrons will have to be injected into the storage ring. The electrons
are typically produced and accelerated in a linear accelerator coupled to a booster ring
and are inserted at ‘full speed’ into the storage ring. The addition of new electrons to
the storage ring may happen continuously (in so-called top-up mode). Alternatively,
depending on the synchrotron design, there is a complete beam-dump every few hours,
after which a full re-injection takes place. A major disadvantage of the latter situation is
that the beam current, and thus the photon flux decreases with time, causing a change
in heat-load onto the optical elements in the path of the synchrotron light, that might
lead to fluctuations in the photon energy arriving at the experiment with time, apart
from the obvious time dependence of the photon flux itself.

Here, a very short introduction to the basic physics behind synchrotron radiation is
given, for a complete review, see Ref. [73]. The electrons in the storage ring travel with
relativistic velocities and the radiation produced by the accelerated electrons should thus
be treated in a relativistic frame-work. A consequence is that the radiation emitted,
becomes highly focused in the forward direction. The typical opening angle of the
radiation $\theta$, emitted by the particle traveling on a radial trajectory with speed $v$, is
given by:

$$\theta \approx \frac{1}{\gamma} = \sqrt{1 - \left(\frac{v}{c}\right)^2}$$ (2.15)

Where $c$ is the speed of light. As $v$ approaches $c$, $\theta$ becomes very small and the radiation
is emitted primarily in the forward direction. The spectrum of radiation is white, i.e.
light of a broad range of frequencies is emitted, see Fig. 2.22b, but the spectrum can
be described with a critical photon energy $\hbar \omega_c$, giving the frequency above and below
which half the total emitted energy is radiated:

$$\hbar \omega_c = \frac{3\hbar c}{2\rho} \left[1 - \left(\frac{v}{c}\right)^2\right]^{-3/2} = 3\langle \epsilon_\gamma \rangle$$ (2.16)

Where $\rho$ is the radius of curvature of the trajectory and $\langle \epsilon_\gamma \rangle$ is the average energy
per emitted photon. Thus, as the electrons travel around the storage ring and pass
a bending magnet, they emit very bright white light. However, experiments such as
photoemission spectroscopy, require mostly monochromatic light. This means that the
emitted synchrotron radiation has to be monochromized and most of the emitted power
Figure 2.22: Synchrotron radiation. (a) Top: photograph of the outside of the experimental hall of the Swiss light source, Villigen, Switzerland. Bottom: schematic of the synchrotron ring BESSYII at the Helmholtz Zentrum Berlin, Germany. (b) Top: electrons at relativistic speed describing a bend trajectory due to a magnetic field, emit radiation ($S$) mainly in the forward direction, taken from Ref. [73]. Bottom: theoretically calculated spectrum of a bending magnet given as the number of photons per second per angle for a 300 mA current of electrons traveling at $E_k = 1.7$ GeV through a magnetic field $B$, of 2 Tesla. The critical photon energy ($h\omega_c \approx 5700$ eV) is indicated. Spectrum taken from Ref. [74]. (c) Top: photograph of the permanent magnet banks of a wiggler at SPring8, Japan [75]. Middle: schematic of the electron trajectory thought an undulator or wiggler. The magnet banks are depicted (atypically) in the horizontal direction. Taken from Ref. [76]. Bottom: the peak magnetic field of a permanent magnet wiggler as a function of the gap between the magnet banks [75]. According to Eq. (2.17), the magnetic field and hence the gap of the wiggler determines the principal wavelength produced by the insertion device.

is wasted. A way to better match the emitted radiation with the required photon energy, is sending the electrons though an undulator. An undulator consists out of two opposing arrays of magnets with alternating polarity, see Fig. 2.22c and can be placed in a straight section of the storage ring. As the electron trajectory is now oscillatory (i.e. ‘bending’ numerous times within a short length), the emitted radiation from the consecutive wiggles will interfere with each other. The result is emitted light with a much higher intensity ($I \propto n^2$ with $n$ being the number of wiggles) than from a bending magnet and a much more narrow spectral width. The fundamental wavelength $\lambda_{ph}$ of order $N$, and the relative line width $\Delta \lambda/\lambda$, of an undulator with a period $\lambda_U$ is given
by:
\[
\lambda_{ph} = N \lambda U \frac{E_0^2}{E_k^2} \left(1 + \frac{k^2}{2} + \frac{E_k^2 \theta^2}{E_0^2}\right) \quad \text{and} \quad \Delta \lambda = \frac{1}{nN}
\] (2.17)

Where \(E_k\) is the kinetic energy of the electrons in the storage ring, \(\theta\) the angle of emission of the light and \(E_0\) the rest energy of an electron. \(k\) is the wiggler parameter of the undulator, that depends on the size of the magnetic field \(B_{max}\) and is given by:

\[
k = \frac{e B_{max} \lambda U}{2 \pi m_e c}
\] (2.18)

Where \(e\) is the elementary charge of the electron and \(m_e\) the rest mass of the electron. By changing the magnetic field, the wavelength of the radiation produced by the undulator will change. In case of an undulator with fixed electromagnets this is done by changing the current through the coils, otherwise the gap between the permanent magnet banks is changed. Note that the more wiggles an undulator has, the more narrow the line width will be, and of course, the more intense the produced radiation will be.

As the electrons that pass through the undulator oscillate in the horizontal plane, the produced radiation is highly linearly polarized in the horizontal direction. By shifting the undulator in the propagation direction of the electrons with half a phase, linear vertical polarization can be achieved. Smaller phase shifts lead to circularly polarized light.

After the insertion device (the undulator) or bending magnet a whole array of optical elements including a monochromator, refocusing mirrors and several slits form the beamline that eventually delivers monochromatic and highly focused light at the experiment. In the previous short explanation about synchrotron light, all the advantages of such a light source have been mentioned: it is capable of producing very intense light with almost any desired polarization or wavelength that is eventually focused into a very narrow beam. In the next sections, two beamlines at BESSYII (at the Helmholtz Zentrum Berlin) are shortly described. These have been used extensively for the experimental work comprising this thesis. First, as an example of a bending magnet beamline, the KMC1 beamline, where HaXPES measurements were performed. Secondly, the UE112-PGM2b beamline, using an undulator as an insertion device.

The KMC1 HaXPES beamline

The KMC1 beamline\(^{17}\) is coupled to a bending magnet with a magnetic field strength of 1.3 T and a bending radius of 4.3m, yielding radiation with a critical energy of 2.5 keV. This beamline is specially designed for the use of x-rays in the 2 to 12 keV regime. Because the reflectivity of x-rays with such short wavelengths becomes very low, few optical elements are placed between the bending magnet and the experiment. An overview of the beamline is depicted in Fig. 2.23a. After the bending magnet an aperture is placed that confines the divergence of the white beam to 6mrad in the horizontal direction and 0.5mrad vertically. After this, an optional Be foil can be placed.

\(^{17}\)For a complete overview of the KMC1 beamline, see Ref. [77]
in the white beam, filtering out the lower wavelengths (typically below 3 keV) to reduce the heat load onto the optical elements downstream to thus achieve a higher stability in terms of the monochromized photon energy.

Next, a toroidal mirror focuses the white beam directly onto the sample position of the experiment. In between, a double Si crystal monochromator is placed. The energy separation is done by Bragg reflection of the radiation from the first Si crystal, which is water cooled, as it has a significant heat load from the white beam (on the order of 20 W at 300 mA ring current). The second crystal mainly functions as a mirror to redirect the monochromated radiation back to the focal position of the toroidal mirror. Rotation of the double crystal selects the wavelength $\lambda$ that is transmitted to the experiment, according to Bragg’s law: $\lambda = 2d \sin \theta$, where $d$ is the $d$-spacing of the Si crystal in use. There are three possible crystal pairs that can be interchanged in vacuum: Si(111), Si(311) and Si(422). These crystals have their maximum resolution at increasingly high...
photon energies, see Fig. 2.23b. The resolution $\Delta E$ of the monochromator is highest in near-backscattering geometry and is given by:

$$\Delta E = E \Delta \theta / \tan \theta$$  \hspace{1cm} (2.19)

Where $\Delta \theta$ is the rocking curve width of the crystal, determined by the intrinsic crystal width (‘Darwin width’) and the beam divergence. The resolution thus obtained for the highest possible $\theta$ is about 300 meV for all three crystals. However, not only first order light is transmitted through to the sample. Also a significant number of higher order wavelengths are passing through the double crystal monochromator, as shown in Fig. 2.23c.

Though these higher order wavelengths can cause extra peaks to appear in the core level spectra taken with lower harmonics, the resolution of the monochromator is much better for the third compared to the first order, because the intrinsic crystal width decreases more then a factor 10 between these photon energies. Yet, both the photon flux (see Fig. 2.23c) as well as the cross-sections for the photoemission process, Ref [70] decrease with increasing photon energies in the hard x-ray regime. This means a significantly extended counting time when measuring in high resolution higher order mode.

The low photo-ionization cross-sections in the hard x-ray regime mean one has to perform the photoemission measurements in an extremely grazing geometry. With an incidence angle of only a few degrees, the penetration depth of the x-ray photons is better matched with the escape depth of the outgoing photoelectrons, thus maximizing the efficiency of the photoionization process compared to the incident photon flux.

**The UE112-PGM2b VUV-ARPES beamline**

The UE112-PGM2b is coupled to an undulator with $n = 32$ and $\lambda_U = 112$ mm, capable of producing photon energies as low as 5 eV. An overview of the beamline is given in Fig. 2.24.\textsuperscript{18} After the undulator, a toroidal mirror collimates the ‘white’ light onto a plane grated monochromator (PGM). The mirror in this case is also used as switching mirror between 3 different beamline branches.

The PGM works with a grating that scatters, via constructive interference, the light at an angle $2\theta = \alpha - \beta$ depending on the wavelength $\lambda$ via the grating equation:

$$Nm\lambda = \sin \alpha + \sin \beta$$  \hspace{1cm} (2.20)

With $N$ is the line density of the grating and $m$ is the diffraction order. This equation for a particular wavelength holds for a finite number of combinations of the incidence angle $\alpha$ and the scattering angle $\beta$. The constant of fixed focus defines these angles as $c_{ff} = \cos \beta / \cos \alpha$ (thus, the more gracing incidence, the larger the $c_{ff}$ value). Larger $c_{ff}$ values correspond to a smaller line width of the monochromized light at the sample position, but a lower intensity and spectral purity (i.e. containing more higher order light). Most commonly, $c_{ff}$ values between 2 and 3 are used.

\textsuperscript{18}Details of a similar optical lay-out are described in Refs. [78] and [79].
Chapter 2. Methods & background

After the monochromator, several optical elements provide focusing of the light beam onto the sample position. The line width of the monochromized light is determined, apart from the quality of the optical components and other engineering factors such as the temperature stability of the grating / mirror combination, by the width by the width of the exit slit, positioned before the last refocusing mirror. As the vertical opening of the exit slit selects radiation out of the vertically dispersed fan made up of different wavelengths, a narrower exit slit improves the resolution, at the cost of the intensity. The resolution in general is higher for lower photon energies. At the UE112-PGM2b beamline however, at photon energies up to $h\nu = 100$ eV, a resolution of the excitation energy better than 7 meV is easily achieved.

Also worth mentioning is that after the monochromator, but before the exit slit, several baffles can be placed in the beam to reduce the spot size, mainly in the horizontal direction. These can also be used to accurately reposition the beam on the sample after an injection, as, due to small changes of the electron orbit in the storage ring, the spot position may vary slightly in between electron injections.

A specific feature of the UE112-PGM2b undulator and beamline is that close to 100% vertical polarization can be obtained at photon energies as low as 30 eV. Often, this is the case only at photon energies around 100 eV.

2.3.2 Low energy electron diffraction

After introducing photoemission spectroscopy (at a straightforward level for length reasons), I turn to the technique of low energy electron diffraction (LEED) which uses elastic scattering of electrons from atoms to determine the lattice symmetry of single crystals. As this technique is ‘electron in - electron out’ and the electrons typically have a kinetic energy between 20 and 400 eV, LEED is very surface sensitive (unlike other structural probes such as for instance x-ray scattering, that has a probing depth in the $\mu$m range). It is thus a technique that is complementary to angle resolved photoemission and can be used to quickly determine the quality and orientation of the in
vacuum cleaved single crystals, before conducting the time-consuming ARPES experiments. Also, the existence of surface reconstructions after in vacuum cleavage of single crystals may not be evident from x-ray or neutron scattering. They will however have a pronounced effect on ARPES measurements and are easily recognized with LEED.

As LEED is one of the most important sample characterization tools for ARPES measurements (and one of the few in situ ones), below the basics of this technique are shortly explained for the interested reader. A typical LEED camera can be bought commercially from several companies such as Specs or Omicron and has about the size of a hat box. The basic lay-out is shown in Fig. 2.25a. At the center of the set-up is an electron gun. Thermal electrons from a glowing filament are monochromized by applying a low and a high pass filter and impinge on the sample surface. The back-scattered electrons pass a series of concentric hemispherical grids that act as a low pass filter, such that only the elastically scattered electrons are detected. The scattered electrons then impinge on a phosphor screen, causing a bright diffraction pattern that can be detected with for instance a CCD camera, see Fig. 2.25b.

As the penetration depth of the electrons in a LEED experiment is very low, the  \( c \)-axis coherence is partly lost, and the Laue conditions are not strictly satisfied in this direction. As a consequence, instead of having sharply defined Bragg reflections in the direction of reciprocal space perpendicular to the sample surface, ‘rods’ of intensity are obtained with smoothly varying intensity as a function of \( c^* \). By recording the intensity of a LEED spot as a function of electron energy, one obtains an \((I,V)\) curve, from which the surface structure can be modeled. One complication in the quantitative interpretation of LEED \((I,V)\) signals, is that one, in order to correctly describe the measured intensity, has to take into account multiple scattering from the atoms.
2.3.3 Other experimental techniques used

Laue diffraction

Laue diffraction is a diffraction technique using ‘white’ x-ray light. The very first x-ray diffraction experiments were in fact using the Laue technique [81]. Laue diffraction, like LEED, is often done in a backscattering geometry. As the incident and backscattered x-rays have a sizable penetration depth in the sample, the scattering is now of three dimensional nature, as opposed to a LEED experiment. The use of polychromatic light facilitates the simultaneous detection of many Bragg spots at once on a detection plate in front of the sample. Because of this, Laue diffraction is particularly handy for determining the orientation of a single crystal. As the x-ray radiation has a large penetration depth in air, the need for UHV is absent and Laue diffraction can be used as a quick check to determine whether a single crystal is of high enough quality, in terms of crystallinity, to be considered for spectroscopy. Also, the existence of multiple crystallites can be determined ex vacuum this way. In our case, Laue is not necessary for the precise orientation of the single crystals, as the c and (a, b) crystallographic axes can in general easily be distinguished: due to the two dimensional nature of LSMO and M122, the large, flat sides of the crystals always correspond to the (a, b) plane. The use of a 5- or 6 axis manipulator and the use of in situ LEED diffraction before commencing the ARPES experiment, further reduce the need for orientation by Laue diffraction.

Magnetometry using a superconducting quantum interference device

Superconducting quantum interference device (SQUID) magnetometers are commercially available. They are able to probe very small magnetic fields from samples with or without external field present and in a temperature range from above room temperature to 4 K (or even down to a few mK, by the use of a dilution fridge). Therefore, they are very useful for measuring the ferro- to paramagnetic transition temperature and its width of the manganites as well as for instance the diamagnetic signal below the transition temperature of superconductors. All the manganite samples that have been measured with photoemission have been characterized with SQUID magnetometry to determine the magnetic properties and hence the crystal quality. The reason a SQUID is able to detect very small magnetic fields, is the use of Josephson junctions: loops of superconducting wire containing a very thin insulating barrier. A voltage change occurs across these junctions upon applying very small magnetic fields.

This characterization method is extremely convenient, as (the sharpness of) the transition temperature of very small samples (about \(1 \times 1 \times 0.1 \text{ mm}^3\)) can be measured, without the need of gluing contacts, as would be required for transport measurements.

2.3.4 Single crystal growth

Although not part of the actual experimental work embodied in this thesis, single crystal growth has been a very important factor in the experiments described here. Without high quality single crystals it is nigh impossible to conduct a proper ARPES experiment. In Amsterdam we are fortunate to have our own facilities for single crystal growth, that
have allowed us to obtain high quality single crystals of the iron pnictide superconductors quite soon after their discovery and moreover, be very critical about the crystal quality of the LSMO samples.

A large portion of the after-growth cutting of the single crystals, the preparations for gluing them onto the sample holders for spectroscopy and the quality checks with Laue diffraction and magnetrometry have been done under own supervision, but the actual single crystal growth is a highly specialized occupation, that requires years of experience and could thus not be part of the experimental work during a 4 year PhD trajectory. Nonetheless, because of its importance to our research group, the following text explains very shortly the main steps of the crystal growth process.

The LSMO single crystals were grown in Amsterdam by Dr. Y. Huang and in Oxford by Dr. D. Prabhakaran with the optical floating zone technique. The latter samples were kindly provided to us by Prof. A. T. Boothroyd. Typically, the starting materials are mixed in appropriate amounts in the form of powdered oxides (La2O3, SrCO3 and MnO2) and are very finely dispersed and thoroughly mixed with a ball-mill. Next, the actual chemical reaction takes place during several repeated cycles of heating (between 800 and 1500° for 12 to 24 hours) and re-milling. Before the last heating cycle, the powder is pressed in a rod and sintered. This poly-crystalline rod of LSMO is the starting material for the actual single-crystal growth process.

The rod is then placed, hanging down, as a feed rod in an optical floating zone furnace, where, with the use of focusing mirrors and halogen lamps a small section at the bottom end of the rod is brought carefully to a molten state. This section is located directly above a seed rod (an old piece of LSMO single crystal, or a poly-crystalline sintered rod). The molten liquid is kept between the rotating feed and seed rod by surface tension. With time, the rods are moved down with respect to the hot zone, such that progressively, the molten zone moves through the feed rod, transforming the seed rod into a growing single crystal or crystals. The growth direction of the LSMO single crystals is in the (a,b) direction, meaning that the long axis of the grown ingot actually does not corresponds to the long c crystallographic axis. Needless to say, there are many parameters that regulate the crystal growth, such as the temperature and the rotation and translation speed.

From the resulting ingot, some 10 cm long and up to 1cm in diameter, that consists out of several (or, in some cases many) single crystals, samples have to be cut with a convenient size for our spectroscopy measurements, typically 2×2×0.2 mm³. The cutting can be done with a diamond saw or, in some cases with a sharp scalpel. As the surface of the bilayered LSMO crystals can be a little rough and sometimes contains a skin of foreign phase (most notably LSMO113), before gluing and further characterization, they are first ground flat.

The pnictide single crystals were grown in Amsterdam by Dr. Y. Huang (Ba122) and in Goettingen University by dr. H. Jeevan (Eu122). The latter crystals were kindly provided to us by Prof. dr. Gegenwart via Prof. dr. J. Fink. The pnictide single crystals were grown using the Bridgeman method. This method entails dissolving the starting materials, preferably well mixed and finely dispersed, in a liquid solvent, contained in an ampule. By applying a temperature gradient over the ampule, single crystals
will form at the cold part and will grow throughout the liquid. The liquid can be
decanted while still being above the melting point of the matrix, or it can be etched
away after cool down. During the first months after the discovery of HTSC in pnictides,
the samples were grown almost exclusively with Sn-flux, but this leads to Sn inclusions
in the single crystals, most probably by substitution at the Fe sites [82, 83]. A more
controlled way of crystal growth is by so-called self-flux, where the amount of FeAs
starting material is much higher than the corresponding stoichiometric amount of M-
cation starting material, thus acting as reactant as well as solvent. This prevents the
inclusion of foreign elements in the pnictide single crystals [84]. To date, floating zone
furnace grown pnictide single crystals are scarce.

2.4 Experimental details and samples

All the samples used in the experiments described in this thesis have been high quality
single crystals. To ensure the results from our spectroscopy measurements have a gen-
eral validity, great care has been taken throughout the work described in this thesis in
characterizing the measured samples. Electron probe micro-analysis measurements on
selected LSMO samples of $x = 0.30, 0.36$ and $0.40$ revealed that the true composition
of the single crystals was within a few percent of the nominal doping and did not vary
substantially across the entire crystal.

Optical inspection in air of all samples ensured that only those with flat and shiny
surfaces were considered for spectroscopy. All measured crystals, bilayered LSMO and
pnictide parents compounds, were characterized prior to the spectroscopy measurements
in term of the temperature and sharpness of the bulk transition by magnetometry (using
a superconducting quantum interference device) and dc resistivity, respectively. The bulk
crystallinity of all LSMO samples and few selected pnictide samples has been checked by
Laue x-ray diffraction. Of the former, only samples displaying sharp and single LAUE
diffraction spots were selected. The pnictide samples in general showed very sharp and
clean Laue patterns.

All selected samples were cleaved in vacuum at temperatures lower than $T = 50$ K
and at pressures better than $2 \times 10^{-10}$ mbar, with the exception of the crystals used in
the HiKE experiments, described in Chapter 4. Those were cleaved at room temperature
at a pressure better than $1 \times 10^{-9}$ mbar.

The quality of all the cleavage surfaces was checked using low energy electron diffrac-
tion (LEED). Only cleavage surfaces displaying sharp and single LEED patterns were
taken in consideration for the spectroscopy measurements.

Referencing of the binding energy was done by measuring the Fermi edge of a freshly
evaporated gold film (ARPES) or the Au 4f core lines of a gold foil (HaXPES) in electrical
contact with the measured samples. Samples were conductively attached to the copper
sample holders. The poorly conducting LSMO samples were coated with graphite around
the sample edge as an extra measure to prevent electrostatic charging. Furthermore, the
measured cleavage surfaces were tested not to be charging electrically (either due to
the contact resistivity of the sample mounting or an intrinsically low conductivity of
the samples, that can result in charge accumulation during the ionizing photoemission
2.4 Experimental details and samples

experiment), by varying the incident photon flux of the experiment and confirming that spectral features did not shift in kinetic energy. The further experimental details are listed per chapter in the following.

2.4.1 Experimental details Chapter 3

Experiments used the UE112-PGMa beamline at BESSY coupled to an SES100 analyzer and the SIS beamline at the Swiss Light Source equipped with an SES2002 analyser and a 50 µm-sized light spot (µ-ARPES). The total experimental energy broadening at 25K was 30 meV at BESSY and 20 meV at the SLS. The momentum resolution was 0.01 π/a at the excitation energies used. Single crystals of bilayered LSMO with doping level x = 0.36 were grown in Amsterdam using the optical floating zone technique. The Curie temperature of the samples was determined using SQUID magnetometry to be 131 K.

2.4.2 Experimental details Chapter 4

Experiments with photon energies around hν = 2 and 6 keV were performed at the double crystal monochromator KMC-1 beamline at Helmholtz Zentrum Berlin, Berlin, coupled to the Scienta R4000 analyzer of the HiKE endstation [77]. Experiments were carried out in a grazing incidence geometry with a total energy resolution of 300 and 180 meV for hν = 2 and 6 keV, respectively, as determined from the width of the Fermi edge of a piece of gold foil. Single crystals of LSMO were grown using the traveling floating zone technique in Amsterdam (x = 0.30, 0.36 and 0.40) and in Oxford (x = 0.30, 0.325, 0.35, 0.375, 0.40, 0.425 and 0.475) [85, 86]. The results obtained from crystals from both Amsterdam and Oxford with the same nominal doping level were identical. The experiments on the core level shift versus doping were repeated with a lab-based Al Kα source from VG-Scienta coupled to a Specs PHOIBOS 100 hemisperical analyzer with a total energy resolution of ≈ 1 eV. The results obtained from the lab-system were identical to the results obtained with hard x-ray radiation at the synchrotron.

During the x-ray core level spectroscopy measurements at the Helmholtz centrum, focused on core level shifts in the order of 50 meV, i.e. much smaller than the experimental resolution, extreme care was taken to avoid the influence of small drifts in the photon energy. This drift occurs due to a slow decrease of the current in the storage ring with time, causing a change in the heat-load on the optical elements in the beam line. The accuracy of the binding energy referencing was better than 50 meV and 100 meV for the experiments with hν = 2010 and 6000 eV, respectively (whereby this error is dominated by the mentioned drift in temperature of the monochromator crystals).

Angle resolved photoemission experiments performed at the Helmholtz Zentrum Berlin used the UE112-PGM beamline coupled to a Scienta SES100 analyzer, as well as the ‘1-cubed’ end station equipped with an R4000 hemispherical analyzer. Additional measurements were performed at the SIS-HRES photoemission beamline at the Swiss Light Source equipped with an SES2002 and an R4000 analyzer and a light spot in the order of 100 µm (µ-ARPES). All ARPES measurements were done in ultra high vacuum at temperatures between T = 20 and 250 K. During temperature dependent measurements special care was taken that the sample manipulator position did not change (within the
size of the light spot) due to thermal contraction or expansion. Temperatures were cycled to check and confirm the absence of surface degradation during warm-up or cool-down.

2.4.3 Experimental details Chapter 5

Experiments with photon energies $h\nu = 2010$ and 3000 eV were performed at the KMC-1 beamline at the Helmholtz-Zentrum Berlin, coupled to the Scienta R4000 analyzer of the HiKE endstation. [77] Experiments were carried out at room temperature in a grazing incidence geometry with a total energy resolution of 300 and 450 meV for $h\nu = 2010$ and 3000 eV, respectively, as determined from the width of the Fermi edge of a piece of gold foil. Single crystals of Ba122 larger than $1 \times 1$ mm$^2$ were grown from Sn flux and cleaved in a vacuum better than $1 \times 10^{-9}$ mbar, resulting in shiny, flat cleavage surfaces. The level of tin impurities in the crystals was estimated from core-level intensities to be in the order of 7 atomic % and these single crystals show a magnetic and structural transition at a reduced temperature of 60 K, instead of the familiarly observed 140 K for Sn impurity-free samples. [33]

Experiments with $h\nu = 125$ and 140 eV were carried out at the UE112–PGMa beamline at the Helmholtz-Zentrum Berlin using an SES100 electron analyzer and were performed both at room temperature and at low temperature (25 K), with an experimental energy resolution of 30 meV. These experiments were performed on the same batch of single crystals as the HiKE experiments, and on sample surfaces cleaved both at room and at low temperature in a vacuum better than $2 \times 10^{-10}$ mbar. The results obtained did not depend on the temperature at which the crystal was cleaved. Spectra were taken in transmission ($k$-integrating) mode of the electron energy analyzers.

2.4.4 Experimental details Chapter 6

Temperature dependent ARPES was performed at the UE112-PGM beamline at the Helmholtz-Zentrum Berlin, coupled to a Scienta SES100 analyzer with a total energy resolution of 27 meV (at $T = 20$ K, $h\nu = 75$ eV) and a resolution of better than 0.02 $\pi/a$ along the slit. The analyzer slit was perpendicular to the scattering plane of the incoming light and the outgoing photoelectrons. The polarization vector of the light was perpendicular to this plane. Additional, detailed FS mapping experiments were performed at the SIS-HRES beamline of the Swiss Light Source, using a Scienta R4000 analyzer with a total energy resolution of 16 meV (at $T = 10$ K, $h\nu = 84$ eV) and better than 0.05 $\pi/a$ along the slit. FS maps were collected with an angular step of 0.5°, scanning in the direction perpendicular to the analyzer slit (denoted $k_\parallel$ forthwith), which is comparable to the resolution along the analyzer slit. The small beam spot-size ($\approx 100$ $\mu$m) assured a minimal influence of surface roughness on the ARPES experiments and aided in the achievement of very high effective contrast in $k$-space. During the SLS experiments the analyzer slit and the polarization vector of the synchrotron radiation were parallel to the scattering plane formed by the incoming light and the outgoing photoelectrons.

Single crystals of Eu122 were grown using the Bridgeman and Sn-flux method at Goettingen University [87]. Their magnetic transition temperature was determined to
be about 190 K, with an additional AFM ordering of the Eu moments around 18 K [88].

The depicted LEED experiments were performed on BaFe$_{1.86}$Co$_{0.14}$As$_2$ and Fe$_y$Se$_{1-x}$Te$_x$

single crystals grown in Amsterdam using the Bridgeman and self-flux method.
Quasiparticles and a gap–less
Fermi surface in
La\(^{(2-2x)}\)Sr\(^{(1+2x)}\)Mn\(_2\)O\(_7\) with \(x = 0.36\)


Abstract
In this chapter we report detailed, temperature dependent, angle resolved photoemission data from La\(^{(2-2x)}\)Sr\(^{(1+2x)}\)Mn\(_2\)O\(_7\) single crystals with a doping level of \(x = 0.36\). The first important result is that there is no sign of a pseudogap in the charge excitations of this material for temperatures below the Curie temperature \(T_C\). The data show unprecedentedly sharp spectral features, enabling the unambiguous identification of clear, resolution-limited quasiparticle features from the bilayer split 3d\(_{x^2-y^2}\)-derived Fermi surfaces both at the zone face and zone diagonal \(k_F\) locations. The data show that these low temperature Fermi surfaces describe closed shapes in \(k_{||}\), centered at the \((\pi/a,\pi/a)\) points in the 2D Brillouin zone, and are not open and arc-like in nature. The second important result concerns the temperature dependence of the electronic states. The spectra display strong incoherent intensity at high binding energies and a very strong temperature dependence, both characteristics reminiscent of polaronic systems. However, the clear and strong quasiparticle peaks at low temperatures are difficult to place within a polaronic scenario. Careful analysis of the temperature dependent changes in the Fermi surface spectra both at the zone face and zone diagonal regions in \(k\)-space indicate that the coherent quasiparticle weight disappears for temperatures significantly above \(T_C\), and that the \(k\)-dependence of the \(T\)-induced changes in the spectra invalidate an interpretation of these data in terms of the superposition of a ‘universal’ metallic spectrum and an insulating spectrum whose relative weight changes with temperature. In this sense, our data are not compatible with a phase separation scenario. Additional data for other doping levels of \(0.30 < x < 0.50\) show results highly similar to those of \(x = 0.36\).
3.1 Introduction

After the high temperature superconductors, one of the most studied correlated electron systems in condensed matter physics are the colossal magnetoresistant (CMR) manganites. The bilayered, strontium doped manganites (La$_{2-x}$Sr$_{x+2}$Mn$_2$O$_7$) with $x \approx 0.3-0.4$ (abbreviated forthwith LSMO) show on cooling an insulator-metal transition associated with the onset of long range ferromagnetic order. This transition occurs at a maximum Curie temperature $T_C$, of approximately 130 K (for $x=0.36$) [89, 90] and goes paired with colossal changes in the magnetoresistance (CMR) [91], which in turn have been linked to the large number of spin and orbital degrees of freedom accessible to the near-Fermi-level electronic states.

The ability to alter the electronic properties of these materials by applying a magnetic field makes them very interesting for applications. From a more fundamental point of view though, despite years of research, the microscopic origin of the colossal magnetoresistance effect in these systems is still the subject of much debate.

In general, metallic electrical transport requires the existence of a Fermi surface (FS) upon which quasiparticles (QP’s) reside. In this context, LSMO is remarkable, as recent ARPES experiments deep in the ferromagnetic, metallic state indicate the existence of two highly differing regimes. Firstly, for $x=0.40$ [23], LSMO is reported to possess a discontinuous FS in the form of arcs centered upon the Brillouin zone diagonal, with a strong pseudogap opening up towards the Brillouin zone face. In contrast, at an only 2-4% lower doping level of $x=0.36-0.38$ [24], the published spectra exhibit clear quasiparticles at the Brillouin zone face, leaving open the issue as to the situation at the zone diagonal.

A second, equally important issue regards the temperature dependence of the QP’s. Seeing as the metallic behaviour in LSMO is symbiotic with the ferromagnetic order, one would expect coherent QP’s at the FS of LSMO to disappear at $T_C$. This appears to be the case at the Brillouin zone diagonal in crystals with $x=0.40$ [23]. Therefore, a recent report proposing both that zone face-QP’s exist well above $T_C$ for $x=0.36$ [25] and that metallic behaviour is seen in the ARPES spectra up to a $T^*$ of 300 K has stimulated much discussion.

The layered managanites play a special role within the CMR family, as they enable exploitation of powerful, direct experimental probes of the electronic states in both real (STM/STS) and reciprocal space (ARPES). Therefore, it is of paramount importance that the two central issues sketched above of whether the FS of LSMO is pseudogapped below $T_C$, and whether QP’s exist above $T_C$ are investigated in detail.

Here, a thorough ARPES study is presented of these key issues in LSMO single crystals with $x=0.36$. Improved sample quality means we are now able to unambiguously show the existence of QP’s at the zone face for both the antibonding and bonding c-axis bilayer split 3d$_{x^2-y^2}$ bands and crucially, also for the zone diagonal direction in the same samples, meaning the 3d$_{x^2-y^2}$-derived FS has no pseudogap at low temperatures. Furthermore, careful analysis of the $k$-dependence of the data recorded at different temperatures provides strong evidence against a scenario of phase separation into microscopic metallic and insulating ‘patches’ [25].
3.2 The fermiology of LSMO with $x = 0.36$

A typical $(E, k)$-image, taken at cut 1 of Fig. 3.1a, is shown in Fig. 3.1b. A ‘U-shaped’ band - in this case the $3d_{x^2-y^2}$ anti-bonding bilayer-split band - disperses from a band-bottom located at ca. $\approx 450$ meV towards the Fermi level, where each branch displays a sharp feature at low energies indicative of the existence of QP’s. In panels (c) and (d) the $(E, k)$-images and energy distribution curves (EDC’s) from $k_F$ locations on the FS are shown. In the former, it is evident that low energy spectral weight survives all the way from the Brillouin zone face (ZF) to the zone diagonal (ZD) region of $k$-space. $^1$ In panel (d), the QP’s show up as a small, yet clearly discernable peak at $E_F$, followed by a hump, at least part of which is due to emission from the deeper lying bonding band (see Fig. 2 and Ref. [18]).

If one takes the presence of low energy spectral weight plus a peaked EDC as a working definition of a QP-signal, it is evident from Fig. 1 that the $d_{x^2-y^2}$ bands support QP’s all round the FS. Consequently, for $x = 0.36$, these FS’s are not zone-diagonal ‘Fermi arcs’ and do not support a pseudogap for $T < T_C$. This is quite unlike the situation reported for $x = 0.40$ [23], thus making pseudogap behavior for this latter doping level not typical for the layered managanites in general (as similar behavior as for $x = 0.36$ can also be shown for LSMO with other doping levels in the metallic region of the phase diagram, see Section 3.4).

In the preceding, two criteria were applied to the data to define whether a QP existed or not. Naturally, it is of interest to examine just how well defined these excitations appear to be in both $k$ and $E$. It is known that effective cleavage surface flatness - over the entirety of the illuminated and analyzed area - can limit the sharpness of ARPES features. The bilayer managanites do not possess a Van der Waals bonded cleavage plane as the ARPES and STM ‘standard’ oxide Bi$_2$Sr$_2$CaCu$_2$O$_8$ does, and therefore measurements on LSMO utilizing a highly focused ‘micro’ excitation spot could deliver better defined QP features.

Figure 3.2 shows $(E, k)$-images recorded using the 100 µm light spot at the SLS, together with their corresponding $E_F$-MDC’s (upper panels) and $k_F$-EDC’s (lower panels). It is clear from the $(E, k)$-image in (a) that the qualitative features are very similar to those of Fig. 3.1b. The big advantage of the ‘µ-ARPES’ approach can be seen clearly in the top panel of Fig. 3.2a. Here the $E_F$ MDC’s at $(\pi, 0)$ for the conventional and micro-spot measurements are overlain. The FWHM of the leading peak of the former is of order 0.06 $\pi/a$, a value equal to the state-of-the-art in the literature (Refs. [23, 24]). The small spot data is almost two times narrower, with a FWHM of only 0.035 $\pi/a$. The corresponding $k_F$ EDC shows a more pronounced peak at $E_F$, whose width is essentially resolution-limited, as would be expected for a quasiparticle.

Fig. 3.2b shows the same $(\pi, 0)$ cut for $h\nu = 73$ eV. This photon energy is reported to strongly favor emission from the bonding band [24], and indeed a further U-like feature is seen, with a band bottom located at ca. 800 meV and $k_F$-wavevectors some 0.1 $\pi/a$ greater than those for the anti-bonding band. The bonding band $k_F$ EDC shows

$^1$For the ZD direction, the bonding and antibonding bilayer split FS’s almost touch. Exactly which of these FS’s dominates the observed intensity is a moot point.
Figure 3.1: (a) Schematic of the FS features of LSMO, showing the 3d$_{x^2-y^2}$-based Γ-centered pocket (purple) and the zone corner-centered FS barrels from the 3d$_{x^2-y^2}$-based bonding (green) and anti-bonding (blue) bilayer split bands. The k-space cuts taken are marked in red. (b) (E, k)-image from LSMO with x = 0.36 taken at the (\pi, 0) point in k-space [cut 1 in panel (a)]. (c) zoomed images taken at the k-slices shown in panel (a). (d) $k_F$ EDCs from the images shown in (c). The inset (highlighted in purple) shows a zoom of the EDC for $k_x = 1.8 \pi/a$. The red shading emphasizes that this EDC also supports a small QP peak on top of a sloping background. All data is recorded with $h\nu = 56$ eV and $T = 30$ K.

Consideration of both panel (a) and (b) of Fig. 3.2, reveals a surprising feature of the $\mu$-ARPES measurements on LSMO in the form of an extra, V-shaped, weak feature indicated in the (E, k)-image of Fig. 3.2b with a black dotted line. This feature disperses in a parabolic manner around the (\pi, 0)-point (as do the anti-bonding and bonding bands). From an extrapolation, its $k_F$ exceeds 0.5 $\pi/a$, a value that is far from a small, narrow peak at $E_F$ signalling the QP, followed by two hump-like features at higher energy.
3.2 The fermiology of LSMO with $x = 0.36$

Figure 3.2: $\mu$-ARPES data for LSMO with $x = 0.36$ at $T = 30$ K (a) at the zone face with $h\nu = 56$ eV, (b) $h\nu = 73$ eV and (c) near the zone diagonal, $h\nu = 56$ eV. In each case, the upper panels contain $E_F$ MDCs [in panel (a) overlaid with the $E_F$-MDC from the data shown in Fig. 3.1b as a dotted line], the central panels the $(E,k)$-images and lower panels the $k_F$ EDCs. The white and black solid arrows mark the $k_F$-location for the bonding and anti-bonding bands, respectively.

Given the identification of well-defined QP features for both $(\pi,0)$ centered FSs, one can then move on to examine their nesting characteristics. Fig. 3.1c shows significant nesting in the ZF region for the anti-bonding band (the $k_F$ vectors remain constant over a fair range in $k_x$). The nesting vector (expressed in units of $2\pi/a$) is simply the $k_F$ value of $q = 0.19$. For the bonding band at $(\pi,0)$, the analogous value would be $q = 0.28$, matching any FS crossing in band structure calculations [18]. At present the origin of this feature, which gives rise to the high energy hump in the EDC indicated with an arrow in Fig. 3.2b, is unknown.

Fig. 3.2c shows data taken in the region of the ZD with $h\nu = 56$ eV. Once more a sharp QP peak is seen at $E_F$, whose intensity, although greater than in the conventional measurement shown in Fig. 3.1c and d, is still small compared to that seen at the ZF for the same photon energy.
making it a much closer match with q-vectors at which Jahn-Teller correlations above $T_C$ give broad regions of incommensurate x-ray scattering centered at $(±\epsilon, 0, ±1)$ with $\epsilon = 0.3$ [14]. This may lie behind the significantly weaker intensity of the QP feature for the bonding band EDC as compared to the analogous anti-bonding band EDC seen in Fig. 3.2, although one should bear in mind that the polaron correlations seen in x-ray experiments collapse for $T < T_C$ [14].

To summarize this part of the results, the observation of persistent and resolution-limited QP signals at all $k_F$ locations probed on the 3d$_{x^2−y^2}$-derived FSs using $\mu$-ARPES measurements is not only fully consistent with non-gapped $(\pi,0)$-centered FSs in LSMO with $x = 0.36$ at low temperature, but also sets the standard for the sharpest photoemission data on the bilayer manganites recorded to date.

### 3.3 The temperature dependence of the QP peaks

We now turn our attention to the issue of the temperature dependence of the Fermi surface electronic states. Fig. 3.3 shows data from the $(\pi,0)$-point taken at temperatures from 25 K up to 185 K, the latter well above the $T_C$ of 131 K. Panel (a) contains EDMs showing one of the branches of the anti-bonding band. It is clear that – apart from thermal broadening – all the EDMs look comparable. It should be noted that the spectral weight of the QP peak does decrease steadily with temperature, as can be seen from the EDCs shown in Fig. 3.3b. We note here that this decrease in intensity with increasing temperatures is larger than the change in thermal broadening can account for on going from 30 to 185 K. Nevertheless, even at 185 K some spectral weight at $E_F$ still remains as a step in the EDC, although the sample is in the paramagnetic, insulating part of the phase diagram. None of the spectra in Fig. 3.3 show a gap within the experimental resolution and the accuracy of the energy referencing used. This can be seen from the symmetrized $k_F$-EDCs displayed in panel (b), although the peak in the 185 K symmetrized spectrum is very small and this EDC might actually be close to being gapped, hinting that a true gap in the charge sector might be opening at even higher temperatures. The fact that spectral intensity at $E_F$ near $(\pi,0)$ exists even 50 K into the paramagnetic region of the phase diagram [25] seems at odds with the globally insulating transport characteristic at these elevated temperatures of bilayered LSMO with $x = 0.36$. Therefore, drawing together what our T-dependent data show us up to this point: (i) the QP-peak at lowest energy disappears at or very close to the bulk Curie temperature, yet (ii) at the zone face, there remains (non-peaked) spectral weight at $E_F$ until temperatures of the order of 50 K above $T_C$.

To further investigate this anomalous temperature dependence, spectra were taken with improved statistics and over a wider binding energy range, both the ZF and ZD regions of the $(\pi,\pi)$-centered Fermi surfaces at low temperature and just below and above $T_C$. These data are shown in Figure 3.4. Panel (a) contains the (zoomed) EDMs and (b) the accompanying $k_F$ EDCs.

In panels (c) and (d) of Fig. 3.4 symmetrized versions are depicted of the EDCs shown in panel (b). Although, as asserted below, the low binding energy coherent spectral weight disappears steadily with increasing temperature at both $k$-points, the
3.3 The temperature dependence of the QP peaks

![Figure 3.3: (a) T-dependence for LSMO \(x = 0.36\) at \((\pi,0)\) (\(h\nu=56\) eV, left hand branch). The MDC peak maxima are overlaid using a black solid line. (b) EDCs at \(k_F\) for all temperatures, normalized to the intensity at 150 meV BE, and (c) their symmetrized versions (all EDCs are offset vertically).]

symmetrized spectra show that at the ZF and the ZD again no gap in the charge sector is opening at temperatures up to 140 K.

One striking feature in these T-dependent data, both at the ZF and ZD regions, is that the aforementioned reduction in spectral weight extends over an energy scale of up to 700-800 meV, which is obviously an energy range far in excess of the change in thermal energy. Such large changes have been reported previously for the ZF region in Ref. [25], and their T-dependence has been put forward as an argument for microscopic phase separation, whereby local metallic and insulating regions change their relative abundance steadily with temperature. Vital for this model is that the difference spectra between pairs of \(k_F\) EDCs (recorded at different temperatures) can be collapsed onto a single, universal ‘metallic EDC’ [25]. The two difference spectra from our data recorded from the ZF region are shown in Fig. 3.4e. At first glance, they do look to be scaled versions of one another, but closer inspection reveals that the weight of the QP-peak in the original EDCs decreases much faster between 95 and 145 K than it did between 30 and 145 K, meaning that the difference spectra lose their low energy peak as temperature increases. As illustrated in the inset of Fig. 3.4e, this decrease in spectral weight of the QP in the difference spectra persists -though less prominently- if the original EDCs
Figure 3.4: (a) EDMs of LSMO ($h\nu = 56$ eV, $k_x = 1.0\pi/a$) at the ZF and ZD point in $k$-space at three different temperatures. (b) EDCs at $k_F$ from the EDMs shown in panel (a) (indicated there with red dotted lines). EDCs are normalized to the high BE intensity, which is equivalent to normalizing to the intensity above $E_F$. (c) Symmetrized EDCs near $E_F$ (scaled at intensity at 200 meV BE) for the three temperatures at the ZF and (d) at the ZD. (e) The scaled difference between the 30 and 95 K EDC (blue curve) and the 95 and 145 K EDC (red curve) for the ZF. The inset shows the same spectra over 300 meV BE for EDCs that are first broadened to match the Fermi-Dirac-distribution at 145 K before subtraction (see text). (f) The scaled difference EDCs of 30 − 145 K EDC (blue curve) and 95 − 145 K EDC (red curve) for the ZD.

taken at 30 and 95 K are first broadened using an additional Fermi-Dirac distribution (matching the temperature broadening of the spectra recorded at 145 K) before the subtraction takes place. This proves that the decrease in QP spectral weight cannot be attributed to temperature broadening alone. If, for the sake of argument, one were to assign the difference spectra in Fig. 3.4e to a metallic phase as was done in Ref. [25], the data here show clearly that this ‘metallic’ spectrum loses its coherent QP spectral weight as the temperature climbs above $T_C$.

An additional, powerful test of this phase separation scenario is given by the $k$-dependence of the spectral changes with temperature. If temperature essentially only alters the relative percentage of the metallic and insulating patches, then various difference spectra at a FS location other than the ZF should also collapse onto a ‘universal metallic EDC’ specific for that point of $k$-space. From Figs. 3.1 and 3.2, it is clear that LSMO with $x = 0.36$ also supports QPs in the zone diagonal region, thus offering the
3.3 The temperature dependence of the QP peaks

Figure 3.5: Large $k_{||}$–area Fermi surface maps (signal integrated over $E_F \pm 10$ meV) for LSMO with $x = 0.30$, 0.35 and 0.425 taken at $T = 20$ K with $h\nu = 56$ and 76 eV. The point density perpendicular to the analyzer slit is $\approx 0.08\pi/a$ (for $h\nu = 56$). The large arrow in the top-left FS map, indicates an unexpected electron-like Fermi surface pocket around the $(\pi, \pi)$ point of $k$-space, that is alluded to in the next chapter. The displayed data has been interpolated with two extra slices along the angular scanning direction (i.e. along the $(0, 0) - (\pi, \pi)$ direction). The two right most panels show the fitted positions of the identifiable $E_F$ crossings in the raw FS maps for both photon energies. Results for the various doping level are overlain to allow for easy comparison. The error bars in the fitted positions are smaller than the symbol size.

The ZD difference spectra shown in Fig. 3.4f clearly differ significantly up to binding energies of 300 meV, thus one cannot speak of a universal ‘metallic EDC’ growing monotonically with decreasing temperature for the ZD region of $k$-space. This, in turn, provides a strong argument against the phase separation model presented in Ref. [25] as being a complete description of the $T$-dependence of these $k$-dependent data, as this scenario would demand that the change in spectral weight happens in a similar fashion at both high symmetry points of the Brillouin zone. At this stage, it is interesting to recall that a recent $T$-dependent STM study of LSMO with $x = 0.30$ [92] found no signs of a bimodal gap distribution in tunnelling data across more than 2000 different surface locations, which - taken at face value - also argues against phase separation, albeit for a
different composition.

Thus, the challenge faced is to reconcile the following four main characteristics of these new, highly-resolved LSMO data for $x = 0.36$:

i. Existence of clear and sharp QP peaks at all $3d_{x^2−y^2}$-derived $k_F$ locations probed at low $T$.

ii. Strong high BE spectral weight at all temperatures.

iii. $T$-dependent changes in the spectra on a scale of up to 800 meV BE.

iv. Clear differences in the temperature induced effects between the ZF and ZD regions of $k$-space.

Phase separation as described above would have offered a route to reconcile points (i)-(iii), but cannot account for point (iv). On the other hand, behavior such as described in points (ii)-(iv) has been reported for photoemission from polaronic systems [93, 94], in which most of the higher binding, energy intensity is due to multiphonon satellites, and a vanishingly weak QP (the ‘zero phonon line’) is left at $E_F$. The kind of electron-phonon coupling strengths required to generate all the observed high BE incoherent weight seen in these data from LSMO would lead to the complete suppression of the QP feature at $E_F$, something that evidently does not occur here for $T << T_C$ [point (i), above].

From the above, it is apparent that some pieces of the puzzle that are required for a complete and consistent description of the ARPES data from these systems (and their temperature dependence) must still be missing. Despite this pointer towards future work in this area, the data do result in a number of unambiguous and important conclusions. Firstly, that the ($\pi,\pi$)-centered Fermi surfaces of the layered CMR manganite La$_{1.28}$Sr$_{1.72}$Mn$_2$O$_7$ support quasiparticles, both at the diagonal and the face of the 2D Brillouin zone at low temperatures. This system, therefore, has no pseudogap in the charge sector, thereby excluding the use of the epithet ‘nodal metal’ for this class of materials in general. Secondly, we find that the temperature dependent behavior of both the quasiparticles and of higher lying spectral weight is different at the Brillouin zone face and diagonal. This argues against a model describing the metal-insulator transition as stemming from a percolative growth of metallic clusters in an insulating matrix.

### 3.4 Results from other doping levels

The temperature dependence reported above for the QP spectral weight of the $x = 0.36$ sample does not, at first glance, correspond to the bulk temperature dependence of bilayered LSMO. After all, above $T = 130$ K, in the high temperature insulating phase, no spectral weight at $E_F$ would be expected. The data presented here however do correspond with the temperature dependence and fermiology of LSMO reported in Ref.

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2We note that the $k_F$ EDCs as presented in this paper also contain spectral weight due to bands located at higher BE, for example the bonding band and the third, at present unidentified feature mentioned earlier.
3.4 Results from other doping levels

[24] for the doping levels \( x = 0.36 \) and \( x = 0.38 \). In contrast, the studies reported in Ref. [23], and [26] on LSMO with a doping level of \( x = 0.40 \), show quite a different behavior: that of a metal with a discontinuous Fermi surface (i.e. displaying ‘Fermi arcs’) at low temperature that loses all coherent QP spectral weight at \( E_F \) upon crossing the bulk metal-to-insulator transition. Thus, in the latter case the temperature dependence of the QP peaks can be unified with the bulk physical properties of bilayered LSMO, while their fermiology is rather exotic. For the slightly different doping levels presented in Refs. [24] and [25] and in the above, the low temperature fermiology is that of a more conventional metal, but the temperature dependence of the QP peaks seems not be connected to the bulk metal-to-insulator transition in a simple way.

In order to investigate whether the difference between these data sets has a physical origin and is due to a subtle doping dependence of the electronic structure of bilayered LSMO, we have scrutinized many other doping levels across the metallic part of the phase diagram of La\(_{2-x}\)Sr\(_{x}\)Mn\(_2\)O\(_7\). FS maps of three representative samples with different doping levels, being \( x = 0.30 \), \( x = 0.35 \) and \( x = 0.425 \), are depicted in Fig. 3.5. The data for all three compositions are very similar to the data presented above for \( x = 0.36 \): all of the doping levels display a continuous Fermi surface with sharp and intense QP peaks, both in the ZD and the ZF direction of \( k \)-space.

The typical temperature dependence of the electronic states at \((\pi, 0)\) of the same three doping levels is depicted in Fig. 3.6. The peak width of the \((I, k)\)-curves at \( E_F \) \((W)\), is a direct measure of the scattering rate of the low lying electronic excitations (assuming that other sources of broadening are negligible). The temperature dependence of this peak width as a function of temperature is plotted in panel (b) for the \( x = 0.35 \) sample and increases smoothly upon warming-up. There is no sign of a clear increase in the scattering rate at or around the bulk transition temperature of the \( x = 0.35 \) sample \((T = 135 K)\), which is at odds with the sharp increase in the bulk resistivity at this temperature.

The evolution of the QP spectral weight with temperature is plotted in Fig. 3.6d for the doping levels \( x = 0.30 \), \( 0.35 \) and \( 0.425 \). In all three cases, the QP spectral weight decreases with temperature in an almost linear fashion and in all three cases there is significant spectral weight at \( E_F \) at temperatures as much as 100 K above the bulk metal-to-insulator transition temperature. So, although the ARPES studies reported in Refs. [23] and [26] for \( x = 0.4 \) are in disagreement with this data, over many investigated cleavage surfaces and a broad range of compositions all across the ferromagnetic metallic phase-space, we find that both the evolution of near-\( E_F \) spectral weight and the lifetime of these near-\( E_F \) electronic states do not seem to be influenced by the bulk electronic transition.

A data collection including a broad range of doping levels, also enables one to investigate the evolution of the FS as a function of hole-doping. For La\(_{2-2x}\)Sr\(_{1+2x}\)Mn\(_2\)O\(_7\), an increasing strontium content corresponds to an increasing number of holes in the Mn 3\(d\) manifold. As the Fermi surface area (in two dimensional systems) in general is directly proportional the number of charge carriers, this should be reflected in the Fermi surface areas of the \((\pi, \pi)\)-centered hole-like anti-bonding and bonding band and the \(\Gamma\) centered electron pocket. The highest and lowest doped compositions shown in Fig. 3.5 differ
12.5% in hole doping, thus an equal change in Fermi surface area is expected between $x = 0.30$ and $x = 0.425$. From LDA calculations [18], the $2k_F$-values at $(\pi, 0)$ for the anti-bonding and bonding band are expected to change between these two doping levels from $0.54\pi/a$ and $0.90\pi/a$ to $0.48\pi/a$ and $0.65\pi/a$, respectively.

The right-most panels of Fig. 3.5 show the fitted $k$ positions from the FS maps of the three doping levels overlain on top of each other. Noticeably, the data points for the three samples fall almost exactly on top of each other. This means that their Fermi surface areas are almost the same, despite the significant change in nominal hole concentration. The respective $2k_F$ values at the $(\pi, 0)$-point are $\approx 0.46$ and $\approx 0.36\pi/a$ for the $h\nu = 73$ (bonding band) and $56$ eV (anti-bonding band) data, respectively. Compared to the predictions from LDA, this would correspond to a doping level of $x \approx 0.50$, thus a hole count some 10 to 20% higher than nominal for the doping levels discussed here. Important to note is that a doping level of 50% corresponds to an insulating, anti-ferromagnetically ordered low temperature phase of LSMO, that is not expected to support spectral weight at the Fermi level. Over many measured cleavage surfaces of different doping levels, some scatter (about 10%) has been observed in these respective $2k_F$-values of the anti-bonding and bonding band QP peaks, but no systematic
change in the area of the Fermi surface that scales with the hole doping is evident in our substantial collection of high resolution ARPES data.

We can summarize our investigation of the FS topology and temperature dependence of La\(_{(2-2x)}\)Sr\(_{(1+2x)}\)Mn\(_2\)O\(_7\) as follows: on the fast majority of cleavage surfaces and doping levels within the metallic region of the phase diagram \(^3\) we have been able to detect QP peaks. Whenever QP peaks are observed, they form a closed FS centered around the \((\pi, \pi)\) point of \(k\)-space. Typically, the spectral weight at \(E_F\) decreases linearly with temperature and remains significant at temperatures far in excess of the determined bulk transition temperatures of the measured single crystals. Very little systematic variation is seen as a function of doping in the area of the FS and the FS sheets assigned in the above and other ARPES studies [23–25] to the anti-bonding and bonding band would correspond to a doping level of \(x = 0.50\), as predicted by LDA calculations [18]. Thus, in short, both the temperature and the doping dependence of the QP peaks seemingly do not correspond to the expected behavior for bulk ferromagnetic, metallic, bilayered LSMO.

A possible origin for the discrepancy between the bulk electronic structure of a compound and the electronic structure as probed with photoemission is a difference between the surface and the bulk of a single crystal in terms of electronic structure or doping. Another possibility would of course be that the nature of the metallic state of La\(_{(2-2x)}\)Sr\(_{(1+2x)}\)Mn\(_2\)O\(_7\) is of such an exotic origin, that the expectations based on experience with more conventional metallic substances, or other groups of unconventional metals such as the cuprate high \(T_c\) superconductors, are not a good description of the bilayered manganites. To investigate the differences between the surface and bulk electronic structure of bilayered LSMO and to get a handle on the origin of the anomalous temperature and doping dependence of the low lying electronic states, a detailed hard X-ray photoemission study combined with additional APRES measurements is presented in the following chapter.

\(^3\)An exception are the samples with doping level \(x = 0.40\). On these samples, both from Amsterdam and Oxford, data containing clear QP-peaks has never been obtained, despite a large number of experiments on high quality cleavage surfaces. At present, we cannot explain why samples of this doping level would be an exception to the other compositions.
Phase separation and the true spectral signature of colossal magnetoresistant \( \text{La}_{(2-2x)}\text{Sr}_{(1+2x)}\text{Mn}_2\text{O}_7 \)


Abstract

In the first part of this chapter angle integrated photoemission data taken with hard x-ray radiation on cleaved single crystals of the bilayered, colossal magnetoresistant manganite \( \text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7 \) (LSMO) with \( 0.30 \leq x < 0.50 \) are presented. Making use of the increased bulk-sensitivity upon hard x-ray excitation it is shown that the core level footprint of the electronic structure of the LSMO cleavage surface is identical to that of the bulk. Furthermore, by comparing the core level shift of the different elements as a function of doping level \( x \), it is shown that microscopic phase separation is unlikely to occur for this particular manganite well above or below the Curie temperature.

The second part of this chapter deals with angle resolved photoemission on the same doping series of bilayered LSMO. As phase separation does not occur at high and low temperatures, the discrepancy between the bulk transport behavior and the temperature dependence of the quasiparticle peaked ARPES spectra described in the previous chapter can definitely not be explained with such a scenario. It is shown that the quasi particle peaked signature in APRES experiments does not, in fact, belong to bilayered LSMO, but to local stacking faults in the crystal, which posses a more robust metallic character than the bilayered matrix they reside in. The real spectroscopic signature of bilayered LSMO is that of a psuedo-gapped semi-metal, without a real Fermi surface. This would reconcile the electronic structure as probed with ARPES with bulk probes such as transport and optical conductivity.
4.1 Introduction

As already alluded to in the introduction about colossal magnetoresistance (CMR) (Chapter 2.1.3), early theoretical attempts to explain this phenomenon focused on the double exchange mechanism. Ferromagnetism then facilitates metallicity in a strongly Hund’s rule coupled system, by increasing the hopping parameter of an \( e_g \) electron that is aligned parallel to the \( t_{2g} \) electrons of the neighboring manganese sites, compared to anti-parallel or randomly aligned spins [95]. The double exchange mechanism however, can only account for a change of resistivity of about 30 percent across the ferro-to-paramagnetic transition, while some of the CMR manganites, such as \( \text{La}_{2-1.5x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7 \) (abbreviated forthwith LSMO, with \( x \) being the hole doping, i.e. increasing the \( \text{Mn}^{4+} \) to \( \text{Mn}^{3+} \) ratio), display changes that are almost a factor 100 larger [12, 91].

One of the main contemporary groups of models attempting to explain the CMR effect is based on an electronic phase separation scenario, that focuses on the idea that with hole doping, instead of a continuous change, the density of the \( \text{Mn} \ e_g \) electrons is unstable for certain doping concentrations leading to a spatial separation of charge into patches of higher and lower than nominal hole doping, while the distribution of dopant atoms would be homogeneous in the sample [96]. The propensity toward phase separation is expected to be especially high near the transition from the metallic to insulation phase and near half-doping, where most manganites show anti-ferromagnetic, orbital and charge order due to the charge disproportionation into equal amounts of formally \( \text{Mn}^{4+} \) and \( \text{Mn}^{3+} \) ions.

Much of the experimental support for phase separation comes from studies involving surface sensitive techniques such as scanning tunneling microscopy/spectroscopy (STM/STS) [97–100] or (angle resolved) photoemission [(AR)PES] [25, 101, 102]. As both techniques have direct access to the electronic structure of a material they would be well suited to address the issue of CMR, as the root of this phenomenon clearly lies in the electronic structure of the manganites. Moreover, STM has the advantage to be a spatially resolving technique on the micro- to nanometer scale, and would thus be extremely useful in (dis-)proving a phase separation scenario. Yet, the reported length scales at which the phase separation would be evident range from micro- to nanometers and often the reported phase separation has little correspondence with the magnetic transition temperature. So in many cases the observed phase separation could well be caused by –for instance– sample inhomogeneity or (for thin films, substrate induced) lattice strain, rather than by electronic phase separation.

From the (AR)PES side, in particular focusing on (bilayered) LSMO, some studies carried out in the metallic part of the phase diagram report a pseudo-gapped Fermi surface [22, 28] while others have reported the existence of small quasiparticle-like (QP) peaks at the Fermi level [1, 23–26, 103], followed by a large incoherent spectral weight at higher binding energies. One would expect the temperature dependence of these quasiparticle peaks, which normally are associated with the metallic phase, to track the bulk Curie temperature, but it does so only in a small subset of the available datasets [26]. In other studies the sharp quasiparticle-like feature persists up to temperatures of order two times \( T_C \), thus well into the insulating regime [1, 25]. Furthermore, an x-ray
4.1 Introduction

Figure 4.1: Sample and cleavage surface quality of the LSMO crystals. (a) Magnetization versus temperature for an $x = 0.36$ sample measured using SQUID magnetometry. Data taken after zero field cooling, with an external field $B = 100$ G $\parallel c$. The sample shows a sharp transition from a paramagnetic (PM) to a ferromagnetic (FM) state at $T_C = 130$ K with a total width smaller than 5 K. (b) Magnetic transitions as measured using SQUID magnetometry of LSMO with $x = 0.30$ ($T_N$) and $0.325 \geq x \geq 0.425$ ($T_C$), plotted on top of the magnetic phase diagram, taken from Ref. [89]. Depicted are the onset, midpoint and endpoint temperatures of the transition (triangles, circles and squares). (c) STM topograph ($150 \times 150$ nm$^2$) of an in vacuum cleaved LSMO crystal ($x = 0.35$), taken at $T = 4$ K showing three flat atomic terraces. The white line indicates the trace of the line scan depicted below the topograph. The step heights correspond to half the $c$-axis length of the tetragonal unit cell (11 Å). The terraces themselves are very smooth, with a height corrugation of the order of only 1 Å over tens of nanometers. The STM data is courtesy of F. Massee. (d) LEED image of a typical LSMO sample, $E = 400$ eV showing a very clear tetragonal pattern, without any signs of a structural reconstruction. The inset shows a cleaved crystal on top of a cleavage post, with a smooth and mirror-like surface over millimeters.

resonant magnetic scattering/ STS study on air-cleaved bilayered LSMO single crystals found the first bilayer at the surface of this material to be insulating and magnetically unordered at low temperatures, in contrast to what was found for the bulk [104]. In this light an STM/ STS study on the anti-ferromagnetic $x = 0.30$ compound is also worth mentioning, where the tunneling spectrum of the entire probed surface (over many thousands of measurements) of a sample cleaved in vacuo seemed to be gapped (hence insulating), while bulk- resistivity measurements showed an in-plane metallic characteristic [92].

All in all, the picture arising from the mentioned STM and ARPES studies is rather diffuse, sometimes even inconsistent and often in contrast with the physical properties measured by bulk probes such as resistivity and magnetization versus temperature. An important question is therefore whether the surface electronic structure of bilayered LSMO is indeed identical to the bulk one. The cleavage plane of this compound is generally assumed to be in between two rock-salt layers. The (La,Sr)O surface termination
Figure 4.2: (Hard) x-ray photoemission data on LSMO ($x = 0.30$) at room temperature. 

(a) Overview core level spectrum taken with $h\nu = 2160$ eV, with the main core levels labeled. Auger peaks are indicated with the according Auger process. 

(b) Zooms of representative core levels for all four elements of LSMO: La 3d$_{3/2}$, Mn 2p$_{3/2}$, O 1s and Sr 3d$_{3/2,5/2}$ taken with $h\nu = 2010$ and 6030 eV. Only the O 1s core level peak shows a small surface contribution, either from adsorbed residual gas on the sample surface or from the sample holder, indicated with ‘S’ in the O 1s spectrum. The inset in the La 3d spectrum illustrates schematically the increased bulk sensitivity of the data recorded using 6030 eV radiation compared to $h\nu = 2010$ eV.

In this chapter, we present a doping dependent hard x-ray photoemission study of bilayered LSMO, La$_{2-x}$Sr$_{1.5x}$Mn$_2$O$_7$, with $0.30 \leq x \leq 0.475$. Although several x-ray photoemission studies of (perovskite) LSMO exist in the literature, for example Refs. [105] and [106], the majority has been conducted either on polycrystals or on single crystals cleaved in air or poor vacuum, disqualifying a comparison between surface and bulk electronic properties. This study is conducted on in vacuum cleaved single crystals and carried out using excitation radiation in the hard and soft x-ray regime on a wide range of doping levels across the metallic part of the phase diagram. Making use of the increased bulk sensitivity with higher excitation energies (several nanometers for 6 keV radiation, instead of a typical $\approx 1$ nm for VUV excited ARPES experiments and Al K\(\alpha\) x-ray photoemission studies), owing to the increased mean free path length of escaping photoelectrons with higher kinetic energy, we show that the surface electronic structure of bilayered LSMO is identical to that of the bulk at room temperature and far below the metal-to-insulator transition temperature. Furthermore, evaluating the core level shift...
per element as a function of doping, we show that the chemical potential of bilayered LSMO is not pinned upon approaching half doping, proving that phase separation is not present for these compounds at temperatures well above the transition temperature.

Having shown that the bulk and surface electronic structure of LSMO are identical and that electronic phase separation does not occur on a global length scale at low temperatures, we are still faced with the question what causes the anomalous temperature and doping dependence of the QP peaks. To answer this pressing question, we will proceed with a detailed spatially and angle resolved photoemission study on the cleavage surface of bilayered LSMO as a function of doping and find that the QP peaked signature in APRES is in fact not representing bilayered LSMO, but stacking faults at or near the crystal surface with a higher dimensionality than the bilayered bulk of the
Chapter 4. Phase separation and spectral signature of LSMO

4.2 Hard X-ray core level spectroscopy

Before presenting the results from spectroscopy, we show that the bulk physical properties of the LSMO single crystal used in these studies are in correspondence to what has been reported in the literature for these compounds. The quality of the crystals, the Curie temperature and the sharpness of the metal-to-insulator transition were checked by magnetometry measurements using a superconducting quantum interference device (SQUID) and were corresponding to the phase diagram from literature, see Fig. 4.1a and b. The cleavage surfaces obtained from the in vacuum cleaved single crystals were of excellent quality, as shown by STM measurements and low energy electron diffraction on similarly prepared LSMO crystals, yielding topographs with very clean, flat surfaces and perfectly tetragonal diffraction patterns without any signs of reconstructions whatsoever, see Fig. 4.1c and d.

In Fig. 4.2a an overview spectrum of LSMO taken with $h\nu = 2160$ eV is shown, displaying many identifiable core level lines. Zooms of representative core levels for all four elements taken with $h\nu = 2010$ and 6030 eV are depicted in panel (b) of Fig. 4.2. Comparing the more bulk sensitive 6030 eV with the more surface sensitive 2010 eV data, it is immediately clear that the binding energies are almost identical and that the line shapes exactly match. Only the O 1s spectrum shows a small surface related shoulder at the high binding energy (BE) side of the main line, but it is likely that this feature either comes from a small amount of residual gas adsorbed on the sample surface, or from the sample holder and mount. For all measured crystals and doping levels, the 6030 eV and 2010 eV data were similar to a very high degree, like the data shown in Fig. 4.2b.

In Fig. 4.3a an angle integrated photoemission spectrum taken with an excitation energy of 140 eV, displaying the valence band and several shallow core levels is shown. At these photon energies the escape depth of the excited photoelectrons is minimal and will hardly exceed the first unit cell of bilayered LSMO. Still, the shallow core levels depicted do not show any sign of significant shoulders or a peak form deviating from a simple, single Gaussian-broadened Lorentzian, thus providing more evidence that the surface and bulk electronic structure are indistinguishable.

Figure 4.3b shows the Sr 3d core level spectra ($h\nu = 2010$ eV) for all measured doping levels. Clearly, the core level spectra shift (almost monotonically) toward lower binding energy with increasing hole doping, but their peak form is basically unaltered. The Sr 3d spectra are also representative for the doping dependent behavior displayed by the La and O core levels, all of which shift rigidly toward lower BE without changing peak form as the doping level of the single crystals is increased. This is in contrast with the Mn core levels. Figure 4.3c shows that the Mn core levels remain essentially unshifted with increased doping, but they do change their peak form slightly. The rather broad

\[^1\text{Due to the extreme grazing incidence geometry necessary to better match the inelastic mean-free path length of the photoelectrons and the penetration depth of the hard x-rays, it is unavoidable to also pick up signals from the sample mounting.}\]
Mn 2p$_{3/2}$ peak consists of several components, with a feature at BE $\approx 639$ eV associated with a non-locally screened core hole \[107\] (see blue arrow in Fig. 4.3c) and around 642 eV two distinguishable locally screened features associated with Mn$^{4+}$ (higher BE) and Mn$^{3+}$ (lower BE) \[108\], whose relative intensity alters qualitatively in line with the expected trend for increased hole doping (indicated with yellow arrows in Fig. 4.3c). The measured increase in the Mn 4+ to Mn 3+ ratio also corresponds to the observed trend in Mn valence by x-ray emission \[109\]. The inset to Fig. 4.3c shows the Mn 3d dominated valence band spectra of all doping levels recorded with $h\nu = 2010$ eV. Similar to the Mn 2p core levels, the depicted valence bands do not notably shift over the entire doping series. Also obvious changes in their line shapes do not occur within the noise of the experiment.

### 4.3 Discussion of the HaXPES data

From the characterization of the bilayered LSMO crystals by measurement of their bulk magnetization versus temperature, Fig. 4.1b, it is clear that the magnetic properties of the samples are in line with what is expected from literature for their nominal doping \[89\]. One extra check to ensure that the measured cleavage surfaces are representative for their expected hole doping, is to compare the evolution of the ratio between the La and Sr core level photoemission peaks throughout the doping series, as this quantity should change in a predictable manner. The straight black line in 4.4a shows the stoichiometric La to Sr ratio versus doping, normalized to that of $x = 0.30$. The black symbols are the measured and normalized intensity ratios between the La 4d and Sr 3d core levels. The error in the measured values is mainly due to a variation in the background intensity from sample to sample. Despite this uncertainty, the measured La/Sr ratios agree (within the error bars) with the expected doping dependence, indicating that the measured cleavage surfaces are indeed representative for their nominal doping level.

Now let us look a little bit closer at the surface versus bulk issue as regards the electronic structure of LSMO. As mentioned in the previous section, both photoemission spectra taken with VUV and hard x-ray radiation do not resolve surface related features for the core levels, strongly suggesting the existence of a similar surface and bulk electronic structure for bilayered LSMO. There is, however, a small but detectable shift of binding energy between the data taken with $h\nu = 2010$ eV and 6030 eV. In Fig. 4.4b this shift is plotted for all four elements and for all measured doping levels. The error bars are mainly determined by the binding energy referencing of the $h\nu = 6030$ eV data, which could be executed with an accuracy of about 100 meV. As can be seen from the gray shaded band in panel (b), the majority of the data points fall within the error bars. Taking the averages of the shift for all elements per doping level, only a very weak downward trend with increasing hole doping is visible, with a change of shift that is only 50 meV over the entire doping series. We can therefore safely conclude that also the apparent shift between the $h\nu = 2010$ eV and 6030 eV data is not indicating a systematic, significant difference between the bulk and surface of bilayered LSMO in
Figure 4.4: Doping dependence of the core level data taken with $h\nu = 2010$ eV at room temperature. (a) The relative intensity ratio of the La 4d and Sr 3d core level peaks. The solid line is the expected ratio from the stoichiometry of the nominal compositions. For details on the normalization, see footnote [2]. The error bars for the measured intensity ratio are caused by uncertainty in the background subtraction procedure and in the correction of the decaying beam intensity versus time. (b) Relative shift in binding energy between the core levels measured with $h\nu = 6030$ and 2010 eV. The shift of the 6030 eV data with respect to the 2010 eV data is given for all doping levels and all four elements (a positive shift means one toward lower binding energy). The filled black triangles are the averaged value per doping level over all 4 core levels. The dotted line is a linear fit to these averaged values. The error margin in the determination of the relative shift is indicated with the black box. The individual error bars for the data points in panel (b) have been omitted for clarity.

terms of hole doping level or charge transfer.

In Fig. 4.5 the results for the shift in binding energy per element as a function of doping are summarized. The shifts are plotted relative to the binding energy measured for $x = 0.30$, thereby setting the shift for this doping level to zero. The shift values were determined by cross-correlating the core level spectra of one particular element for the different doping levels with each other, which is justified as the form of the core levels hardly changes with doping. As mentioned (and also shown in Fig. 4.3), all core levels shift toward lower binding energy with increasing doping (a positive shift), except for the Mn peaks, which stay constant in BE. Taking the averages of the La, Sr and O shifts,

\[ \text{The measured intensities of core levels for the different elements are determined not only by their relative stoichiometry, but also by their (photon energy dependent) photoionisation cross-sections. To allow a comparison between the measured La/ Sr ratio and the ratios expected from the nominal doping levels, the measured La 4d to Sr 3d peak area ratio versus doping has been scaled such that the average measured value over all doping levels coincides with the average ratio predicted from stoichiometry over the entire doping range. Thereafter, all data in the plot has been scaled such that the predicted ratio for } x = 0.30 \text{ is set to 1. This way the reported, experimentally determined ratios are independent of the cross-sections for the La 4d and Sr 3d core levels.} \]

\[ \text{It was checked and confirmed that binding energy shifts versus doping, obtained by either a Voigt-peak fitting procedure or a center of gravity determination of the core level spectra, yielded the same result as the cross-correlation procedure.} \]
4.3 Discussion of the HaXPES data

Figure 4.5: Shift in binding energy versus doping with respect to $x = 0.30$ for the La 3d, Sr 3d, Mn 2p and O 1s core levels ($h\nu = 2010$ eV, room temperature). The filled black triangles are the averaged shift per doping level of La 3d, Sr 3d and O 1s. The dotted line is a linear fit to these averaged values. The error bars for all data points are represented by the error bar depicted for the $x = 0.475$ Mn 2p data point: the rest of the error bars have been omitted for clarity. The inset shows the chemical potential shift with respect to $x = 0.30$ for perovskite LSMO (LSMO 113) after Ref. [105] compared to the measured chemical potential shift for bilayered LSMO (LSMO 327, open symbols). Note that in contrast to the bilayered case, doping levels below $x = 0.30$ can be obtained for the perovskite.

A linear trend is evident for bilayered LSMO, as shown by the black dotted line in Fig. 4.5. These results fall exactly in line with the doping dependence of the binding energy for the perovskite analogue $(\text{La,Sr})\text{MnO}_3$ [105], see the inset to Fig. 4.5. As also argued in Ref. [105], in general, the shift of a core level $\Delta E$ can be explained by a number of terms given by the following formula:

$$\Delta E = \Delta \mu + K \Delta Q + \Delta V_M - \Delta E_R,$$

where $\Delta \mu$ is the change in the chemical potential, $K \Delta Q$ the change in the number of valence electrons of the atom under consideration (the chemical shift), $\Delta V_M$ the change in the Madelung potential, and $\Delta E_R$ is the change in the extra-atomic relaxation energy due to polarizability of the atoms and the conduction electrons surrounding the created core hole [66]. A significant contribution of the Madelung potential to the shift in binding energy seen in Fig. 4.5 can be excluded since the O 1s and the Sr 3d and La 4d shift in the same direction and the Madelung term has opposite sign for anions and cations. Moreover, the contribution due to changes in the screening of the core-hole potential by polarizable surrounding ions and conduction electrons ($\Delta E_R$) can be disregarded as the measurements are performed at room temperature, i.e. in the insulating regime, and, additionally, the polarizability is not expected to change with Sr doping, as La$^{3+}$ and Sr$^{2+}$ have a very similar cation radius (and thus polarizability, which is proportional to the size of the atom). As also the number of valence electrons of La, Sr and O are not
expected to change across the doping range, the observed linear trend in the binding energy shift for these three elements reflects the shift of the chemical potential with hole doping. The observation that the Mn core levels show no shift may be due to the fact that with doping the Mn valency does change, whereby this chemical shift counterbalances the shift of the chemical potential. This also holds for the measured valence bands depicted in Fig. 4.3c, which have a considerable Mn 3d partial density of states at the Fermi level, down to $BE \approx 8$ eV [18]. We note that this is in contrast with the Al Kα x-ray study on bilayered LSMO reported in Ref. [110], where a binding energy shift of both the valence band and the Mn 2p core level peaks with doping is observed. Also, in the study on thin perovskite LSMO films (that have been in contact with air) in Ref. [108] the 3+ component of the Mn 2p core level is shown to shift with doping, unlike what we observe here for bilayered LSMO. The results reported here are, however, fully consistent with the findings of Ref. [105], and can be taken as representative for the bulk electronic structure of bilayered LSMO, due to both the use of hard x-rays as the excitation source and high quality, in situ cleaved single crystals.

This result directly gives important insight into the applicability of phase separation scenarios to the bilayered manganites. Several numerical studies [19, 96] have shown that phase separation in manganites in the clean limit would lead to a pinning of the chemical potential as a function of doping. Chemical potential pinning has indeed been shown for the perovskite manganite (Pr,Ca)MnO$_3$, that has a narrow bandwidth compared to LSMO and a larger propensity toward charge and orbital order [102]. From simulations it has been predicted that disorder in the lattice (by for instance cation substitution that leads to significant local changes in the tolerance factor) can lift the pinning of the chemical potential [20]. The chemical disorder in LSMO however is not of the type leading to large variations in the tolerance factor, owing to the similar cationic radius of La$^{3+}$ and Sr$^{2+}$, and LSMO would thus be a good candidate for chemical potential pinning if phase separation were to occur. Although this scenario often discussed in connection with the metal to insulator transition temperature, a similar model has been used to explain the occurrence of metallic like features in ARPES spectra well above room temperature [25]. However, our observed monotonic shift of the chemical potential with doping rules out the existence of electronic phase separation around room temperature. Also the proximity of the charge and orbitally ordered phase at $x = 0.475$ (that is within a few percent of the half doped case, with a Néel temperature above 200 K) does not seem to provoke macroscopic phase separation around room temperature in the LSMO case.

The data presented in Fig. 4.6 show that the conclusions drawn above for room temperature also hold at temperatures well below the metal-to-insulator transition. Panel (a) shows the measured Sr 3d core level spectrum of an $x = 0.325$ sample for $T = 290 \text{ K}$ and 20 K. It is clear that no broadening of the peak occurs upon lowering the temperature, meaning that no additional surface and/or bulk component is formed as the temperature is lowered. This in turn signifies that the surface and bulk electronic structure of bilayered LSMO are identical, also at low temperatures, well in the metallic regime.

In Fig. 4.6b the average core level shift at low temperature is plotted on top of that
4.4 The origin of the QP peaks

4.4.1 Real-space ARPES mapping of the cleavage surfaces

Having shown in the previous section that there is no differentiation between the surface and bulk electronic structure of LSMO, nor that there is evidence for electronic phase separation at low or high temperatures, the origin of the anomalous behavior of the
Figure 4.7: The ARPES signature across a typical cleavage surface of LSMO. (a) Optical image of a cleavage surface (for \( x = 0.375 \)). The red grid lines indicate a 100 × 100 µm mesh. At every grid point inside the thick blue line an ARPES spectrum was collected. The beam spot size was 100 × 30 µm and is indicated in the panel. (b) Typical ARPES \( E(k) \) image (\( T = 20 \) K, \( h\nu = 56 \) eV) collected on the green shaded areas in panel (a), showing sharp peaks at \( E_F \). These parts of the crystal surface are dubbed ‘quasi particle (QP) areas’. The inset to the spectrum shows a schematic of a two dimensional projection of the Brillouin zone of LSMO (after Ref. [18]). The spectrum was collected along the cut in \( k \)-space indicated with a thick blue line (\( k_y = \pi/a \)). (c) A typical ARPES spectrum (\( T = 20 \) K, \( h\nu = 56 \) eV, taken along the same cut in \( k \)-space as the spectrum in panel [b]) collected on the non-shaded areas in panel (a), showing a strongly suppressed spectral weight for the near \( E_F \) electronic states. These parts of the crystal surface are dubbed ‘non QP areas’. (d) \((I,E)\)-curves at \( k_F \) for the spectra in panel (a) and (b), from cuts through the respective \( E(k) \) images, indicated with a red and blue dotted line.

quasiparticle peaks compared to the bulk physical properties is still not clear. In order to determine the origin of this behavior we have conducted a very extensive ARPES study on dozens of cleavage surfaces on single crystals covering essentially the full composition range in the phase diagram for which LSMO possesses a ferromagnetic ground state.

We have noticed, after measuring many high quality single crystals, that not on all cleavage surfaces, and often only after searching across the surface of the cleaved crystals, were we able to detect the QP peaks discussed in the previous chapter. In order to obtain a more qualitative feeling for the abundance of these QP-peaked areas on a typical cleavage surface, a surface-exploration procedure was developed, where the entire crystal surface (of several mm\(^2\)) is meticulously mapped in real space, by taking ARPES spectra at low temperature over a square grid with interval steps of only
4.4 The origin of the QP peaks

Figure 4.8: $k_z$ Mapping of a QP peaked and a non-QP spot (at $T = 20$ K) on the same $x = 0.375$ cleavage surface. (a) Panel (right): a schematic representation of the 3 dimensional Brillouin zone of LSMO. Varying the photon energy corresponds to altering the $k_z$ value of the cut in $k$-space (indicated with a green thick line). Other panels show the fitted $k_F$ loci from a $(\pi, 0)$ cut through the Fermi surface as a function of photon energy (i.e. $k_z$) for both the QP-peaked and non-QP areas. The error bars of the fitted $k_F$ locations are smaller than the symbols used. The position of the smallest observed $k_F$ for the QP-peaked spot is indicated with yellow diamonds in the panel showing data from the non-QP spot. In panel (a) we also show the raw $(I, k)$ curves (intensity in gray scale), stacked for the different $h\nu$’s. (b) Representative $(E, k)$ images for the QP-peaked and non-QP spot. The $(I, k)$ curves at $E_F$ are displayed with red symbols. The respective fitted Lorentzians are displayed as shaded areas in the figure. The blue solid lines represent the total of the fitted Lorentzians. The determined $k_F$ loci are indicated with large colored triangles.

100 µm.$^4$

$^4$From the hard X-ray measurements, it was clear that the cleavage surface of the single crystals is identical to their bulk. However, the HaXPES measurements are conducted in a grazing incidence geometry. As a consequence, the light spot has a footprint of several mm$^2$ on the crystal surface. The HaXPES experiments are thus spatially averaging over the major part of the cleavage surface. Experiments done with VUV radiation at modern synchrotron beam lines, have a much smaller spot size (down to $100 \times 30$ µm$^2$), and would thus be able to pick up local (but macroscopic) differences across a cleavage surface, that would not be detectable in a HaXPES experiment.
An example of such a surface mapping run is shown in Fig. 4.7a. The entire surface within the thick blue line was explored and at each grid point of the red mesh an ARPES spectrum has been taken. One can immediately see that the area with significant QP-peak spectral weight [indicated with green shading in panel (a)] is a minority of the mapped cleavage surface. The majority of the flat, mirror-like parts of the cleavage surface show typical ARPES spectra such as shown in panel (c), with vanishingly small spectral weight at $E_F$. This type of spectral response will forthwith be referred to as ‘non-QP spectrum’. We must note that, with $\approx 10\%$ of the surface area displaying QP peaks, the sample shown in Fig. 4.7a is an exception: the QP-peaked to non-QP surface area ratio is in the order of $1:100$ on a typical LSMO cleave.

The difference between the two types of spectra typically obtained is underlined in Fig. 4.7d, where the $(I, k)$-curves at $k_F$ are depicted for the spectra from panel (b) and (c). The QP-peaked spectra show a sharp peak at $E_F$ (indicated with a star), followed by a broad hump (indicated with an arrow), while this peak is completely absent for the non-QP spectrum and only the high binding energy (BE) hump is observed in the latter case.

As mentioned, the QP-peaked area on the sample depicted in Fig. 4.7a is particularly abundant. Irrespective of the doping level, the typical proportion of the cleavage surface displaying ARPES spectra with peaks close to $E_F$ is only in the order of $1\%$. Also, reduction of the beam spot size, e.g. by introducing beam blockers or closing down exit slits, often increased the QP-peak signal with respect to the high BE hump. This indicates that the actual area producing the QP-peaked signal is smaller than the typical spot size of the ARPES experiments. Thus, although one can almost always find some part of a bilayered LSMO cleave that shows QP peaks, this type of spectral signature is certainly the exception rather than the rule. Having made this important observation, we are left with the following question: which of the two typically obtained spectral signatures is intrinsic to bilayered LSMO and what causes the appearance of the other signal?

In order to answer this pressing question, we first focus on the FS topology of the QP-peaked areas, as these have received much attention in the ARPES literature over the years [1, 23–26]. As discussed in Chapter 1, the hole doping obtained from the measured Fermi surface area in general does not correspond to the nominal hole doping of the crystals under scrutiny, if one takes the ARPES features into account that have been ascribed to the bonding (thought to be resolved with $h\nu = 73$ eV) and the antibonding band (supposedly resolved with $56$ eV) in earlier photoemission studies [1, 24]. However, on undertaking a more detailed ARPES study on the Fermi surface here, an even more remarkable difference between the expected FS for bilayered LSMO [18] and the measured FS on many of the examined QP spots is brought to light.

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5As the non-QP spectra have vanishingly small spectral weight at $E_F$, they do not display a real Fermi crossing. The $k_F$ values of such spectra are determined throughout this chapter by taking an integral over the spectral weight between $E_F$ and $BE = 100$ meV and taking the maxima of the resulting $(I, k)$-curves.

6An exception are the samples with doping level $x = 0.40$. On these samples, both from Amsterdam and Oxford, we have never observed clear QP-peaked spectra, despite many attempts on a large number (> 15) of cleavage surfaces.
By varying the photon energy one is able to pick up electronic states with different \( k_z \) values in an ARPES experiment, thus investigating the dispersion of the band structure in the \( k_z \) direction. This is schematically depicted in the three dimensional Brillouin zone in Fig. 4.8a. The variation in photon energy also affects the matrix elements, causing a change in spectral weight as a function of \( k_z \) between the different bands resolved in an experiment. While the dispersion of the bands should (of course) be periodic in \( k_z \) with the reciprocal c-axis lattice vector, this need not per se hold for the matrix elements.

In Fig. 4.8a, a detailed comparison of the \( k_z \) dependence of the electronic states around \((k_x, k_y) = (\pi, 0)\) for a QP-peaked and non-QP-peaked area on the same cleavage surface of an \( x = 0.375 \) sample is shown. The gray scale plot displays the \((I, k_x)\)-curves at \( E_F \) as a function of \( k_z \). The variation of the matrix elements with photon energy is evident in both cases as a strong, non-periodic change in intensity of the bands. However, \( k_z \) dispersion is notable by its absence, both in the QP peaked and non-QP case, as there is very little variation in the \( 2k_F \) values with photon energy. The band structure of both the non-QP and QP-peaked areas is thus quasi two dimensional, in correspondence with LDA calculations [18].

The surprise lays in the fact that the ARPES spectra obtained from the QP-peaked spot contain three distinguishable \( k_F \) values from hole-like bands centered around the \((\pi, \pi)\) point of \( k \)-space (with \( 2k_F \) values of 0.34, 0.46 and 0.56\( \pi/a \)), instead of two, as one may expect from a bilayered system. Though the intensity of the band with the largest \( 2k_F \) value is weak compared to the inner two bands, it is clearly observed at numerous photon energies (e.g. \( h\nu = 80 \text{ eV} \)). At photon energies of \( h\nu = 56 \text{ eV} \) and 73 eV, those previously associated with the AB and B band, the inner and middle band, respectively, have by far the largest intensity, making the outer band (with the largest \( 2k_F \) value) difficult to observe. But clearly, the number of Fermi surface sheets around \((\pi, \pi)\) is larger than two, questioning whether we are really dealing with a bilayered system, and by consequence, making the assignment of a bonding and anti-bonding band erroneous. In contrast, for the non-QP area only two pairs of \( k_F \) values are distinguishable, with \( 2k_F \) values of 0.44 and 0.60\( \pi/a \). These values correspond much better to the predictions for bilayered LSMO from LDA calculations [18].

Over many measured cleavage surfaces, the observation of deviating \( k_F \) values and a too large number of Fermi surface sheets is very common for the QP peaked spots, although, on a case-by-case basis, there is a rather large variation in the \( 2k_F \) value of the outermost, third band. The fitted \( k \) positions of the measured FS of an \( x = 0.36 \) sample are displayed in Fig. 4.9a. Again three distinct hole barrels around \( X \) are present, but the outer band has now a much larger \( 2k_F = 0.83\pi/a \), and in this case has significant spectral weight at \( h\nu = 73\text{ eV} \). As discussed in the previous chapter, the inner two bands, with \( 2k_F \approx 0.56 \) and 0.34\( \pi/a \), correspond well to the predicted Fermi surface for LSMO with a doping level of \( x = 0.50 \). Taking also the outer band into account, the hole count, inferred from the Fermi surface area, corresponds much better to the nominal doping level of \( x = 0.36 \).

Another interesting observation is presented in Fig. 4.9b. The ARPES spectra, taken at the \((\pi, 0)\) point of \( k \)-space on a small QP-peaked area (\( < 50 \times 50\mu\text{m}^2 \)) of another \( x = 0.36 \) cleavage surface, reveal as many as 4(!) distinct \( k_F \) values associated with \((\pi, \pi)\)
Figure 4.9: Comparison of fitted $k_F$ values between QP peaked and non-QP spectra. 

(a) Fitted $k_F$ values for a QP peaked area of the cleavage surface of an $x = 0.36$ sample. Data taken with $h\nu = 56$ and 73 eV at $T = 20$ K. Note that in this case two distinct pairs of $k_F$ values are present in the 73 eV data (with $2k_F = 0.83$ and 0.56$\pi/a$ spanning the $[\pi, 0]$ point of $k$-space. For $h\nu = 56$ eV, $2k_F = 0.34\pi/a$ at $[\pi, 0]$). The error bars of the fitted $k_F$ locations are smaller than the symbol size. The fitted data is overlain on top of a calculated Fermi surface from Ref. [18] for $x = 0.50$. The insets show the measured $(E, k)$ images for both photon energies at $k_x = -\pi/a$. The gray symbols in panel (a) are mirrored from the measured positions (colored symbols). 

(b) As many as four identifiable pairs of $k_F$ locations (QP peaks) on a different $x = 0.36$ sample. Data taken at $T = 20$ K at $(\pi, 0)$. The $(I, k)$-curves at $E_F$ are displayed in red. 

(c) Fitted $2k_F$ values at $(\pi, 0)$ for non-QP spectra as a function of doping. The $k_F$ values were inferred from a fit with two pairs of Lorentzian peaks on $(I, k)$-curves integrated over $100 < BE < -100$ meV. Error bars are represented by the black tick at $x = 0.46$. The dotted lines are linear trend-lines through the inner (blue) and outer (red) fitted $2k_F$ values. The yellow diamonds are the $2k_F$ values predicted for LSMO by LDA calculations, Ref. [18]. The red and blue shaded areas represent the distribution of most prominently present $2k_F$ values as a function of doping observed on QP peaked areas, recorded with $h\nu = 73$ and 56 eV, respectively.

centered Fermi surfaces. We note that the symmetric intensity distribution of the peaks at positive and negative $k_x$ and the switching of intensity among the different features between the spectra taken with different photon energy make it highly unlikely that the multitude of peaks is caused by simultaneous measurement of several crystallites with different doping level or surface angles with respect to each other. This is thus a genuine observation of four distinct pairs of $k_F$s on a QP peaked surface location of a bilayered LSMO crystal. Panel (c) of the same figure, displays the $k_F$ values at $(\pi, 0)$ obtained from a collection of non-QP areas on single crystal with different doping levels. Though some scatter is present in the data, the general trend in doping corresponds rather well the predicted $k_F$ values from band structure calculations.

Furthermore, another discrepancy between the QP-peaked FS and the predicted band structure for bilayered LSMO is a feature visible in all four FS maps displayed in Fig. 4.5. Indicated with a large arrow in top-left FS map in that figure, is a small circular
4.4 The origin of the QP peaks

Figure 4.10: The QP-peaked areas of a cleavage surface show a $\sqrt{2} \times \sqrt{2}$ reconstruction. $(E,k)$ image obtained from an $x = 0.375$ sample ($h\nu = 56$ eV, $T = 20$ K) showing a copy (indicated with open triangles) of the main band (indicated with a closed triangle). The $(E,k)$ image was recorded along the $(0,0) - (\pi,\pi)$ direction in $k$-space, as indicated with a thick purple line in the small FS map (top right). The inset to the $(E,k)$ image shows a second derivative of a similar spectrum for $x = 0.30$, with in red the fitted peaks of the $(I,k)$- curves for the main band and one branch of the diffraction copy. The bottom right schematic FS illustrates how folding of the bands due to the presence of a $\sqrt{2} \times \sqrt{2}$ reconstructed (smaller) Brillouin zone can lead to the observed band with its band bottom at $(\pi,\pi)$.

pocket, which is electron-like around $X$ (and is thus markedly different from the ‘extra’ band structure features discussed up to now, that were all hole-like around the $X$ point). The dispersion of the additional electron pocket can be seen in the $(E,k)$-image cutting through $k$-space along the $(\pi,\pi) - (-\pi,-\pi)$ direction depicted in Fig. 4.10. The most intense feature in the spectrum is the main band, either the $d_{z^2-r^2}$ or the anti-bonding or bonding $d_{x^2-y^2}$ band that has its band bottom below $BE = 1$ eV at $\Gamma$. Two other Fermi crossings, forming the extra electron pocket, can be seen in the image (indicated with open triangles).

Taking a second derivative of the spectrum (in $k$) enhances the contrast between the main band and these features. Such a second derivative spectrum is depicted in the inset to the large $(E,k)$-image. The fitted band dispersions are plotted on top of the derivative spectrum and show that the extra features mirror the main band dispersion perfectly. Such a copy of the main band(s) can only occur if these are folded back around a smaller Brillouin zone boundary, resulting from a larger periodicity in real space than the tetragonal unit cell. From the observed dispersion of the diffraction copies, we deduce that the reconstruction of the tetragonal unit cell is most likely of $\sqrt{2} \times \sqrt{2}$ origin and the diffraction copy is that of the $d_{z^2-r^2}$ hole pocket around $\Gamma$, as illustrated in the bottom right inset to Fig. 4.10. 

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Footnote: Although not all the main bands appear to have diffraction copies in Fig. 4.5 and Fig. 4.10, it
From the above observation, it follows that QP-peaked spots of an LSMO cleavage surface do not possess a $1 \times 1$ tetragonal unit cell. This is in sharp contrast with the bulk crystal structure of bilayered LSMO in the ferromagnetic metallic low temperature phase, which is strictly tetragonal. In addition, a surface sensitive diffraction technique such as LEED (that is however spatially averaging over $\approx 1\text{mm}^2$) yields a strictly $1 \times 1$ tetragonal diffraction pattern with a unit cell of 3.8 Å. Interestingly, no diffraction copies are observed on the non-QP peaked areas of a cleavage surface. Thus, observations of the $\sqrt{2} \times \sqrt{2}$ reconstructed crystal structure are confined to the QP-peaked spots only.

At this stage we can summarize our investigation of the FS topology of the bilayered LSMO by listing the experimental observations described up to now in this and the previous chapter:

i. The fast majority of a typical cleavage surface of bilayered LSMO in the low temperature metallic phase yields photoemission spectra with vanishingly small spectral weight at $E_F$. The estimated $k_F$ values from these spectra seem to correspond well to the predicted band structure from LDA calculations and show an evolution with nominal doping level, tracking the expected number of charge carriers.

ii. Only a very small fraction of a typical cleavage surface of bilayered LSMO (mostly smaller than a few percent) has a signature in $(E,k)$ space displaying intense, sharp peaks at $E_F$, although the majority of the ARPES literature on bilayered LSMO discusses the physical properties of these QP-peaks.

iii. The temperature dependence of the QP-peaked areas does not track the bulk transport properties of bilayered LSMO. Even 100 K above the bulk Curie and metal-to-insulator transition temperature, the APRES spectra obtained from these spots have significant spectral weight at $E_F$, unlike what is expected (and indeed generally measured) for ARPES from insulating materials.

iv. The Fermi surface area obtained from the QP-peaked regions either does not correspond to the expected nominal doping, and/or instead of bilayer splitting, ‘tri-’ or even ‘quadruple’ layer splitting is observed, unlike what is expected for a bilayered compound. The number of observed bands and their $2k_F$ values differ from QP-peaked to QP-peaked spot (even within the cleavage surface of one single crystal, in case multiple QP peaked areas are present).

v. The QP-peaked spots show diffraction replicas of (some of) the main bands corresponding to a $\sqrt{2} \times \sqrt{2}$ reconstruction of the tetragonal unit cell. Such reconstructions are not observed for the bulk of metallic, bilayered LSMO crystals, nor do they form an intrinsic property of the cleavage surface, as is a well known fact that in an ARPES experiment the back-folded bands can have strongly varying intensity at different $k$ values. Their observability may also strongly depend on measurement geometry and photon energy.
they do not turn up in LEED diffraction experiments and the majority non-QP surface.

The results presented above strongly point towards a scenario in which the minority area of an LSMO cleavage surface, giving sharply peaked spectroscopic features, is in fact not representative for bilayered LSMO with the nominal doping levels discussed here. This would in turn mean that the intrinsic low temperature \((E, k)\) space signature of bilayered LSMO as probed by ARPES is that of a pseudo-gapped ‘bad metal’ with vanishingly small spectral weight at \(E_F\). Below we will discuss the physical implications of this conclusion, and we will give an explanation for the observation of the QP-peaked spots.

### 4.4.2 Quasiparticle peaks: the signature of stacking faults

Having gathered evidence that the QP-peaked ARPES signature does not correspond to the electronic structure of bilayered LSMO, the question remains: what is the origin of the QP-peaks? First we look into the possibility that the QP peaked areas do represent bilayered LSMO, but with a very different doping level from the nominal one. It is not inconceivable that, due to instabilities in the growth of the single crystalline ingot, the La/ Sr ratio may fluctuate and some parts of the sample are left with a different doping level. This scenario is not very likely though, as the magnetic phase diagram of LSMO, outside the ferromagnetic region, is dominated by anti-ferromagnetic insulating compounds. An anti-ferromagnetic metallic line phase has been observed around a narrow doping region near \(x = 0.60\) [103, 111, 112], however at temperatures around 160 K orbital ordering sets in, and these compositions become insulating as well. Thus, it is unlikely that this scenario leads to the observation of QP-peaks at all, or at least at temperatures far in excess of 150 K. Also, the observed ‘trilayer splitting’ can of course not be explained this way.

In Fig. 4.11, two shallow core level spectra are depicted, one obtained from a QP-peaked spot and one from the non-QP area on the same \(x = 0.425\) cleavage surface. By measuring the shallow core levels with a photon energy of \(h\nu = 140\) eV, one can make use of the very small beam spot size available in a VUV-PES experiment (thus enabling one to discriminate between the small QP-peaked spots and the majority non-QP surface). From the two spectra it is immediately clear that the Mn, Sr, and La shallow core levels are almost identical, both in intensity and \(BE\) position. However, looking more closely at the valence band region recorded on the two spots (the inset to Fig. 4.11), obvious changes can be seen up to a \(BE \approx 6\) eV. This means that the QP-peaked and non-QP areas, though quite similar in chemical composition, are rather different in coordination chemistry or crystal structure.

To put all the pieces of the puzzle together and thus arrive at a fitting explanation for our observations, we now take a step back, and take a closer look at the physical properties of the LSMO Ruddleston-Popper family as a whole, displayed in Fig.4.12. From the figure it is clear that with an increasing number of stacked MnO planes \((N)\) in between a double rock-salt layer, the metallic phase space of the manganite increases, as the ferromagnetic ordering becomes more robust with respect to both temperature
and doping variation and the propensity towards (static) charge and orbital ordering decreases. While the single layer analog displays no metallic phase whatsoever, the bilayered compound is reported to show metallic-like behavior in the narrow doping range between \(0.30 < x < 0.45\). The \((a,b)\)-plane resistivity of the latter however is (just) above the Mott minimum conductivity limit of \(10^{-3} \ \Omega \text{cm}\) \([113, 114]\) and can therefore not be assigned as a proper metal, for which the mean free path length of the quasi particles is longer than the interatomic spacing \(a\) \([115]\). Of the three members of the LSMO family displayed in Fig. 4.12, only the perovskite \((N = \infty)\) shows real metallic behavior.\(^8\)

The metallic behavior in the manganites seems to be strongly coupled to the lattice degrees of freedom. Bilayered LSMO, a particularly bad metal, has, on average, severely elongated apical Mn-O bonds at the outer side of the bilayer at low temperature, while the more metallic perovskite analog has more regular MnO octahedra. In the latter case however, electron delocalization can also be prevented by a sufficiently large Jahn-Teller distortion \([116]\). Stacking a larger number of MnO octahedra in between the double rock-salt layer apparently allows the octahedra to relax and obtain a more regular shape, thus enhancing metallic behavior.

It is well known that almost every, if not all, single crystals of bilayered LSMO (or other manganites) have a small volume fraction of stacking faults included in the bilayered matrix \([119–123]\). These inclusions are evident from muon scattering experiments \([123]\), but are also visible in the magnetization versus temperature of bilayered manganites, as small steps at temperatures far above the bulk transition temperature \([120, 121]\). In Fig. 4.7a a transmission electron micrograph of such a stacking fault with \(N = 5\) inside the bilayered matrix (with \(N = 2\)) is displayed, taken from Ref. \([120]\). Panel (b) of the same figure shows a typical magnetization curve of an \(x = 0.30\) sample with several

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\*Data in the literature on other members of the Ruddleson-Popper series, e.g. \(N = 3, 4, \ldots\) is very scarce, probably largely in part due to the difficulty of controlling the single crystal growth process and maintaining a regular stacking order for the higher-end members.\*
4.4 The origin of the QP peaks

Figure 4.12: Magnetic and transport properties of the LSMO Ruddleston-Popper series. (a) Magnetic phase diagram of \((\text{La,} \text{Sr})_{(N+1)}\text{Mn}_N\text{O}_{(3N+1)}\) as a function of Sr doping for the perovskite \(N = \infty\) (left, after Ref. [4]), the bi-layered \(N = 2\) (middle, after Ref. [89, 111]) and single layered \(N = 1\) (right, after Ref. [117]) analogues. (b) Resistivity as function of temperature for various metallic compositions of perovskite LSMO (from Ref. [118]). (c) Resistivity as function of temperature for bi-layered LSMO with \(x = 0.4\) (from Ref. [10]).

High temperature transitions belonging to such inclusions. As these stacking faults have a higher dimensionality than bilayered LSMO, they are much more robustly metallic in character, and hence they have a higher Curie temperature (or vice versa) than the bilayered matrix they reside in. This is in keeping with the strong dimension dependence of the degree of apparent metallic character seen in the three phase diagrams displayed in Fig. 4.11 for \(N = 1, N = 2\) and \(N = \infty\).

The volume fraction of these inclusions is small, but noticeable: around 1 volume percent [119–123], the same average proportion of the surface area typically showing a QP peaked spectral signature. Upon cleaving a bilayered LSMO single crystal, it will be inevitable that the cleavage surface at certain spots is formed by such an \(N = 3, 5, 7\ldots\) stacking fault rather than a bilayered MnO block. This in turn means the APRES signal obtained from a small part of the sample surface will belong to these stacking faults. As a consequence, it is our conviction that the QP-peaked areas of a bilayered LSMO cleavage surface are in fact formed by these inclusions, as sketched in Fig. 4.7c. Most of the anomalous behavior of the QP peaks can naturally be explained within this scenario:

i. The volume fraction of the stacking faults as determined from magnetization measurements [120, 121] matches the typical surface abundance of the QP peaked spots.

ii. The elevated Curie temperature (and concurrent enhanced metallic character) of the stacking faults compared to the bilayered matrix corresponds very
well with the observation that significant QP spectral weight remains at \( E_F \) at temperatures in excess of 100 K above the bulk \( T_C \) of the bilayered system. The Drude weight of cubic LSMO \( (N = \infty) \) in optical conductivity studies decreases linearly with temperature [124]. Taking this behavior as generic for the higher-end members of the Ruddledson-Popper series, this corresponds well to the linear decrease in QP spectral weight with temperate evident from our ARPES data.

iii. The multitude of hole-like FS sheets observed around the \((\pi, \pi)\) point in \( k \)-space in our ARPES experiments can be explained by the increased stacking number, \( N \). Rather than a bilayer splitting, these inclusions will very likely have a larger degree of band-splittings, either due to the hybridization of a larger number of MnO planes in the \( c \)-axis direction, or due to a doping imbalance between eg. the outer and central planes \( (N = 3 \text{ or } 4) \), or also in planes sandwiched between those \( (N = 5 \text{ or higher}) \).

iv. The overall scatter in \( k_F \) values and the varying number of observed hole bands around \((\pi, \pi)\) from the QP-peaked spots can naturally be ascribed to the freedom in the number of additionally stacked MnO planes and an uncertainty in how the La/Sr/Mn ratio or hole doping is affected by these stacking errors.

v. Small area electron diffraction experiments in transmission electron microscopy studies on bilayered LSMO with \( x = 0.40 \) have shown that these inclusions have a \( \sqrt{2} \times \sqrt{2} \) reconstructed unit cell, with respect to the tetragonal structure of the bilayered matrix [119]. This would be exactly the type of reconstruction that is needed to explain the observed diffraction copies in our photoemission data (see Fig. 4.10).

An alternative explanation for the origin of the QP-peaked areas could be the existence of oxygen vacancies. This would affect the hole-doping level (although oxygen vacancies correspond to electron doping, while we observe a too large number of holes) and possibly cause tilting of the MnO octahedra in the bilayers, thus giving rise to a \( \sqrt{2} \times \sqrt{2} \) reconstructed unit cell. Still, the anomalous temperature dependence and the observation of tri-layer splitting cannot be explained this way. Another possibility would be the existence of local strain fields due to small imperfections or inclusions in the crystal lattice. Thin films of \( \text{La}_{(2-2x)}\text{Sr}_{(1+2x)}\text{Mn}_2\text{O}_7 \) can be heavily strained due to the substrate and have been metallic up to temperatures of 250 K [125]. Like oxygen non-stoichiometry, strain effects can possibly cause tilting of the octahedra and thus lead to a reconstructed lattice. Optical measurements on such films have however shown the presence of pseudo-gap [125], which is thus not in correspondence with the observation of sharp QP-peaks in our photoemission data from the QP-peaked areas of the sample surface.

Taking all of the above together, it is highly likely that the quasiparticle peaks observed in our angle resolved photoemission experiments on \( \text{La}_{(2-2x)}\text{Sr}_{(1+2x)}\text{Mn}_2\text{O}_7 \) with \( 0.30 < x < 0.50 \) are in fact not representing the intrinsic electronic structure of this
compound, but belong to stacking faults with an increased \( \text{MnO}_2 \) plane stacking number \( N \). This in turn leads to the conclusion that the intrinsic \((E,k)\) space signature of bilayered LSMO is that of a pseudogapped ‘bad metal’ with vanishingly small spectral weight at \( E_F \): a material lacking a true Fermi surface populated by quasiparticles. In short: bilayered LSMO is not a metal.

## 4.5 Bilayered LSMO: a psuedo-gapped bad metal

Over time, several photoemission studies in the literature have reported a psuedo-gapped \( k \)-space signature with vanishing spectral weight at \( E_F \) for \( \text{La}_{(2-2x)}\text{Sr}_{(1+2x)}\text{Mn}_2\text{O}_7 \)[22, 27, 28]. In the previous sections we have shown that this most probably the true spectroscopic signature of bilayered LSMO: the absence of quasi particle peaks is a consequence of the mechanism behind the charge transport of this compound, and has nothing to do with extrinsic properties such as differences between the surface and bulk electronic structure. Bulk sensitive probes, such as optical conductivity, have reported the strongly incoherent nature of the charge carriers for bilayered LSMO. An important conclusion of those studies [126, 127] was that the \( c \)-axis transport of bilayered LSMO is insulating over the entire regime, also in the low temperature ferromagnetic phase. Additionally, the in-plane Drude weight, even at very low temperatures, is extremely small or even absent [11]. The effective mass of the charge carriers is ten times heavier than the free electron one and the transport characteristics of LSMO are consistent with small polarons, even at low temperatures in the ferromagnetic phase. These observations would be hard to reconcile with a Fermi surface displaying sharp and well defined QP peak features in an ARPES experiment.

Comparing, within this picture, the ARPES data of LSMO presented in this chapter with data from another polaronic system, \( \text{Ca}_2\text{CuO}_2\text{Cl}_2 \) (CCOC), it is evident that the data of both compounds are highly similar [94, 128]. With the maximum of the incoherent hump of LSMO at a binding energy of \( BE \approx 450 \) meV and a characteristic phonon frequency of \( \approx 50 \) meV, the average number of phonons dressing the polaron \( \hat{n} = 9 \), which is a value comparable to that for CCOC [128] and well into the small polaron limit, where the QP spectral weight is expected to become vanishingly small and the signature of ARPES spectra is expected to be that of an insulator.

In this respect it is interesting to take another look at STM/STS measurements on bilayered LSMO. The study by Rønnow et al. reported in Ref. [92] and mentioned earlier, found tunneling behavior displaying a gap at all temperatures for LSMO samples with doping level \( x = 0.30 \). The temperature dependence of this charge gap indicated an activated transport behavior. This behavior was ascribed to the insulating nature of the \( c \)-axis transport (as the tunneling from tip to sample or vice versa happens along the \( c \)-axis), mainly due to the anti-ferromagnetic ordering of the bilayers in this direction. We find a similar STS signature for LSMO in the ferromagnetic part of the phase diagram, see Fig. 4.13, displaying gapped spectra down to temperatures of 4 K. Looking at another highly anisotropic material with in-plane metallic character but insulating \( c \)-axis transport properties, normal-state, over-doped \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \), it is striking that the tunneling characteristics are non-gapped for break junction tunneling [129] and scanning
Figure 4.13: QP-peaked spots of a cleavage surface are formed by surface inclusions with an MnO octahedra stacking number $N > 2$. (a) Transmission electron microscopy image taken from Ref. [120] of an $x = 0.30$ bi-layered LSMO crystal having an $N = 5$ inclusion (indicated with the vertical thick red bar). (b) Magnetization as function of temperature for bi-layered LSMO with $x = 0.3$ ($H = 100$ Oe and $H \parallel c$). The inset shows a zoom of the temperature interval between $T = 260 - 320$ K (after Ref. [120]). (c) Schematic representation of such an inclusion (with $N = 5$) at the cleavage surface of a bi-layered ($N = 2$) crystal. The true spectroscopic signature in an ARPES experiment of the $N > 2$ stacking faults that happen to be just beneath the termination surface give rise to the QP-peaked spectra. (d) Scanning tunneling spectroscopy data on an $x = 0.36$ sample. The main panel shows a typical $dI/dV$ curve, as obtained from numerous spots of the same cleavage surface of a sample. The insets show the measured $I/V$ curve (left) and a typical STM topograph (right). The STM data is courtesy of Freek Massee.

tunneling spectroscopy experiments [130], despite having a c-axis resistivity of the same order of magnitude as bilayered LSMO [131].

In general the tunneling matrix elements are rather poorly understood in an STS experiment and the relative contribution of the different parts of $k$-space to the total tunneling signal is not clear, thus one should be cautious with linking tunneling spectral weight directly to the spectral weight observed in an ARPES experiment. Yet, both by tunneling spectroscopy and photoemission we find a vanishingly small spectral weight at $E_F$ for LSMO, which is fully consistent with the findings from optical spectroscopy [11, 126, 127].

To conclude, by taking the fully soft-gapped, ghost-like Fermi surface as the true spectral signature of bilayered LSMO, we reunify the findings from APRES with those from other important bulk and surface electronic probes. We thus argue that the trans-
4.6 Outlook

The almost inevitable presence of inclusions in the bulk of bilayered LSMO crystals and thus also in the sub-surface region after cleavage may seem to complicate experimental work on these systems considerably, but at the same time they might present a unique opportunity to investigate interesting physical phenomena, such as the influence of dimensionality on the metallic behavior and the ARPES signature of a compound. If one could devise a way to characterize the local stacking faults \textit{in situ} in terms of doping and stacking number, than this would be a unique chance to study some of the higher-end members of the Rutherford-Popper series, as single crystals of these compounds are generally unavailable and thin films are difficult to grow and suffer from strain effects and oxygen vacancies. Moreover, these inclusions might be the only way to investigate cubic-like manganites in a controlled fashion using surface sensitive techniques. Perovskite manganites lack a natural cleavage plane and thus, upon cleaving, one is left with a very rough surface, displaying either severe structural reconstructions or electronic charge transfer to avoid a polar catastrophe. To date, no ARPES data from these compounds has appeared in the literature displaying sharp, well identifiable features. Thin films of these compounds are available, but in general suffer from oxygen vacancies and show transition temperatures and transport behavior that do not correspond to the bulk properties of (La,Sr)MnO$_3$. A problem more specific to ARPES is that the significant $k_z$ dispersion of the band structure of cubic manganites leads to additional broadening of the spectra, an issue which might be circumvented in the case of cubic samples with a very small crystal size in the c-axis, as $k_z$ is no longer a proper quantum number in that case. Recent developments in photoemission electron microscopy and low-energy electron microscopy (PEEM-LEEM), enabling one to obtain a real space microscopic image of a sample surface and perform ARPES from a very local spot almost simultaneously, might make such a directed study of these stacking faults feasible in the near future.
5

Core level and valence band spectroscopy of iron pnictides


Abstract

Photoemission data taken with hard X-ray radiation on cleaved single crystals of the barium parent compound of the \(M\text{Fe}_2\text{As}_2\) pnictide high temperature superconductor family are presented. Making use of the increased bulk-sensitivity upon hard X-ray excitation, and comparing the results to data taken at conventional VUV photoemission excitation energies, it is shown that the \(\text{BaFe}_2\text{As}_2\) cleavage surface provides an electrostatic environment that is slightly different to the bulk, most likely in the form of a modified Madelung potential. However, as the data argue against a different surface doping level, and the surface-related features in the spectra are by no means as dominating as seen in systems such as \(\text{YBa}_2\text{Cu}_3\text{O}_x\), we can conclude that the itinerant, near-\(E_F\) electronic states are almost unaffected by the existence of the cleavage surface. Furthermore, exploiting the strong changes in photoionisation cross section between the Fe and As states across the wide photon energy range employed, it is shown that the degree of energetic overlap between the iron 3d and arsenic 4p valence bands is particularly small at the Fermi level, which can only mean a very low degree of hybridization between the Fe 3d and As 4p states near and at \(E_F\). Consequently, this means that the itinerancy of the charge carriers in this group of materials involves mainly the Fe 3d - Fe 3d overlap integrals with at best a minor role for the Fe 3d - As 4p hopping parameters, and that the states which support superconductivity upon doping are essentially of Fe 3d character.
5.1 Introduction

The recent discovery of an entirely new class of high \( T_c \) superconductors based on (quasi) two-dimensional FeAs-layers, rather than on CuO-layers \([32, 132]\), has caused significant excitement in the field of condensed matter physics. The discovery of a new family of superconductors with high transition temperatures, large critical fields and more isotropic properties than the cuprates also gives a window of opportunity in terms of future applications. Moreover, many hope that these iron pnictides can help us to gain more insight into the mechanisms that lead to unconventional superconductivity in general, or may even help unravel a now twenty year old mystery: what makes the high \( T_c \) cuprates superconduct? From the beginning of the cuprate era, surface sensitive probes such as (angle resolved) photoemission (AR)PES, and scanning tunneling spectroscopy (STS), have played an important role in determining the electronic structure of the high \( T_c \) superconductors \([30, 133]\). Crucial pieces of the high \( T_c \) puzzle have been supplied by these experimental techniques, for instance insight into the superconducting order parameter and coupling to identifiable bosonic modes \([30]\). In this light, it will be no surprise that also the iron pnictides are already being studied intensively using the aforementioned techniques \([58, 59, 134–138]\).

One important point to keep in mind, however, is that the surface electronic structure of a material can differ from the bulk electronic structure, in which case detailed knowledge regarding the origin and nature of these differences is required in order to fully exploit the strong points of techniques such as ARPES and STS to investigate bulk superconductivity.

The pnictides are quasi two-dimensional materials, like the cuprates, where one can assign a formal charge to each layer of the crystal structure. As the crystal symmetry at the surface is broken, one can be left with a polar surface and the possibility of having a diverging electrical field at the cleavage plane. To avoid this ‘polarization catastrophe’, the surface of a material can be reconstructed, both structurally and/or electronically. An interesting example of the latter is thought to occur at the interface of perovskite heterostructures, such as LaAlO\(_3\) / SrTiO\(_3\). Such heterointerfaces are conducting \([139]\), although both oxides have a band gap of several electron volts. The diverging electrical field is quenched in LaAlO\(_3\) / SrTiO\(_3\) by means of a partial charge transfer, giving the interface layer half the charge and opposite sign with respect to the charge of the layer below.

In order to compare the surface and bulk properties of a material one would want to be able to tune the probing depth of the experiment. In a photoemission experiment the escape depth of the photoelectrons is sensitive to their kinetic energy, i.e. the excitation energy of the photons. Conventional (AR)PES experiments are performed with photon energies typically between 20 and 100 eV \([\text{in the (V)UV range}]\), coinciding with a minimum in the electron escape depth and thus probing only the first few Ångstroms below the surface. By choosing higher excitation energies in the hard X-ray regime \((h\nu\text{'s of several keV})\), the probing depth is increased to nanometers or even tens of nanometers.

In this chapter, we present results from a photoemission study of the undoped parent compound of one of the main pnictide high \( T_c \) superconductor families, BaFe\(_2\)As\(_2\).
Figure 5.1: Hard X-ray photoemission data from Ba122. All data taken at room temperature. (a) Overview spectrum taken with $h\nu = 3000$ eV. The inset shows a scanning tunneling microscopy topograph (150 × 150 Å$^2$) from room temperature cleaved Ba122, displaying a clear surface reconstruction that lacks long range order, taken from Ref. [140]. (b) Zoom of the near valence band region displaying the Ba5p (green shaded) and As4s core levels (red shaded) and an approximate inelastic background in blue. Representative core level spectra ($h\nu = 2010$ eV) for all three elements are shown in (c). Displayed are spectra taken in a normal emission geometry (black) and 35° off normal (red), the latter decreasing the bulk sensitivity, as the mean free path length of the electron is determined by the photon energy and the escape depth thus by the emission angle (illustrated schematically in the inset of the right-most panel). The Fe 2p$_{3/2}$ peak is fitted with a single Doniac-Sunjic line shape, displayed in green. The inset to the Fe 2p$_{3/2}$ core level spectrum shows a broadened and background corrected version of this spectrum including the Fe 2p$_{1/2}$ line (blue) together with Fe2p core lines from metallic Fe(111) taken from Ref. [141] in green. Note the excellent resemblance. For the Ba 3d$_{3/2}$ line shown in the right-most panel of (c), the difference between normal and off-normal emission is highlighted in green.
(abbreviated forthwith as Ba122), presenting core level and \( k \)-integrated valence band spectra for this composition. Ba122 has been reported to become superconducting by both hole doping (substituting K for Ba) and electron doping (substituting Co for Fe), with a maximum \( T_C \) of 40 K and 22 K, respectively [33, 34].

Reports in the literature have pointed out that the cleavage plane of single crystalline Ba122 is most likely to be the Ba block-layer [137, 140]. As this compound consists of FeAs layers separated by a single Ba layer, this means that (in order to obtain a symmetric cleave and maintain charge neutrality) the top barium layer on the surface termination after the cleave should contain half the number of atoms compared to the bulk Ba layers. The surface of Ba122 is thus expected to differ from the bulk, structurally. This has been shown to be the case by several groups doing scanning tunneling microscopy, where a clear reconstruction of the tetragonal unit cell is visible [59, 137, 140]. The nature of the reconstruction has been reported to be 2x1 [59], or with larger period [140], but upon cleavage at room temperatures it lacks sufficient long range order to be observed using low energy electron diffraction [140]. An example of such a disordered, reconstructed Ba122 surface is shown in the inset of Fig. 5.1a. The question is, of course: what will be the effect of these specifically surface-related phenomena on the electronic structure of the surface and near surface region?

By comparing photoemission measurements carried out using hard X-ray radiation and data taken at conventional excitation energies, we find that the former give information mainly about the bulk electronic structure of Ba122, while the latter data show signs of an additional surface electronic structure component, representing a minor alteration of the electronic environment at the termination surface compared to the bulk. We can therefore conclude that the surface of this parent compound of the pnictide 122 high \( T_c \) superconductors is electronically reconstructed with respect to the bulk electronic structure, but that the deviation from the bulk situation is modest. The implications of this altered surface structure are expected to be small for the near-E\( _F \) electronic states.

Having clarified this point, we are able to use data recorded with widely differing photon energies to show that the majority of the As 4p and Fe 3d states that make up the valence band (VB) of Ba122, possess relatively little overlap in energy. This means that the degree of hybridization between iron 3d and arsenic 4p orbitals is quite small for this compound compared to the Cu-O hybridization in the high \( T_c \) superconducting cuprates. Importantly, the near-E\( _F \) states are almost exclusively Fe 3d, thus the hopping of the itinerant charge carriers in this parent compound of the pnictide high temperature superconductors involves mainly the Fe 3d- Fe 3d overlap integrals.

## 5.2 Hard X-ray data on BaFe\(_2\)As\(_2\)

In Fig. 5.1a an overview spectrum of Ba122 taken with \( h\nu = 3 \) keV is shown, displaying many core level lines. The small O 1s, C 1s and Ag 3d signals come from surface contamination of the sample holder and the silver loaded epoxy that was used to attach the Ba122 crystal to the sample holder \(^1\). The binding energies of identifiable core levels

\(^1\)Due to the extreme grazing incidence geometry necessary to better match the inelastic mean-free path length of the photoelectrons and the penetration depth of the hard X-rays, it is unavoidable to
Table 5.1: Binding energies (BE) in eV of the measured core levels of Ba122, \(h\nu = 3000\) eV, \(T = \) room temperature. The Fermi level was determined from the Fermi cut-off of piece of gold foil. The accuracy of the binding energy determination is \(\pm 100\) meV. The Fe 3s line coincides with the Ba 4d lines and could thus not be resolved. The Fe 3p spin-orbit splitting could also not be resolved.

<table>
<thead>
<tr>
<th>Core level</th>
<th>BE (eV)</th>
<th>Core level</th>
<th>BE (eV)</th>
<th>Core level</th>
<th>BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As 2(\text{p}_{1/2})</td>
<td>1358.1</td>
<td>Fe 2(\text{p}_{3/2})</td>
<td>706.5</td>
<td>Ba 4(\text{d}_{5/2})</td>
<td>89.5</td>
</tr>
<tr>
<td>As 2(\text{p}_{3/2})</td>
<td>1322.4</td>
<td>Ba 4s</td>
<td>252.9</td>
<td>Fe 3(\text{p}_{1/2,3/2})</td>
<td>52.7</td>
</tr>
<tr>
<td>Ba 3s</td>
<td>1292.8</td>
<td>As 3s</td>
<td>204.2</td>
<td>As 3(\text{d}_{3/2})</td>
<td>41.4</td>
</tr>
<tr>
<td>Ba 3(\text{p}_{1/2})</td>
<td>1136.0</td>
<td>Ba 4(\text{p}_{1/2})</td>
<td>192.2</td>
<td>As 3(\text{d}_{5/2})</td>
<td>40.7</td>
</tr>
<tr>
<td>Ba 3(\text{p}_{3/2})</td>
<td>1062.1</td>
<td>Ba 4(\text{p}_{3/2})</td>
<td>178.1</td>
<td>Ba 5s</td>
<td>29.6</td>
</tr>
<tr>
<td>Fe 2s</td>
<td>844.9</td>
<td>As 3(\text{p}_{1/2})</td>
<td>145.0</td>
<td>Ba 5(\text{p}_{1/2})</td>
<td>16.3</td>
</tr>
<tr>
<td>Ba 3(\text{d}_{3/2})</td>
<td>795.1</td>
<td>As 3(\text{p}_{3/2})</td>
<td>140.1</td>
<td>Ba 5(\text{p}_{3/2})</td>
<td>14.4</td>
</tr>
<tr>
<td>Ba 3(\text{d}_{5/2})</td>
<td>779.7</td>
<td>Fe 3s</td>
<td>- -</td>
<td>As 4s</td>
<td>11.6</td>
</tr>
<tr>
<td>Fe 2(\text{p}_{1/2})</td>
<td>719.6</td>
<td>Ba 4(\text{d}_{3/2})</td>
<td>92.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

are listed in Table 5.1. Figure 5.1b shows a zoom of the near-\(E_F\) region with clearly distinguishable, spin orbit split Ba 5p lines at a binding energy (BE) of 15 eV, the As 4s line at 12 eV and the valence band (VB) between BE\(\approx\) 8 eV and \(E_F\). We note that the As 4s line at 12eV has been confused in the literature with a charge transfer satellite coming from the Fe 3d states of the valence band [142]. This spectral feature however is unlikely to originate from a satellite, as its spectral weight at \(h\nu = 3\) keV is comparable to the entire valence band. At lower excitation energies its relative weight becomes significantly smaller, see for instance the inset of Fig. 5.2b taken with \(h\nu = 125\) eV. The spectral weight of the 12 eV feature traces the tabulated photoionisation As 4s cross-section values [70] \(^2\) for these two photon energies, thus supporting an assignment to the As 4s shallow core level.

Figure 5.1c shows spectra of representative core levels from the three elements in Ba122: As 2p, Fe 2p and Ba 3d, taken with a photon energy of 2010 eV. Comparing the line shapes of the three core levels, it is immediately clear that while the As 2p and Ba 3d peaks are quite symmetric, the Fe 2p line is not. The Fe 2p peak can be fitted with a single, Gaussian-broadened Doniak-Sunjic line shape with asymmetry parameter \(\alpha = 0.44\), a value that is identical to reported values for elemental Fe [141].

If the asymmetry in the Ba122 Fe core lines was caused by the presence of high BE charge transfer satellites, one could expect the signature of a shoulder in the spectrum, but instead the high BE side of the core line is completely smooth. The inset in Fig. 5.1c shows the measured Fe 2p spectrum together with a Fe (111) 2p line from the literature [141]. The measured spectrum has been broadened with a Gaussian with full

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\(^2\)The listed values for photoionization cross-sections used throughout this document, taken from Ref. [70], are values for the atomic PIXs and are not necessarily directly applicable to more complicated compounds, but can be well used as an estimate to the real values.
width of half maximum FWHM= 700 meV to compensate for the higher resolution of our experiment and additionally a smooth Shirley-like background has been subtracted from the hard X-ray excited data presented here so as to enable a reasonable comparison of the two spectra. One can see that the two spectra coincide perfectly. \(^3\) This feature is thus not a property of the Fe (111) Fe 2p core level line shape.

The fact that the Ba122 Fe core level lines are so identical to those of elementary Fe means that the asymmetry of the core lines is best though of as caused by the significant partial density of states (pDOS) of Fe at the Fermi level. This enables a continuum of possible excitations during the creation of the core hole, leading to a smooth ‘loss-tail’ at the high BE side of the core level line. In turn, the fact that the As 2p core line in Fig. 5.1c is so symmetric (a fit with a Doniac-Sunjic line form yields an \(\alpha\) of only 0.06), means that the As pDOS at the Fermi level is almost negligible in comparison with the Fe3d contribution.

The core level lines were recorded both in normal emission geometry, as well as with an emission angle of 35° off-normal. The latter geometry increases the surface sensitivity of the experiment, see the inset in 5.1c, but yields almost identical results as normal emission for the Fe 2p and As 2p core lines. The Ba 3d line, however, is broader when recorded in off-normal emission, as can be seen in the right-most panel of Fig. 5.1c. Although the difference is quite small, it is evident that there is a small surface contribution for the Ba core lines, causing a (modest) asymmetry in the Ba 4d line shape.

### 5.3 Valence band data

Now focusing on the near \(E_F\) electronic states, a zoom of the valence band region taken with \(h\nu = 2010\) eV is depicted in Fig. 5.2a. One can see that the total bandwidth of the valence band is about \(6–8\) eV, displaying a sharp peak close to \(E_F\) (the maximum being centered at about 350 meV BE) and a broad hump between 3 to 7 eV. From our core level data it is already evident that the DOS closest to \(E_F\) consists primarily of Fe3d states, but at this particular photon energy \((h\nu = 2010\) eV\), the photoionization cross-sections (PIXS) \([70]\), for Fe 3d and As 4p are roughly equal, meaning that we cannot - a priori - distinguish between Fe and As pDOS.

At photon energies around 100 eV however, the PIXs favor Fe 3d with respect to the As 4p states by a factor 70, making spectra measured with these photon energies representative for the Fe 3d pDOS. In Fig. 5.2a one can also see a valence band spectrum recorded with \(h\nu = 125\) eV \(^4\), with a large peak at \(E_F\) and hardly any sign of a hump at higher binding energies, showing that the Fe 3d states are indeed located close to or

\(^3\)The literature spectrum of Fe (111) shown in Fig. 5.1c has a small satellite around a binding energy of 712 eV, which is due to the fact that this data was taken with a Mg K\(\alpha\) lab source.

\(^4\)We note that, due to the small angular acceptance of the SES100 analyzer, the \(k\)-space integration of the \(h\nu = 125\) eV spectra is over only part of the 2D Brillouin zone. The depicted spectra are integrated over 40% of the Brillouin zone area around \(\Gamma\). Using a polar rotation of the sample it was checked and confirmed that integration around different parts of the Brillouin zone, for instance \((\pi,0)\), yielded very similar spectra.
5.3 Valence band data

Figure 5.2: Comparison of x-ray and VUV photoemission valence band data (a) Valence band spectra taken with \( h\nu = 2010 \text{ eV}, T=\text{room temperature} \) and \( h\nu = 125 \text{ eV}, T=20\text{K} \), see also footnote [5]. The inset shows a broadened version of the \( h\nu = 125 \text{ eV} \) spectrum, representing the Fe 3d pDOS of the valence band. This curve has been subtracted from the one in the left panel to obtain the As 4p pDOS (shown as the red curve in the inset), (b) Shallow core levels of Ba122 recorded with \( h\nu = 125 \text{ eV}, T=20\text{K} \). The inset shows a zoom of the Ba 5p and As core levels, with their Lorentzian peak fits (grey shaded areas).

at \( E_F \) and that the As 4p states are mainly responsible for the spectral weight between 3 and 7 eV in Fig. 5.2a.

The inset in Fig. 5.2a shows the difference between the measured spectra in panel (a), whereby the \( h\nu = 125 \text{ eV} \) spectrum has been broadened with a Gaussian of 350 meV to account for the difference in resolution and temperature between the two measurements. This subtraction spectrum gives an estimate for the As 4p density of states. One minor remark is that the relative spectral weight of the As 4p to the Fe 3d states would then be roughly 2:1 for the hard X-ray data, judging from the area under the curves in the inset of Fig. 5.2, which is a factor two too high if compared to tabulated photoionization cross-sections. These cross-sections however are listed for atomic values and it is not certain they are strictly applicable to the valence band of a material such as Ba122 (as shown in Chapter 2, the PIXs in a solid material show an oscillatory behavior, in contrast to those for atomic species). The important, qualitatively robust point we make here is that there is little overlap in energy between the main maxima of the Fe 3d (350 meV) and the As 4p states (4 eV).

In the literature, several studies, both theoretical [143] and experimental [144], have suggested that the Fe 3d and As 4p states are strongly hybridized, thereby trying to rationalize the small measured Fe magnetic moment compared to predictions from LDA calculations. Others, however, have argued that the Fe-As overlap is small [57].

\(^5\)Although the hard X-ray and VUV valence band spectra in Fig. 5.2a are taken with different temperatures, it was checked and confirmed that data taken at room temperature with VUV radiation did not differ significantly from the low temperature data.
though, from our data it is hard to make a quantitative statement about the hybridization between Fe and As, it is clear that electronic states between $E_F$ and the first 1.5 eV, that determine the physical properties such as magnetism and superconductivity, are (almost) exclusively of Fe 3d character.

This would not mean the As 4p states are of no importance: our data would not exclude an important role for the As atoms as a source of screening of the iron on-site Coulomb repulsion [57]. We stress here that our use of the Ba122 compound enables us to draw these conclusions regarding the Fe-As covalence in a reliable manner. Many photoemission studies in the literature have been carried out on the structurally related 1111-pnictides [144–146] that, besides arsenic, also contain oxygen. The O 2p states of these compounds overlap in energy with the As 4p states [57, 147] and give a strong contribution to the valence band spectral weight, both at low as well as at high photon energies, thus making a trustworthy disentanglement of the As and Fe partial density of states practically impossible.

### 5.4 Shallow core level data

Now zooming in on the form of the As 3d and Ba 4d levels, it is evident that for both core levels the main lines have shoulders, see panel (a) of Fig. 5.3, taken with $h\nu = 140$ eV. The weight of these features varies slightly from cleavage surface to cleavage surface. Note that whereas the shoulder of the As 3d line is always located at the low binding energy side of the main line, the Ba 4d shoulders are reproducibly situated at the high binding energy side of the main line. The size of the binding energy shift for both elements is similar: $+(-)$ 400 meV for Ba (As). The appearance of these extra core level features is most naturally explained in terms of the existence of a surface and a bulk contribution. By changing the measurement geometry to off-normal emission, the spectral weight of the shoulders increases with respect to that of the main peak, confirming that the former indeed originate from the surface. This is shown in Fig. 5.3b for the Ba 4d lines. The relative weight of these contributions has been determined in panel (a) by fitting the spin-orbit split doublets with, in total, 4 Gaussian broadened Lorentzians, for both the As 3d and the Ba 4d core levels. We mention in passing that the spin-orbit splitting of the As 3d core level is 670 meV, which is very close to the value found for metallic arsenic [148], and thus we are of the opinion that this value itself cannot be taken as a signal of strong Fe - As hybridization, as was done recently in a photoemission study of a member of the 1111-pnictide family [144].

From Fig. 5.3a one can see that with respect to that of As, the surface contribution for Ba is very large and significantly broadened when compared to the bulk states, which would support a picture in which the Ba atoms indeed make up the termination surface after UHV cleavage of Ba122 single crystals. The broad energy distribution of the Ba surface states might partly be due to adsorption of residual gas from the vacuum onto the surface, or, more significantly, to the absence of long range structural order in the topmost Ba layer (as shown in the inset in Fig. 5.1a) [59, 140]. The fact that the surface contribution for arsenic is much more narrow than for Ba can also be rationalized within the same picture, as the ‘sub-surface’ As layer is far less perturbed by the cleavage,
and possesses a markedly reduced variation in electronic environments compared to the top-most Ba layer. Furthermore, the small spectral weight of the surface features in the As spectra compared to the Ba case can be taken as evidence that the effect of the presence of the surface is rapidly screened away for the atomic layers further below the Ba termination layer.

In Fig. 5.3c the same core level spectra as in panel (a) are plotted, overlain with the same core levels measured with $h\nu = 3$ keV. It is evident that the (much more surface sensitive) $h\nu = 140$eV data for Ba 4d (left panel) are much broader at the base, although they were recorded with much higher resolution than the hard X-ray data. Broadening of the VUV-excited Ba 4d data, to correct for the difference in experimental resolution, gives an asymmetric line shape with much more spectral weight at the high binding energy side than the $h\nu = 3$ keV data, emphasizing the fact that the hard X-ray data is indeed probing the electronic structure representative for the bulk of Ba122. The As 3d peaks, as measured with $h\nu = 140$eV, are significantly narrower compared to the X-ray data and broadening yields a spectrum that is, despite the non-negligible surface component, almost identical to the 3 keV data. This also explains why the surface contribution for As could not be resolved from comparison between the 3 keV and 2010 eV X-ray data, while it was evident for the Ba core levels. Also the Fe 3p core level (not shown) shows an altered peak form when measured with $h\nu = 140$eV compared to the hard X-ray data, although the VUV excited signal is very weak, and thus not amenable to further analysis. In addition, the small spin-orbit splitting and the Doniac-Sunjic peak form for this line disqualify a disentanglement of the surface and bulk contributions for the Fe 3p signal.

An important point to unravel is, of course, the exact origin of the difference between the surface and the bulk electronic environments of Ba122. As explained in the introductory chapter on photoemission (Chapter 2), the shift of a core level $\Delta E$ can be explained by a number of terms given by the following formula:

$$\Delta E = \Delta \mu + K \Delta Q + \Delta V_M - \Delta E_R,$$

where $\Delta \mu$ is the change in the chemical potential, $\Delta Q$ the change in the number of valence electrons of the atom under consideration, $\Delta V_M$ the change in the Madelung potential, and $\Delta E_R$ is the change in the extra-atomic relaxation energy due to polarizability of the atoms and the conduction electrons surrounding the created core hole [66]. In the case of Ba122 it is a non-trivial exercise to determine exactly the role played by each of these terms at the surface. One may expect, at least, that the polarization and the Madelung potential are different at the surface, although it is difficult to disentangle these two contributions. A good starting point would therefore be to compare the measured data for Ba122 to a known case from the literature, in which (electronic) surface renormalization is known to play an important role.

Let us first consider the possibility of a (grossly) different charge carrier concentration at the surface, i.e. an altered surface doping level. From photoemission investigations it is known that certain cuprates which lack a natural cleavage plane, such as YBa$_2$Cu$_3$O$_{x - 7}$ - YBCO for short - show such a surface doping effect [150–152]. For YBCO this
Figure 5.3: Surface versus bulk electronic states of Ba122 from comparison of x-ray and VUV photoemission data (a) Ba 4d (left) and As 3d (right) core levels recorded with $h\nu = 140$ eV (black). The surface (S), and bulk (B), contributions have been determined by a fit with 4 Gaussian broadened Lorentzians and are shown with blue and green shaded areas, respectively, (b) Ba 4d lines for different emission angles, taken with $h\nu = 140$ eV on a different sample, (c) For comparison, the same core levels recorded with $h\nu = 3000$ eV (red) are shown together with the data from panel (a) (thin black) and Gaussian broadened versions of the latter (blue) to compensate for the difference in experimental resolution, (d) Ba 4d core levels of cleaved YBa$_2$Cu$_3$O$_x$ ($x = 6.75$) taken with different experimental geometries and photon energies in the hard X-ray regime. Data from Ref.[149]. Note the large spectral weight of the surface contribution here and the large energy difference between bulk (B) and surface (S) states, indicated in the figure with green and blue vertical lines, respectively.
is caused by the fact that the CuO chains are ruptured upon cleavage, remaining behind - in the form of debris - on the termination surface. These chain fragments donate extra holes to the underlying copper-oxygen plane bilayer. The analogy with Ba122, where also only half of a bulk crystal layer remains on the surface after cleavage, is obvious. This type of electronic surface reconstruction for YBCO, however, has a drastic effect on the measured core level spectra, as can be seen in Fig. 5.3d. Depicted are Ba 4d core levels taken, in order of decreasing bulk sensitivity, with $h\nu \approx 6$ keV and $h\nu \approx 2$ keV in normal emission geometry and $h\nu \approx 2$ keV with $35^\circ$ off-normal emission. The difference between spectra recorded with the latter two sets of experimental conditions is still very significant, showing that one has a sizable surface contribution even with an excitation energy of 2 keV. This is not the case for Ba122, Fig. 5.1c, where the difference between normal and off-normal emission is nigh on indistinguishable. Also, the shift of the surface states of YBCO is quite large: about 1 eV with respect to the bulk states, more than twice that seen in Ba122. Moreover, the increased surface doping of YBCO leads to a shift of surface states toward higher binding energy both for the cations and anions ($O^{2-}$), so this mechanism can most likely be disqualified as the cause of the electronic surface reconstruction of Ba122.

The picture for Ba122 shown in Fig. 5.3a is, in fact, very reminiscent of the situation seen in X-ray photoemission from the GaAs (110) surface, where the core levels are known to contain a surface contribution [153]. This surface component has a shift in binding energy (with respect to the main line) that is opposite for the negatively and positively charged As and Ga ions: toward lower and higher binding energy, respectively. This shift has been explained by a change in the Madelung potential at the surface [154–156] with a core level shift that happens to be close to what we find here for Ba122. Therefore, it is quite credible that the altered surface electronic structure of Ba122 is caused by a change in the Madelung potential, with the surface doping level itself being very close or equal to the bulk value for the Ba122 material. The question then arises as to what effect this has on the valence band states, and in particular those close to $E_F$, which are intimately involved in the superconductivity in the doped Ba122 and related materials.

While one may expect the altered surface Madelung potential to have some effect, one should bear in mind that the near-$E_F$ states in these systems are band-like and itinerant in nature, whereas the concept of a Madelung energy is more generally applicable to localized, ionic electronic levels. Secondly, in the case of GaAs (which possesses a band gap in the order of 1 eV), calculations have indicated the presence of occupied surface electronic states attributable to the altered Madelung potential in that system, lying at about 500 meV below the valence band edge. Yet, no sizable, structured contribution from these states has been identified in photoemission experiments [157, 158]. Taking all these considerations together, we conclude that the near-$E_F$ electronic structure at the surface of Ba122 is very close to that of the bulk. Furthermore, the fact that the surface doping level of Ba122 looks to be the same as the bulk (despite the presence of a reconstructed and potentially polar Ba termination layer) provides confidence that STM and ARPES should be representative probes to investigate the bulk properties of Ba122, such as spin ordering transition temperatures and superconductivity, both in terms of
critical temperature and superconducting gap sizes as a function of temperature and doping.

5.5 Conclusions

We have presented high-resolution photoemission data taken with hard X-ray and VUV photon beams on single crystals of the undoped parent compound of the electron and hole doped pnictide high temperature superconductor, BaFe$_2$As$_2$. From the line shape of the core levels it could be deduced that the near-$E_F$ electronic states are primarily of itinerant Fe 3d character. By comparing the hard X-ray excited data with results obtained using conventional VUV excitation energies, we were able to disentangle the approximate Fe and As partial densities of states in the valence band and show that the contribution of the As 4p states near the Fermi level is very small indeed. Seeing as this energy region is where the Fe 3d partial density of states is maximal, this strongly suggests that the degree of hybridization between the Fe 3d and As 4p states is minimal at and near $E_F$ for these states, a fact that could be of considerable significance in relation to the issue of the small magnetic moment found at the Fe sites in these compounds.

The exploitation of two widely differing regimes of photoelectron kinetic energies has also enabled us to examine whether the electronic structure of the cleaved Ba122 surface is the same as or close to that of the bulk. By comparison with the well studied case of GaAs, we find that the termination surface - which comprises the Ba layer of the quasi-2D crystal structure - is likely to possess a modified Madelung potential, compared to the bulk. However, the core level data do provide evidence against the existence of a surface region with differing doping level. The departure of the surface contribution to the electronic structure in Ba122 from the bulk situation is very modest in the iron pnictide. Therefore, the distorting effects of the real cleavage surface on the investigation of bulk-representative, near-$E_F$ electronic properties of Ba122 and related compounds with surface sensitive probes such as angle resolved photoemission and scanning tunneling spectroscopy are found to be minor in nature.
6 Angle resolved photoemission of an anti-ferromagnetic pnictide parent compound


Abstract

Using angle resolved photoemission it is shown that the low lying electronic states of the iron pnictide parent compound EuFe$_2$As$_2$ are strongly modified in the magnetically ordered, low temperature, orthorhombic state compared to the tetragonal, paramagnetic phase above the spin density wave transition temperature. Back-folded bands, reflected in the orthorhombic/anti-ferromagnetic Brillouin zone boundary hybridize strongly with the non-folded states, leading to the opening of energy gaps. As a direct consequence, the large Fermi surfaces of the tetragonal phase fragment, the low temperature Fermi surface being comprised of small droplets, built up of electron and hole-like portions. These high resolution ARPES data are therefore in keeping with quantum oscillation and optical data from other undoped pnictide parent compounds.
6.1 Introduction

The electronic structure and properties of the newly discovered iron-pnictide superconductors [32, 132] are a focus of much research. A central theme is the understanding of the origins of the magnetic ordering and its possible interplay with superconductivity. The characteristics of the low-temperature, orthorhombic, anti-ferromagnetic (AFM) phase have been experimentally determined, for example for the undoped 122-parent compounds, $MFe_2As_2$ (with $M = \text{Ca, Sr, Ba, Eu} \ldots$). A common proposition is that the magnetism is of an itinerant, spin density wave (SDW) type, connected to nesting of the warped cylindrical Fermi surfaces (FS’s) centered at the $(0,0)$ (Γ) and $(\pi,\pi)$ points (X) of the tetragonal Brillouin zone (BZ) [50]. Such an SDW would have dramatic consequences for the band structure and Fermi surface, leading to reconstruction, the opening of gaps and major Fermi surface depletion.

Recently, quantum oscillation (QO) experiments have presented evidence for Fermi surfaces comprising small pockets - due to the effects of the SDW order - in SrFe$_2$As$_2$ [52] and BaFe$_2$As$_2$ [53]. Both studies find the existence of three distinct orbits, with FS areas of only 0.3%, 0.6% and 1.5% of the tetragonal BZ (compared to a total FS area larger than 20% in the tetragonal phase). In addition, the opening of gaps as well as a dramatic reduction of the free charge carrier density upon entering the orthorhombic AFM state has been concluded from optical conductivity measurements [54, 55].

Given that a FS-nesting-driven SDW is rooted in $k$-space, it is of great importance whether the SDW ‘fingerprints’ of reconstruction, gapping and FS depletion really take place in the $E(k)$-space hosting the electronic states of these materials. Angle-resolved photoemission (ARPES) is a powerful probe of such issues, and consequently there have been numerous studies of the parent compounds of the pnictide superconductors using ARPES. Early studies were unable to detect significant changes below the magnetic ordering temperature [47, 135]. More recently, ARPES studies have shown the existence of small, additional FS pockets (either hole or electron-like) around the $(0,0)$ or $(\pi,\pi)$ point [58, 60, 159, 160], and a detailed temperature-dependent study is reported in [61]. Despite this progress, it could be argued that there are no studies that cover the states around Γ and X on an equal footing, avoiding matrix-element-induced extinction of important states, and there are, in any case, no studies reported of the europium parent compound. On top of this, the issues of the dimensionality of the electronic states [48, 49, 62, 161] and the nature of the cleavage surface of the $MFe_2As_2$ systems [37, 162] are both matters of quite some discussion.

In this chapter we present the first photoemission study on the pnictide parent compound Eu122, showing data of a clarity that makes use of second differentials unnecessary. The local iron moment for Eu122, with $\approx 1\mu_B$ [163], is similar to the other $M122$ compounds, yet in Eu122 the Eu moments also order at low temperatures, having a local moment of nearly $7\mu_B$. Our low temperature ARPES data however do closely resemble those reported for other parent compounds [61, 160], indicating that the ordering of the Eu moments is of little influence on the ordering of the iron moments.

Exploiting matrix elements and polarization-dependent selection rules, we uncover hybridization effects between back-folded hole and electron-like bands both at the $(\pi,\pi)$
Figure 6.1: Temperature dependent Fermi surface (FS) topology of Eu122. (a) Measured FS ($E_F \pm 10$ meV, $h\nu = 84$ eV) of Eu122 at $T = 10$ K. The light polarization $\epsilon$ is indicated. The inset shows a schematic high temperature FS in a two-dimensional projection covering a quarter of the tetragonal Brillouin zone. (b) FS maps ($h\nu = 75$ eV) around the $(\pi, \pi)$-point in $k$-space (purple box in the inset of [a]) at different temperatures. The polarization vector ($\epsilon$) is parallel to the analyzer slit. The top-most 20 K FS map is taken on a fresh cleavage surface, the bottom one after cycling the sample temperature up to 300 K, see also footnote [1].

and $(0, 0)$ regions of $k$-space and provide clear evidence of the resulting energy gaps. As a result, the large FS’s we know from the paramagnetic phase break up into extremely small hole and electron pockets we dub ‘droplets’ on entering the magnetically ordered state.

The exact nature of the AFM phase (localized vs. itinerant) is still subject of debate [51, 164]. We note that our ARPES measurements cannot a priori distinguish between localized versus itinerant magnetic order. Even more so, the folding of the band-structure observed in our experiment could be argued to be more sensitive to the orthorhombic

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Footnote 1: Between the two data sets recorded at $T = 20$ K in panel (c) of Fig. 6.1, several warm up–cool down cycles were performed, resulting in a slightly different spectral weight distribution and $k_F$ loci for the droplet-like FS between the two spectra. The mechanism leading to these small changes is not clear, but the important point to note is the dis- and re-appearance of the small FS droplets above and below the magnetic ordering temperature.
Figure 6.2: Low energy electron diffraction on pnictides. (a) A LEED diffraction pattern from a fresh cleavage surface of cobalt doped Ba122, cleaved and measured at $T = 20$ K. Spots are indexed within the tetragonal unit cell. The white and black circles indicate spots originating from a $2 \times 1$ surface reconstruction, the spots marked with a grey circle correspond to a $\sqrt{2} \times \sqrt{2}$ reconstruction. (b) The same cleavage surface after warming the sample up to $T = 150$ K. The non-integer spots that now have disappeared do not re-appear after cooling down again. (c) A LEED diffraction pattern from a fresh cleavage surface of Fe$_{1+\delta}$(Se,Te) (FST), cleaved and measured at $T = 20$ K. Note the absence of reconstruction spots. LEED data courtesy of F. Massee.

structural distortion than the magnetic ordering. Yet, the back-folding, hybridization and gapping we observe in our ARPES data are consistent with the QO and optical conductivity results on related compounds.

6.2 Results from angle resolved photoemission: temperature dependence

We start with a discussion of the ‘as cleaved’, $T = 10$ K data from EuFe$_2$As$_2$ shown in Fig. 6.1a. The inset shows a cartoon of the $k$-space region under scrutiny, with a simplified representation of the band theory predictions for the tetragonal phase: three hole pockets around $(0, 0)$ (blue circles) and two electron pockets at $(\pi, \pi)$ (red ellipses) [165]. The main part of Fig. 6.1a is a wide $k$-range, low temperature FS map which obviously exhibits quite a different FS topology than the tetragonal expectation.

The most eye-catching difference is the fact that both the large hole-like FS’s at $(0, 0)$ and the electron-like FS’s at $(\pi, \pi)$ and equivalent points have broken up into a number of clearly disconnected ‘droplets’. We stress that this data clearly resolves the structural distortion than the magnetic ordering. Yet, the back-folding, hybridization and gapping we observe in our ARPES data are consistent with the QO and optical conductivity results on related compounds.

2At the $(\pi, \pi)$ point in Fig. 1a, only two of the four droplet FS’s are visible, due to the strong polarisation dependence of the photoemission matrix elements, linked to the presence of a mirror plane
droplet structure of the FS’s at both high symmetry points: there are no large FS’s left. Droplet, or petal-like FS’s have been reported in ARPES studies of differing $k$-space locations of the Sr122 (Ref. [160]), Ba122 (Ref. [61, 159]) and Ca122 (Ref. [49]) parent compounds, as well as from the doped superconductor (Ba,K)Fe$_2$As$_2$ (Ref. [58]). We will zoom in on the Γ and X $k$-space regions for Eu122 later in this chapter. Before doing this, we deal with the issue of surface reconstructions.

Seeing as the simplest SDW scenario involves shifted copies of bands appearing at new $k$-space locations compared to the high-$T$ tetragonal phase, it is important to have a feeling for the impact of (surface) structural reconstructions on the data, particularly as such reconstructions are a common feature of scanning tunneling microscopy data from the MFe$_2$As$_2$ materials [37, 38].

These reconstructions can also be seen in low energy electron diffraction (LEED) patterns that display prominent $2 \times 1$, $1 \times 2$, and less clear $\sqrt{2} \times \sqrt{2}$ reconstruction spots. In Fig. 6.2, LEED patterns obtained from a cleavage surface of the closely related iron pnictide Ba122 are shown for a freshly cleaved sample at $T = 20$ K and for the same sample warmed up to 150 K. The figure also displays a diffraction pattern obtained from the pnictide superconductor Fe$_{1+\delta}$(Se,Te), that lacks the $M$-cation layer in between the iron-pnictide block-layers. The latter compound does not show any sign of reconstructions in the LEED pattern upon cold cleavage. The surface reconstructions of Ba122 (and Eu122) are not robust against thermal cycling up to temperatures above $\approx 150$ K, and do not re-appear in the LEED pattern upon re-cooling the sample, in keeping with their origins in ordering/disordering processes within the partial Eu layer that comprises the termination of the cleaved crystal [37, 162].

In Fig. 6.1b, we show that the FS’s around $(\pi, \pi)$ remain essentially unchanged upon raising the temperature from 10 K to 20 K, at which point the Eu moments become disordered, illustrating that the magnetic state of the Eu sub-lattice does not have a significant effect on the Fe-derived electronic states at the Fermi level as seen with ARPES. The situation is very different at $T = 200$ K: upon exiting the AFM phase for magnetic ordering within the Fe planes, the droplet-like FS structure (indicated with an arrow and appearing as a dumb-bell in the measurement geometry used in Fig. 6.1b due to intensity from a below-$E_F$ band at the X point itself) is no longer observed. At 200 K, the LEED pattern of the cleave shows only 1x1 tetragonal spots. Upon re-cooling to 20K (bottom panel of Fig. 6.1b), the extra, $2 \times 1$ and $\sqrt{2} \times \sqrt{2}$ LEED spots do not re-appear, yet the droplet FS at $(\pi, \pi)$ does, proving that this remarkable FS topology reflects the bulk, magnetic state of the pnictide parent compound, and is definitely not a result of ‘diffraction replicas’ due to surface reconstructions.

in the Fe-plane and the p-polarised synchrotron radiation used. For $k''_{||}$ values well away from zero, this selection rule no longer operates and all four droplet FS’s are seen, such as at $(-\pi, \pi)$. For a short introduction on photoemission matrix elements and selection rules, see Chapter 2.

3We carried out further checks whether the ordering of the Eu moments had any influence on the electronic structure of Eu122 as probed with ARPES, but no difference was found for several different $k$-cuts taken at 10K and well above 20K.
6.3 Low temperature fermiology

Now we are sure that the observed low-\(T\) Eu122 FS is sensitive to the bulk magnetism, we return to the band structure in the orthorhombic phase in more detail. In Fig. 6.3 several \(E(k)\)-cuts through the \(\Gamma\) and \(Z\) \([(k_x, k_y, k_z) = (0, 0, \pi/c)]\) points, parallel to \(\Gamma X\) are shown, taken with \(h\nu = 100\) and 84 eV. The data taken with these two photon energies look, in general, very similar - with FS crossings at very similar \(k\)'s, albeit with (at times strongly) varying spectral weight. As these two photon energies correspond to \(k_z = 0\) (100 eV) and \(\pi/c\) (84 eV), this illustrates that the \(k_z\)-dispersion for this compound is modest.\(^4\)

A second point is that the destruction of the large FS’s to give droplets is clearly present in Eu122 at both \(k_z = 0\) and \(k_z = \pi/c\), unlike what has been reported for Ba and Ca122 [159].

We note that the surface quality and favorable experimental conditions mean that a large number of band features can be distinguished in the \(E(k)\) images shown in Fig. 6.3. We deal firstly with a group of features that clearly possess reversed character with respect to the high-\(T\), tetragonal situation, being hole-like around X and electron-like

\(^4\)The assignment of \(h\nu = 84\) eV as \(k_z = \pi/c\) and \(h\nu = 100\) eV as \(k_z = 0\) is strictly speaking only valid at the \(\Gamma\) point. Due to the necessary tilting of the sample across the recording of the FS map, the \(k_z\) vectors at the X-point are about 15% of the reciprocal c-axis lattice vector smaller.
Figure 6.4: Detailed FS topology around the \((0, 0)\)-points of Eu122 \((T = 10 \text{ K}, \hbar\nu = 84 \text{ (Z)}\) and 100 eV \((\Gamma)\). For each of (a)-(d), the left panels show schematic (top) and measured (bottom) \((E,k)\)-images for the green \(k\)-space cuts shown in the small FS maps (top right panel in each case). In each band structure scheme, electron-pocket bands are labeled ‘e’ and indicated in red, whereas hole-pocket bands get an ‘h’, and are shown in blue. Barely distinguishable features are indicated with dotted lines. Red shading indicates areas in which the symmetry selection rules can lead to suppression of some of the orbital states. The measured FS map in the top right sub-panel in (c) has been replaced with a sketch of the low \(T\) Fermi surface, with the FS predicted for the tetragonal phase shown in grey.

around \(\Gamma(Z)\). These states are marked in Fig. 6.3 using black arrows and a black star, for the hole-like and electron-like features, respectively, and originate from the effects of magnetic order in the Fe plane.
Further inspection of Fig. 6.3, however, shows that there are also ARPES features (marked with gray, open arrows) which seem to match those expected in the paramagnetic, tetragonal state, such as the electron-like feature clearly visible around $(\pi, \pi)$ for $h\nu = 100\text{eV}$. This apparent dichotomy - that both reconstructed and unreconstructed bands coexist - has been reported in ARPES investigations of other parent compounds,\[159, 160\] and will be returned to further on. Dealing with these kind of issues one is confronted with the intrinsic complexity of the low lying electronic structure of these multiband materials. Even adopting the simplest picture of only back-folding the tetragonal band structure yields 8 or 10 bands (starting from 4 or 5 FS’s at high temperature), and if the crystal contains small-scale magnetic twin domains we average over in the ARPES experiment, then this number doubles. It is therefore imperative to zoom-in and take a closer look at the different high symmetry points in $k$-space.

To start off, we zoom-in on the Γ-point in Fig. 6.4. Four $k$-space cuts for the two different photon energies are presented, partnered with a band structure scheme as a guide to the $E(k)$ images. Panel (a) clearly shows the existence of shallow electron-like bands, appearing in the FS map as small, triangular shaped pockets. Cuts through the center of this feature along the $k_x$-direction using $h\nu = 84$ and 100 eV are shown in panels (c) and (d), and reveal that, in fact, it consists of two concentric electron pockets. The cuts shown in Fig. 6.4b illustrate a d-wave like gapping operative around the $(0,0)$ point, with no low energy pockets such as those seen at $k_x \sim 0.2\pi/a$ in panels (c) and (d). The concentric electron pockets have Fermi surface areas of about 1% and 0.3% of the tetragonal BZ. Such small FS areas match those observed in the QO studies of Sr122 and Ba122, although we note that the details of the band structure of the different pnictide parent compounds will depend somewhat on the identity of the $M$-cation.

The important point here is the fact that we are able to detect the disintegration of the large Γ-centered FS’s into very small droplets. As can be seen in the $E(k)$ images, the two different photon energies either more clearly resolve the left (84 eV) or the right side (100 eV) of the small pockets, and this matrix element difference is, in fact, a signal of different orbital character for either side of the pocket. A natural explanation for this would be that these multiple, orbitally-split pockets consist of back-folded and hybridized hole-like and electron-like bands which started life as the Γ and X-point band structure features in the tetragonal phase, respectively.

As the $E(k)$-sketches indicate, the data still contains remnants resembling the tetragonal bands. However, these interact with the back-folded bands such that the former do not cross the Fermi energy, and thus do not give rise to large FS’s around Γ. In Fig. 6.4c one can also see a further case of interaction between a folded and non-folded band in that the blue hole-like band - which is well below the Fermi level - is not symmetric around $k_x = 0$ but is further pushed down by the presence of the lower binding energy back-folded bands on the right. These data, then, do not support a picture of selective modification of bands from the tetragonal band structure,\[160\] in which only some bands interact with the back-folded structures, a point we will return to when discussing the zoom-in on the X-point in a moment.

We now turn to the states around the X or $(\pi, \pi)$ point, which - in general - have received less attention in ARPES papers on the parent compounds than have those
around $\Gamma$. In Fig. 6.5a and b, data recorded with 84eV photons are presented. Cut 1 in panel (b) clearly shows two pairs of hole-like features crossing $E_F$, giving rise to the two pairs of blue features shown along cut 1 in the main FS sketch [panel (a)]. This is in contrast to cut 2, which reveals that the hole-like bands do not approach $E_F$: their spectral weight is suppressed up to a binding energy of about 70 meV, which, as also noted in Ref. [160], corresponds rather well to the gap observed in optical conductivity measurements (with $2\Delta \approx 90$ meV for Eu122 [55]). Thus, cut 2 of Fig. 6.5 attests to the opening of a gap, leading to the break-up of the large elliptical X-point FS’s into significantly smaller structures.

The data of cut 3 take us a step further: here the cut just grazes the end of the longer hole-like arc, and if we take this result at face value the droplet-like FS would, in fact, have to be ‘open’. Thus, for the $k_z$ value close to $\pi/c$ (i.e., that relevant for $h\nu = 84$ eV) if we were conducting a quantum oscillation experiment, there would be no closed FS orbits measurable in the $k_{x,y}$ plane near $(\pi, \pi)$. The $E(k)$-image along $k$-space cut 4 clearly shows that the hole-like bands bend back into an electron-like feature around X that has its band bottom at a binding energy $BE \approx 100$ meV. This delivers the clue that the crescent-shaped, gapped, FS segments around the X-point in the AFM orthorhombic phase arise from hybridization of the X-centered electron pockets with the back-folded hole-like bands from the $\Gamma$ point.

We now switch in Fig. 6.5c to data recorded with $h\nu = 100$ eV (for which $k_z \approx 0$). Comparing the FS maps of panels (a) and (c) and the data of cuts 1 and 5, we note that for 100 eV photons a clear electron-like feature is observed, located at the opening of the hole-like arc seen also for 100 eV photons in cut 6. These electron-like sections can be seen to act as a ‘gate’, closing off the arc into a continuous, droplet-like FS.

Thus, these data from the X-point can support two scenarios: i) firstly, if the lack of hole-like bands in cut 1 is taken to be an initial state effect (i.e., is not simply due to a low matrix element), then we see a $k_z$-dependence in which for $k_z = 0$ ($h\nu = 100$ eV) there are small FS droplets around the $(\pi, \pi)$ points, whereas for $k_z = \pi/c$ ($h\nu = 84$ eV) the hole-like arcs remain open and thus no closed FS exists near X for this $k_z$ value. ii) the alternative is to posture that there are electron-like ‘gates’ closing the hole-like arcs for all $k_z$ values (i.e., the droplets are, in fact thin, roughly triangular prisms with their long axis along $k_z$), but that they carry no spectral weight for $h\nu = 84$ eV. Although scenario (ii) seems the more likely, whichever scenario is correct as regards the $k_z$ behavior, in both cases the large, elliptical FS’s at X that mark the tetragonal, paramagnetic phase are broken up into much smaller structures on entering the AFM phase, either with or without continuity along $k_z$.

Thus, bringing together the conclusions from both the $\Gamma$ and X-point data, we can state the following by way of summary:

i. This first ARPES study of the EuFe$_2$As$_2$ parent compound of the pnictide high $T_c$ superconductors has yielded data of high quality, with excellent ‘contrast’ in $k$-space, enabling a detailed discussion of all Fermi surfaces near both the $(0, 0)$ and $(\pi, \pi)$ points on an equal footing.

ii. On cooling well below the magnetic ordering temperature of the iron planes,
the large FS’s (reversibly) break-up into small droplet-like structures, supporting only a fraction of the original, high temperature FS areas.

iii. The fact that both electron-like features are found at (0,0) and hole-like at
(\pi, \pi) suggests that back-folding of the high-T band structure takes place via reflection in the new Brillouin zone boundaries.

iv. The back-folding picture is strongly supported by clear evidence for hybridization between the back-folded and non-folded bands, resulting in shifting of bands and the opening of d-wave-like energy gaps of order 50-70meV.

v. Comparison of data probing different locations along the \( k_z \) axis suggest that either the small FS structures near the \((\pi, \pi)\) point might indeed be droplets—without continuity along \( k_z \)—or they take the form of prisms stretching along \( k_z \).

vi. Finally, the ordering of the Eu moments below ca. 20K does not have a noticeable impact on the ARPES data.

Taking points 2)–4) together, we can close this chapter by stating that these ARPES data are in keeping with the conclusions from recent quantum oscillation and optical data on other \( MFe_2As_2 \) parent compounds [52–55], that offer support for a large suppression of the number of near \( E_F \) electronic states in the low temperature magnetically ordered orthorhombic phase. Additionally, we have shown that the ordering of the Eu moments is of little influence on the reconstruction of the tetragonal band structure.
Some of the most intensively studied contemporary physical phenomena, have their origin not in the properties of single particles, but in the interplay between many particles (most notably electrons) comprising the system. Two examples of such emerging physical phenomena are high temperature and unconventional superconductivity (HTSC) and colossal magnetoresistance (CMR).

Superconductivity is the complete loss of electronic resistance below a critical temperature. This temperature ($T_c$) is typically well below 30 K for conventional superconductors, but certain compounds, such as the cuprates and the (more recently discovered) iron pnictides, display high temperature superconductivity: their $T_c$ is far in excess of that of conventional superconductors. The CMR effect is observed in perovskite (\textit{-like}) manganites and is also associated with a large change in resistivity that coincides with a para- to ferromagnetic transition upon lowering the temperature. This transition temperature can be influenced strongly by applying an external magnetic field: a field of several Tesla can boost the transition temperature by as much as 100 K.

These phenomena arise from the collective behavior of many electrons in the solid, their mutual interactions, as well as their interactions with for instance the crystal lattice they reside in. The fact that these physical properties are rooted in the intrinsically many-body properties of the system makes them fundamentally hard to understand. Despite a huge body of theoretical and experimental work, the mechanisms behind both HTSC and the CMR effect are still not fully understood to date.

This thesis is comprised of two (more or less) independent parts, that are dealing with the two phenomena mentioned above. These parts are summarized in separate sections below. The CMR effect is addressed as it occurs in the material La_{2-2x}Sr_{1+2x}Mn_{2}O_{7}, a bilayered manganite that has received considerable attention from the condensed matter physics community over the years. The issue of high temperature superconductivity is not addressed directly, instead a study is presented of some of the more fundamental electronic properties of the (non-superconducting) iron pnictide parent compounds BaFe$_2$As$_2$ and EuFe$_2$As$_2$. These parent compounds can be made superconducting by cation substitution (or application of pressure) and it is believed that their physical properties are intimately connected to the HTSC itself.

As these phenomena, HTSC and CMR, both have their roots in the electronic structure of the system at hand, including the many-body interactions, an experimental technique is required that can image these directly. Therefore, the experimental technique of choice throughout this thesis is (angle resolved) photoemission, (AR)PES. This is a photon-in, electron-out technique that is capable of directly probing the band structure of a single-crystalline material. Moreover, the electron-electron and electron-phonon interactions, as well as possible interactions between the electronic system and collective excitations of the spin system can also be uncovered in (AR)PES experiments, mak-
ing this technique extremely suitable to gain knowledge about physical phenomena that depend on electron interactions.

**Manganites and CMR**
The first part of this thesis is dedicated to La$_{(2-2x)}$Sr$_{(1+2x)}$Mn$_2$O$_7$ (LSMO for short): a bilayered manganite that shows the CMR effect in a narrow Sr doping range, where metallic-like behavior is observed at low temperatures (for $0.30 < x < 0.50$). In the introduction the crystal structure and the relevant physics of LSMO are discussed. The high temperature electron transport in this material (and the CMR manganites in general) is believed to be governed largely by polarons and their hopping. This is due to the large the Mn crystal field splitting and associated Jahn-Teller distortions, combined with a large Hund’s rule coupling. These interactions favor (insulating) super exchange leading to anti-ferromagnetic and orbital ordering. In the doped case, combination (or competition) with a mixed valence character, leads to ferromagnetic double exchange interaction, giving rise to carriers in the form of fluctuating, correlated polarons, which possess a hugely increased effective mass compared to free electrons. Although this behavior seems rather well established in the high temperature, paramagnetic and insulating regime, it is still not known how the insulator-to-metal transition comes about upon lowering the temperature below $T_C$. Also its connection to the CMR effect is not yet exactly known.

This state of uncertainty is even more relevant to the subject of the (low temperature) electronic structure of these systems. There is still much debate as to what - for instance - the spectral signature of a polaronic metallic conductor should be as seen in an ARPES experiment. Previous ARPES measurements have ranged from showing that La$_{(2-2x)}$Sr$_{(1+2x)}$Mn$_2$O$_7$ to is a psuedo-gapped material, without spectral weight at $E_F$ to showing it to be a material having a psuedo-gap at specific points in $k$-space, while showing sharp quasi particle (QP) peaks at $E_F$ in other $k$-space regions. In Chapter 3 we have shown that in fact these QP peaks can be obtained at all $k$-space locations, but that the temperature and Sr doping dependence is very unusual and not corresponding to the bulk physical properties of La$_{(2-2x)}$Sr$_{(1+2x)}$Mn$_2$O$_7$.

In Chapter 4 we have presented a detailed hard x-ray photoemission study on LSMO to try to explain this anomalous doping and temperature dependence. From these measurements we have concluded that phase separation does not occur for LSMO at temperatures well above and below $T_C$ and can hence not explained the observed anomalies. This study further showed the surface and bulk of LSMO to be highly similar in terms of doping.

Additional detailed ARPES measurements we carried out, reveal that the actual QP peaked spectral signature originates typically from a very small area of the cleavage surface. Taking this fact, in combination with the anomalous behavior, we conclude that the QP peaked, gap-less, metallic Fermi surfaces are not representative of bilayered LSMO. Instead they originate from naturally occurring stacking faults within the pseudo-perovskite crystal structure, which lead to small inclusions of LSMO with a larger number of stacked MnO$_2$ planes and thus physical properties more like those of the cubic, three-dimensional perovskite manganites. More importantly, we therefore interpret the true spectral signature of bilayered LSMO as that of a psuedo-gapped ‘bad’-metal, lack-
ing sharp near-\(E_F\) peaks anywhere in \(k\)-space, and supporting vanishingly small spectral weight at the Fermi level. This is in accordance with observations from optical spectroscopy studies and general considerations from a bulk transport point of view. The interpretation of the QP peaked spectral signature seen in ARPES in terms of extrinsic inclusions also gives an explanation for the inconsistencies between the majority of the different ARPES studies.

**Iron Pnictides**

The second part of this thesis deals with the electronic structure of the parent compounds of the newly discovered iron pnictide superconductors. Superconductivity in these materials was discovered in early 2008 and has spurred an enormous research effort into the synthesis and investigation of the physical properties of these systems, both experimentally and theoretically. Being a very young field, many fundamental issues concerning these systems are not yet settled. It is for instance not still known how correlated the pnictides are (although the metallic nature of the parent compounds reveals that they are less strongly correlated than the other big family of HTSC, the cuprates). Also, the nature of the anti-ferromagnetic ordering of the parent and low-doped compounds is not understood, as is their band structure. Moreover, one could even argue that the details of the generic pnictide phase diagram are not yet clear (issues such as first versus second order transitions and coexistence of superconductivity and magnetic order vary wildly between the different studies and pnictide compounds).

In Chapter 5, we present angle integrated PES and x-ray photoemission measurements on \(\text{BaFe}_2\text{As}_2\), in an attempt to clarify some of the more fundamental issues of this pnictide parent compound. We show that the surface electronic of this compound is different from the bulk, due to the lack of a natural cleavage plane. However, the effect of the surface termination is likely to be only relevant for the top-most As and (half-closed) Ba layer, and of little influence on the near-\(E_F\), Fe 3d derived electronic states. Furthermore, we prove that there is little hybridization between the Fe 3d and As 4p occupied electronic states in the crucial energy region near-\(E_F\).

In Chapter 6, we focus on another pnictide parent compound, \(\text{EuFe}_2\text{As}_2\). We investigate the low temperature orthorhombic and anti-ferromagnetically (AFM) ordered phase of this system, which sets itself slightly apart from other \(M122\) (\(M=\text{Sr, Ba, Ca, }\ldots\)) compounds, as, besides the Fe moments, the Eu moments show an additional AFM ordering at low temperatures. By making use of variable light polarization and different photon energies, we show, with unprecedented clarity, that the large Fermi surfaces of this pnictide parent compound observed in the tetragonal high temperature phase, break up into small droplet-like Fermi surfaces in the AFM phase whereby the carrier density is suppressed to only a fraction of its original value. Our observations are in correspondence with optical conductivity and quantum oscillation studies.
Bibliography


A. Revcolevschi, and D. S. Dessau. Quasiparticle-like peaks, kinks, and electron-phonon coupling at the \((\pi, 0)\) regions in the CMR oxide \(La_{2-2x}Sr_{1+2x}Mn_2O_7\). Phys. Rev. Lett., 97, 056401 (2006).


[32] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono. Iron-based layered superconductor \(La(O_{1-x}F_x)FeAs\) (\(x=0.05-0.12\)) with \(T_c=26\) K. J.Am.Chem.Soc., 130, 3296 (2008).


[90] M. Kubota, H. Fujioka, K. Ohoyama, K. Hirotab, Y. Moritomod, H. Yoshizawa, and Y. Endohb. *Neutron scattering studies on magnetic structure of the double-layered manganite La$_{2-x}$Sr$_{1+2x}$Mn$_2$O$_7$ (0.3 < x < 1.0)*. J. Phys. Chem. Solids, 60, 1161 (1999).


Bibliography


NEDERLANDSE SAMENVATTING

Enkele van de heden ten dage meest bestudeerde fysische verschijnselen vinden hun oorsprong in de gezamenlijke interactie tussen de vele deeltjes (en dan met name de elektronen) waaruit het systeem is opgebouwd. Als een fysisch fenomeen niet een eigenschap is van de aparte deeltjes in een systeem, maar alleen van een verzameling van de deeltjes, dan wordt deze eigenschap emergent genoemd.

Hoewel dit misschien exotisch klinkt, zijn wij zelf een voorbeeld van een (biologisch) emergent systeem: het leven. Alleen de hele verzameling van water, eiwitten, vetten, DNA, suikers, zuren, ionen, etc. die een cel omvat maken het tot een levend systeem. Afzonderlijk is elk van deze bouwstenen slecht een levenloos object.

Twee van de meest bestudeerde fysische emergente systemen zijn materialen die hoge temperatuur en onconventionele supergeleiding (HTSC) en kolossale magneetweerstand (CMR) vertonen. Supergeleiding is het verlies van elektrische weerstand en treedt slechts voor bepaalde materialen op beneden een specifieke kritische temperatuur.

Supergeleiding is overigens een Nederlandse ontdekking: in 1911 nam Heike Kamerlingh Onnes in Leiden waar dat de weerstand van kwik beneden 4 K oneindig klein werd. Sindsdien is gebleken dat vele metalen, waaronder titanium, zink, aluminium, tin, wolfraam en lood (en verschillende legeringen) supergeleiders zijn, de meeste met een transitietemperatuur ver beneden de 10 K.

In 1986 werd er echter een grote groep stoffen ontdekt, die in sommige gevallen supergeleiding vertonen bij temperaturen boven de 100 K (!), terwijl de overgangstemperatuur ($T_c$) voor conventionele supergeleiders bijna nooit boven de 30 K ligt. Deze groep stoffen zijn opgebouwd uit lagen van koperoxide afgewisseld met andere tussenlagen en worden als geheel de cupraten genoemd. Deze ontdekking is bijzonder, ten eerste omdat koper zelf geen supergeleider is en ten tweede omdat deze materialen een gecompliceerde, gelaagde kristalstructuur hebben, in tegenstelling tot de doorgaans simpele metalen die tot de conventionele supergeleiders behoren.

In 2008 is een tweede groep hoge temperatuur supergeleiders ontdekt, ditmaal bestaande uit ijzer verbindingen. Wederom is ijzer zelf geen supergeleider. Sterker nog: ijzer is een ferromagneet en ferromagnetisme en supergeleiding sluiten elkaar meestal wederzijds uit. De materialen die in 2008 ontdekt zijn heten ijzer pnictides en stellen, samen met de bovengenoemde cupraten, de moderne wetenschap voor een aantal grote en belangrijke vragen: wat is het mechanisme achter deze hoge temperatuur supergeleiding en kunnen wij, als we dit mechanisme begrijpen, supergeleiders met een overgangstemperatuur in de buurt van kamertemperatuur ontwikkelen? Kamertemperatuur supergeleiding zou een technologische revolutie betekenen die zijn weerga niet kent.

Ook het CMR effect heeft zijn wortels in een grote verandering van de elektrische weerstand als een functie van temperatuur. Deze weerstandsverandering valt samen met een overgang van een paramagnetische naar een ferromagnetische toestand. Het
CMR effect behelst dat de overgangstemperatuur sterk beïnvloed kan worden door het aanleggen van een extern magnetisch veld: in sommige materialen kan een veld van een paar Tesla de transitie temperatuur ongeveer 100 K omhoog stuwen.

Het CMR effect is de overtreffende trap (in termen van weerstandsverandering) van het gigantische magneetweerstands effect (GMR). GMR is het fysische verschijnsel wat ten grondslag ligt aan het mechanisme om harddisks uit te lezen en wordt als zodanig op grote schaal toegepast in ons dagelijks leven. De ontdekkers van het GMR effect hebben hiervoor overigens in 2007 de Nobelprijs ontvangen.

Het CMR effect wordt voornamelijk bestudeerd in een specifieke groep materialen, de manganiëten. Dit zijn stoffen die allemaal gebaseerd zijn op mangaan dat in de kristalstructuur octaedrisch wordt omringd door zes zuurstof atomen.

Zoals gezegd vinden zowel HTSC als het CMR effect hun oorsprong in het collectieve gedrag van de vele elektronen, hun onderlinge interacties alsmede de interacties met het kristalrooster van de vaste stoffen die deze fenomenen tentoonspreiden. Het feit dat HTSC en CMR geworteld zijn in de intrinsieke veel-deeltjes eigenschappen van het systeem, maakt ze fundamenteel moeilijk om te begrijpen. Het mag dan ook geen verbazing wekken dat, ondanks een enorme verzameling experimenteel en theoretisch werk, het mechanisme achter deze twee fenomenen tot op de dag van vandaag niet volledig begrepen is.

Dit proefschrift is opgebouwd uit twee (min of meer) onafhankelijke delen, die de twee bovengenoemde fysische fenomenen behandelen. De twee delen worden hieronder in aparte secties samengevat. Het CMR effect wordt aangehaald in verband met de verbinding \( \text{La\,(2-2x)Sr\,(1+2x)MnO}_7 \), dubbellaags LSMO (of kortweg LSMO), een systeem dat al gedurende vele jaren in het middelpunt van de aandacht staat van de fysische gemeenschap die gecondenseerde materie bestudeert. Hoge temperatuur supergeleiding wordt niet direct behandeld, echter, er wordt wel een studie gepresenteerd naar de fundamentele elektronische eigenschappen die ten grondslag liggen aan de supergeleiding van de ijzer pnictides. De behandelde materialen in deze context zijn BaFe\(_2\)As\(_2\) en EuFe\(_2\)As\(_2\), zogenaamde moederverbindingen die supergeleidend gemaakt kunnen worden door kation substitutie (of drukverhoging). Een algemene aannames is dat hun fysische eigenschappen sterk verbonden zijn met de hoge temperatuur supergeleiding zelf.

Omdat deze fenomenen, HTSC en CMR, beide hun oorsprong vinden in de elektronische structuur, inclusief de veel-deeltjes interacties, van het betreffende materiaal, vergt hun bestudering een experimentele techniek die idealiter deze structuur direct kan meten. Zo een techniek is hoekopgeloste foto-emissie spectroscopie (ARPES).

Hoekopgeloste foto-emissie is een foton-in, electron-uit techniek. Door monochromatisch licht op een te onderzoeken materiaal te schijnen, worden elektronen vanuit de vaste stof in het vacuüem geëmitteerd. De snelheid en emissiehoek van de geëmitteerde elektronen zijn te meten. Deze twee grootheden zijn direct te linken aan de bindingsenergie en het kristalmoment van de elektronen in de vaste stof. Aangezien deze laatste twee grootheden de toestand van het elektron in het materiaal bijna volledig definiëren, is ARPES in staat om alle mogelijke informatie te verschaffen over de elektronische structuur van het te onderzoeken systeem.

\(^5\)Een derde relevante grootheid voor elektronen is hun spin. Het is ook mogelijk om een spinopgelost
ARPES is dus in staat de bandenstructuur van een één-kristal direct af te beelden. Ook de elektron-elektron en elektron-foon interacties en de mogelijke interacties tussen de elektronen en de collectieve excitaties van het spinsysteem kunnen ontsluisert worden met behulp van een foto-emissie experiment. Dit maakt ARPES de techniek om informatie in te winnen over fysische processen die gebaseerd zijn op elektroninteracties. Logischerwijs is ARPES de techniek van keuze voor het experimentele werk dat in dit proefschrift behandel wordt.

**Manganieten en kolossale magneetweerstand**

Het eerste deel van deze dissertatie is gewijd aan La\((2-2\times)\)Sr\((1+2\times)\)Mn\(_2\)O\(_7\): een dubbellaags manganiet die CMR laat zien in een smal gebied van het (magnetische) fasediagram (temperatuur tegen Sr dotering), waar tevens mettallisch gedrag waargenomen wordt bij lage temperaturen. Dit gebied komt overeen met een Sr dotering 0,30 < x < 0,50.

In de inleiding van de dissertatie worden de kristalstructuur en de relevante fysica van LSMO behandeld. Elektronentransport in dit materiaal (en de CMR manganieten in het algemeen) bij hoge temperaturen vindt, naar men aannemt, plaats middels het hoppen van polaronen. Dit is te wijten aan het grote kristalveld en de daarmee samenhangende Jahn-Teller deformatie van het kristalrooster, in samenspel met een grote waarde voor de Hund’s regel koppeling. Deze interacties leiden, via super exchange, tot een antiferromagnetische spin ordening, orbitaal ordening en tot een isolerend gedrag qua elektronentransport.

In geval van dotering krijgt LSMO een gemengd valentie karakter en kunnen de bovenstaande mechanismen in competitie geraken met een ferromagnetische dubbel exchange interactie, hetgeen leidt tot ladingsdragers in de vorm van fluctuerende, gecorreleerde polaronen. Dezen bezitten een zeer sterk toegenomen effectieve massa in vergelijking met het vrije elektron. Hoewel dit gedrag vrij goed te beschrijven lijkt in de isolerende, paramagnetische toestand bij hoge temperaturen, is het nog steeds niet bekend hoe de isolator-naar-metaal overgang in LSMO en aanverwante stoffen bewerkstelligd wordt als de temperatuur beneden de Curie temperatuur van het betreffende materiaal wordt gebracht. Tevens is de connectie met het CMR effect nog onbekend.

Deze onzekerheden gelden met name voor de elektronische structuur bij lage temperatuur. Er is heden ten dage veel discussie over de spectrale signatuur van een polaronische geleider (zoals dus LSMO) in een hoekopgelost foto-emissie experiment. ARPES metingen in het verleden op LSMO hebben een grote spreiding laten zien: van een materiaal met een pseudo-kloof, zonder spectraal gewicht aan het Fermi niveau tot een materiaal met een scherp gepiekt spectraal gewicht aan het Fermi niveau, ook wel quasi deeltjes (of QP-pieken) genoemd, op specifieke punten in k-ruimte. In Hoofdstuk 3 tonen we aan dat deze scherpe QP-pieken zelfs waargenomen kunnen worden bij alle k locaties op het Fermi oppervlak van dubbellaags LSMO. Echter, de temperatuur afhankelijkheid en de ontwikkeling als functie van Sr dotering van deze QP-pieken is hoogst ongebruikelijk en komt niet overeen met de fysische eigenschappen van de bulk van de betreffende LSMO één-kristallen.

In Hoofdstuk 4 presenteren we een gedetailleerde hoekgeïntegreerde foto-emissie
studie, gebruikmakend van harde Röntgen straling. Met deze metingen kunnen we aantonen dat fasescheiding niet voorkomt in LSMO bij temperaturen ver boven of onder de overgangstemperatuur en dat de ongewoonlijke eigenschappen van de QP-pieken dus niet met een dergelijk scenario verklaard kunnen worden. Deze studie laat tevens zien dat het oppervlakte en de bulk van LSMO in hoge mate overeenkomen in termen van dotering.

Additionele, gedetailleerde hoekopgeloste PES metingen laten zien dat het QP-gepiekte spectrale gewicht dicht bij het Fermi niveau eigenlijk afkomstig is van een fractie van het gehele breukoppervlak van het één-kristal. Dit feit, in combinatie met het ongewone gedrag van de QP-pieken, leidt tot de conclusie dat het QP-gepiekte, kloofloze, metallische Fermi oppervlak niet representatief is voor dubbellaags LSMO. In plaats daarvan is het afkomstig van inherent stapelfouten in de pseudo-pyroksietkristalstructuur van dubbellaags LSMO, die tot kleine inclusies leiden met een groter aantal opeenvolgende MnO2 vlakken. Dientengevolge hebben deze inclusies dus fysische eigenschappen die meer lijken op de driehoekige perovskietmanganieten.

Belangrijker is dat we daaruit kunnen afleiden dat de ware spectrale signatuur van dubbellaags LSMO die van een pseudo-gekloofd ‘slecht metaal’ is, dat nergens in k-ruimte scherp piekt en deel van het Fermi-niveau heeft. Deze observaties zijn in overeenstemming met optische spectroscopie studies en meer algemene beschouwingen vanuit het oogpunt van bulk transportmetingen. Bovendien geeft de interpretatie van het gepiekte spectrale gewicht aan $E_F$ een verklaring voor de inconsistenties tussen de meerderheid van de verschenen APRES studies op dit materiaal.

**IJzer Pnictides**

Het tweede deel van dit proefschrift heeft de elektronische structuur van de moeder-verbindingen van de recent ontdekte ijer pnictide supergeleiders als onderwerp. De ontdekking van supergeleiding in de pnictides (de stoffen zelf waren overigens al jaren bekend) in 2008 heeft geleid tot een enorme onderzoekseinspanning naar de synthese en de fysische eigenschappen van deze stoffen, zowel experimenteel als theoretisch. Omdat de pnictides een jong onderzoeksveld zijn, zijn veel van de fundamentele vraagstukken nog onbeantwoord. Het is bijvoorbeeld nog niet bekend hoe gecorreleerd het elektronensysteem van de pnictides is (hoewel het metallische karakter van de moederverbindingen laat zien dat de pnictides in ieder geval minder gecorreleerd zijn dan de andere grote familie van hoge temperatuur supergeleiders, de cupraten).

Ook de oorsprong van de antiferromagnetische ordening van de moeder- en laag gedoterde verbindingen wordt nog niet begrepen. Dit geldt ook voor hun bandenstructuur. Men zou zelfs kunnen beweren dat er nog steeds over de details van het generieke fase diagram van de pnictide familie gedebatteerd wordt: zaken als eerste versus tweede orde fase overgangen en de coëxistentie van supergeleiding en antiferromagnetisme verschillen sterk tussen de vele verscholen studies.

In Hoofdstuk 5 presenteren we hoekgeïntegreerde PES en Röntgen foto-emissie metingen aan BaFe$_2$Fe$_2$, om enkele van de meer fundamentele aspecten van deze verbinding op te helderen. We laten zien dat de elektronische structuur van de bulk en het oppervlakte verschillend zijn, wegens het ontbreken van een natuurlijk breukvlak in de kristalstructuur. Echter, het effect van de resulterende, afwijkende elektronische struc-
tuur aan het oppervlakte is alleen relevant voor de bovenste As en (halfgesloten) Ba lagen en heeft weinig tot geen effect op de Fe 3d toestanden dicht bij het Fermi niveau, zoals die waargenomen worden in een foto-emissie experiment. We laten ook zien dat de hybridisatie tussen de Fe 3d en As 4p toestanden minimaal is dicht bij het Fermi niveau.

In Hoofdstuk 6 verleggen we onze focus naar een andere moederverbinding, namelijk EuFe$_2$As$_2$. We onderzoeken de bij lage temperatuur orthorhombisch en antiferromagnetisch (AFM) geordende fase van dit materiaal, dat zichzelf onderscheid van de overige $M122 \ (M = \text{Sr, Ba, Ca, . . .})$ verbindingen doordat, behalve de ijzermomenten, ook de spinmomenten op Eu ordenen en wel op AFM wijze en bij 20 K. Door gebruik te maken van variabel polariseerbaar licht en verschillende fotonenergieën, laten we, met niet eerder vertoonde helderheid, zien dat de grote Fermi oppervlakken in de tetragonale hoge temperatuur fase van dit materiaal opbreken in kleine druppelvormige Fermi oppervlakten in de lage temperatuur fase. Hierbij wordt de vrije ladingsdragersdichtheid decimeerd tot een fractie van de oorspronkelijke waarde. Onze observaties zijn in overeenstemming met bevindingen uit optische conductiviteits- en quantumoscillatiestudies.
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