Probing quantum materials with novel scanning tunneling microscopy techniques

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Introduction

In this thesis we will deal with the quantum matter realized in electron systems in the structural arrangements of atoms that form a solid. This may sound as a cryptic sentence at first look, but it connects some basic ingredients that form the starting point for this dissertation; it contains the notion that the *electronic* phase and the *structural* phase of a material can be viewed as two distinct properties, which, remarkably, do not need to be the same states of matter. This can be illustrated by the following example: Say you would be asked to think of an electrically conducting material, probably the first thing that comes to mind is a *solid* material, probably a metal. A structural solid is characterized by a close packing of the constituent particles (atoms), and, in the example of a metal, this packing of atoms is regularly ordered in a repeating pattern which gives it its stability and definite shape and volume. In such a solid, because of the rigid (crystalline) arrangement, the constituent particles cannot move freely throughout the material; the constituent particles don't flow. But what about the electronic phase of this material? Each atom in the material brings a set of electrons. If these constituent particles of the electron system would also be rigidly arranged the system would act like a solid; the electrons would not be able to move through the material, as in an electronic insulator. However, in a conducting material the electrons are mobile and thus its electronic phase cannot be equivalent to a solid. As it turns out, we describe the electronic phase of most simple metals by a *gas* or *liquid* phase, which allows us to reproduce many of is electronic properties reasonably well [1, 2].

Using Landau's theory of electronic liquids we can describe the electronic properties

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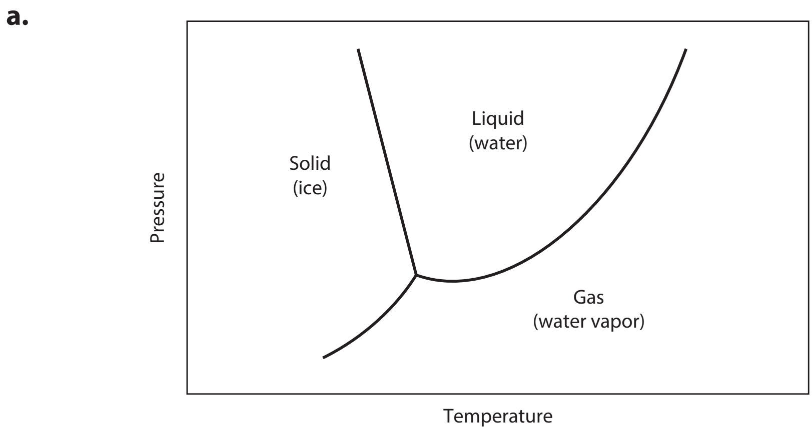

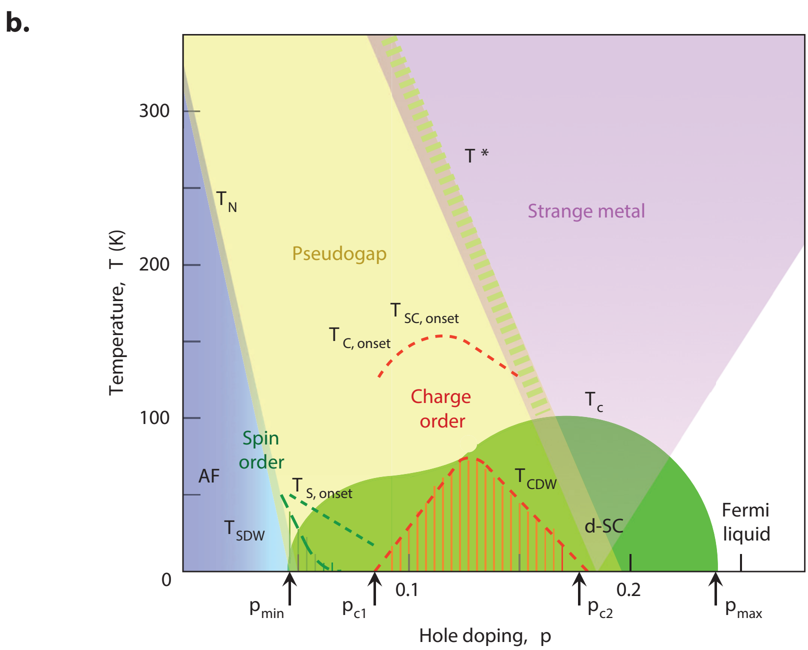

Figure 1.1: **Phase diagrams. a.** A typical phase diagram of a simple single substance (for example water). In the temperature - pressure plane, the phase-equilibrium lines separate the three different types of phases. In this case: solid, liquid and gas. **b.** Electronic phase diagram of the cuprate high-temperature superconductor, where as function of temperature and carrier doping the various different electronic phases are shown, presented in a similar fashion as the structural phase diagram of a simple substance (a.). Figure reproduced from Keimer *et al.* [3].

of most simple metals by a non-interacting single-particle picture. But what about materials where the interactions between the particles become so strong that the simple single-particle description starts to fail? Now we enter the realm of the *quantum materials*. Here the independent single-electron picture breaks down since the constituent electronic particles start to notice and influence each other, becoming so-called *strongly correlated*. The collective behavior of all the electrons will start to dictate the general electronic properties of the material. Out of this microscopic strongly correlated electron soup, macroscopic properties can emerge that are quantum mechanical of nature. Superconductivity might be the prime example, where pairing of the electrons induces a new state of matter which can be described by a single macroscopic quantum mechanical wave function. It are not only the strong electronic correlations that that can lead to the emergence of complex macroscopic states, making quantum materials stand out from ordinary matter. Such complex electronic states can also require other ingredients such as topological order or quantum criticality, bringing 'quantum' in the material.

The most well studied quantum materials to date are arguably the copper oxide (*cuprate*) high-temperature superconductors. Their rich phase diagram shown in figure 1.1 illustrates the wild zoo of different electronic phases found in these materials. However, despite the large number of experimental and theoretical effort, our contemporary understanding of the microscopic details of these copper oxides still fails to reproduce their emerging macroscopic features and electronic states [3]. For several decades now, the field of condensed matter physics is challenged to understand these emerging states of matter, as well as their driving forces. Interestingly though, the interplay between the electronic and structural phases seems to play an important role. Therefore, in this thesis, in our personal search for understanding, we will employ an experimental technique that can visualize the electronic and structural phases of a material, simultaneously, on the atomic level. We will build upon the existing experimental foundations and add new tools that will allow us to explore the uncharted territory of quantum matter in strongly correlated electron systems.

In the following sections we will introduce a scanning probe technique that will form the point of departure for the work presented in this thesis. We will take this local probe and dress it up with two novel tools, to be able to investigate the relevant quantum mechanical degrees of freedom in strongly correlated quantum matter. After a brief introduction of the scanning probe, we will introduce the concepts of *noise* and *Josephson* scanning tunneling microscopy, followed by a further outline of this thesis.

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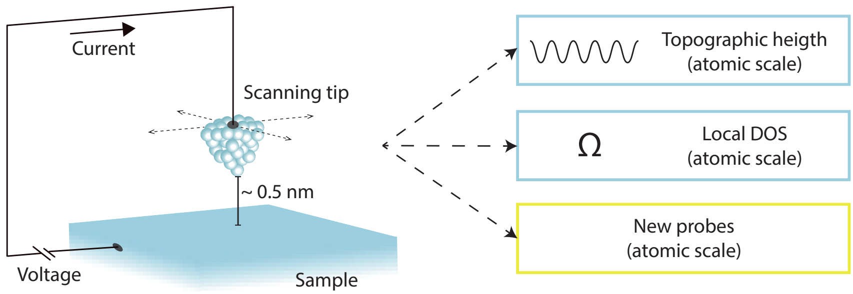

Figure 1.2: **Scanning Tunneling Microscopy (STM).** A schematic picture to illustrate the experimental setup of STM. An atomically sharp scanning tip is brought in the close vicinity of the sample under investigation (also atomically flat). Applying a bias voltage over the tip-sample junctions results in a measurable tunneling current. This is used to obtain topographic and spectroscopic (local density of states (DOS)) information about the sample. In this thesis we will add two new ingredients by introducing new probes.

1.1. A SCANNING TIP TO EXPLORE QUANTUM MATTER

A scanning tunneling microscope (STM), illustrated in figure 1.2, is an instrument that is designed to visualize the surface of a material on the atomic level. It has established itself as one of the powerful experimental tools to investigate strongly correlated quantum matter. This is, for a large part, due to the fact that STM can spatially resolve the structural and electronic phases with atomic-scale precision. In the following paragraphs we will briefly discuss the basic principles of STM. For all further details we refer to some excellent descriptions elsewhere, see references [4, 5].

STM is based on the concept of quantum tunneling. An (atomically) sharp metallic tip (scanning tip in figure 1.2) is brought in the close vicinity of the clean and atomically flat sample surface. Tip and sample are separated by a thin vacuum barrier (typical tunneling distance ~ 0.5 nm). When a bias voltage is applied over the tip-sample junction, electrons are allowed to tunnel through the vacuum barrier, generating a tunneling current (typically in the pA to nA range) which scales exponentially with the tip-sample separation distance. The tip can be scanned over the sample surface while employing a feedback loop that keeps the tunneling current constant by adjusting the tip-sample separation distance. By measuring the vertical position of the tip while scanning over the sample surface a topographic height image of the surface is made with atomic-scale resolution, allowing for visualization of crystalline atomic structure of the sample. Later on we will refer to such an image as 'topograph'.

The true power of using STM for investigating quantum matter lies in the combination of performing topographic and spectroscopic measurements in the same field of view, both with atomic scale resolution. This allowed for example for the visualization of charge order in cuprate high-temperature superconductors [6–8] and its nanoscale electronic disorder [9–11]. Also it shed light on Cooper pairing in heavy fermion systems [12, 13] and the nematic electronic structure in an iron-based superconductor [14, 15]. Spatially resolving the electronic structure is done by measuring the local density of states as function of energy (local DOS in figure 1.2), while scanning the tip over the sample surface. The tip is stopped at an equally spaced grid of points to measure the differential conductance (dI/dV) in a set energy window. In this way a three-dimensional dataset is constructed by registering the local density of states as function of spatial coordinates and energy, providing a measure on a broad set of electronic properties of the sample.

We will build on these foundations of STM as a powerful probe to investigate quantum matter. We are challenged by the idea that the decisive information needed to explain most of the complex physical phenomena observed in the phase diagram of quantum matter (see i.e. the phase diagram in figure 1.1) is still missing. Therefore this thesis is devoted to adding new experimental tools to the STM toolset, in order to access physical parameters that are not accessible yet. Our motivation for both new tools will be discussed in the following two sections. Later in this thesis we will develop these techniques and employ them on quantum matter, in order to shed light on (new) physical phenomena, trying to bring us one step closer to decoding the microscopic nature of the phase diagram of quantum materials.

1.2. THE NOISE AS THE SIGNAL

"The noise is the signal." These words by Rolf Landauer are the inspiration for the first new technique we will introduce in this thesis. What Landauer meant was that fluctuations in time of a measurement can be a source of information that is not present in the time-averaged value [16]. What does this mean for the tunneling current between the STM tip and the sample? The basic flow of electrons between the two leads is a purely Poissonian process, meaning that the electrons are completely uncorrelated (they don't influence each other) and transfer at random moments in time between both electrodes. The net amount of charge that these electrons transfer per unit time is what we generally consider as the (time-averaged) magnitude of the current. The deviation from this mean value is what we usually call the *noise*, as illustrated in figure 1.3.

The current noise in a tunnel junction originates from the fact that the flow of charge carriers is discrete (it consists of small packages of charge: electrons)[17]. Since it is the quantized nature of the tunneling current itself that gives rise to the noise, it is also linked to electron-electron correlations and other dynamical charge phenomena. Imagine one would be able to probe the magnitude of these electronic correlations and visualize it on the atomic scale. One could apply it to quantum matter,

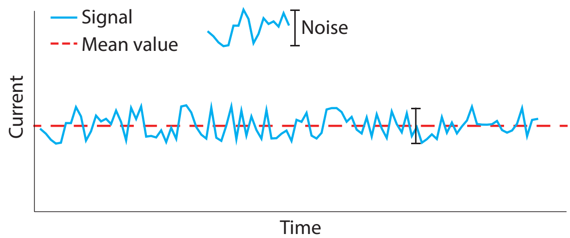

Figure 1.3: **Illustration of 'signal' and 'noise' in a current-time trace.** The tunneling current flowing through the tip-sample junction is the 'signal'. In conventional STM a time averaged value of the tunneling current is measured, here indicated by the red dashed line 'mean'. In this thesis we will improve the temporal resolution of STM in order to also measure the 'noise'.

where the strong electron correlations make up the collective electronic behavior, with the aim to investigate how these electronic correlations make up the emerging states of matter. Unfortunately, one of the main limitations of STM is that the time resolution of the measurement is limited due to the technical details of the experimental setup (which will be discussed in detail later in this thesis), allowing only the measurement of the time-averaged value of the tunneling current (red dashed line in figure 1.3). This prevented quantification the local noise in a scanning tunneling setup up till now. In this thesis we will overcome this limitation and present spatially resolved noise measurements.

In order to add atomic-scale spectroscopic noise measurements to the STM toolbox, we will build on pioneering experiments in STM [18, 19] and high precision quantum transport technologies [20] to tailor the scanning tip into a device that measures the local noise associated with the tunneling current. In this thesis we will discuss this development and unleash it on quantum matter.

1.3. PROBING THE CONDENSATE

The second new technique we will utilize is based on the *Josephson* effect [21]. By using a superconducting STM tip and bringing it in tunneling contact with a superconducting sample, we couple two superconducting macroscopic objects through a thin insulating vacuum barrier, creating a scannable Josephson junction. The tunneling current can now be carried by Cooper pairs, rather than quasiparticles carrying single electron charge, granting direct access to both superconducting condensates.

We will keep the further details of this technique for the later chapters in this thesis, but already we would like to point out the advantage of Josephson STM. While (conventional) STM is a widely used and powerful technique to investigate the superconducting phase of a material, it remarkably doesn't probe the superconducting state directly. Instead it only accesses the single-particle channel, where Bogoliubov quasiparticles with energies larger than the pair-breaking gap transport the charge. Although this already provides an insight into the superconducting phase, we would also like to get access to the Cooper pair channel. Pioneering work by the group of Dynes guides the route of how this should be approached experimentally [22–24]. Recently the first atomic-resolution Josephson experiment on a conventional superconductor [25] and first visualization of an unconventional high-temperature superfluid [26] were reported.

We will take the next step and for the first time visualize the superfluid of an unconventional high-temperature superconductor with atomic-resolution by spatially resolving the Josephson current, while simultaneously also registering the topographic and single-particle electronic properties.

1.4. OUTLINE OF THIS THESIS

In this thesis we will introduce new techniques for scanning tunneling microscopy and use them to reveal uncharted physical phenomena and insights in various quantum materials. The thesis is further organized as follows.

In *chapter 2* we discuss the development, build-up and testing of a novel amplification circuit to measure the tunneling current in the MHz regime, in order to uncover the *shot noise* caused by the tunneling electrons. We demonstrate the unique performance of our amplifier by spatially mapping the noise on a Au(111) surface with atomic resolution in the giga-Ohm regime. We also show differential conductance measurements at 3 MHz, which yields superior performance over the conventional STM spectroscopy techniques.

In *chapter 3* we utilize this newly developed scanning *noise* spectroscopy technique to elucidate the properties of the atomically thin insulating layers in a cuprate high-temperature superconductor. We discover atomic-scale noise centers that exhibit MHz current fluctuations up to 40 times the of the expected noise, which we can attribute to trapping of charge. The results presented in this chapter provide a new picture of how these materials should be looked at: an atomic stacking of atomically thin metallic layers separated by polarizable insulators withing a three-dimensional superconducting state.

In *chapter 4* we combine the scanning *noise* technique with a *Josephson* STM. We image the current noise with atomic resolution on a superconducting Pb(111) surface using a superconducting Pb STM tip. By measuring the current noise as function of applied bias, we reveal the change from single electron tunneling above the superconducting gap energy to double electron charge transfer below the superconducting gap energy, and we spatially map this noise doubling over the sample surface.

In *chapter 5* we use atomic-resolution *Josephson* scanning tunneling microscopy to reveal a strongly spatially imhomogeneous superfluid in an iron-based superconductor. By simultaneously measuring the topographic and electronic properties we find that this inhomogeneity in the superfluid is correlated with the coherence of the quasiparticles (electrons / holes) meaning that superconductivity appears to be needed for coherent quasiparticles, locally on the length scale of Cooper pairing.

In *chapter 6* we visualize the electronic properties of an *iridate* sample while crossing the phase transition from a solid electronic phase (Mott state), melting into the so-called pseudogap phase. We show that when extra charge carriers are added into the material a phase-separated state appears along with emergent electronic order and we are able to precisely decode how this state develops from the Mott insulating state. While the material is chemically very different, the phenomena we observe are very similar to that observed in the cuprate high-temperature superconductors. Therefor we attribute them as generic features of doped Mott insulators, disregarding their chemical make-up.

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