Of spin and charge in the cuprates
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Chapter 1

Introduction

1.1 Magnetism, Superconductivity, and Correlated Electrons

Magnetism and superconductivity have very different histories. Magnetic phenomena have been known for a few thousand years [1, 2], and it is easy to imagine how fascinating the properties of lodestone must have been to our ancestors. The influence of magnetism on human thought and history can thus not be underrated. Thales for example ascribed magnetism to an attractive “soul” in the lodestone. A similar idea might have inspired the so called animal magnetism or mesmerism, which dealt with the healing powers of hypnosis in the 18th century: it was believed that the mesmerist “magnetized” his patient just as a magnet “influences” his surroundings. An early application of magnetism with a major impact on human life on earth was the compass, which is reported at least as early as the 12th century, perhaps dating back even to 2600 B.C. [1]. Nowadays, making use of magnetic phenomena has become a daily routine. This thesis for example relies heavily on the information storage capability of magnetic media, and many people of my generation might get sentimental about the magnetic tape recordings of their adolescence.

On the contrary, superconductivity is truly a 20th century phenomenon, since it does not occur at room temperature. It was found at 4 K (see Fig. 1.1) in Leiden in 1911 in the group of Heike Kamerlingh Onnes [3], who usually gets the credit.* History has almost forgotten the very important contribution of his assistant and later professor Gilles Holst. The impressive evolution of the maximum transition temperature $T_c$ observed over the years is shown in Fig. 1.2, the current record being 134 K (at ambient pressure) [4]. It explains the high expectations that were raised around 1990 on an even higher $T_c$ and possible applications, but up till now there is not too much to get sentimental about, unless you are a scientist. An ambitious report of superconductivity at 250 K had to strike its flag again [5]. It is amusing to speculate on how different human society would be today if

*H.K. Onnes actually predicted that “the resistance would, within the limits of experimental accuracy, become zero. Experiment has completely confirmed this forecast”, which “was based upon the idea of resistance vibrators.” See Communication No. 119 [3].
superconductivity was and always had been a common room temperature phenomenon. A microscopic theory of superconductivity was one of the great outstanding problems of solid state physics until 1956, when Bardeen, Cooper and Schrieffer formulated their theory of bound electron pairs [6]. The advent of superconductivity at “high” temperatures, i.e., above 30 K in the cuprates in 1986 [7] reanimated the problem once again, and since then a fascinating multitude of “anomalies” have been reported in the field, giving rise to many controversies — and to this thesis.

Despite their very different history, magnetism and superconductivity are both very active fields of solid state physics. It is their quantum nature which places them in the 20th century, and it is the many-body aspects of magnetism and superconductivity which make them fascinating, exceedingly difficult and very hot topics. Many-body physics is intriguing and beautiful, but unfortunately a large number of theoretical many-body models is unsolvable. We owe a large part of our understanding of the solid state of matter to the fact that many-body effects can be neglected in many simple metals. It is a surprising

Figure 1.1: First observation of superconductivity in 1911 by Heike Kamerlingh Onnes, Gilles Holst and Dorsman in resistivity data of Hg [3].
Figure 1.2: Evolution of the record transition temperature $T_c$ over the years as given in Ref. [8].

present of mother nature to us that many materials are described rather well by the independent electron approximation. It is in fact the Pauli exclusion principle that explains why this independent electron approximation works so well, since even for large electron-electron interactions, the exclusion principle reduces the available phase space drastically for excitation energies small compared to the Fermi energy. Hence the effect of the interactions can be very small. It was a very important argument by Landau that in many cases even strong interactions can be captured by renormalizing the properties of the electrons, calling the renormalized objects quasiparticles. This is known as the Landau Fermi liquid concept [9].

Dealing with independent electrons, the Bloch-Wilson band theory [10] successfully distinguished metals and insulators in 1929, which counts as an early success of quantum
mechanics. But there are limits to this approach, and that’s where very interesting physics arises. Already at a conference in 1937 de Boer and Verwey [11] pointed out that the insulator NiO should be a metal according to band theory, and in the discussion Peierls proposed electron-electron correlations as the origin for this discrepancy [12, 13]. An intuitive understanding of strong correlations can be obtained by considering an array of hydrogen atoms [12]. If the atoms are close enough to form a solid the electrons will form a half-filled band, hence we expect a metal. If, on the other hand, the atoms are very far apart from each other, we of course expect an “insulator”. For intermediate distances there will be a range where the large on-site electron-electron Coulomb repulsion still wins over the finite overlap of the wave functions and suppresses charge fluctuations, i.e., where an insulator — the so-called Mott insulator — will be formed although in principle the band is half-filled. This explains the insulating properties of NiO and other transition metal oxides. The importance of correlations hence is determined by the ratio of the on-site Coulomb repulsion to the hopping matrix element.

The impact of interactions is enhanced in lower dimensions. In one dimension (1D) spin-charge separation occurs, i.e., the excitations are not Fermionic quasiparticles and Fermi liquid theory breaks down [14–16]. For the case of 2D we witness a very controversial discussion, as to whether the cuprates are Fermi liquids or not [17]. Some of the normal state properties (i.e. $T > T_c$) such as the linear resistivity, the non-Drude optical conductivity, a Raman “background” extending up to some tenths of 1 eV and in particular the peak width of photoemission spectra, do not agree with conventional Fermi liquid theory, turning the term “normal state” into a misnomer. We will briefly discuss the spectrum of ideas — from exotic to more conventional — put forward in order to account for the anomalies of the normal state in section 2.3. In what concerns magnetism, the situation is in some sense similar. Again in 1D the excitations are different from the ones known from higher dimensions: the well-defined magnon dispersion is replaced by a spinon continuum [18]; and again, two dimensions are the stage for a kind of crossover. Long range order is impossible in 1D at all temperatures, and the same is true for 2D at finite temperatures. Nevertheless, long range order is observed due to a small 3D coupling. The magnetic ground state is unknown for a 2D square lattice, but for real materials the Néel state is thought to be a good approximation. However, magnetic flux phases have been claimed to be lower in energy [19], and the resonating valence bond state is not too far away either [20, 21]. The character of the magnetic excitations in a 2D $S = 1/2$ square lattice antiferromagnet will be discussed in section 2.2.

Strong correlations are encountered in transition metal compounds with their rather localized $d$-electrons [22, 23], giving rise to, e.g., metal-insulator transitions, colossal magnetoresistance or high temperature superconductivity. In this thesis we will focus on the cuprates and will be dealing with (a) the antiferromagnetic correlated insulating state at half-filling, (b) the peculiar situation of doping in such a correlated insulator and (c) the superconducting state evolving at higher doping levels.
1.2 Optics in Cuprates

Advantages of optical spectroscopy in a practical sense are that rather small samples are sufficient (we will present reflectivity data on samples with dimensions down to 500 µm and transmission measurements of a 200 × 200 µm² crystal face), that no contacts need to be applied, that it is not surface sensitive and that collecting high quality data does not require large scale technical facilities. As a result, optical data are available on all the different cuprates for many different doping levels and temperatures, whereas for example neutron scattering has focused mainly on La₂₋ₓSrₓCuO₄ and YBa₂Cu₃O₇₋₅ and angle resolved photo emission on Bi₂Sr₂CaCu₂O₈₋ₓ. At the same time, the broad frequency range from millimeter wavelengths up to the ultra violet allows the simultaneous study of quasi-free and bound carriers, of phonons and other low lying excitations. This broad frequency range goes hand in hand with a very high resolution, accurate absolute values and well determined line shapes, which is in particular very helpful for the study of the interactions of all different kinds of excitations.

One of the most popular words in strongly correlated cuprate physics is the term “anomaly”. Optical spectroscopy has had and still has important contributions in terms of revealing how unusual the carrier dynamics really are in the cuprates. A comparison of the optical properties of the cuprates with the behavior found in conventional and other exotic superconductors has recently been published by Timusk [24]. A prominent experimental anomaly which triggered a lot of theoretical research is the non-Drude like 1/ω fall-off of the optical conductivity σ(ω) for electrical fields parallel to the CuO₂ layers. This is the optical equivalent to the famous linear temperature dependence of the resistivity and points strongly to a non-Fermi liquid or “marginal” Fermi liquid behavior (see chapter 2.3.2). It has been suggested that the deviations from a 1/ω² Drude behavior are due to a mid-infrared band that has to be added to a conventional Drude peak (see the reviews by Timusk and Tanner [25]). In particular at low doping levels a distinct peak is clearly observable in the mid-infrared, but it has also become clear that the physics in the cuprates changes quite strongly with doping, and that for example the linearity of the resistivity over a wide range of temperatures is observed only in a very narrow doping range. As an alternative to the existence of a distinct mid-infrared band, the low energy electronic response has been analyzed in terms of a memory function (see section 3.2.1), i.e., a frequency dependent scattering rate [26–30] as opposed to the constant scattering rate for the quasiparticles in the Drude model. Besides visualizing the non-Drude 1/ω behavior of the optical conductivity as a linear frequency dependence of the scattering rate, this analysis also reveals a suppression of the scattering rate at low frequencies in underdoped samples for temperatures well above Tc [30, 31]. This is one of the many faces of the so-called pseudogap, a partial gap opening in the normal state (see section 2.3.1). It was the e-axis optical conductivity [32] which first revealed that the now widely discussed pseudogap is not only a spin- but also a charge-gap. At the same time, the more obvious gap to look

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¹We apologize to the reader unfamiliar with the field for using cuprate terminology already in this part of the introduction. For structural and other details see chapter 2.
for, namely the superconducting one, or a fingerprint of it appearing at $T_c$, had not been observed [25]. The smooth evolution with decreasing temperature of the pseudogap into the superconducting gap that has meanwhile been established with other techniques (see section 2.3.1) is but one of the reasons for the absence of a distinct feature arising at $T_c$. There are at least two more good reasons for that: the cuprates are in the clean limit, i.e., the in-plane mean free path is substantially larger than the correlation length, and the superconducting order parameter follows $d$-wave symmetry. In the clean limit, absorption above the gap is weak and therefore hard to measure, and the $d$-wave gap is responsible for a finite amount of spectral weight at all frequencies. The combination of these effects makes it very difficult to establish the observation of a gap from the experimental data. The linear temperature dependence of the penetration depth observed in microwave data of single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_{6.65}$ [37] clearly pointed towards the existence of nodes of the order parameter, but a definite proof of the $d$-wave symmetry required of course phase sensitive techniques [33–35]. Making use of a grazing angle of incidence our group has succeeded in showing a disagreement of optical data with an isotropic $s$-wave gap and has confirmed the $d$-wave order parameter [36].

Two-dimensionality is a central issue in the cuprates, and optical spectroscopy is one of the best suited tools to probe the strong anisotropy for carrier dynamics parallel and perpendicular to the CuO$_2$ layers [38, 39]. Contrary to the above described response in the $ab$-plane, the $c$-axis optical conductivity develops a true Drude peak only in overdoped samples, whereas a very broad overdamped electronic response is encountered at optimal doping and below [40]. This qualifies for incoherent behavior, at least in a phenomenological sense. At the same time a very sharp plasma edge is observed along the $c$-axis in the superconducting state, which has been attributed to a Josephson plasmon, a collective mode in a stack of Josephson coupled 2D superconducting layers. This discrepancy between the overdamped electronic dynamics in the normal state and the existence of a very sharp, undamped plasmon in the superconducting state is a key ingredient in one of the most influential theories on high $T_c$ superconductivity, Anderson’s interlayer tunnelling model. However, predictions of the theory for a relation between the superconducting plasmon frequency and $T_c$ have recently been found to disagree strongly with optical data [41, 42]. A more detailed discussion of the intriguing $c$-axis optical properties will follow in chapter 8, where we will describe the excitations of a Josephson coupled stack of bilayers [43], in which case two longitudinal and therefore also one optical, i.e. a finite frequency transverse plasmon, arise.

The Josephson plasmon is only one of the fascinating excitations the very complex cuprates offer, and this thesis focusses on some of them. We mentioned above that interactions between different excitations can be studied in detail in optical spectra. In the undoped insulating regime the low energy electronic excitations are magnetic. A coupling of these magnetic excitations to phonons nevertheless allows us to study even the spin degrees of freedom with optical techniques, and we will argue that the accurately determined line shape of the optical conductivity is better suited to give an adequate picture of the magnetic excitations than the usually studied neutron or Raman scattering spectra. Adding a few carriers to the undoped magnetic insulator produces a highly complicated
excitation spectrum [44, 45]. The doped carriers interact with magnetic excitations, with phonons, and with impurities simultaneously, and at least phenomenologically the excitation spectrum can be described in terms of spin polarons, magneto-elastic polarons, and impurity bound states.

Interesting phenomena have also been discussed in the phonon spectra of the high $T_c$ cuprates. For a review we want to refer the reader to the work of Litvinchuk, Thomsen and Cardona [46].

1.3 Scope of this Thesis

In the past 12 years a few 10,000 papers have been published about the cuprates and high $T_c$ superconductivity, which turns it into an uneasy field. Many different issues have been addressed, many have been solved, and although 12 years is not such a long time the transparency is small compared to the effort. This has two implications: one is that the race is still on, the challenge is there and fascinating problems have to be solved, the other that it looks like “everything has been done” already. Measuring infrared spectra of compounds that have been studied more extensively than any other and on which literally hundreds of papers with infrared data have been published might look like an unprofitable enterprise. However, the cuprates have a rich capacity for “anomalous” behavior, which provides us with a lot of work still to be done. There are two stages in the life of an anomaly: first it has to be recognized as a deviation from what is expected, then it has to be turned into the “normal” behavior of a well-understood problem. The central issues of this thesis focus on both aspects. In chapter 5 we claim the observation of anomalous behavior in the antiferromagnetic insulators, and in chapter 8 we explain a “strange bump” observed in the c-axis infrared data of superconducting samples. Having solved one problem and pointing out another one we have at least not increased the number of open questions in the field, and one might argue that posing the right questions is better than giving the wrong answers.

In order to set the stage for our own results we present the following introduction: chapter 2.1 will deal with the structural and electronic properties of the cuprates, and in sections 2.2 and 2.3 the state of the art of magnetism and superconductivity in the cuprates will be discussed. We will focus mainly on those aspects which are either important for the results of this thesis or which relate the two phenomena to one another.

In chapter 3 we will give an introduction to the experimental method, optical spectroscopy, and discuss some models of the quantity we want to determine, namely the dielectric function. The following chapters describe the results of this thesis and deal with the undoped parent compound (chapters 4 - 6), the low doping regime (chapter 7) and the superconducting phase (chapter 8).