Visualizing strongly-correlated electrons with a novel scanning tunneling microscope

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Introduction

1.1 Studying correlated electrons with a scanning tunneling microscope

Modern solid-state physics successfully describes the electronic properties of many solids within the framework of band theory [1]. Its most surprising aspect is the assumption that the interactions between the valence electrons are negligible, despite them carrying charge and therefore being subject to Coulomb repulsion. Many electronic and thermal properties of conventional materials can, indeed, be described in this independent-electron approximation, where the electron interactions are treated as a perturbation of the single-electron properties. These concepts are the foundation of Landau's Fermi-liquid theory. In this theory, the electronic properties of materials are described by single particle-like excitations that are called *quasiparticles*. Quasiparticles can be considered as electron-like particles that have renormalized properties, such as their mass, in order to take the interactions into account [2].

There are materials, however, where the Coulomb interaction between electrons is so strong that it cannot be treated by Landau's theory. These materials go under the name of *strongly-correlated electron systems*. The Fermi-liquid description fails to reproduce their physical properties, because the picture of independent quasiparticles does not hold any longer. These systems are characterized by emerging collective behavior that cannot be simply described by adding single-particle excitations. To quote P.W. Anderson: 'More is different' [3]. Strongly-correlated electrons are found

in a variety of materials, and are responsible for some of the most intriguing phenomena in condensed-matter physics, including high-temperature superconductivity, Mott physics and quantum criticality.

The field of correlated-electron systems has been initially driven by the experimental discovery of a number of novel, engineered materials. In the last thirty years, progress in material science has facilitated the growth of better crystals, and improvement of scientific instrumentation has brought to the acquisition of data with ever-increasing quality. We believe that these advances, combined with the efforts in the development of new theoretical techniques, are key to understand the emergent collective properties of quantum materials.

Among the experimental techniques that are used to study strongly-correlated electron systems, spectroscopic-imaging scanning tunneling microscopy (SI-STM) stands out for its ability to resolve electronic inhomogeneities at the atomic scale [4]. The power of SI-STM lies in its ability to directly measure the local density of states (LDOS) of the sample with very high energy and spatial resolution. This allows, for instance, the visualization of the effect of a single impurity atom on the electronic structure. This (otherwise unattainable) resolution achieved by STM is particularly important in the study of strongly-correlated electron systems, that are often characterized by nanoscale inhomogeneities in the electronic structure.

In the last twenty years, SI-STM has proven to be very successful in the study of correlated-electron systems. However, performing SI-STM experiments is technically challenging: most prominently, the technique is extremely sensitive to external vibrations, that easily impact the data quality and bury important features in the noise. For this reason, specially designed equipment is required to achieve good data quality.

This thesis discusses our contribution to the progress of the field of strongly correlated-electron systems in two main areas. The first is the construction of a new, home-built, cryogenic STM that is stiffer than any other reported in literature to date (where stiffness directly implies high stability against vibrational noise and thus better data quality). The second is the study of the physics of lightly doped Mott insulators, a prototypical example of how strong electron-electron correlations give rise to unusual phases of matter.

In the remainder of this introduction, we first give a general overview to the physics of Mott insulators, and then briefly review cuprate high-temperature superconductors, as an example of the exotic phases of matter that appear upon doping a Mott insulator (Sec. 1.2). This allows us to introduce several concepts that will be used throughout this thesis. Finally, in Sec. 1.3, we give an outline of the thesis.

1.2 From Mott insulators to high-T_c superconductors

Mott insulators are the simplest example of the effect of strong electron-electron correlations. Band theory fails to describe them, predicting that they would be metallic. Their theoretical description, however, is very simple once electron-electron repulsion is taken into account. It was first proposed by Nevill Mott as follows [5–7]: consider a lattice model as illustrated in Fig. 1.1a, with a single orbital per atom and one electron on each site (half filling). When the electrons move through the lattice with (hopping) kinetic energy t[1], some sites occasionally become doubly occupied. This is opposed by the on-site Coulomb repulsion U. If $U \gg t$, the hopping of the electrons from site to site is energetically suppressed. Electrons then localize on the atomic sites, and the material becomes insulating simply because the electrons can not move. They can be thought of as frozen at their atomic locations. Even if the electrons are localized, their spins are in principle still free to point in all possible directions. However, their interaction energy is minimized when they are either in parallel or antiparallel configuration. By considering virtual hopping processes, it is shown that they organize in an antiferromagnetic ground state [7].

From a different point of view, one can see how 'switching on' the Coulomb interaction affects the density of states [8]. This is schematically illustrated in Fig. 1.1b. For $U = 0$, i.e. without electron-electron correlations, a single band of width W forms from the overlap of the atomic orbitals; with single occupancy of each site, the system is metallic. The bandwidth W can be obtained from tight-binding calculations as $W =$

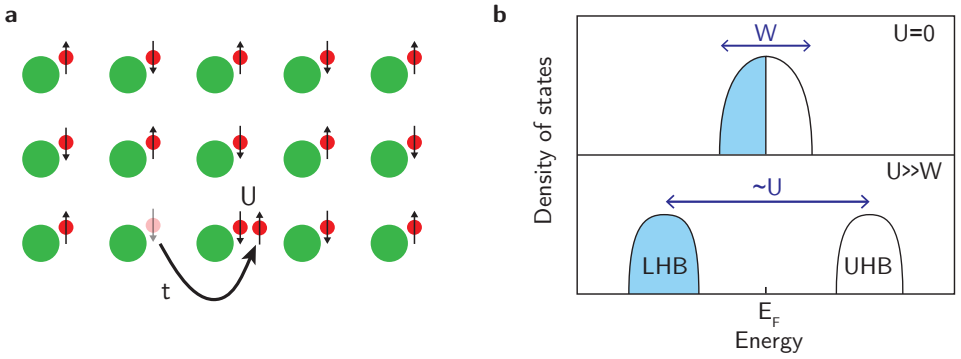

Figure 1.1: **a**, Cartoon picture of a Mott insulator. The kinetic hopping energy t competes with the on-site Coulomb repulsion U. **b**, Schematic illustration of the opening of the Mott gap, with the formation of a filled lower Hubbard band (LHB) and an empty upper Hubbard band (UHB); adapted from Ref. [8].

[1]Here, t represents the hopping matrix elements as defined in standard tight-binding models, and it contains the kinetic energy associated with the motion through the lattice.

$2zt$, where t represents the hopping matrix elements and z is the number of nearest neighbors, e.g., z=2 in one dimension, z=4 in a square lattice. The bandwidth is therefore related to the kinetic energy of the electrons. If $U \gg W$, a gap opens around the Fermi level, with the creation of two subbands. The lower band represents states with singly-occupied sites, while the upper band corresponds to states with doubly-occupied sites. These bands are called lower and upper Hubbard bands, respectively. Note how different this is from a band insulator or a semiconductor: instead of an energy gap determined by the periodic potential of the crystal lattice, we now have a gap that is entirely due to electron correlations.

But which materials are most likely to be Mott insulators? In other words, what governs the relation between U and W, and what are typical values in real materials? In a solid, the atoms are close together: the closer the atomic orbitals are to each other, the more the hopping term t (and therefore the bandwidth W) increases. At the same time, the bare Coulomb interaction U gets screened and becomes smaller. Transition metal oxides with $3d$ valence electrons are very good candidates to become Mott insulators, with a relatively narrow bandwidth ($W \approx 1 - 3\,\mathrm{eV}$) and large Coulomb interaction ($U \approx 5$ eV). Indeed, some of the vanadates, nickelates, cobaltates, and, most prominently, cuprates, are found to be Mott insulators. When moving in the periodic table towards the more spatially extended orbitals of $4d$ and $5d$ transition metal oxides, the bandwidth increases and the electron correlations are reduced. As we show in chapter 6, the $4d$-transition metal oxide rhodate Sr_2RhO_4 is a correlated metal that can almost perfectly be described by Fermi-liquid theory. With increasing atomic numbers, however, other quantities become relevant, in particular spin-orbit coupling. We will show in chapter 4 that indeed the interplay of bandwidth, Coulomb interaction and spin-orbit coupling can cause the $5d$-transition metal oxide iridate Sr_2IrO_4 to be a Mott insulator, even if Coulomb interactions for $5d$ transition metal oxides are strongly reduced and the bandwidths are larger.

The physics of Mott insulators as discussed thus far is well understood within the framework of the Hubbard model, and can be described by the Mott-Hubbard Hamiltonian:

$$H(t,U) = -t \sum_{<i,j>} c^{\dagger}_{i\sigma} c_{j\sigma} + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow} \tag{1.1}$$

where $< i, j >$ indicates the sum over nearest neighbors, $c^{\dagger}_{i\sigma}(c_{i\sigma})$ creates (annihilates) an electron with spin σ on a lattice site i, and $n_{i\sigma} = c^{\dagger}_{i\sigma} c_{i\sigma}$ is the number operator. The model considers only electrons in a single band. Despite this being a considerable simplification, low-energy properties of several real systems are well-described by this model, because typically only a small number of bands (sometimes just one) are crossing the Fermi level [6].

If the description of a Mott insulator is relatively simple and successful, the situation becomes more complicated very quickly once one moves away from the Mott insulating state. This can happen by tuning external parameters like pressure, temperature or insertion of extra carriers (doping) [6, 9]. Due to the strong electron correlations, small changes of these external parameters strongly influence the properties of the system, giving rise to fascinating, emergent, collective behaviors and complex phase diagrams.

One of the most interesting and studied phases emerging from doped Mott insulators is unconventional, high-temperature superconductivity. In the remainder of this section, we will focus on cuprates, copper-oxide-based high-T_c superconductors, and we will give a description of their phase diagram.

Cuprates are a family of layered materials with perovskite crystal structure, characterized by the presence of CuO_2 planes. Since the discovery of high-temperature superconductivity in 1986[2], the chemical composition of cuprates has been tuned until reaching $T_c = 135\,\mathrm{K}$ [11]. Typically, their unit cells are large and complex, containing heavy elements such as Bi, Hg, and Ba.

In the parent state, without the insertion of extra carriers, the copper atoms are in the Cu^{2+} $3d^9$ configuration with half-filled $d_{x^2-y^2}$ orbitals. They are typical Mott insulators, with the localized spins arranged in an antiferromagnetic ground state. When doped with extra carriers[3], they show a wide number of different behaviors, as illustrated in the phase diagram in Fig. 1.2. Importantly, the strong Coulomb repulsion, that causes the parent compound to be a Mott insulator, keeps being the dominant interaction, also in the doped compound. The electrons are thus strongly correlated even in the phases that appear upon doping, and Fermi-liquid theory is unable to describe them. Understanding the cuprates phase diagram indeed remains one of the biggest open problems in condensed-matter physics [11].

We will now give a very brief overview of the electronic phases that are encountered in the phase diagram. We mainly follow Ref. [11], and, as a conclusion, emphasize the main contributions that the use of scanning tunneling microscopy has given to the field.

High-T_c superconductivity emerges at low temperatures upon doping, and spans a dome-shaped area around the so-called optimal doping level, where the highest T_c is achieved. The electron-pair wave function (also called order parameter) has d-wave symmetry, making it an unconventional superconductor — opposed to conventional

[2]High-T_c superconductivity was first found in $La_{2-x}Ba_xCuO_4$ ($T_c \approx 30\,\mathrm{K}$) by Bednorz and Müller [10], who were awarded the Nobel prize for the discovery in 1987.

[3]The highest T_c and the most interesting electronic phases are observed upon hole-doping. The effects of electron-doping cuprates have also been studied (see Ref. [12] for a review); here, we focus on hole-doped cuprates.

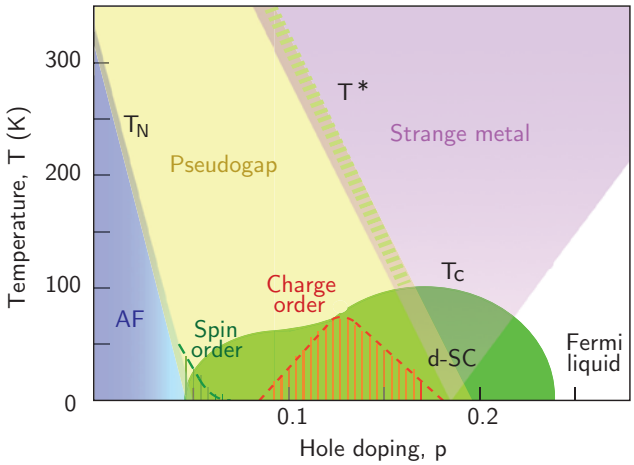

Figure 1.2: Phase diagram of cuprates, as a function of hole doping and temperature. Adapted from Ref. [11].

BCS superconductors, where the superconducting wave function has s-wave symmetry. This causes the superconducting gap to be anisotropic in momentum space.

When the temperature is raised, a variety of exotic electronic behaviors emerge, most of which are not yet fully understood. At low doping and high temperature, a very mysterious phase appear at the threshold indicated by T^*. It is called the *pseudogap* phase, because it is characterized by a depletion of the density of states close to the Fermi level, measured by several experimental techniques. Its origin is still under debate; one hypothesis is that at T^* electron pairs already start to form, however the superconducting order is suppressed by phase fluctuations. Between the pseudogap and the superconducting phase, at relatively low temperatures, a series of *intertwined orders* appear [13]. Their origin can be ascribed to the short-range antiferromagnetic correlations inherited from the Mott state, and they are believed to compete with superconductivity.

At high temperature, around optimal doping, cuprates enter the so-called *strange metal* phase. The name is due to the fact that the transport properties are remarkably different from the ones of 'normal' metals. The most striking example is the behavior of the resistivity ρ as a function of temperature: while in a normal Fermi liquid ρ grows quadratically with temperature and finally saturates according to the Mott-Joffe-Regel criterion[4], in cuprates $\rho \propto T$, and this behavior persists up to very high temperature. The strange metal phase has been proposed to be related to quan-

[4]The Mott-Joffe-Regel criterion puts a lower limit to the conductivity of metals, corresponding to a minimum mean free path equal to the lattice constant. This, in turn, puts an upper limit to the resistivity [14].

tum criticality emerging from the presence of a quantum critical point under the superconducting dome near optimal doping. This would imply the absence of quasiparticle excitations in this phase of matter.

Scanning tunneling microscopy greatly contributed to the understanding of the phase diagram of the cuprates, and allowed, among others, the visualization of nanoscale electronic disorder [15–17], the determination of the superconducting gap structure by quasiparticle interference [18], and the imaging of local symmetry breaking in the pseudogap phase [19, 20]. In the present work, we use STM to elucidate the transition between the Mott insulating state and the pseudogap phase for the iridate Sr_2IrO_4, that we find has striking similarities to the cuprates.

1.3 Outline of this thesis

In this thesis we aim to better understand correlated electron systems using spectroscopic-imaging STM. To this end, we both develop new scientific instrumentation and study correlated electron systems with an emphasis on lightly doped Mott insulators. The thesis is organized as follows.

Chapter 2 gives an introduction to the experimental technique of spectroscopic-imaging scanning tunneling microscopy and to the interpretation of its data.

Chapter 3 describes the design, construction and performance of our newly built ultra-stable scanning tunneling microscope, which we called *Dome*[5]. The microscope is the stiffest against external vibration reported to date, which makes it particularly suited to study quasiparticle interference. It lead to the experimental results presented in chapter 6.

Chapters 4 and 5 are dedicated to the study of lightly doped Mott insulators. The measurements have been performed with a commercial STM, in parallel to the construction phases of the home-built microscope. In chapter 4, we investigate the melting of the Mott state upon the addition of extra carriers in the Mott insulator Sr_2IrO_4. We show the appearance, at sufficient doping, of a pseudogap phase and of emergent order, and we are able to precisely elucidate how this state develops from the Mott insulating phase. In chapter 5, we focus on the special situation that is encountered when STM experiments are performed on materials with poor electronic screening. Our motivation stems from the results of chapter 4, where, at very low doping levels, we find discrepancies with other experimental techniques. Here, we develop a model that explains our results and reconciles them with literature.

[5]Referring, among other things, to the superconducting dome of unconventional superconductors.

Chapter 6 shows quasiparticle interference measurements on the correlated metal Sr_2RhO_4, which is an example of a 2D Fermi liquid. These are the first measurements that we perform with the home-built STM described in chapter 3.

Finally, chapter 7 gives some concluding thoughts and an outlook of the possible measurements that can be performed with the microscope *Dome* in the near future.