A tunneler’s view on correlated oxides and iron based superconductors
Massee, F.

Citation for published version (APA):
Massee, F. (2011). A tunneler’s view on correlated oxides and iron based superconductors Ipskamp drukkers

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Within the field of condensed matter physics many materials can be found that have complex, often exotic and usually not well understood properties. Aside from the drive to understand what brings about these properties, the prospect of putting such materials to use for applications is one of the main motivations to study them. The work described in this thesis is concentrated on two different families of such complex materials, namely the superconducting iron based pnictides and the colossal magnetoresistive manganese. Although the properties of these two families are rather different, comparisons can still be drawn between them. For instance, in both systems magnetism plays a crucial role and the interplay between the lattice and the electronic structure, although different in detail, is important in both cases. Unlike their famous cuprate cousins, an important part of the complexity both these quantum matter systems lies in their orbital degrees of freedom, whereby the frontier electronic states have two or more different 3d orbitals to choose from. The explicit role of - for example - orbital ordering has been clear in the manganites from the outset, while this realisation is currently growing in the iron pnictides. Interestingly, the crystal structure of the manganites is nearly identical to that of the cuprates, whereas many properties of these cuprates are, in turn, seen back in the pnictides. Therefore, even though this thesis is split into two seemingly independent parts, the underlying physics describing both emergent types of complex matter systems might in fact be very similar.

1.1 Iron based high temperature superconductivity

While trying to find a transparent oxide semi-conductor, H. Hosono and co-workers stumbled upon an iron based material with an unusually large superconducting transition temperature of 26 K [1]. Within a short period of time several different families of iron based materials were found with superconducting transition temper-
atures reaching as high as 55 K [2], well in excess of the originally predicted limit of ∼ 40 K for conventional superconductors [3]. These discoveries resulted in a world wide drive to study the origin of superconductivity in these iron based materials, partly in the hope it could add to the ongoing debate on the physics driving superconductivity in the well established family of high-\( T_c \) superconductors, the cuprates, but also from an applications point of view. For instance, although these newly discovered materials are, like the cuprates, layered, their anisotropy is generally much smaller, and the parent compounds are metallic. Moreover, as the pairing symmetry is now believed to be of s-wave character, grain boundaries will pose less of a problem than they are for instance for d-wave cuprate superconducting wires. Lastly, the mechanical properties are considerably advantageous over those of the cuprates as wires are for instance more easily drawn.

At the time of the discovery of the iron based superconductors, the main focus of the Ph.D. work presented here was the investigation of the colossal magnetoresistant manganites. However, when synthesis of the ‘122’ family of pnictides was achieved in our research group by Y. K. Huang, it was decided to also investigate the pnictides. At that time, only two preprints reporting scanning tunneling microscopy and spectroscopy (STM/S) measurements on pnictides existed, and the field was fresh and wide open: basically everything was uncharted territory. Having got up to speed with the STM/S system on the bilayered manganites - and after getting the machine up and running on typical calibration samples such as graphite, writing analysis programs and modifying the setup to increase its capabilities and effectiveness - the pnictides formed a welcome change of subject displaying a zoo of surface topographies and strongly varying superconducting gaps, all of which are discussed in the first four experimental chapters.

1.2 Colossal magnetoresistant manganites

Next to the high temperature superconductors, the colossal magnetoresistant manganites are one of the main thrusts of both theoretical and experimental investigations in complex hard condensed matter physics. Despite years of research, the physics underlying the colossal change in resistivity upon application of a magnetic field is not fully understood and remains a hot topic. For application purposes, this knowledge is essential for the tuning of the transition temperature and of the magnitude of the change in resistivity. The existence of coherent quasi-particle weight at the Fermi level seen with angle resolved photoemission (ARPES) on the bilayered material \( \text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7 \), despite evidence from bulk probes that this material is a poor metal at most, i.e. one with a relatively high resistivity, has started a lively discussion as to the origin of these truly metallic spectra, all the more since ongoing research within our research group found that only a very small portion of the sample surface displays such peaked spectra [6].

\footnote{although Refs. [4, 5] have shown that this limit is actually not a limit at all, it is still commonly seen as a special temperature for a \( T_c \) to exceed}
In an effort to elucidate the origin of these quasi-particle peaked regions and to find an explanation for the colossal magnetoresistive effect that is particularly strong in these bilayered manganites, the focus of this part of the Ph.D. research was to try and find such regions and determine their properties on the atomic scale using the newly installed scanning tunneling microscope. The first year and a half of the research presented in this thesis were therefore devoted to scanning surfaces of bilayered manganites with various doping concentrations. Combined with the ARPES investigations, a compelling explanation of the quasi-particle peaked areas and the ‘metallic’ bilayered manganites as a whole was found, which is presented in chapter 9.

1.3 Outline of this thesis

The first ‘real’ chapter of this thesis, chapter 2, introduces the technique of scanning tunneling microscopy and spectroscopy (STM/S), both from a theoretical and experimental point of view, and gives an introduction to low energy electron diffraction (LEED). To improve the readability of the chapter, details on the art of making tips, tip characterisation and a number of calibration measurements are given in the various appendices.

Having introduced the experimental setup, the main body of the thesis is divided into two parts. Part I describes the research done on the iron based superconductors, and Part II that on the bilayered manganite La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$.

The first chapter of part I, chapter 3 introduces superconductivity in general and the iron based pnictides in particular by giving a short overview of the existing literature on the subject. Chapter 4 then tackles an important part of any surface sensitive study: the cleavage surface of the ‘122’ pnictide family of materials. Before being able to make any statement about a material from its investigation with a surface sensitive technique such as STM/S or angle resolved photoemission (ARPES), one should know what the properties of the surface layer are and whether or not the presence of a surface affects the results obtained by the study. In this chapter a combination of temperature dependent STM, STS and LEED investigations on various ‘122’ pnictide systems demonstrate that cleavage of these systems occurs within the Ba layer, leaving half a Ba layer on each side of the cleave. This Ba layer is shown to be disordered or to be ordered into $(\sqrt{2} \times \sqrt{2})$ and $(2 \times 1)$ structures, all of which can cross over into one another. A considerable, non-reversible temperature dependence of the structures is furthermore observed. At the end of the chapter a simple model explaining the various surface appearances is presented.

Having thoroughly investigated the properties of the cleavage surface, chapter 5 describes the investigation of the electronic states of the optimally doped Ba122 compound, focusing in particular on the superconducting energy gap. In the first place, it is found that the electronic states as seen with STM are little affected by the details of the surface topology. Secondly, a large variation in the peak-to-peak separation, which is interpreted as the superconducting gap size, is found as a func-
tion of real space position. A correlation between the peak height, gap size and zero bias conductance is found in the system, similar to what is seen in the cuprates. As measurements on non-doped Ba122 show relatively small variation in zero bias conductance, the variation seen in the electronic properties of the superconductor are shown to be connected to the superconducting state and not the material in general. The size of the normalised gap is shown to be well beyond the BCS s- and d- wave values, suggesting an unconventional mechanism of superconductivity. By examining the autocorrelation traces of gap maps, the length scales of the variation in gap magnitude are seen to be on the order of the Co-Co separation, hinting at a connection between these two.

The observation of a large spatial variation in peak-to-peak separation in the tunneling spectra discussed in chapter 5 are very reminiscent of the cuprate systems, where similar variations have been observed, which turned out to be related to a pseudogap rather than the superconducting gap. In order to see whether in the pnictides this variation is also related to a pseudogap that does not close at $T_c$, temperature dependent measurements of the superconducting gap have been performed for various doping concentrations. It is shown that the observed gaps all close at $T_c$, ruling out a pseudogap and assigning the peak-to-peak separation to the superconducting gap.

In chapter 7, the origin of the large variation in superconducting gap size is further investigated by a detailed doping dependent study and measurements on differently doped Ba122 materials.

Part II of this thesis describes the STM/S investigations performed on the bilayered colossal magnetoresistant manganite $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, which was the original subject of this Ph.D. research. Various doping concentrations of this manganite material were investigated using STM/S, at the same time as detailed ARPES investigations were performed on identical crystals during numerous visits to large scale light source facilities in Berlin and Villigen (CH). After introducing the manganite family of materials and in particular the bilayered manganite $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ in chapter 8, the last chapter will discuss these STM/S investigations, which taken together with ARPES form the basis of a compelling description of the manganites and their colossal magnetoresistant effect in terms of polaronic conduction close to a metallic breakdown, contrary to the commonly adopted picture of a double exchange driven metal to insulator transition.

This thesis describes the first Ph.D. research at the van der Waals Zeeman Institute performed with a Createc ultra high vacuum, low temperature scanning tunneling microscope. To benchmark the system, measurements on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and $\text{Pb}_x\text{Bi}_{2-2x}\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ which have been intensively studied in the literature, have been performed, which are discussed in appendix A. It will be shown that with the commercially available setup used it is possible to obtain not only high resolution topographic images, but also spatial maps of the energy gap over large fields of view as well as maps of the local density of states at energies that show quasi-particle interference scattering patterns. Following the literature on
these two systems closely, all these different types of measurement and their analysis will be presented.

As considerable time in this research has been devoted to the art of making one of the crucial elements in tunneling microscopy, the tip, appendix B reviews various methods used to produce both tungsten and platinum-iridium tips and the characterisation thereof on a Au(788) sample. Adaptations to the setup to incorporate in situ oxide removal of tips and to have a higher measurement efficiency will also be discussed.

Appendix C will discuss the calibration of the temperature of the STM, using a thermometer in the place of a sample holder in the STM and by temperature dependent measurements on the BCS superconductor Nb. Experimental and thermal broadening of the spectra will be discussed in detail, which are relevant in the discussion of the temperature dependence of the pnictide superconductor data presented in chapter 6.

The resolution of any STM is mainly limited by noise, both electromagnetic and vibrational. Appendix D will therefore discuss the detection and reduction of noise in the setup and will give an overview of the noise present in the system used and its effect on the resolution.

In the last appendix (E), the software written throughout this research will be briefly discussed, focusing on the routines used to load data saved by the Createc measurement software into the analysis program Igor. It should be noted that this appendix is rather specific and therefore less of general interest, most probably being of more use to following generations of STM practitioners in Amsterdam than to for instance members of the Ph.D. committee. It is (like the other appendices) not required for a full understanding of the work described in this thesis. The algorithm used to construct gap maps will be described and the appendix will close with a section on various parameters used throughout this work on different systems (setup currents, modulation frequencies, approach settings, etc.).