Of Spin and Charge in the Cuprates The front cover depicts a portrait of Charles Augustin de Coulomb (1736-1806). The font set (including the "spins") is inspired by the music and writings of John Cage (1912-1992); it was produced by P22 TYPE FOUNDRY for the Museum of Contemporary Art, Los Angeles. There is music in the spins! The back side cover shows the tower of the Martini church in Groningen.

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# Of Spin and Charge in the Cuprates

Proefschrift

ter verkrijging van het doctoraat in de Wiskunde en Natuurwetenschappen aan de Rijksuniversiteit Groningen op gezag van de Rector Magnificus, dr. D.F.J. Bosscher, in het openbaar te verdedigen op vrijdag 17 september 1999 om 16.00 uur

 $\operatorname{door}$ 

Markus Uwe Grüninger

geboren op 22 maart 1967 te Offenburg (Duitsland) Promotores: Prof. Dr. D. van der Marel Prof. Dr. G.A. Sawatzky Denn soviel sei für jeden wachen Zeitgenossen gewiß, daß ein magnetisches Millenium anbreche, mit dessen Beginn alle bisherige Geschichte der Menschheit zu einer bloßen Vorgeschichte herabsinkt.

The mesmerian *LeBrasseur* in Peter Sloterdijk's *Der Zauberbaum*, Die Entstehung der Psychoanalyse im Jahr 1785.

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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

<sup>\*</sup>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].



Figure 1.1: First observation of superconductivity in 1911 by Heike Kamerlingh Onnes, Gilles Holst and Dorsman in resistivity data of Hg [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 1.2: 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 electronelectron 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  $\mu$ m and transmission measurements of a 200 × 200  $\mu$ m<sup>2</sup> 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 La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> and angle resolved photo emission on Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+ $\delta$ </sub>. 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  $1/\omega$  fall-off of the optical conductivity  $\sigma(\omega)$  for electrical fields parallel to the CuO<sub>2</sub> layers.<sup>†</sup> 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  $1/\omega^2$  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  $1/\omega$  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  $T_c$  [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 *c*-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

<sup>&</sup>lt;sup>†</sup>We 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 YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub> [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).

## Chapter 2

# The Cuprates: Magnetism and Superconductivity in the late 20th Century

### 2.1 Structural and Electronic Properties of the Cuprates

### 2.1.1 Crystal Structure of $YBa_2Cu_3O_{7-\delta}$

Since the original discovery of superconductivity in a cuprate compound in 1986 [7] the number of structures belonging to the high  $T_c$  cuprate family has become quite large and keeps increasing. The driving force of this growth is the quest for higher and higher superconducting transition temperatures, which have evolved from the original 30 K in a La-Ba-Cu-O compound [7] to the current 134 K in HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+y</sub>. This can even be increased to 164 K by applying pressure [47–49]. The family is divided into several subgroups which are classified according to their cation structure. The most widely studied systems are La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4+ $\delta$ </sub> (214), YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> (123) and Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+6</sub> (2201, 2212, and 2223 for n = 1, 2 and 3). The essential ingredient that all cuprate compounds share are 2D CuO<sub>2</sub> layers, whereas everything else is subject to change and thereby appears to be detail. However, it has been noticed that  $T_c$  is enhanced if the "stuff" around the CuO<sub>2</sub> layers contains Cu, Tl, Hg, Bi or Pb cations in a closed shell  $d^{10}$  or  $s^2$  oxidation state [50]. These specific cations have low lying  $nd^{10} \leftrightarrow nd^9(n+1)s$  excitations and hence show a strong tendency to polarize the oxygen ions via  $s - d_{3z^2-r^2}$  hybridization.

The CuO<sub>2</sub> layers and the apical oxygen ions form a square lattice of corner sharing CuO<sub>6</sub> octahedra or CuO<sub>5</sub> pyramids, giving rise to a tetragonal symmetry. In many materials a slight orthorhombic distortion is observed. The behavior of most cuprates can be varied on a broad scale — from insulating to superconducting — by controlling the carrier concentration via doping. Often the highest  $T_c$  is reached for non-stoichiometric samples. For a detailed description of the crystal structures, lattice parameters and interatomic dis-



Figure 2.1: Elementary cells of insulating  $YBa_2 Cu_3 O_6$  and superconducting  $YBa_2 Cu_3 O_7$ .

x	a	b	С	Cu2-O2	Cu2-O3	Cu2-O4	Cu2-O2-Cu2	Cu1-O4	Cu1-O1
6	3.86		11.80	1.94		2.45	$167^{\circ}$	1.80	
7	3.82	3.89	11.68	1.93	1.96	2.27	$164^{\circ}$	1.84	1.94

Table 2.1: Lattice parameters, Cu-O interatomic distances (in Å) and Cu2-O2-Cu2 angle of  $YBa_2 Cu_3 O_x$  at 300 K as given by Hazen in Ref. [51].

tances of various cuprates we refer the reader to Ref. [51]. This thesis concentrates on the  $YBa_2Cu_3O_{7-\delta}$  system,<sup>\*</sup> the first material to support superconductivity at liquid nitrogen temperatures [52]. The elementary cells of the two limiting cases of oxygen content, x=6 and 7, are shown in Fig. 2.1. The sandwich structure of CuO, BaO and CuO<sub>2</sub> layers is obvious. The lattice parameters and typical Cu-O interatomic distances are given in Table 2.1. A more artistic impression of what it "feels" like to roam through the landscape of layers and chains is given in Fig. 2.2.

 $YBa_2Cu_3O_{7-\delta}$  belongs to the class of bilayer materials, *i.e.*, there are two closely spaced  $CuO_2$  layers per unit cell, and the inter-bilayer distance is much larger than the intra-bilayer

<sup>&</sup>lt;sup>\*</sup>Our convention for the various ways of labelling the oxygen content will read  $YBa_2Cu_3O_{7-\delta}$ ,  $YBa_2Cu_3O_{6+y}$  and  $YBa_2Cu_3O_x$ .



Figure 2.2: A more artistic view of superconducting  $YBa_2 Cu_3 O_7$ , emphasizing the dominance of the  $CuO_2$  bilayers and the CuO chains. Pyramids and diamonds denote  $CuO_5$ and  $CuO_4$  units, respectively.



Figure 2.3: Experimentally determined phase diagram of  $YBa_2 Cu_3 O_{6+x}$  as given by Rossat-Mignod in 1990 [53]. Note the different scales for  $T_c$  and the Néel temperature  $T_N$  and the different definition of the oxygen content  $(x \rightarrow 6+x)$  in the figure as compared to the main text.



Figure 2.4: Superconducting transition temperature  $T_c$  as a function of annealing temperature for  $YBa_2 Cu_3 O_{7-\delta}$  and  $NdBa_2 Cu_3 O_{7-\delta}$  [54]. Higher annealing temperatures correspond to a lower oxygen content.

one. In general,  $T_c$  within one cuprate subgroup increases from single layer to bilayer to trilayer compounds, a fact which is not understood and barely addressed [55–57]. This neglect may for example be justified by a  $T_c$  as high as 90 K encountered in the single layer material  $Tl_2Ba_2CuO_6$ , which has a comparably large layer-to-layer distance of 11.6 Å. Most of the cuprate structures show some distortion of the CuO<sub>2</sub> layers. In YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> the planar oxygen ions are shifted towards the interior of the bilayer, giving rise to the so-called buckling with an angle of 164 – 167°.

Neglecting covalency, the oxidation states in the tetragonal insulator YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> are  $Y^{3+}$ , Ba<sup>2+</sup>, O<sup>2-</sup>, Cu<sup>2+</sup> for the planar Cu ions and Cu<sup>1+</sup> for the linearly twofold coordinated Cu1 ion on the so-called chain site, *i.e.*, all ions but the two Cu<sup>2+</sup> are in a closed-shell configuration. The system can be doped by adding oxygen on the O1 or O5 sites (see below for the doping mechanism). A structural transition from tetragonal to orthorhombic occurs at an oxygen content of about x = 6.4. In ideal stoichiometric YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> all O1 sites are populated and form the so-called chains along the *b*-axis, whereas all O5 sites (along *a*) are empty. The orthorhombic distortion gives rise to twinning of samples. For intermediate oxygen concentrations superstructures can be formed, leaving for example every second (third) chain empty in the Ortho II phase (Ortho III) for x = 6.5 (x = 6.66).

Many groups have emphasized the possibility that the apical oxygen ions play an important role (O1 in Fig. 2.1). However, the in-plane Cu-O distance is typically of 1.94 Å, whereas the planar Cu to apical O distance is much larger, about 2.3 Å (see Table 2.1). It

is interesting to note that the position of the apical oxygen is actually determined by the much stronger and shorter (1.80 Å) bond to the Cu1 on the chain site. This short bond is typical for the case of a linear twofold coordination of a Cu<sup>1+</sup> ion. Possible implications for the electronic structure will be discussed in more detail in chapter 6. It is obvious that the apical oxygen as well as the other "stuff" have some influence on the electronic properties. Certainly, the negatively charged  $(CuO_2)^{2-}$  layers would be unstable without the compensating "stuff". However, we strongly believe that one "miracle" is enough, *i.e.*, that there is only one mechanism for high  $T_c$  superconductivity, and that the key to the fundamental physical properties lies within the CuO<sub>2</sub> layers, and that everything else only enhances or degrades these properties, but is not its very origin.

An early phase diagram of  $YBa_2Cu_3O_x$  is given in Fig. 2.3. The system is an antiferromagnetic insulator with a Néel temperature of up to 500 K for oxygen contents close to 6. It undergoes a metal-insulator transition to a superconducting phase for x = 6.4. Often the existence of two superconducting plateaus with transition temperatures of 60 and 90 K has been claimed (see Fig. 2.3). However, it appears that especially the 60 K plateau is related to formation of the above mentioned chain superstructures with local variations in oxygen content near, e.g., x = 6.5 and 6.66. Recent work by Erb [54] suggests the absence of the 60 K plateau in homogeneous samples (see Fig. 2.4; higher annealing temperatures correspond to a lower oxygen content). The absence of a 90 K plateau had been realized already long before. Instead of saturating with increasing oxygen content,  $T_c$  goes through a maximum at high doping concentrations, which indeed is typical for all cuprates (at least for those that allow doping on a broad range). A similar plot of  $T_c$  in Ca doped (Y,Ca)Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> shows the maximum more clearly (see Fig. 2.34 (c) on page 72) and confirms the absence of plateaus. Nowadays, the doping concentration with the highest  $T_c$  is called optimal doping, whereas samples with a lower  $T_c$  are either called underdoped (towards the insulating phase) or overdoped. In YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> optimal doping corresponds to an oxygen content of x = 6.93. For details and controversies about "up-to-date" phase diagrams see section 2.3.1.

#### Carrier Doping in $YBa_2Cu_3O_{7-\delta}$

The obvious way of doping a cuprate such as  $La_2CuO_4$  is to replace the trivalent  $La^{3+}$  by divalent ions such as  $Sr^{2+}$ . This can be achieved in  $YBa_2Cu_3O_6$  by substituting  $Y^{3+}$  with  $Ca^{2+}$ . In this case the concentration of doped carriers equals the concentration of Sr or Ca impurities. However, the way usually chosen to change the doping level in  $YBa_2Cu_3O_{6+y}$ is to play with the oxygen content, which influences the doping in a more subtle way. Fig. 2.5 shows a *bc*-face side view of several unit cells of  $YBa_2Cu_3O_{6+y}$  with some excess oxygen ions (large light balls). A single, isolated excess oxygen ion takes one electron from each of its Cu1 neighbors, thereby turning them from  $Cu^{1+}$  to  $Cu^{2+}$  (lower part of Fig. 2.5). The CuO<sub>2</sub> layers only become doped with carriers if chain fragments are formed (upper part of Fig. 2.5). In a CuO chain every oxygen can take at most one electron from the Cu1 site of its own unit cell, since the  $Cu^{3+}$  state is suppressed by the strong on-site Coulomb repulsion in the Cu 3*d* shell (see below). This lack of electrons produces holes in the chain oxygen bands. Doping of an adjacent CuO<sub>2</sub> layer takes place by partially filling the "chain



Figure 2.5: The mechanism of carrier doping via changing the oxygen content in  $YBa_2 Cu_3 O_{6+y}$ . Only ions lying within the same plane of the bc-face are shown, Y and Ba sites are left out for the sake of simplicity.

holes" with electrons from this  $CuO_2$  layer. If the excess oxygen ions are arranged in a checker board pattern superstructure (full-empty-full-empty), it is in principle possible to have 50% occupancy of oxygen chain sites without any carrier doping of the  $CuO_2$  layers.

The superconducting transition temperature for the maximum oxygen content of x = 7is only slightly reduced from that for optimal doping (89 K as compared to 93 K). In order to advance further into the overdoped region a combination of O and Ca doping has to be used. A nice example for the equivalence of the two dopants as far as low energy electronic properties are concerned is the infrared study of the *c*-axis optical conductivity of Ca-doped (Y,Ca)Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> by Bernhard and co-workers [58].

### 2.1.2 Electronic Structure and Microscopic Models

In order to describe low energy phenomena such as magnetism or superconductivity, one has to derive an effective Hamiltonian from the multitude of electronic bands lying a few eV above and below the Fermi energy.<sup>†</sup> A simple counting of formal valencies for the so-called parent compound  $YBa_2Cu_3O_6$  shows that all atomic shells are completely filled with the single exception of the nine electrons in the *d*-band of  $Cu^{2+}$ . The orbital degeneracy of the 3*d*-band is lifted by ligand fields, resulting in a single hole in the  $d_{x^2-y^2}$ orbital and a half-filled band. Accordingly, band structure calculations predict a nonmagnetic metallic state [64], in contrast to the insulating gap of order 1.5 eV observed in optical spectra [25, 65]. This spectacular failure of band theory is due to electronic correlations caused by the large on-site Coulomb repulsion *U*, which forces the electrons to stay out of each others way as much as possible. The most favorable solution is to have one hole localized on every Cu site. Kinetic energy is partly recovered by forming an antiferromagnetic state, which allows for some "excursions" to the nearest neighbors. Already in 1987 Anderson proposed that the single-band Hubbard model

$$H = -t \sum_{\langle ij \rangle, \sigma} (c_{i,\sigma}^{\dagger} c_{j,\sigma} + H.c.) + U \sum_{i} n_{i,\downarrow} n_{i,\uparrow}$$
(2.1)

captures the essential physics of the cuprates [20]. Here, the operators  $c_{i,\sigma}^{\dagger}(c_{i,\sigma})$  create (annihilate) a hole with spin  $\sigma$  at site *i* on a square lattice, and the  $n_{i,\sigma} = c_{i,\sigma}^{\dagger}c_{i,\sigma}$  are the hole number operators. The first sum is carried out over nearest neighbor sites  $\langle ij \rangle$  only. In addition to the Hubbard *U* term, which counts the doubly occupied sites, the model contains the kinetic energy in terms of the nearest neighbor hopping matrix element *t*. Here we adopt hole notation, which treats the state with completely filled shells as the vacuum of the Hilbert space. This model might look simple, but turns out to be a wolf in sheep's clothing, calling for further simplification. This is achieved in the strong coupling limit  $U \gg t$ , in which the one-band Hubbard model can be reduced to the most studied Hamiltonian in the field of high T<sub>c</sub> superconductivity, the t-J model

$$H = -t \sum_{\langle ij \rangle,\sigma} \left( \hat{c}^{\dagger}_{i,\sigma} \hat{c}_{j,\sigma} + H.c. \right) + J \sum_{\langle ij \rangle} \left( \mathbf{S}_{i} \cdot \mathbf{S}_{j} - \frac{1}{4} n_{i} n_{j} \right)$$
$$-\frac{t^{2}}{U} \sum_{\langle ijk \rangle,\sigma} \left( \hat{c}^{\dagger}_{k,\sigma} n_{j,-\sigma} \hat{c}_{i,\sigma} - \hat{c}^{\dagger}_{k,\sigma} \hat{c}^{\dagger}_{j,-\sigma} \hat{c}_{j,\sigma} \hat{c}_{i,-\sigma} + H.c. \right), \qquad (2.2)$$

where the abbreviation  $\hat{c}_{i,\sigma}^{(\dagger)} = c_{i,\sigma}^{(\dagger)}(1-n_{i,-\sigma})$  for projecting out doubly occupied sites has been used. The  $\mathbf{S}_i = c_{i\alpha}^{\dagger} \boldsymbol{\sigma}_{\alpha\beta} c_{i\beta}$  are the spin operators at site *i* for S = 1/2, and  $\boldsymbol{\sigma}_{\alpha\beta}$ designates the Pauli spin matrices. The exchange coupling constant is given by  $J = 4t^2/U$ . The last term is a three-site hopping term (with *i* and *k* being nearest neighbors of *j*)

<sup>&</sup>lt;sup>†</sup>The fundamental electronic structure of the cuprates forms the very basis for any discussion about high  $T_c$  superconductivity. It has been described extensively by many authors, allowing us to mention only the key ingredients and to refer the reader for further details to, *e.g.*, the contributions of Sawatzky, Emery and Rice to Ref. [59] or to the more recent reviews by Dagotto, Brenig and Kampf [60–62]. "Some unusual aspects" are treated in the thesis of Henk Eskes [63].



Figure 2.6: A sketch of four unit cells of a  $CuO_2$  layer showing the most relevant orbitals,  $3d_{x^2-y^2}$  on Cu and  $2p_{x,y}$  on O, and the most important electronic parameters. The white signs in the lower left unit cell give the orbital phases. The dashed circle on the upper right denotes a Zhang-Rice singlet, where the black signs indicate the relevant symmetry.

Table 2.2: A widely accepted standard set of typical parameter values (in eV) as given in Refs. [63, 66, 67].  $\Delta = \epsilon_p - \epsilon_d$ 

which usually is omitted for the sake of simplicity, since it is proportional to both the small parameters  $t^2/U$  and doping concentration  $\delta$ . It is worth noting that the discussion whether the t-J model is a valid description of the low energy physics has been and still is controversial. Lately it has been realized that the next nearest and third nearest neighbor hopping integrals t' and t'' and the related exchange constants J' and J'' are important for the description of experimental results, at least at low doping levels.

At exactly half-filling the charge excitations are gapped and the low energy degrees of freedom of the t-J model are magnetic and can be described by the Heisenberg model

$$H = -J \sum_{\langle ij \rangle} \left( \mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} n_i n_j \right).$$
(2.3)

The term  $\frac{1}{4}n_in_i$  contributes only a constant energy shift and is usually dropped.

In order to obtain realistic values for the model parameters we have to relinquish the simple ionic view and incorporate hybridization of Cu and O orbitals. It is important to note that the Cu-O charge transfer energy  $\Delta = \epsilon_p - \epsilon_d$  in fact is smaller than the

on-site Hubbard U, which places the cuprate parent compounds on the "charge transfer insulator" side of the Zaanen-Sawatzky-Allen scheme (see Fig. 2.7) [68], as opposed to the above described Mott-Hubbard insulator. Including the planar oxygen  $p_{x,y}$  orbitals which have a large  $\sigma$ -type overlap with the Cu  $d_{x^2-y^2}$  (see Fig. 2.6) brings us to the three-band Hubbard model as proposed by Emery [69], which reads

$$H = \epsilon_d \sum_{i,\sigma} n_{i,\sigma}^d + \epsilon_p \sum_{j,\sigma} n_{j,\sigma}^p + \sum_{\langle ij \rangle,\sigma} t_{pd}^{ij}(d_{i,\sigma}^{\dagger}p_{j,\sigma} + H.c.)$$
(2.4)

$$+ \sum_{\langle jj'\rangle,\sigma} t_{pp}^{jj'}(p_{j,\sigma}^{\dagger}p_{j',\sigma} + H.c.) + U_d \sum_i n_{i,\uparrow}^d n_{i,\downarrow}^d + U_p \sum_j n_{j,\uparrow}^p n_{j,\downarrow}^p + U_{pd} \sum_{\langle ij\rangle,\sigma,\sigma'} n_{i,\sigma}^d n_{j,\sigma}^p$$

Here, the index i(j) denotes Cu (O) sites, and the operators  $d_{i,\sigma}^{\dagger}(d_{i,\sigma})$  and  $p_{j,\sigma}^{\dagger}(p_{j,\sigma})$  create (annihilate) a hole with spin  $\sigma$  in the Cu  $d_{x^2-y^2}$  and O  $p_{x,y}$  orbitals, respectively. The  $n_{i,\sigma}^d = d_{i,\sigma}^{\dagger} d_{i,\sigma}$  and  $n_{j,\sigma}^p = p_{j,\sigma}^{\dagger} p_{j,\sigma}$  are the hole number operators for the corresponding orbitals. The Cu (O) on-site energy is given by  $\epsilon_d(\epsilon_p)$ , with  $\Delta = \epsilon_p - \epsilon_d$  being positive in hole notation, and the  $t_{pd}^{ij}(t_{pp}^{ij'})$  describe the Cu-O (O-O) hybridization with the appropriate phase factors according to the orbital symmetries indicated in Fig. 2.6. The terms proportional to  $U_d$ and  $U_p$  count the doubly occupied sites on Cu and O, respectively, and the  $U_{pd}$  term takes the inter-site Coulomb repulsion into account. A widely accepted standard set of typical parameter values is given in Table 2.2, which underlines the dominant importance of  $U_d$ and hence of the small radius of the Cu 3d shell for the electronic correlations. The other key parameter is the charge transfer energy  $\Delta$ , which — being much smaller than  $U_d$  places the "action" into the oxygen band upon hole doping. Often  $U_p$  and  $U_{pd}$  are neglected for the sake of simplicity.

In the three-band model, the exchange interaction between nearest neighbor Cu spins is mediated via the oxygen orbitals. Therefore J has become a *super*exchange constant [70] and is given to the first non-vanishing order by [71]

$$J = \frac{4t_{pd}^4}{(\Delta + U_{pd})^2} \left(\frac{1}{U_d} + \frac{2}{2\Delta + U_p}\right).$$
 (2.5)

The thus obtained remarkably large value of J compares favorably with the experimental result of 100 - 130 meV, which however turns out to be mere coincidence [63]. A more detailed discussion of J will be given in chapter 5.1.

At this point it is important to notice another, even stronger exchange interaction, namely the one between the spin of a doped hole — residing mainly on O — and the Cu hole spin (again to first non-vanishing order, neglecting  $U_p$  and  $U_{pd}$ ),

$$J_{Cu-O} = t_{pd}^2 \left(\frac{1}{\Delta} + \frac{1}{U_d - \Delta}\right).$$

$$(2.6)$$

The large value of the exchange interaction is due to the hybridization which is strongest if the doped hole is put into a fully symmetric linear combination of the four oxygen  $p_{\sigma}$ 



Figure 2.7: Zaanen-Sawatzky-Allen scheme as described by Horsch and Stephan in Ref. [72]. (a) In the absence of correlations the Cu  $d_{x^2-y^2}$  and O  $p_{x,y}$  bands form bonding (B), non-bonding (NB) and anti-bonding (AB) combinations. With the five electrons present in the three orbitals we thus have two full bands and one half-filled anti-bonding band. (b) If the Hubbard U is larger than the band width, the anti-bonding band splits in a lower (LHB) and an upper Hubbard band (UHB), turning the system into a Mott-Hubbard insulator. (c) The lower Hubbard band shifts below the oxygen bands, if U is larger than the Cu-O charge transfer energy  $E_{CT}$ . The system will be a charge-transfer insulator. (d) Hybridization with the upper Hubbard band splits the bonding band into triplet and singlet bands in a charge-transfer insulator. The Zhang-Rice singlet is the first electron removal state.

orbitals surrounding the Cu hole. The entity residing on the central Cu d orbital and the four ligand O p orbitals is called a Zhang-Rice singlet (ZRS) [73, 74]. The large  $J_{Cu-O}$ produces a large singlet-triplet splitting (3.5 eV [63, 74]) and hence the triplet can be neglected. This essentially brings us back to the one-band Hubbard model of Eq. 2.1. albeit with a parameter U which is of the order of  $\Delta$  — the lower Hubbard band mimics the charge transfer band — and a hopping parameter  $t \approx t_{pd}^2/\Delta \approx 0.5$  eV given by the singlet hopping matrix element. The Zhang-Rice singlet corresponds to a spinless fermion moving in the background of Cu spins without doubly occupied sites, *i.e.*, it can be viewed as an *empty* site in the 2D square lattice of Cu spins. Concerning the stability of the Zhang-Rice singlet and the applicability of a one-band model Eskes and Sawatzky pointed out that "Zhang-Rice singlets are not singlets" [63, 75], *i.e.*, that they are not clearly separated from other states, but that these other states are not included in both the oneand three-band models. Finally it has to be noted that the Zhang-Rice singlet state was derived for a  $CuO_4$  cluster, and that therefore "neighboring" Zhang-Rice singlets are not orthogonal. A summary of the above mentioned models and their classification in the Zaanen-Sawatzky-Allen scheme is given in Fig. 2.7.

A note of caution: not one of the above mentioned Hamiltonians has been solved ex-

actly, and not even the zero temperature ground state of the seemingly simple Heisenberg Hamiltonian of Eq. 2.3 is known. Therefore numerical methods such as exact diagonalization of small clusters have been popular, and they indeed have proven very helpful. This is due to the *local* character of the correlations, which can be captured in a finite cluster. However, one has to be aware of the present limitations, best expressed in cluster size. Using exact diagonalization studies of the optical conductivity as an example, we find clusters of up to 26 sites for the t-J model [76], of  $4 \times 4$  sites for the one-band Hubbard model [77] and of only  $2 \times 2$  sites for the three-band model [78]. The Hilbert space for the one-band Hubbard model on a  $4 \times 4$  cluster has already a dimension of the order of  $10^8$  [77]. The present "record" cluster solved for the t-J model contains 32 sites [79], which requires handling of matrices with dimensions up to  $3 \cdot 10^8$ . A larger cluster size is not only important for allowing a finite size scaling analysis, but the 32-site cluster is the smallest with the full rotational symmetry that contains the important  $(\pi/2, \pi/2)$  point without the accidental degeneracies of, for example, the widely studied 16-site cluster. In the 16-site cluster a "single" doped hole already amounts to 6.25% of doping, which has to be compared with the optimal doping concentration of about 15% in the cuprates. Many of the important questions, such as whether a "single" doped hole has a finite quasiparticle pole strength or whether there is superconductivity in these models, have therefore not been answered satisfactorily to date. Lately one-dimensional insulating cuprates such as the spin chain system  $Sr_2CuO_3$ , the spin-Peierls material  $CuGeO_3$  or the spin ladder compound  $Sr_{14}Cu_{21}O_{42}$  have been "en vogue". The 1D case bears the advantage of offering models that are exactly solvable, but it is also attractive for numerical studies, since large clusters can be treated and comparison with exact solutions is possible. The dimensional "crossover" in terms of ladders with an increasing number of legs is very interesting [80], and good agreement between a three-leg ladder and the behavior of underdoped cuprates has been claimed [81].

In spite of the difficulties and controversies of the 2D case, one can state that the basic applicability of the correlated models to the cuprates has nevertheless been proven experimentally, first of all by the successful description of experimental data at "halffilling" by the Heisenberg Hamiltonian (for details and limitations, see chapters 2.2 and 5). Direct evidence comes also from photoemission spectroscopy, showing the Cu  $d^8$  like electron removal states at much higher energies than the  $d^{9}\underline{L}$  states [82], where  $\underline{L}$  denotes a ligand hole. Another beautiful example is the transfer of spectral weight with doping which is intrinsic to correlated electron physics [83]. Adding a dopant to a conventional insulator does not influence the spectral weights of the valence and conduction bands. In the Hubbard model, however, the situation is very different. Removing an electron with spin  $\sigma$  from the lower Hubbard band on site *i* removes the state with spin  $-\sigma$  from the upper Hubbard band and shifts it to the lower one! Appealing verifications of this spectral weight transfer are observed in the doping dependence of  $La_{2-x}Sr_xCuO_4$  in optical spectroscopy [65], x-ray absorption [84] and EELS experiments [85]. This basic applicability however refers to an intermediate energy scale, and a valid description of the real low energy physics is still open to debate.

Going beyond the "simple" models described here one can include further neighbors or

take into account oxygen-oxygen hybridization and the large oxygen bandwidth. Varma and collaborators have claimed the importance of possibly low lying charge transfer excitons [86,87], whereas others believe in low lying d-d excitations  $(d_{x^2-y^2} \rightarrow d_{3z^2-r^2})$  [88,89]. Feiner and co-workers [90] find that the apical oxygen sites differentiate between different classes of cuprates, and that  $T_c$  increases within one class with decreasing interaction strength between planar and apical orbitals. A particular influence of out-of-plane ions seems to be present in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub>, for which band structure calculations indicate a Fermi surface which is rotated by 45° with respect to the prototypical La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> system. Hybridization with apical oxygen states has been claimed to be responsible for this phenomenon [91], while an effective description within the one-band Hubbard and t-Jmodels in terms of a next-nearest neighbor hopping matrix element  $t' \approx 0.45t$  yields the same rotation [92]. Feiner and collaborators [90] argue that for symmetry reasons structural differences between various cuprates enter only in  $t_{-} \equiv t' - 2t''$ , where t'' describes a nextnext-nearest neighbor hopping. They argue that the Fermi surface shape depends on  $t_{-}$ and that this explains the variation in the maximum  $T_c$  obtainable in the different cuprates.

### 2.1.3 Sample Quality

Imperfections such as inhomogeneities, impurities or disorder are a serious issue in the cuprates. In most cuprates, the optimal doping concentration (the highest  $T_c$ ) is obtained for a non-stoichiometric case. Using  $La_{2-x}Sr_xCuO_4$  as an example, optimal doping corresponds to 15/2 % of Sr ions on La sites, which turns the system rather into a random alloy and explains the existence of a spin-glass phase observed at low doping levels. The presence of 1D chains in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> leads to twin domains, even in the stoichiometric case, and detwinning procedures such as applying uniaxial pressure can induce serious strain in a sample. All systems experience some kind of tilting, buckling or other modulations of particular units within the unit cell, which often obscures the interpretation of experimental data. In the following we give a short list of some of the ambiguous issues that are, or might be, connected to sample quality or experimental problems. This list is not intended to find fault in what other people did, in fact we put ourselves on there as well.

• The most entertaining example to us is the case of  $Y_{1-y}Pr_yBa_2Cu_3O_7$  [93]. Substitution of Pr for Y was known to suppress  $T_c$  rapidly, and  $PrBa_2Cu_3O_7$  was assumed to be an insulator. This has for example been exploited to study whether a single *isolated* CuO<sub>2</sub> layer in a PrBCO/YBCO/PrBCO superstructure supports superconductivity. In the discussion about the microscopic origin for the insulating behavior of  $PrBa_2Cu_3O_7$  the valency of the Pr ions was heavily debated, but the case was settled with a model by Fehrenbacher and Rice [94], who attributed hole localization to hybridization between O p and Pr f orbitals. This at least was the case until recently, when  $PrBa_2Cu_3O_7$  was found to be a superconductor, in fact the one with the highest  $T_c$  [*sic*] in the 123 family, reaching 106 K under pressure [95]. Nevertheless, the Fehrenbacher-Rice model turns out to be essentially right, a decision worthy of King Solomon: Mazin points out that the physics in  $PrBa_2Cu_3O_7$  indeed

is governed by pf-hybridization, but that the corresponding band is *itinerant*, not localized. The evil is due to Ba-Pr disorder, which easily localizes the heavy carriers in the pf band. It was known already for a long time that partial substitution of La or Nd for Ba reduces  $T_c$  significantly [51]. This disorder can only be suppressed in very clean single crystals, which are now available [96]. In the end, PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> is again an exception, but an even more extraordinary one than it was from the very beginning: it is the only high  $T_c$  "cuprate" in which superconductivity is not fully dominated by Cu-O pd bands.

- The same disorder on the Ba site prevented the advent of high T<sub>c</sub> superconductivity in 1981, when Er-Rakho and co-workers [97] synthesized La<sub>3</sub>Ba<sub>3</sub>Cu<sub>6</sub>O<sub>14</sub>, a true 123 isomorph [51]. Their sample was not superconducting, most likely due to the La-Ba disorder.
- The potential use of  $YBa_2Cu_3O_{7-\delta}$  in technical applications was promoted by an *increase* of the critical current in high magnetic fields far above the lower critical field  $H_{c1}$ . Due to the shape of the magnetization curve this was known as the fishtail anomaly. Recently it was shown that the anomaly is only due to strong pinning caused by clusters of O vacancies, and that it can be suppressed reversibly by controlling the clustering [98].
- The so-called infinite layer compound  $(Sr,Ca)CuO_2$  with a  $T_c$  of about 100 K was believed to be exceptional in that it was the only hole-doped cuprate superconductor without apical oxygen ions. However, these samples are phase impure and in 1995 superconductivity was solely attributed to phases of  $\operatorname{Sr}_{n+1}\operatorname{Cu}_n\operatorname{O}_{2n+1+\delta}(n=2,3,\cdots)$ , which comprise apical oxygen ions [50, 99]. The interesting counterpart of this story is that all *electron*-doped versions of high  $T_c$  superconductors do *not* have apical oxygen ions [99]. In the model *insulating* parent compound  $Sr_2CuO_2Cl_2$  the apical oxygens are replaced by  $Cl^{1-}$  ions, and it is believed that this compound cannot be doped. This and other insulating  $M_2CuO_2X_2$  materials were actually studied already in 1975 by Müller-Buschbaum and collaborators [100]. However, one can easily be fooled by such reasoning. The isomorph  $Ca_2CuOCl_2$  has recently been turned into the 26 K superconductor  $Ca_{0.96}Na_{0.04}CuO_2Cl_2$  by Hiroi *et al.* [101]. It was synthesized under 6 GPa oxygen pressure. Via high-pressure synthesis the 24 K superconductor  $(Ca,K)_2CuO_2Cl_2$  was also produced [103]. Another example of a hole doped superconductor without apical oxygen ions is  $Sr_2CuO_2F_{2,33}$ , in which superconductivity was reported at 46 K [102].
- The highest  $T_c$  in the  $La_{2-x}Sr_xCuO_{4+\delta}$  system is obtained not for the mostly studied case of Sr doping, which allows a maximum  $T_c$  of  $\approx 38$  K, but for doping with interstitial excess oxygen, in which case a  $T_c$  of 45 K can be reached (in the absence of Sr). Unlike the disordered Sr dopants, the excess oxygen ions order in a superstructure of regularly spaced interstitial planes, a phenomenon called staging [104, 105].

- The temperature dependence of the spin-lattice relaxation rate of Cu nuclei indicates the opening of a spin-gap in for example the underdoped phase of the bilayer compound YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> (see below). No such indication was found in the single layer material La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>, which inspired Millis and Monien to propose an explanation based on the finite exchange coupling between the two layers of one bilayer [106]. Nowadays, there are indications that the previously labelled "spin-gap" is accompanied by a charge-gap (see below), and the NMR mystery of La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> is attributed to impurities, since, *e.g.*, Zn impurities are known to suppress the phenomenon in bilayer compounds as well [107]. However, the same issue arises around the resonance observed in neutron scattering at 41 meV and below (depending on doping) [108]. Millis and Monien in a later paper propose a bilayer origin [109]. Lately, the same resonance has been found in another bilayer material, Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+ $\delta$ </sub> [110].
- In the case of  $Bi_2Sr_2CaCu_2O_{8+\delta}$  it is not trivial to determine whether a sample with a reduced  $T_c$  is underdoped or overdoped.
- Magnetic spin fluctuations observed in underdoped compounds were found initially to be incommensurate in  $La_{2-x}Sr_xCuO_4$  and commensurate in  $YBa_2Cu_3O_{7-\delta}$ . This was attributed to a different shape of the Fermi surface [111, 112]. Recently incommensurate spin fluctuations have been discovered in  $YBa_2Cu_3O_{7-\delta}$  [113] and probably in  $Bi_2Sr_2CaCu_2O_{8+\delta}$  as well [110].
- We observed a very intriguing sharp feature in the mid-infrared conductivity spectrum of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> and explained it in terms of direct excitation of optical magnons [114] (see chapter 5.1). Even today this is the scenario that describes the shape of the mid-infrared absorption in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> better than any other. However, neutron scattering experiments tell us that the optical magnon branch lies at a three times lower energy [115, 116]. Since then we have observed that this sharp peak is hardly affected by varying several parameters, which calls for an interpretation in terms of impurities. This is hard to reconcile with the fact that additional structures similar to the sharp peak appear in cleaner samples. We will present the current understanding of this puzzle in chapter 6.

Some effects such as the disorder of dopant ions or irregularities of the crystal structure can not be circumvented in most cases, but one can work on the purity of the samples. Compared to semiconductor standards the purity of high  $T_c$  compounds is really poor,

Crucible	$Al_2O_3$	Au	MgO	$Y_2O_3$ stab. $ZrO_2$	${ m BaZrO_3}$
impurities	Al	Au	Mg	Mg, Zn, Al, Fe, Mn, Ti	La, Sr, Zr
in at. $\%$	5	1.5	1	0.07 - 0.14	0.0005 - 0.0014

Table 2.3: Crucible materials used for the growth of  $YBa_2 Cu_3 O_{7-\delta}$  single crystals and the contaminants found in them [118].

and a well known bon mot states that if the available purity of semiconductors was as bad as in the cuprates the world would still be waiting for the first transistor to work. The main problem is the corrosion of the container used for crystal growth. In the case of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> an inert crucible material, namely BaZrO<sub>3</sub>, was only developed recently [117]. All crucible materials used before were known to react with the melt. State of the art single crystals were grown in  $Y_2O_3$  stabilized  $ZrO_2$  crucibles, but even in these a whole variety of impurities can be found which stem from the sintering aids used in the industrial production of the crucibles. Usually, these additives are an industrial production secret and hence are not mentioned [118]. A list of crucible materials and the amount of impurities typically found in samples grown in them are reproduced from Ref. [118] in Table 2.3. The heavily contaminating  $Al_2O_3$  crucibles were often used because they produced large crystals, in particular along the *c*-axis. These samples tend to be underdoped, since Al prefers the chain sites and likes to be sixfold coordinated, which destroys the chain structure and reduces the transfer of carriers into the  $CuO_2$  layers. This is only one reason for the sometimes confusing disagreement between experimental data of different sources on samples with the same oxygen content. The advantage of the new samples grown in  $BaZrO_3$  has been demonstrated by the suppression of the fishtail effect [98] (see above), the observation of the vortex lattice in  $YBa_2Cu_3O_{7-\delta}$  (although the material cannot be cleaved) [119], and the melting transition of this vortex lattice [120].

### 2.2 The 2D Spin 1/2 Square Lattice Heisenberg Antiferromagnet

Few subjects in science are more difficult to understand than magnetism. Encyclopaedia Britannica, 15th Edition, 1989.

#### 2.2.1 Some Theory

The undoped antiferromagnetic phase of the cuprates with exactly one hole per Cu site is the best realization of a two dimensional spin 1/2 square lattice Heisenberg antiferromagnet known. The non-existence of experimental data on such a system marked an important unexplored region of quantum statistical mechanics before 1986. Magnetic models had always been in the very focus of quantum and statistical mechanics. The absence of long-range order even at T = 0 in the one-dimensional S = 1/2 quantum Heisenberg antiferromagnet was already proved by Bethe in 1931 [121]. In 1966/67 Hohenberg [122] and Mermin and Wagner [123] demonstrated that no long-range order exists in 2D at finite temperatures if the order parameter is continuous. For  $S \ge 1$  the existence of an ordered ground state in 2D at T=0 was established only in the 1980's [124, 125]. This leaves the case of the extreme quantum limit spin 1/2 in two dimensions as the last point in this T-D-S phase space open for debate. Evidence for long-range order is being collected; for reviews see Refs. [105, 126]. Very influential in this discussion was the proposal of Chakravarty, Halperin and Nelson [127], who claimed that the long-wavelength low-temperature behavior is described by the quantum non-linear  $\sigma$  model in two space plus one (imaginary) time dimension. The imaginary time incorporates the effect of quantum fluctuations. The model is a field theory used in statistical mechanics and particle physics [18]. The phase diagram in the q-Tplane<sup>‡</sup> is sketched in Fig. 2.8. For g smaller than a critical value  $g_c$  the T = 0 ground state is ordered (thick line). At finite temperatures, long-range order is lost but the correlation length diverges exponentially for  $T \rightarrow 0$ . The long-wavelength low-temperature behavior can be mapped onto a *classical* model in this regime, and the parameters are simply renormalized by quantum fluctuations, giving that part its name: "renormalized classical". At high temperatures "quantum critical" behavior is predicted, which dominates even for T=0 at the quantum critical fixed point  $g=g_c$ . Here, the only relevant energy scale is the temperature itself, and the correlation length varies linearly with T. For  $g > g_c$  quantum disordered behavior rules the low temperature range, the system has an excitation gap and the correlation length stays constant. The properties of antiferromagnets near to criticality have been explored by Chubukov, Sachdev and Ye [128].

In the renormalized classical regime, the coupling constant has been given as [127]

$$g/g_c = \left(1 + \frac{2\sqrt{2}\chi_{\perp}\hbar c}{Ng_L^2\mu_B^2 a}\right)^{-1}, \quad g < g_c,$$
(2.7)

where  $\chi_{\perp}$  denotes the susceptibility perpendicular to the orientation of the order parameter, c the spin wave velocity, N the number of spins,  $g_L$  the gyromagnetic Landé factor,  $\mu_B$ the Bohr magneton and a the lattice constant. Within spin wave theory the parameters equal  $\chi_{\perp} = N g_L^2 \mu_B^2 Z_{\chi}/(8J)$  and  $\hbar c = \sqrt{2} Z_c J a$  [105], where  $Z_{\chi}$  and  $Z_c$  are quantum renormalization parameters (see below). Hence we obtain

$$g/g_c = \frac{1}{1 + Z_\chi Z_c/2}, \quad g < g_c,$$
 (2.8)

and finally, using the values given in the last row of Table 2.4 below, we obtain an estimate for the coupling constant g of the 2D spin 1/2 square lattice Heisenberg antiferromagnet of  $g/g_c = 0.73$ , which is far enough from 1 to support the belief in long-range order at T = 0. It is worth mentioning that the predicted crossover with increasing temperature from renormalized classical to quantum critical behavior has not been found experimentally [89, 129], even in a system with  $J \approx 80$  K, allowing experiments in a wide range of T > J [129]. Furthermore we want to emphasize that the quantum non-linear  $\sigma$  model is a *continuum* model that is only meant to describe the *long-wavelength* behavior.

The T = 0 ground state, however, might look like an academic issue, since in the real materials long-range antiferromagnetic order sets in at temperatures up to 500 K. This is

<sup>&</sup>lt;sup>‡</sup>The coupling constant g acts like 1/zS, where z is the number of nearest neighbors, and measures the strength of quantum fluctuations.



Figure 2.8: Schematic phase diagram of the quantum non-linear  $\sigma$  model [127]. The thick line depicts the T = 0 ordered state for  $g < g_c$ .

due to deviations from truly two-dimensional behavior, giving rise to anisotropies in the Hamiltonian (for a tetragonal system)

$$H = J\left(\sum_{\langle ij\rangle} \mathbf{S}_i \cdot \mathbf{S}_j + \alpha_{XY} \sum_{\langle ij\rangle} S_i^c S_j^c + \alpha_{\perp} \sum_{\langle ik\rangle} \mathbf{S}_i \cdot \mathbf{S}_k\right), \qquad (2.9)$$

where  $\alpha_{XY} > 0$  denotes the easy-plane XY-anisotropy, *i.e.*, the difference in energy for "rotating" a spin in-plane or out-of-plane, and  $\alpha_{\perp}$  is the coupling between adjacent layers, where  $\langle ik \rangle$  denotes a pair of nearest-neighbor spins along c. The sum over  $\langle ij \rangle$  is again running over nearest-neighbor spin pairs in the CuO<sub>2</sub> plane. In comparison to Eq. 2.3 we have dropped the irrelevant constant energy shift and the minus-sign, which means that now a positive value of J corresponds to antiferromagnetic coupling. The parameters differ slightly among the classes of cuprates, but a good estimate is given by the canonical values  $J \approx 100$  meV,  $\alpha_{XY} \approx 10^{-4}$  and  $\alpha_{\perp} \approx 10^{-5}$ . Note that the spins are oriented in the *ab*-plane. Since we want to keep the "textbook" orientation of the staggered magnetization along the z-axis we have to live with z being different from c and lying in the "XY"-plane. In La<sub>2</sub>CuO<sub>4</sub> further complications arise due to the orthorhombic symmetry, which adds an antisymmetric Dzyaloshinski-Moriya term proportional to  $\mathbf{S}_i \times \mathbf{S}_j$  to the Hamiltonian, causing a finite canting of the spins out of the CuO<sub>2</sub> layers and weak ferromagnetism in an applied field. Another extension is necessary in tetragonal YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> due to the coupling between nearest-neighbor layers in a bilayer

$$H_{12} = J_{12} \sum_{i} \mathbf{S}_{1,i} \cdot \mathbf{S}_{2,i}$$
(2.10)

where *i* again labels all Cu sites in a 2D square lattice, and  $\{1, 2\}$  count the two planes in a single bilayer. Actually, a Dzyaloshinski-Moriya term is present in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> as well. It arises from the buckling of the layers, the fact that the plane of O sites is shifted with respect to the plane of Cu sites, leading to a Cu-O-Cu bond angle of 167°. In a single layer, this term would promote a spiral spin ordering [130], but in a bilayer the spiraling is frustrated by the interlayer coupling  $J_{12}$  and disappears for  $J_{12} \gtrsim 10^{-3} J$  [131].

Let us go back to equation 2.9 in order to estimate within a mean-field argument the three-dimensional order temperature caused by the anisotropies. We may assume that the transition occurs when the asymmetric terms in the Hamiltonian Eq. 2.9 times the number of spins within an area determined by the correlation length are of the order of  $k_B T$ . Accordingly, the single layer compound  $Sr_2CuO_2Cl_2$  is the material closest to the ideal case because (a) it is tetragonal and (b) the  $\alpha_{\perp}$  term is almost fully frustrated, since the spins form a body-centered lattice, every spin sitting above the middle of the spin plaquette of the adjacent layer. The strongest remaining anisotropy results from spin-orbit corrections to superexchange, which also makes the  $CuO_2$  plane the easy-plane [132]. Despite its tiny value it still yields a 3D ordering temperature of 256 K [105], which is due to the very large in-plane exchange coupling of the order of 1500 K. The larger anisotropies in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> allow for ordering already at about 500 K, and in  $Ca_{0.85}Sr_{0.15}CuO_2$  a Néel temperature  $T_N$  as high as 540 K is observed [133]. One has to realize that the correlation length is already quite large above  $T_N$ , and hence the phase transition is not very spectacular from a thermodynamic point of view, the specific heat "jump" is unmeasurably small [105]. Despite the absence of a signature in the specific heat data, the interesting range for comparison of experimental results, such as neutron scattering measurements, with the 2D spin 1/2 Heisenberg model is restricted to high temperatures,  $T > T_N$ .

The presence of 3D long-range order is convincingly established by the appearance of a Bragg peak at  $(\pi, \pi)$  in neutron diffraction studies. The magnetic unit cell is doubled due to the antiparallel alignment of neighboring spins. The resultant magnetic Brillouin zone follows the tight-binding Fermi surface for half-filling and is shown in Fig. 2.9. Thus far we have avoided calling the ordered state a Néel state, as is usually done. The excitations of the Néel state are spin waves, and spin wave theory is supposed to describe them rather well even for S = 1/2 in 2D. We want to argue that the current belief that the Néel state approximates the true ground state well enough is based on *long-wavelength* physics. Detailed comparisons of the high temperature correlation length with theoretical predictions for the 2D spin 1/2 Heisenberg model are indeed very



Figure 2.9: Magnetic Brillouin zone (dashed line) and definition of high symmetry points.

valuable and tell us the validity of the approach for *long wavelengths*, but celebrating the Heisenberg Hamiltonian the way it is done closes our eyes for the probably more important *local* physics. Inelastic neutron scattering experiments observed a well-defined spin-wave peak even at the Brillouin zone boundary, which has led people to believe that spin-waves tell the full story. We want to claim that fascinating physics is hidden in the "background",

and that the full line shape has to be analyzed, not just the width of the main peak.

In the following we first want to present the spin wave scenario. Alternative models such as the resonant valence bond (RVB) state or flux phases will be mentioned, and the excitation spectrum will be discussed. Then we want to discuss the problems encountered in describing neutron and Raman scattering with spin wave theory. We will argue that the mid-infrared optical conductivity spectrum most directly offers some "line shape", which we will discuss in chapter 5.1, and that the line shape gives a fingerprint of the excitations. We want to emphasize that *short-range* physics become dominant in the presence of doped holes, and we will discuss the shortcomings of a spin-wave scenario using angle-resolved photoelectron spectroscopy (ARPES) data. This will serve as a bridge to the discussion of the superconducting phase, in particular concerning the underdoped regime, in section 2.3.1. Our main conclusion in this introduction will be that the key to the anomalous behavior encountered in the underdoped phase is hidden in the "dressing" the doped carriers have to carry around, and that we can only hope to understand that if we are able to describe the excitations which form the "dressing", *i.e.*, the excitations of the antiferromagnetic state.

We start with introducing the concept of spin wave theory, the obvious idea of which is to describe the magnetic excitations as small deviations from the broken symmetry ground state, just as we are used to doing with phonons. In an antiferromagnet it is convenient to rotate one of the two equivalent sublattices A and B. We hence define

$$\tilde{S}_{j}^{z} = -S_{j}^{z}, \quad \tilde{S}_{j}^{x} = S_{j}^{x}, \quad \tilde{S}_{j}^{y} = -S_{j}^{y}, \quad j \in B,$$
(2.11)

where z denotes the orientation of the staggered magnetization. Now we can rewrite the isotropic Heisenberg Hamiltonian [18]

$$H = \frac{J}{2} \sum_{\langle ij \rangle} \left( S_i^+ \tilde{S}_j^+ + S_i^- \tilde{S}_j^- \right) - J \sum_{\langle ij \rangle} S_i^z \tilde{S}_j^z \quad , \tag{2.12}$$

where  $i \in A$ ,  $j \in B$  and the  $S^+$  ( $S^-$ ) are spin raising (lowering) operators. The somewhat unconventional  $S^+S^+$  combinations which replace the familiar  $S^+S^-$  terms stem from the rotation in Eq. 2.11. This rotation simplifies our next step, since it allows one to define the Holstein-Primakoff transformation from spin to Bose operators in the same way on both sublattices,

$$S^+ = \left(\sqrt{2S - n_b}\right)b \tag{2.13}$$

$$S^{-} = b^{+} \left(\sqrt{2S - n_b}\right) \tag{2.14}$$

$$S^z = -n_b + S \tag{2.15}$$

where the  $b^+$  (b) are Boson creation (annihilation) operators, and  $n_b$  is the corresponding number operator. The physical states are of course restricted to  $\{|n_b\rangle\}_S = \{|0\rangle, |1\rangle, \ldots, |2S\rangle\}$ , other states have to be projected out. Now we expand the square root in Eqs. 2.13 and

$\langle S^z \rangle$	$Z_c$	$Z_{ ho}$	$Z_{\chi}$	order	Ref.
0.303	1	1	1	0	[138]
0.303	1.158	0.601	0.448	1/2S	[139]
0.307	1.179	0.724	0.514	$(1/2S)^{2}$	[135]
0.308	1.172	0.720	0.525	QMC	[134]

Table 2.4: Magnitude of the order parameter  $\langle S^z \rangle$  and renormalization factors obtained in up to second order of spin wave theory. A recent quantum Monte Carlo result is given in the last line.

2.14 in 1/2S,

$$\sqrt{2S - n_b} = \sqrt{2S} \left( 1 - \frac{n_b}{4S} - \frac{n_b^2}{32S^2} \cdots \right).$$
 (2.16)

Often, spin wave theory is called a 1/S expansion, but 1/2S might be more suitable. The truncation of the expansion to low orders connects physical and unphysical subspaces. It can be justified if  $\langle n_b \rangle \ll 2S$ . The expansion shows that the classical limit of non-interacting magnetic excitations is realized for  $S = \infty$ . Non-interacting spin waves are also the result of *linear* spin wave theory, which keeps only the zeroth order term of Eq. 2.16 even for the case of finite spin. The Hamiltonian can then be diagonalized by making use of a Bogoliubov transformation, the resulting Bosons being called magnons. The Bogoliubov transformation mixes an arbitrary number of "Holstein-Primakoff Bosons", *i.e.*, spin-flips into the classical Néel ground state, which reduces the order parameter. The resulting "quantum Néel" state is kind of a classical Néel state with "short spins". The magnon dispersion for a 2D spin 1/2 isotropic Heisenberg model on a square lattice is given by

$$\hbar\omega_{\mathbf{q},0} = zJS\left(1 - \gamma_{\mathbf{q}}^2\right)^{1/2}, \quad \gamma_{\mathbf{q}} = \frac{1}{2}\left[\cos(q_x a) + \cos(q_y a)\right]$$
 (2.17)

where z = 4 counts the number of nearest neighbors, a denotes the lattice parameter, and  $\mathbf{q} = (q_x, q_y)$  designates the wave vector. The index 0 denotes the "semi-classical" zeroth order limit. The dispersion is twofold degenerate due to the two interchangeable sublattice directions. For small  $\mathbf{q}$  the dispersion is linear,  $\hbar\omega_{\mathbf{q},0} = \sqrt{8} JSa|\mathbf{q}|$ , and the spin wave velocity c is defined via the slope,  $\hbar c_0 = \sqrt{8} JSa$ . The spin-stiffness constant  $\rho_{s,0} = JS^2$  measures the increase in ground state energy upon rotating the staggered order parameter. The staggered magnetic moment per spin is  $g\mu_B \langle S^z \rangle$ , and  $\langle S^z \rangle \approx 0.3$ . The magnetic susceptibility for a magnetic field perpendicular to the orientation of the order parameter is expressed as  $\chi_{\perp,0} = Ng_L^2\mu_B^2/8J$ , where N is the number of spins,  $g_L$  denotes the gyromagnetic Landé factor, and  $\mu_B$  is the Bohr magneton.

Switching on the interaction between spins, *i.e.*, allowing for quantum fluctuations by including higher terms of Eq. 2.16 is described by using the following three renormalization
factors  $Z_c$ ,  $Z_\rho$  and  $Z_{\chi}$ :

$$c = c_0 Z_c = \sqrt{8JSaZ_c} \tag{2.18}$$

$$\rho_s = \rho_{s,0} Z_\rho = J S^2 Z_\rho \tag{2.19}$$

$$\chi_{\perp} = \chi_{\perp,0} Z_{\chi} = \frac{N g_L^2 \mu_B^2}{8J} Z_{\chi}$$
(2.20)

Note that the factors are not independent,  $Z_c^2 = Z_{\rho}/Z_{\chi}$ , which follows from  $c^2 \propto \rho_s/\chi_{\perp}$ . The quantum fluctuations are essentially reduced to a renormalization of the energy scale, and are assumed not to change qualitatively the character of the excitation spectrum. Values of the renormalization factors and the average spin  $\langle S^z \rangle$  found in up to second order in 1/2S are collected in Table 2.4. We also included a recent quantum Monte Carlo result [134]. The influence of a next-nearest neighbor coupling J' on the renormalization parameters has been studied by Igarashi in spin wave theory up to second order and up to J'/J = 0.4 [135]. A more complete list for J'=0 including results from other calculational techniques can be found in the recent review of Johnston [105]. The general agreement is usually interpreted as an indication of the surprising validity of the spin wave approach even for spin 1/2, where 1/2S is not really a small number. Note that the normal ordering of operators necessary for the higher order terms is already a laborious task in first order. The first order correction to  $Z_c$  is known as the Oguchi-correction. In order to obtain the value of J from experimental data often  $Z_c = 1.18$  is used, since this second order result agrees with the value obtained in a high temperature series expansion [136, 137]. We want to mention that the series expansion indicates that the renormalization of the dispersion is not uniform, the magnon energy being larger at  $(\pi/2, \pi, 2)$  than at  $(\pi, 0)$  by 7% [137]. A marked difference between these two points is found in ARPES data of the insulating cuprates which is not explained by the simple nearest neighbor t-J model (see below).

#### Alternative models

It is well known that the Néel state serves only as an approximate ground state. A straightforward way for trying to improve on this is the use of variational wave functions, the most famous being the (nearest neighbor) resonant valence bond (RVB) state proposed by Anderson [20]. Originally, the RVB state was proposed by Anderson in 1973 for the description of the triangular lattice [140]. A valence bond state is a state which consists only of singlet pairs. Even if we restrict ourselves to only nearest neighbor singlet pairs the number of possible states or coverings is exorbitant, in which case the term *resonant* valence bond state is used. In general different coverings are not orthogonal, which complicates the problem significantly. The ground state in this model is a linear combination of all degenerate states of singlet pairs. The ground state energy is lowered by the strong quantum fluctuations between the different coverings of the two-dimensional plane. A compact wave function is however only known for the nearest neighbor RVB state [141].

Other spin liquid states have been proposed such as the flux phase [19, 142] with diamagnetic currents flowing around a plaquette. Photoemission studies of antiferromag-

	t'/t	$J \ ({\rm meV})$	$J' \ (meV)$	J'/J	$J_{12} \ (\mathrm{meV})$
$\rm La_2CuO_4$	-0.3	166	15	0.09	
$\mathrm{YBa}_2\mathrm{Cu}_3\mathrm{O}_6$	-0.45	163	33	0.20	8.4

Table 2.5: Exchange constants as derived by Morr [153] from fits to experimental neutron scattering data, using values for the next-nearest neighbor hopping t' which were obtained from band structure calculations and ARPES data.

netic  $Sr_2CuO_2Cl_2$  [143, 144] (see below) find comparable excitation energies at the (0,0) and (0,  $\pi$ ) points, which agree with expectations for a  $\pi$ -flux spectrum [19, 145] (see also Refs. [146, 147]). This has been taken as an indication that the antiferromagnetic state may resemble the  $\pi$ -flux state at short distances. Anderson's interlayer tunnelling theory for high T<sub>c</sub> superconductivity relies on the separation of spin and charge in 2D, and the related slave-boson mean-field theories [145, 148] suggest a  $\pi$ -flux phase for half-filling. Obviously, the discussion about the correct ground state of the cuprate parent compounds is highly relevant to the field of high T<sub>c</sub> superconductivity and vice versa.

It has been argued that the RVB state is not realized in the nearest neighbor Heisenberg model [149]. However, if the Néel state is really so close to the true solution of the simple nearest neighbor Heisenberg Hamiltonian but does not — as we hope to show later on — capture the relevant physics of the insulating cuprates, then we have to look for the most important extensions to the model. Already in the original paper in 1987 [20] Anderson mentioned that the RVB state will be promoted by either a frustrating nextnearest neighbor coupling or a virtual phonon interaction which is not strong enough to favor a spin-Peierls state. Also Chakravarty, Halperin and Nelson [127] mentioned already in their original paper in 1989 that the critical parameter g in the quantum non-linear  $\sigma$ model depends on a frustrating next-nearest neighbor coupling J'. They suggested that for a large enough value of J' the T = 0 ground state possibly could be quantum disordered. They, however, concluded that this is not the case in  $La_2CuO_4$ . The characters of the phases arising with finite J' have been discussed controversially. Kampf [62] noted that the spin wave velocity vanishes for J' = J/2, the same value at which the Néel state disappears in the *classical* Heisenberg model [149]. In the classical limit, a four-sublattice antiferromagnet with antiparallel alignment within each of the former sublattices A and B arises. Kotov and co-workers [150] report a critical value of  $(J'/J)_c \approx 0.38$  for the quantum transition from Néel order to quantum disorder in the form of spontaneous dimerization.<sup>§</sup> For J'/J > 0.65 a collinear magnetic ordering with columnar stacking of up and down spins arises, a precursor of the four-sublattice phase [151, 152]. The magnon dispersion in the presence of a finite J' has recently been calculated for single and bilayer materials by

<sup>&</sup>lt;sup>§</sup>Studies which focus on the quantum transition or the quantum disordered phase usually call the Hamiltonian the  $J_1 - J_2$  model, which for the case of a 2D square lattice is equivalent to our J - J' model with  $J \equiv J_1$  and  $J' \equiv J_2$ .

Morr [153]. The bilayer result reads

$$\hbar\omega_{ac,op}(\mathbf{q}) = 2J \left\{ \left[ 1 \mp \gamma_{\mathbf{q}} + \frac{J_{12}}{2J} - \frac{J'}{J} \left( 1 - \cos(q_x)\cos(q_y) \right) \right] \times \left[ 1 \pm \gamma_{\mathbf{q}} - \frac{J'}{J} \left( 1 - \cos(q_x)\cos(q_y) \right) \right] \right\}^{1/2}, \qquad (2.21)$$

where the upper (lower) sign denotes the acoustic (optical) magnon branch,  $J_{12}$  is the exchange coupling between layers as defined in Eq. 2.10 and  $\gamma_{\mathbf{q}}$  was defined in Eq. 2.17. The single layer result is readily obtained by putting  $J_{12} = 0$ . One interesting feature of this dispersion is that the finite value of J' lifts the degeneracy between  $(\pi/2, \pi/2)$  and  $(\pi, 0)$  by about 10%, a point of major importance in the discussion of single hole dynamics and ARPES data (see below). Using values for the next-nearest neighbor hopping t' obtained from band structure calculations and ARPES data, Morr [153] derived the exchange constants from fits to experimental neutron scattering data (see Table 2.5). Moreover, he reported that the quantum renormalization factors (see Table 2.4) are enhanced by a finite J'.

The energy difference between  $(\pi/2, \pi/2)$  and  $(\pi, 0)$  had been noted already in 1988 by MacDonald, Girvin and Yoshioka [154], who had carried out a t/U expansion of the Hubbard model. There, the J' term is accompanied by a 4-spin cyclic exchange term appearing in the same order  $t^4/U^3$ . They concluded that these higher order terms promote valence bond states compared to the Néel state. MacDonald, Girvin and Yoshioka found that in particular the 4-spin cyclic exchange lifts the degeneracy between different valence bond states. Lowest in energy are those states which contain only one singlet bond on the perimeter of a plaquette (see Fig. 2.10 (a)). Interestingly, this disagrees with results for the pure  $J_1 - J_2$  or J - J' model (including some dimerization), for which the covering shown in Fig. 2.10 (b) is the ground state in a certain parameter regime (see Refs. [150,155] and references therein). The important message of MacDonald and co-workers is that the 4-spin cyclic exchange appears in the same order of the t/U expansion as J' and can hence not be neglected. For the expectation values in the Néel state and the most favorable valence bond states MacDonald and collaborators [154] obtain

$$\langle H \rangle_{\text{N\acute{e}el}} = -4t^2/U + 24t^4/U^3 + \cdots , \quad \langle H \rangle_{\text{VB}} = -7t^2/2U + 12t^4/U^3 + \cdots$$
(2.22)

and cite the ground state energy to be  $\langle H \rangle_0 = -4 \cdot 8t^2/U$ . Even though the cuprates do not reach the critical value  $t/U \approx 0.2$  at half-filling MacDonald, Girvin and Yoshioka argued that a spin-liquid state might become important if additional frustration is introduced by doping holes. Oleś [154] commented that this conclusion cannot be drawn from low orders and that the expectation values can be misleading since they do not incorporate quantum fluctuations.

Promotion of the quantum disordered singlet state by a frustrating next-nearest neighbor term is a well known phenomenon in 1D. Consider a chain with an even number of



Figure 2.10: Two distinct nearest neighbor singlet coverings of the 2D square lattice. Note that state (a) has no plaquette with more than one singlet bond on the perimeter.

sites which are antiferromagnetically coupled and obey cyclic boundary conditions. Since it is not long-range ordered, the ground state qualifies for a spin liquid already without frustration, but a state of singlet pairs needs either some external dimerization or some kind of frustration. If the next-nearest neighbor coupling J' is also antiferromagnetic and larger than the critical value  $J'/J \approx 0.241$  then the ground state is a nearest-neighbor spin singlet valence bond state, the so-called dimerized state. A particularly simple exact spin dimer state is realized for J'/J = 1/2, the so-called Majumdar-Gosh point [156]. The two coverings  $12 - 34 - 56 \cdots$  and  $N1 - 23 - 45 \cdots$ , where ij labels a bond of neighboring sites i and j in the N-site chain, are degenerate. These dimerized states have experienced revived interest after the recent discovery of compounds such as  $(VO)_2P_2O_7$  [157] or the first inorganic spin-Peierls compound [158], CuGeO<sub>3</sub>, which allowed for a more precise analysis of the singlet liquid state than the previously known less clean organic examples. A comfortable model that does not have the problem of non-orthogonality is shown for one and two dimensions in Fig. 2.11 [159]. The dimerization pattern drawn defines a unique covering of the structure, the dimerized state is an exact eigenstate. It is easy to convert this pattern into a similar covering for three dimensions [159]. During the writing of this thesis a 2D realization of this pattern was reported [160],  $SrCu_2(BO_3)_2$ , which additionally seems to be very close to the critical coupling ratio [159]. New structures are reported at a high rate during these days, and interesting physics is ahead.

Another route towards a spin liquid but without frustration is to consider a spin 1/2 two-leg ladder in the case that the coupling across the rung  $J_{\perp}$  is much larger than along the leg (J) of the ladder. For J = 0 the ground state obviously consists of independent spin singlet bonds, one on each rung, with a gap to (triplet) spin excitations. A finite J will drive the system into a resonating valence bond state. What comes as a surprise is that the spin gap most likely remains finite for any finite ratio  $J_{\perp}/J$  [80, 161]. Even



Figure 2.11: Examples of exact dimer ground states in one and two dimensions, reproduced from Ref. [159]. The solid lines denote the dimers.

more surprising is that this demonstrates a profound difference between spin 1/2 evenand odd-leg ladders. It is believed that all even-leg ladders have a spin-gap, whereas all odd-leg ladders are similar to the single isolated chain and have gapless excitations [80]. The underlying physics is that an even number of spin 1/2 particles can form a total S=0singlet with a gap to the triplet excitations, whereas an odd number of spins combines at least to total S = 1/2. Odd-leg ladders are hence like single chains with an effective coupling  $J_{eff}$  between total S=1/2 states. Note that a frustrating next-nearest neighbor coupling along the leg will change the physics again (see below).

A similar geometry is encountered in another popular system for the study of singlet liquids, the bilayer, which undergoes a transition to an interlayer singlet pair state if  $J_{12}$ rises above the critical value,  $J_{12}/J \approx 2.5$  [162–164]. The phase diagram of a bilayer including also the next nearest neighbor in-plane exchange J' has been discussed in Refs. [165, 166]. In YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> and other cuprates the coupling  $J_{12}$  is too small to form a quantum disordered state, but recently copper silicates and germanates (BaCuSi<sub>2</sub>O<sub>6</sub> and CaCuGe<sub>2</sub>O<sub>6</sub>) have been discovered which represent the opposite limit. In the 2D S = 1/2square lattice bilayer BaCuSi<sub>2</sub>O<sub>6</sub> Sasago and co-workers [167] find  $J_{12}/J \approx 24$  and the excitations are local single-dimer excitations hopping from one site to another. Obviously, experiments on a bilayer closer to the critical ratio  $J_{12}/J \approx 2.5$  would be very interesting.

An at first sight surprising, and in this context very interesting, result is the coexistence of dimerization (spin singlets) and antiferromagnetism in a 1D spin chain in the presence of impurities. Experimental indications for this coexistence in the spin-Peierls compound  $CuGe_{1-y}Si_yO_3$  or  $Cu_{1-x}Zn_xGeO_3$  came from neutron scattering experiments [168]. A theoretical model able to describe the coexistence was developed by Fukuyama [169].

Matthew Fisher and co-workers have argued recently that in the case of the cuprates, which are rather in an intermediate t/U coupling regime, subsuming the Fermionic degrees of freedom in an effective spin model is "throwing out the baby with the bath water" [170].

They developed the notion of a "nodal liquid" and view the underdoped and undoped cuprates as a quantum disordered version of a *d*-wave superconductor. At half-filling the nodal liquid is a Mott insulator with a charge gap. It does not have broken symmetries, but nevertheless possesses gapless spin excitations, but these stem from *Fermionic* degrees of freedom. These "nodons" are charge neutral descendants of the quasiparticles of the superconducting state (via a gauge transformation), which live in the nodes of the *d*-wave gap. Fisher and collaborators claim that the behavior of a two-leg ladder is reminiscent of that encountered in the cuprates. At the present state, however, the details of the magnetic insulating state and the relevance to the undoped cuprates have not been worked out.

A central issue in the discussion of quantum disordered states is of course the character of the elementary excitation spectrum. In 1979 it was realized by Andrei and Lowenstein [171, 172] and in 1981 by Faddeev and Takhtajan [173] that the true excitations in the 1D spin 1/2 Heisenberg chain are what we call spinons<sup>¶</sup> today, a spin 1/2 soliton, a topological kink of the order parameter. An external probe such as neutrons will see a two-spinon continuum, since the spin-flip (or equivalently spin 1 magnon) induced by the probe decays into two spinons that can share energy and momentum in different ways, giving rise to a two-particle continuum. The other obvious excitation in a singlet liquid is a spin 1 triplet excitation. Only recently ideas about confinement of spinons into bound states by introducing external dimerization have been formulated [174, 175]. The external dimerization  $\delta$  is expressed as a  $J \sum_{i} (-\delta)^{i+1} \mathbf{S}_i \cdot \mathbf{S}_{i+1}$  term. It favors the  $12 - 34 - 56 \cdots$ covering over  $23 - 45 - 67 \cdots$ . A spinon travelling along the chain shifts the dimers from the favorable to the unfavorable state, the energy cost being proportional to the length of the "long-dimer" segment, *i.e.*, the distance between two spinons (see Fig. 2.12). A similar confinement of spinons was reported for a frustrated two-leg ladder and a 2D array of coupled 1D chains [176]. In the presence of spinon confinement the excitation spectrum shows multiple singlet and triplet excitations [176].

Recently, Eder elaborated upon the 2D nearest neighbor RVB state [21]. He showed that the elementary excitations are not spinons due to the non-orthogonality with the ground state, but spin 1 dimer excitations. The non-orthogonality is specifically problematic for the 2D square lattice case, since for example in a two-leg ladder a unique dimer covering exists. Eder derived the dispersion relation for the triplet excitations of the dimers and found at T=0 a condensation of triplets at  $(\pi, \pi)$ , which produces antiferromagnetic order. The relevance of this "triplet condensation" will reveal itself in the discussion of the SO(5) symmetry model for the superconducting state on page 79. The propagation of excited dimers is similar to the excitations found in the two- or even-leg ladders. The paradox behind this similarity has been pointed out by Dagotto and Rice [80]: The underdoped

<sup>&</sup>lt;sup>¶</sup>The credits for the first description of spinons usually go to Faddeev and Takhtajan [173]. However, Andrei and Lowenstein "discovered" the spinon in Ref. [171] in the context of the Gross-Neveu model. They proved that the excitations carry spin 1/2 and that they are created only in pairs. In Ref. [172] they calculated the spinon S-matrix, *i.e.*, the complete solution for the spin excitations. Andrei and Lowenstein do not explicitly mention the Heisenberg antiferromagnet in their papers, but the Bethe ansatz equations used for the Gross-Neveu model hold also for the Kondo problem and the Heisenberg antiferromagnet. The same is true for the character of the spinons and their S-matrix.



Figure 2.12: Spinon confinement in (a) a dimerized chain and (d) a frustrated ladder consisting of two weakly coupled Majumdar-Gosh chains [176]. (a) In (1) a dimerized 1D chain is shown in which the singlets prefer the  $J + \delta$  bonds over the  $J - \delta$  ones. (2) depicts a triplet excitation that decays in (3) into two spinons. The spinon confinement is obvious from (4): in the region between the two spinons the unfavorable  $J - \delta$  bond singlets are formed, and therefore the excitation energy increases with the distance between the spinons. (b) and (c) show two possible versions of two weakly coupled (small  $J_{\perp}$ ) dimerized Majumdar-Gosh chains (a frustrated ladder), where (b) is lower in energy than (c) [176]. In (d) two spinons have been excited in one of the two chains, and the region between the two spinons is turned into an energetically unfavorable state that confines the spinons, similar to case (a).

2D cuprates resemble the two-leg ladders in that they show a spin-gap and d-wave pairing. Superconductivity had been predicted for the two-leg ladder and has meanwhile indeed been observed [177]. At the same time, however, the long-range magnetically ordered state in the undoped 2D cuprates evolves smoothly from the nearly ordered character of the odd-leg ladders.

In the preceding paragraphs we have studied excitations possible beyond the spin wave approach. The "anomalous" excitations we found are the "normal" excitations of a spin liquid ground state. Yet another possibility is to stick to the Néel ground state but to consider excitations other than the "small amplitude" spin waves such as topological excitations, vortices [1]. In 2D the order parameter rotates on any closed path around a vortex core by  $2\pi n$ , where the integer number n denotes the winding number. The energy of a vortex increases with the size of the (spherical) sample with radius R like  $\ln R$  [1] and a single vortex is hence not a very likely state to occur. This changes if we consider a vortex-antivortex pair with winding numbers +n and -n. Such a pair is similar to a dipole and their disturbances cancel at large distances, resulting in a finite energy for the pair creation. Kosterlitz and Thouless obtained a strong influence of vortex-antivortex pairs on the temperature dependent behavior of the classical 2D XY-model [178]. A visual impression of a vortex and a vortex-antivortex pair is reproduced from Ref. [19] in Fig. 2.18 (a) and (b) on page 50. We want to postpone the discussion to the section dealing with hole doping, since vortices and related objects such as Skyrmions and merons have mainly been studied in connection with doping in the context of the cuprates. However, we want to mention that the occurrence of vortices around doped holes is promoted if the underlying antiferromagnetic background is not a Néel state but a so-called spin flux state [19]. In the spin flux phase on the 2D square lattice the spin part of the electron wavefunction experiences a rotation by  $2\pi$  on encircling a plaquette [19]. Berciu and John included a next-nearest neighbor Coulomb repulsion in the one-band Hubbard model and claimed that in mean field the spin-flux phase has a lower ground state energy than the conventional antiferromagnet [19]. This energy gain can be expressed in a very interesting way: in the conventional state all points of the Brillouin zone edge belong to the nested tight binding Fermi surface, whereas in the spin-flux phase all points are lowered in energy with respect to the four points at  $(\pm \pi/2, \pm \pi/2)$  [19]. This has meanwhile been confirmed experimentally and will be discussed in connection with the pseudogap observed in underdoped cuprates (see Fig. 2.33 on page 70).

## 2.2.2 Neutron and Raman Scattering in Undoped Cuprates

#### **Correlation Length**

The strongest support for a Néel-type of ordering in the insulating 2D cuprates is believed to come from neutron experiments. The 3D ordering at the Néel temperature is convincingly established by the observation of a Bragg peak at  $(\pi, \pi)$  (for a recent review, see Kastner *et al.* [89]). The study of the 2D Heisenberg antiferromagnet is thus restricted to  $T > T_N$ . Above  $T_N$  the correlation length is determined from the now quasi-elastic peak at  $(\pi, \pi)$ . Correlations are found to be truly two-dimensional and rather long-range due to the large value of J. Initially, the correlation length  $\xi(T)$  was reported to vary approximately linearly with 1/T at high temperatures even in the undoped case, which was — following the quantum non-linear  $\sigma$ -model [127] — attributed to quantum critical behavior and the quantum critical point was placed at zero doping, x = 0 [179]. Later measurements [180–182] extending to lower and higher temperatures showed an exponential divergence in 1/T, pointing towards long-range order at T = 0. The temperature

	$Z_{\chi}$ $(\chi)$	$Z_{\chi}~(\xi)$
$YBa_2Cu_3O_6$	$0.4 \pm 0.1 \; [189]$	
${ m La}_2{ m CuO}_4$	$0.39 \pm 0.1 \; [189]$	
${ m La}_2{ m CuO}_4$	0.36 [190]	$0.52 \pm 0.04$ [190]
$\mathrm{Nd}_{2}\mathrm{CuO}_{4}$	0.28 [190]	$0.46 \pm 0.04$ [190]
$\mathrm{Pr}_{2}\mathrm{CuO}_{4}$	0.28 [190]	$0.43 \pm 0.04$ [190]

Table 2.6: Experimental results for the quantum renormalization parameter  $Z_{\chi}$  as determined from (left column,  $\chi$ ) the spin susceptibility measured in absolute units or (right column,  $\xi$ ) the correlation length. A recent quantum Monte Carlo simulation yields  $Z_{\chi} = 0.525$  [134] (see Table 2.4).

dependence and even the absolute value of  $\xi(T)$  agree very well with renormalized classical behavior as calculated by Hasenfratz and Niedermayer [134, 183] and with Monte Carlo simulations [184]. The long-wavelength physics are determined by thermal fluctuations, quantum fluctuations only renormalize the correlation length, even though in a dramatic way for S = 1/2 [182], and the overall behavior is very similar to the classical case. However, the excellent agreement between experiment and theory is spoiled by the disagreement observed for the S = 1 systems La<sub>2</sub>NiO<sub>4</sub> [185] and K<sub>2</sub>NiF<sub>4</sub> [180]. There, the spin stiffness  $\rho_s$ has to be reduced by 20% in comparison to the spin-wave result in order to retrieve agreement, *i.e.*, the renormalization due to quantum fluctuations is stronger than predicted. This issue has been addressed by Elstner and co-workers [186] and Beard and collaborators [134]. They conjecture that the experimental data most likely are not in the asymptotic scaling regime [89, 134, 186], *i.e.*, that the experimental accessible correlation lengths are too short for present theory to apply, and that excellent agreement had been claimed for a temperature range where the theory should in principle not hold anymore. The discrepancy for S=1 however shows that this excellent agreement for the S=1/2 case is partly accidental. Moreover, the peak intensity of the static structure factor, which measures instantaneous spin-spin correlations, is predicted to obey  $S(0) \propto T^2 \xi^2$  [127, 187], whereas in both S = 1/2 and S = 1 systems a dependence  $\propto \xi^2$  is observed [179, 180, 182, 185]. Interestingly, Greven and collaborators argue that the discrepancy might be due to the fact that the non-linear  $\sigma$  model is a continuum model which does not describe shortwavelength spin-waves properly [180]. Recent data on the S = 5/2 system Rb<sub>2</sub>MnF<sub>4</sub> [188] agree with the theoretical prediction  $S(0)\xi^{-2} \propto T^2$ , but also show a cross over to a weaker temperature dependence. We want to remark that the high temperature behavior is not entirely conclusive for the low temperature state. Just as 2D behavior is encountered only above  $T_N$  where temperature destroys the interplane correlations, a similar effect might reduce the frustration due to a next-nearest neighbor coupling J' at high temperatures, but the frustration might still be substantial at lower temperatures. Note that in mean-field the interplane correlations vanish for  $k_B T$  of order  $J_{\perp} \xi^2 / a^2$ , where a is the lattice spacing, but that thermal fluctuations overrule J' already for  $k_B T$  of order z'J', where the number of next-nearest neighbors z' equals 4. Another remark concerns the experimental result for the correlation length in the case of finite doping concentrations [179], which will be discussed in the next section.

Theoretically, the values of the renormalization parameters  $Z_c$ ,  $Z_{\chi}$  and  $Z_{\rho}$  seem to be very well known, as indicated by the good agreement in Table 2.4 between higher order spin wave theory and quantum Monte Carlo results. Experimentally, the case is still open. Since  $Z_c$  renormalizes the overall energy scale it cannot be determined from experiment. On contrary, the other two can be obtained from neutron scattering data, but Bourges and collaborators pointed out a discrepancy between the two ways to determine  $Z_{\chi}$  and  $Z_{\rho}$  [190]. One way is to measure the spin susceptibility in *absolute units*, which allows one to determine  $Z_{\chi}$  if  $Z_c$  is known [189, 190]. The second estimate can be obtained from  $Z_{\rho} = 4\rho_s/J$ , where  $\rho_s$  is derived from a fit of the correlation length  $\xi \propto \exp\left(2\pi\rho_s/k_BT\right)$ . Also here knowledge of  $Z_c$  is required (to yield the correct value of J), and  $Z_{\chi}$  can then be obtained from  $Z_{\chi} = Z_{\rho}/Z_c^2$ . Bourges and co-workers [190] point out that the two ways yield results that disagree, and that moreover the renormalization parameters depend on the material studied (see Table 2.6). In general the experimental values are smaller than the theoretical results summarized in Table 2.4. Note that Itoh and collaborators [191] have given  $\langle S \rangle = 0.17$  for La<sub>2</sub>CuO<sub>4</sub>, in agreement with the small values given in Table 2.6. One problem in the determination of the absolute value of the spin susceptibility is the atomic form factor of the  $Cu^{2+}$  spins, which is not known precisely. Bourges and collaborators [190] use an asymmetric form factor, whereas Itoh and co-workers choose the free ion form factor [191]. Also the Landé factor  $g_L$  is not known accurately, since electron spin resonance measurements did not succeed in finding a resonance in the cuprates. Bourges et al. [190] use  $g_L = 2$ , whereas 2.1 [192] and 2.2 [193] have been claimed to be typical. In fact,  $g_L$ is anisotropic. Kaplan and collaborators state that the experimental value of  $Z_{\chi}$  should be much smaller than the theoretical one, since a large additional reduction is expected from covalency [194]. Also the second method of determining  $Z_{\rho}$  and  $Z_{\chi}$  has its traps. Johnston [105] pointed out that in order to determine  $Z_{\rho}$  one should not use the exponent of a purely exponential fit to the correlation length  $\xi$  (as done above), since the exact functional form given by Hasenfratz and Niedermayer [183] reads

$$\xi \propto \frac{1}{2\pi\rho_s} \exp\left(\frac{2\pi\rho_s}{k_B T}\right) \cdot \left(1 - 0.5 \frac{k_B T}{2\pi\rho_s} + O\left(\frac{k_B T}{2\pi\rho_s}\right)^2\right).$$
(2.23)

Discrepancies between the values of the ordered moment determined from neutron scattering or local probes such as muon spin rotation ( $\mu$ SR), nuclear quadrupole resonance (NQR) and Mössbauer spectroscopy have been pointed out by Johnston [105]. With increasing doping concentration the Néel temperature is rapidly reduced. Neutron data indicate that the ordered moment drops rapidly with  $T_N$ , whereas for local probes the reduction is observed to be much more gradual [105]. This results in a discontinuity of the ordered moment at  $T_N$  in for example NQR data [195], whereas neutron measurements show a smooth reduction to zero [196].

#### Inelastic Neutron Scattering

Another important milestone in the celebrated victory of spin wave theory comes again from neutron scattering results. Hayden and collaborators observed well-defined peaks at



Figure 2.13: (a) Neutron scattering cross section emphasizing the Brillouin zone boundary. A lifetime  $< 10/\omega$  is deduced. Dashed line: nearest neighbor spin wave theory. (b) Spin wave dispersion. Full (open) symbols: data from spallation source (reactor). The detectors integrate over the wave vector range indicated by the horizontal bars. Both panels reproduced from Hayden et al. [197].

the Brillouin zone boundary in an assembly of 16 samples of  $La_2CuO_4$  with total mass of 0.1 kg using neutrons from a spallation source [197]. Due to the large value of J the conventionally used thermal neutrons do not allow an exploration of the whole spin wave dispersion. A background corrected scattering cross section which emphasizes the zone boundary contribution is reproduced in the left panel of Fig. 2.13 [197]. The data were collected at 296 K, *i.e.*, above the Néel temperatures of the individual samples ranging from 260 to 290 K. The dashed line depicts a nearest-neighbor spin wave model. A lifetime  $> 10/\omega$  is deduced, which is taken as evidence that spin wave theory indeed gives a valid description of the excitation spectrum. The right panel [197] shows the thus obtained spin wave dispersion, where the full (open) symbols represent data from the spallation source (reactor). The detectors integrate over the wave vector range indicated by the horizontal bars. We agree on the importance of this observation, however we want to point out that this might not be the full story yet. The most interesting information is contained in the line shape, and this cannot be determined satisfactorily. Neutron scattering measures the spin-spin correlation function and hence the expectation value S(S+1). The full intensity amounts to 1/2(1+1/2)=3/4, which is distributed into the Bragg intensity (*i.e.*, the static moment squared), a one-magnon contribution and higher order terms [198]. In a perfectly ordered system the static contribution  $S^2$  of the Bragg intensity and the linear spin wave part S exhaust the full spectral weight. The 2D cuprates show an ordered moment of 0.3, *i.e.*, the Bragg intensity amounts only to 36% of the ideal case; and the one-magnon part is given by  $Z_{\chi}S$ , with  $0.28 \le Z_{\chi} \le 0.5$  (see Table 2.6). The sum of the two describes only 30 to 45% of the full intensity. The important question is in how far it is justified to separate the magnetic excitation spectrum into 60% "background" and 30% simply renormalized classical spin waves (plus the 10% of the static contribution). Let us assume for the moment that the 2D S=1/2 antiferromagnet is a crossover case, in which magnons do not really decay into spinons as in 1D, but they are close to it, *i.e.*, let us assume that magnons can be described as confined spinons. In this case the overall dispersion would very much resemble that of a simple magnon, but the line shape would acquire some tails due to the possibility of excitations of "internal" degrees of freedom of the magnon. We



Figure 2.14: Neutron scattering data of the spinon continuum in 1D, reproduced from Tennant et al. [199]. The largest part of the spectral weight comes from the envelop.

are convinced that this possibility or other similar scenarios cannot be excluded on the basis of the available neutron data.

In order to emphasize this point we show neutron data reported by Tennant and coworkers [199] of the 1D S = 1/2 system KCuF<sub>3</sub> in the lower panel of Fig. 2.14. This is a particularly nice example of an experimental observation of the spinon continuum, but — to cite a german publishing house selling art guides — you only see what you know. The spectral weight is largely determined by the envelope of the continuum, and hence the spectrum might as well be described with a number of well-defined peaks. In fact, the first experimental data of the magnetic excitation spectrum of a 1D S=1/2 system in 1974 by Endoh and collaborators [200] has been interpreted as strong support for the validity of the des Cloizeaux-Pearson spin wave dispersion given in 1962 [201]. We quote [200]: "There are sharp excitations with a dispersion given precisely by Eq. (1)" [The des Cloizeaux-Pearson dispersion relation  $\hbar\omega(q) = (\pi/2)J|\sin q|$  and "We should emphasize that the asymmetric line shapes may be purely due to an instrumental artifact." Of course one cannot blame the authors as the notion of the spinon continuum was developed only in 1979 - 1981 [171–173], as mentioned above (see footnote on page 36). Our aim was rather to show how difficult it indeed is to decide on this point. Of course the experimental technology has advanced dramatically within the last 25 years, but the very large value of J compensates this at least partly. Nevertheless a full continuum of excitations might readily be determined, but a statement about a "tail" of the main line or some asymmetry

is clearly beyond reach. Yet the real physics might be hidden in such a tail.

#### **Raman Scattering**

In contrast to the neutron scattering measurements, the line shape is very well determined in two-magnon Raman scattering. The light scattering process corresponds to the virtual excitation of one hole to a nearest neighbor Cu site. This virtual state relaxes via emitting a photon and two magnons. Due to momentum conservation the total momentum of the two magnons has to be  $k_{tot} = k_1 + k_2 \approx 0$ , and a density of states argument shows that the spectrum is dominated by Brillouin zone boundary magnons with  $k_1 = -k_2$ . A rough estimate of the peak position can be obtained from a local double spin flip picture: two isolated spin flips break four antiferromagnetic bonds each, whereas two spin flips on neighboring sites break only six bonds altogether, reducing the energy from 8SJ to 6SJ =3J. Initially, Raman data of the insulating cuprates were analyzed using the non-resonant Loudon-Fleury Hamiltonian which assumes that the energy of the incoming photon is off-resonance with the virtual excitation. The thus obtained values for J were in good agreement with neutron scattering results, however the line shape was described poorly. The anomaly consists in particular of a very broad line shape, spectral weight at high energies, eventually giving rise to a second peak at 4J, and a finite signal not only in  $B_{1q}$ geometry, but also in  $A_{1q}$  and  $B_{2q}$ . Note that these anomalies are absent in similar systems with S = 1 [204, 205]. In Fig. 2.15 we reproduce Raman data of Blumberg and collaborators [202] of  $Sr_2CuO_2Cl_2$  (two upper panels) and  $YBa_2Cu_3O_{6,1}$  (two lower panels). The figure demonstrates vividly that it is not enough to speak about "the" Raman line shape, but that the data depend drastically on the energy of the incoming photon, *i.e.*, that it is crucial to take the resonance with the charge-transfer absorption at approximately 1.5 - 2 eV into account. Therefore the large body of theoretical work trying to understand the Raman twomagnon line shape while ignoring the resonance has to be viewed as possibly describing additional effects, while the main role is played by the resonance. Let us nevertheless comment on the non-resonant scenarios.

Singh and collaborators argued that spin wave theory underestimates the line width because admixtures to the Néel state with a larger number of inverted spins induced by quantum fluctuations are neglected [206]. They calculated the first three frequency moments of the Raman line shape in a series expansion where the behavior of the Heisenberg Hamiltonian is derived via an extrapolation from the Ising limit. These three moments correspond to the central frequency, the peak width and the skewness of the spectrum, respectively. The first and the third were claimed to be in good agreement with experimental data, whereas the second giving the width was 20% too small [206]. A comparison with the experimental data of Fig. 2.15 shows that *one* set of moments is not sufficient to represent the data, since the line shape depends strongly on the laser frequency. Recently, Sandvik and collaborators [207] have reported frequency moments obtained from quantum Monte Carlo calculations and exact diagonalization of small clusters [207]. Although their result for the line shape is strongly influenced by finite size effects and does



Figure 2.15: Dependence of the Raman spectra of  $Sr_2 CuO_2 Cl_2$  (two upper panels) and  $YBa_2 Cu_3 O_{6.1}$  (two lower panels) on the laser frequency. Reproduced from Blumberg et al. [202].  $x'x' = A_{1g} + B_{2g}$ ;  $x'y' = B_{1g} + A_{2g}$ .



Figure 2.16: Locations in the  $(\Delta \omega, \omega_i)$ plane where the triple resonance condition is fulfilled. Here,  $\Delta \omega$  denotes the Raman shift, and  $\omega_i$  the laser frequency. The solid line depicts the frequency of the two-magnon peak in the non-resonant case. Reproduced from Schönfeld et al. [203].



Figure 2.17: Comparison of experimental data and a result of the triple resonance theory for an intermediate laser frequency  $\omega_{res,1} < \omega_i < \omega_{res,2}$ . Reproduced from Schönfeld et al. [203].

not resemble the experimental data, it nevertheless agrees with Singh's result, which tells us nothing more than that the line shape is not well defined from the first three moments only. Sandvik and co-workers [207] nevertheless argue that the peak width is larger than in spin wave theory and that this result corroborates at least partly the study of Singh and collaborators [206]. There is no second peak around 4J in the numerical data, and the  $A_{1g}$  scattering is zero. Canali and Girvin [208] calculated the four-magnon contribution to the Raman spectrum. They reported a very small weight corresponding to less than 3% of the two-magnon contribution and hence poor agreement with the experimental line shape. Nevertheless the influence on the frequency moments was large because four-magnon scattering peaks at rather high energies and hence changes the ratio of the first two moments by a factor of 2.5, yielding good agreement with the series expansion of Singh and collaborators. Canali and Girvin suggest that the weight might be enhanced by taking interactions of four magnons into account, which is beyond reach due to the great complexity of the calculation.

Other treatments add terms to the Heisenberg Hamiltonian such as a finite spin wave damping due to magnon-phonon interaction [209–215], a next-nearest neighbor exchange coupling or a cyclic four-spin exchange term [216-219]. A coupling to phonons has been claimed to describe the main peak well, albeit the necessary values for the coupling constant being rather large [210–212]. Recently, it has been claimed that a smaller coupling is sufficient if lattice fluctuations are taken into account in the hopping parameter [215], as opposed to modulations of J discussed in the other studies. Sandvik et al. [207] suggest that the strong lattice-induced disorder in J required by the calculation of Nori and collaborators [212] might be at least partly an articlate caused by the  $4 \times 4$  cluster used, since larger clusters yield a broader profile to start with [207]. A major drawback of the above mentioned phonon-magnon interaction scenarios, where the phonons increase the magnon damping, is the inability to produce a second peak at higher frequencies. However, Lee and Min [214] reported a shoulder at the experimentally observed position of 4J, if the magnon-phonon interaction is taken into account explicitly. A definite second peak can be obtained by including a cyclic four-spin exchange process [216–218]. However, the intensity of the second peak remains small. Note that the cyclic four-spin exchange appears in the same order of a t/U expansion of the Hubbard model as the next-nearest neighbor coupling J', as stated above [154]. Recently, an excellent description of the data has been claimed to be obtained by including both phonon-magnon interactions and higher order exchange contributions [219]. This agreement might simply be caused by the large number of parameters available, a meaningful description of the changes of the line shape with laser frequency cannot be reached this way.

Interesting results have been obtained starting from different ground states such as the flux phase proposed by Affleck and Marston [142] as described above. Hsu develops the notion of "spin waves" or paramagnons in a flux phase and argues that they are less incoherent excitations than the conventional strongly interacting spin waves obtained in a Holstein-Primakoff transformation [146]. These flux phase paramagnons have an unusual spectrum with no singularity in the density of states. The resulting two-"magnon" spectrum is hence not that much dominated by the zone boundary and therefore intrinsically broader than in the conventional approach. Hsu claims to obtain a reasonable description of the experimental data with non-interacting flux phase "spin waves". Wang and collaborators extend the 1D Wigner-Jordan transformation to the case of 2D and calculate the excitation spectrum of Wigner-Jordan Fermions in an in-phase flux state [147]. This is particularly interesting since it forms a kind of bridge between the spinon excitation spectrum known from 1D and the magnetic excitations present in two dimensions. They claim that only the Wigner-Jordan transformation satisfies the N identities  $S_i^+ S_i^- + S_i^- S_i^+ \equiv 1$  for every site *i*. The Wigner-Jordan Fermion excitation spectrum is similar to the conventional spin wave spectrum, but as in other treatments of the flux phase [19, 146] the degeneracy between  $(\pi/2, \pi/2)$  and  $(\pi, 0)$  is lifted. Another difference concerns the long-wavelength spectrum: the Wigner-Jordan Fermions stay gapless and show a linear dispersion for small momenta also for finite temperatures, whereas long-wavelength spin waves are not well defined for high temperatures [147]. The description of the Raman spectrum is claimed to be excellent.

In the insulating cuprates, however, all experimental data are collected in resonance, and the Raman intensity indeed vanishes for laser frequencies too far off resonance [202]. A diagrammatic theory for resonant Raman scattering has been developed by Chubukov and Frenkel [220] and independently by Schönfeld, Kampf and Müller-Hartmann [203]. The Raman profile has been given by Schönfeld and collaborators [203] and by Morr and Chubukov [221]. Both groups admit that the experimental peak width is much broader than in the model and state that it was not their major intention to describe the width [203,221]; the possible role of phonons is acknowledged. The bilayer case relevant for  $YBa_2Cu_3O_6$ has been treated explicitly by Morr and collaborators [222]. The theory takes into account the quasiparticle dispersion relevant for the virtual particle-hole excitation of the intermediate state. Different diagrams contribute to the Raman intensity, and in resonance the most singular contribution stems from a diagram of which all three denominators vanish simultaneously under certain conditions. This model is hence called the triple resonance theory. In Fig. 2.16 we reproduce from Ref. [203] the locations in the  $(\Delta \omega, \omega_i)$  plane where the triple resonance condition is fulfilled. Here,  $\Delta \omega$  denotes the Raman shift, and  $\omega_i$  the laser frequency. The solid line depicts the two-magnon Raman peak in the non-resonant case. The triple resonance is restricted to a diagram without magnon-magnon interaction, whereas the dominant peak at about 2.6 J is specifically caused by magnon-magnon interactions, as stated above. The theory hence yields two peaks, the dominant peak at 2.6 Jand the triple resonance peak which shifts with laser frequency according to Fig. 2.16. The weight of the main peak is enhanced for the two values of the laser frequency where the main peak coincides with the triple resonance, *i.e.*, at approximately  $\omega_i = \omega_{res,1} = 2\Delta + 3J$ and  $\omega_{res,2} = 2\Delta + 8J$ , where  $2\Delta$  corresponds to the charge transfer gap. This resonant enhancement has been confirmed experimentally [202]. In particular, the amplitude of the dominant two-magnon peak has been predicted to be proportional to  $(\omega_{res,2} - \omega_i)^{-1}$  for  $\omega_i \rightarrow \omega_{res,2}$  [220], again in agreement with experiment. Moreover, the theory explains why the resonance occurs for frequencies well above the charge transfer gap,  $\omega_{res,1} > 2\Delta$ . These findings establish the validity of the triple resonance theory for the case of the insulating cuprates and show that one cannot hope to find an accurate description of the Raman data

in a non-resonant model. However, we want to argue that also the triple resonance theory does not adequately describe the full set of experimental data. One obvious shortcoming at the present state is that the theory considers only two-magnon excitations and hence has a cut-off at 4J. Moreover, the experimental spectra show a peak at 4J for all laser frequencies, and this peak is in particular well resolved for the *lowest* laser frequency, *e.g.*, 1.92 eV in the  $B_{1q}$  data of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.1</sub> in Fig. 2.15. The resonant energies correspond in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.1</sub> to  $\omega_{res,1} \approx 2.1$  eV and  $\omega_{res,2} \approx 3.07$  eV, and the charge transfer gap is observed at  $2\Delta \approx 1.75$  eV [202]. At a laser frequency of 1.92 eV the triple resonance condition hence is fulfilled *below* the main peak and does not contribute at 4J. Therefore, the 4J peak must be of a different origin. Morr and Chubukov [221] report the Raman profiles for  $\omega_i = \omega_{res,1}$ ,  $\omega_i = \omega_{res,2}$  and an intermediate frequency. They obtain symmetric line shapes for the main peak in the first and second case and an asymmetric line shape for the intermediate laser frequency. They claim full consistency with the experimental data, but in our opinion the discrepancy for the low laser frequency is apparent: the peak at 4J is obviously of different origin. The same might hold for the high laser frequency: on the one hand the more or less symmetric line shape is in agreement with theory, but on the other hand the peak is now so broad that again it is difficult for the model to explain the large amount of high frequency spectral weight. Morr and Chubukov [221] also included a finite next-nearest neighbor hopping matrix element t'. In this case not all three denominators can vanish at the same time anymore, and several double resonances replace the triple resonance. They show the locations of one of the double resonances in the  $(\Delta \omega, \omega_i)$  plane, and this double resonance stays around 4J even for low laser frequencies. However, Morr and Chubukov argue that a finite t' worsens the agreement with experiment. Morr and Chubukov have given the theoretical Raman profiles for three different laser frequencies, as stated above, but so far only Schönfeld and co-workers have plotted a theoretical curve directly on top of experimental data [203]. The curve corresponds to an intermediate laser frequency,  $\omega_{res,1} < \omega_{in} < \omega_{res,2}$ , and is reproduced in Fig. 2.17. The authors consider the agreement as fair, but given the fact that the enhancement of the high frequency spectral weight by the triple resonance is largest for the chosen laser frequency, the total amount of high frequency spectral weight in the experimental data is strongly underestimated by the model. As stated above, both groups [203, 221] admit that the experimental peak width is much broader than in the model. Remarkably, two of the advocates of the triple resonance, Chubukov and Morr, argue in a paper on the single particle spectral function [223] (see below) that the width of the two-magnon Raman peak is much broader than expected for free magnons. This supports our conclusion that the triple resonance is important to understand the experimental data, but does not tell the full story yet.

Sandvik and collaborators argue that resonance effects need to be taken into account to explain the dependence of the Raman spectrum on laser frequency observed experimentally, but that nevertheless the *width* of the spectrum is an intrinsic phenomenon [207]. They claim that indeed spin wave theory fails to describe the line shape, that quantum fluctuations enhance the width and that an additional interaction with phonons describes the full broadening of the spectrum. However, the good agreement between the series expansion [206], quantum Monte Carlo [207] and the two-magnon—four-magnon spectrum [208]

might as well just indicate the failure of the Heisenberg Hamiltonian, as agreement with experiment could not be established conclusively so far. We propose that the infrared absorption spectrum is much better suited to elucidate the intrinsic line shape of the magnetic excitation spectrum, since the resonance problem is absent. The current state of the art is an explanation of the main infrared peak in terms of bimagnon-plus-phonon absorption proposed by Lorenzana and Sawatzky [224], where the main role of the phonon is to make the magnon response infrared active in the first place. Similar to the Raman case the experimental spectra for S = 1/2 differ from the spin wave result in that they show a large amount of high frequency spectral weight and, in particular, peaks at frequencies above the main peak position [225–227]. Moreover, the bimagnon-plus-phonon model gives an excellent description of the experimental absorption spectrum of the S=1 system  $La_2NiO_4$  [224, 228]. We study the mid-infrared spectrum of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> in chapter 5 and show that taking into account magnon-phonon interaction fails to resolve the discrepancy between experimental data and theory for the case of S = 1/2 in 2D. A study of the infrared absorption using other techniques such as series expansion, quantum Monte Carlo or exact diagonalization would be very valuable, but unfortunately this has not been realized sufficiently by the community thus far. The absence of the resonance problem would offer a serious test for the validity of the Heisenberg model for the magnetic excitation spectrum of the insulating cuprates. The price one has to pay is an enhanced calculational effort, since the free choice of the phonon momentum calls for a calculation of the bimagnon spectrum throughout the entire Brillouin zone, as opposed to the much simpler  $\mathbf{k} = 0$  spectrum necessary in the case of Raman spectroscopy.

### 2.2.3 Single Doped Hole in an Antiferromagnet, ARPES

For our purpose there are two points of view on the "single doped hole in an antiferromagnet", *i.e.*, the low doping regime: (i) what do the holes do to the antiferromagnet? and (ii) what does the antiferromagnet do to the holes? The first question is related to the previous paragraphs, and the second is the basis for the discussion of the superconducting phase in the following section. Obviously we touch upon a key issue in the whole field, and one of the very central questions: what role does magnetism play in the high  $T_c$  drama? In order to answer this question much work has focused on point (ii), more in any case than on point (i). We prefer a more dialectic point of view, which is to say that in order to address point (ii) we have to understand the magnetic phase in the first place, but at the same time the study of the doped system can be very helpful for a conclusive picture of the magnetic state.

Let us start with point (i). One point of controversy is whether a doped hole disturbs only the magnitude of the antiferromagnetic order parameter or also the orientation. Concerning the latter, topological excitations such as Skyrmions have been studied by Shraiman and Siggia [229] and Gooding [230]. Gooding found a charged Skyrmion if the motion of a doped hole was restricted to a single plaquette. The stability of this state depends on the next-nearest neighbor hopping [230]. Spiral phases have been found for low doping concentrations under the constraint of homogeneous charge distribution [231, 232]. Relaxing the latter constraint vortices can be formed, but due to its infinite size a vortex around a single doped hole is not favorable [233]. However, this problem can be circumvented by considering two holes: it has been claimed that two holes form the cores of a bound magnetic vortex-antivortex pair [19,233]. Berciu and John claim that a meron-antimeron pair is lower in energy than a spin bag (see below) if the nearest neighbor Coulomb repulsion is included and one starts from a spin-flux phase [19]. We reproduce in Fig. 2.18 the self-consistent spin configurations obtained on clusters for (a) the vortex around a single doped hole, (b) the meron-antimeron pair around two doped holes, (c) the spin bag formed around a single doped hole in a conventional antiferromagnetic background, and (d) a charged stripe domain wall consisting of meron-antimeron pairs for 15% of doping (for the discussion on stripes, see page 78).

Let us continue with the discussion of the correlation length (see page 38 for the discussion at zero doping). It is well known that the Néel temperature is rapidly suppressed by hole doping. Controversy arises about the origin of this drastic effect, whether the disorder induced by the holes or some kind of frustration does the job. Concerning the correlation length, the high temperature 2D behavior has been studied and described in detail (see discussion above, page 38), but the low temperature behavior remains strange. Keimer and collaborators [179] observed that the inverse correlation length follows a universal form at low doping concentrations, which is the one of the undoped case just shifted by the respective finite value at zero temperature (see Fig. 2.36 on page 76). It has been argued that this behavior is very different from predictions of the non-linear  $\sigma$  model, but to make this comparison one has to make a severe assumption. The effect of doping is reduced to tuning the quantum coupling constant q, otherwise a homogeneous model is considered, impurities are neglected. In this case one expects an infinite correlation length for T = 0 for all  $g < g_c$ , a linear inverse correlation length at  $g = g_c$  and finite values of  $\xi^{-1}$ at zero temperature for  $g > g_c$ . This clearly does not agree with the experimental data of Keimer and co-workers [179] (Fig. 2.36). We want to argue that one cannot neglect the impurities and inhomogeneities, in particular not in  $La_{2-x}Sr_xCuO_4$  which is a spin glass in the low doping region at low temperatures, and that an additional important role is being played by phonons. We think that the constant correlation lengths observed below 300 K indicate localization already at this rather high temperature, but want to save this point until page 76. We realize that we are not the first to think in this direction, at least as far as impurities are concerned. Gooding and collaborators [230, 234, 235] proposed a model for the  $La_{2-x}Sr_xCuO_4$  structure, in which the doped holes are bound to the Sr impurities at low temperatures. They neglect the formation of Zhang-Rice singlets and assume that the hole motion is restricted to the four oxygen sites on the  $Cu_4O_4$  square above or below the impurity. The electronic correlations are responsible for a chirality and the hole circulates either clockwise or counter-clockwise [230], giving rise to a spiral twist of the magnetic order parameter. Topologically this state is similar to a Skyrmion. Gooding and co-workers [235] argue that the superposition of the spin distortions of different impurities produces small magnetic domains, giving rise to the spin glass phase. The experimental spin glass temperature is of the order of 10 K [236]. They claim to be able to describe the doping dependence of magnetic and transport properties with this model [235, 237] and



(a) A meron-vortex with winding number 1 in the spin-flux phase with one doped hole. The core is localized in the center of a plaquette [19].



(c) A spin bag in the conventional Néeltype phase with one doped hole [19].



(b) A bound meron-antimeron pair with total winding number zero in the spin-flux phase with two doped holes. The cores are localized on neighboring plaquettes (M and A) [19].

	1	1	1	T	1	T	1	1	1	1	1	
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	7-	Ŷ	↑	ı	♦	↑	↓	ī	↑	↓	↑	-
:	6-	↑	ı	↓	↑	↓	↑	¥	ī	↑	¥	-
J	5-	I	¥	↑	¥	ſ	¥	↑	ı.	¥	↑	-
	4-	↑	ı	♦	↑	↓	↑	ı	¥	↑	↓	-
	3-	Ý	↑	١	♦	↑	1	¥	ſ	↓	↑	-
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	I	1	2	3	4	5	6	7	8	9	10	
	i											

(d) A charged stripe domain wall for 15% doping in the conventional Néel-type phase with cyclic boundary conditions [19].

Figure 2.18: Self-consistent spin distributions of  $i \times j$  lattices obtained in a mean-field Hartree-Fock study by Berciu and John [19].



Figure 2.19: *Pictorial description* of the string picture and of a real space "spin bag" for the case of a single doped hole in a 2D S = 1/2Heisenberg antiferromagnet. Doping a hole at site i produces a sin*qlet.* The dots denote misaligned bonds which are caused by virtual This interaction of the hopping. spin of the doped hole with the antiferromagnetic background leads to two kinds of motion: (i) a rapid oscillation on a scale of t (solid lines) within a region of reduced staggered magnetization (a "spin bag" or spin polaron; dashed circle), and (ii) the coherent motion of this quasiparticle on the scale of J (dashed arrow). See text for details.

attribute also the incommensurability (see the discussion on stripes on page 78) observed for doping concentrations x > 0.05 to the impurity induced domains. However, the model does not convincingly answer the question why the holes should be localized already at high temperatures. Gooding and co-workers claim that the holes are restricted to move along the domain walls from one impurity site to the other at higher temperatures, but these domain walls only appear because the holes were localized to the Sr impurities in the first place. In our view the high localization temperature can only be explained if phonons are also taken into account (see below). Skyrmion textures have also been reported to describe the remarkable behavior of Li-doped  $La_2Cu_{1-x}Li_xO_4$  in which all holes are strongly bound to the vicinity of the Li sites [238]. Despite the very similar suppression of antiferromagnetism upon Li or Sr doping the transport behavior is very different,  $La_2Cu_{1-x}Li_xO_4$ staying insulating even up to x = 0.5. Moreover, the chirality is a specific property of the  $La_{2-x}Sr_xCuO_4$  structure and is absent in  $YBa_2Cu_3O_{6+y}$ . Detailed measurements of the correlation length in  $YBa_2Cu_3O_{6+y}$  would therefore be highly desirable. Furthermore we want to point out that if the disorder is of such a significant importance in the doped case, then one has to worry about the same issue in the "undoped" phase, since the cuprates are not clean materials.

Now we address point (ii), what does the antiferromagnet do to the holes? The central question is whether it makes sense to speak about the doped hole as a quasiparticle or if the interaction is so strong that the quasiparticle pole vanishes, leaving us with an incoherent

excitation spectrum. This issue is still controversial. Detailed discussions of the properties of doped holes in a quantum antiferromagnet can be found in the reviews of Dagotto, Kampf, Brenig and Jaklič and Prelovšek [60–62,239]. Here, we want to start with drawing an intuitive picture of the dynamics of a single doped hole. To do so we will use a "single band" language, *i.e.*, we will draw only the Cu sites, keeping in mind that the first electron removal state is a Zhang-Rice singlet involving the oxygen orbitals (see Fig. 2.19). We initially place the doped hole with, say, spin down on the spin up site i, where the two spins form a singlet. If we allow only for nearest neighbor hopping, the motion of the singlet leaves a trace of misaligned bonds (black dots in Fig. 2.19), which forms a linear potential and ties the doped hole with a "rubber band" to site i. This is known as the string picture. However, the trace can be healed by allowing for spin fluctuations, *i.e.*, after the singlet has moved to site k a double spin flip on sites i and j can reduce the trace by two sites, thereby allowing the excitation to delocalize. Strictly speaking, the localization of the doped hole is not perfect in the absence of spin fluctuations, since complicated paths can be created that heal themselves. For example, circling a plaquette one and a half times translates the excitation across the diagonal [240]. Nevertheless we can qualitatively distinguish between two kinds of motion with different energy scales. The first is the rapid incoherent motion of the doped hole on a scale of t in a finite region around site i (dashed circle in Fig. 2.19). The "rubber band" will dictate a characteristic size of the region. One can visualize this region as an area of reduced staggered magnetization (as opposed to the change of orientation discussed above) and call it "spin bag" [241] or spin polaron. The second motion is dominated by the scale of the spin fluctuations, J, and describes the coherent motion of a quasiparticle (dashed arrow). The rapid oscillation of the doped hole within the spin bag can be viewed as internal excitations of the quasiparticle giving rise to an incoherent part of the excitation spectrum. In other terms, the hole is heavily dressed with spin excitations and thereby acquires a large effective mass. The dressing drastically reduces the bandwidth W = 8t of a free hole to 2.2J. Note that in this semi-localized problem it is misleading to treat the "magnetic dressing" as spin waves [60]. This scenario finds support in the good agreement that has been obtained between exact diagonalization studies of the t-J model [242] and analytical calculations for spin-bag quasiparticles [243]. It is hence no surprise that the theoretical reviews [60-62] conclude that a Fermi liquid scenario with a finite quasiparticle pole strength is most likely to apply. We want to add that a more realistic picture should also include an additional dressing with phonons and the influence of impurities, particularly since both will be more effective in disturbing the already heavy quasiparticle than they would be in case of an otherwise free hole.

Another extension of the model which will be of some importance below is a nextnearest neighbor hopping t'. Note that t' connects sites of the same magnetic sublattice and is therefore not affected by the magnetic order. At the same time, the inter-sublattice hopping t is effectively rescaled to J, as described above. Hence inclusion of a seemingly small value of t' as compared to t can alter the picture significantly, and the parameters to be compared are t' and J. Note that finite values for next-nearest and next-next-nearest

<sup>&</sup>lt;sup> $\|$ </sup> The notion of a spin bag has been introduced in a spin density wave formalism [61,62,241].



Figure 2.20: ARPES spectra of insulating  $Sr_2 CuO_2 Cl_2$  at 150 K along three cuts through the Brillouin zone, reproduced from Kim and collaborators [144]. Numbers label the momentum, and tick marks peak frequencies obtained from curve fitting.

neighbor hoppings follow for the cuprates from realistic multi-band models including outof-plane orbitals (see Ref. [90] and references therein). We want to remark once more that a cyclic four-spin exchange term appears in the same order of the perturbation expansion of the multi-band model as the t'-term [154]. Moreover, one has to reconsider the three-site hopping term of Eq. 2.2 if higher order terms are included.

Opposition to the Fermi liquid quasiparticle scenario has been raised in connection with the Marshall sign rule [18,244], which states that a double spin flip of two antiparallel spins on neighboring sites gives rise to a sign change of the wave function. Sheng, Chen and Weng [245] claim that the rapidly (on the scale of t) oscillating hole picks up a sequence of signs or phases from the antiferromagnetic background and thereby creates a phase string in addition to the above mentioned string of misaligned bonds. The phase string, however, cannot be healed by low-energy spin fluctuations and causes the quasiparticle weight Z to vanish [245]. Note that this result was obtained in the t-J model, and that the Marshall sign rule holds exactly only below a value of  $J'/J \leq 0.2$  [246]. In later papers Weng and collaborators claim that the phase string effect gives rise to spin-charge separation in 2D [247] and that a *bosonic* RVB model which includes the phase string effect explains antiferromagnetism, superconductivity and the underdoped regime in the cuprates [248].

A strong impetus to discussions concerning the single doped hole came from recent angle-resolved photoelectron spectroscopy (ARPES) results on insulating  $Sr_2CuO_2Cl_2$  [143,



Figure 2.21: ARPES spectra of insulating  $Sr_2 CuO_2 Cl_2$ , underdoped and overdoped  $Bi_2Sr_2 CaCu_2 O_{8+\delta}$  and electron doped  $Nd_{1.85} Ce_{0.15} CuO_4$ , reproduced from Kim and collaborators [144].



Figure 2.22: Results of the t-J (left panel) and t-t'-t''-J model (other panels) for the single particle spectral function, reproduced from Kim and collaborators [144]. Parameters and doping levels are indicated in the figure. The spectra of the four right panels can directly be compared with the experimental data given in Fig. 2.21. Note that a Lorentzian broadening of 0.1 eV has been used.

144]. A strong discrepancy with results of the t-J model is observed for both the dispersion of the quasiparticle band and in particular the line shape or width of the quasiparticle peak. Both results strongly question the quasiparticle concept. In the t-J model the smallest energy corresponds to the  $(\pi/2, \pi/2)$  point, in agreement with experiment. However, the t-J model further predicts a very flat dispersion from  $(\pi/2, \pi/2)$  to  $(\pi, 0)$ , *i.e.*, the mass at  $(\pi/2, \pi/2)$  is very anisotropic. Note that in numerical results obtained on  $4 \times 4$  clusters these two points are degenerate due to a hidden symmetry of the cluster. In other clusters the degeneracy is lifted, but the energies are still quite close. Experimentally, the two points differ by almost the full band width, and  $(\pi, 0)$  is almost degenerate with (0, 0) (see Fig. 2.20). Note that the marked difference between  $(\pi, 0)$  and  $(\pi/2, \pi/2)$  is particularly important since in underdoped samples a pseudogap opens at  $(\pi, 0)$ . The close connection between this pseudogap and the insulating phase will become clear in section 2.3.1, to which we want to postpone the discussion of recent ARPES data on insulating  $Ca_2CuO_2Cl_2$  [249]. As a remedy to the discrepancy between experiment and theory the inclusion of nextnearest and next-next-nearest neighbor hoppings t' and t'' has been proposed [144,250-255]. The t-t'-t''-J model has also been claimed to describe the second discrepancy, the indeed spectacular line shape observed experimentally by Kim and collaborators [144]. This, however, is questionable. At  $(\pi, 0)$  the notion of a peak itself can be questioned, since the "peak" width is much larger than the full band width (see left panel of Fig. 2.21). Along (0,0) to  $(\pi,0)$  the authors describe the spectra in terms of two extremely broad humps (see ticks in mid panel of Fig. 2.20), but a continuum with some structure and a cutting edge might be an equally valid picture. At  $(\pi/2, \pi/2)$  a quasiparticle like peak is observed, but the full width at half maximum amounts to approximately 300 meV, which is about the full band width and one order of magnitude larger than the resolution limited true quasiparticle peaks observed in the *superconducting* state at higher doping levels [256,257]. The spectra of underdoped samples will be discussed in section 2.3.1, but as an appetizer it is already worth comparing the different doping levels depicted in Fig. 2.21. At both  $(\pi, 0)$ and  $(\pi/2, \pi/2)$  the peaks seem to sharpen up with increased doping, but the "sharpness" could possibly be caused in large part by the Fermi cut-off. The most important point of the comparison is the proof that the extreme breadth of the experimental features is neither material dependent nor an experimental artefact, since the doped samples show a resolution limited sharp quasiparticle peak in the superconducting state [256, 257], despite the lack of a truly sharp peak in the normal state. These experimental spectra have to be compared with the theoretical results reproduced in Fig. 2.22. The left panel depicts spectra calculated within the t-J model, whereas the other four panels have been derived in the t-t'-t''-J model and correspond to the four panels of Fig. 2.21. The parameters used are t = 0.35 eV, t' = -0.12 eV, t'' = 0.08 eV and J = 0.14 eV [144], *i.e.*, t' is comparable to J. The overall agreement is quite satisfactory. Let us focus on the insulating phase (two left panels of Fig. 2.22). The t-J model clearly fails to describe the experimental data, whereas the t - t' - t'' - J model is able to reproduce the experimental dispersion and the reduced weight at  $(\pi, 0)$ . However, one has to realize that the theory gives  $\delta$ -functions for the response, the width of the displayed curve is simply adjusted by a Lorentzian broadening (0.1 eV in this case). This is a serious shortcoming which indicates that a key ingredient



Figure 2.23: Dispersion of a single hole in a spin flux phase as given in Ref. [19]. Open circles: experimental data of Ref. [143]; solid line: result for the spin-flux phase; dashed line: result for the conventional phase.

of the underlying physics is not understood. At the same time, the relatively large ratio of t'/t necessary to reproduce the experimentally found dispersion possibly indicates that a valid description can be reached by destabilizing the antiferromagnetic order, since the additional hopping possibilities promote a spin liquid state, at least around the doped hole.

A similar effect is achieved by considering not the conventional antiferromagnet in the first place, but a spin flux phase with a nearest neighbor Coulomb repulsion [19] as discussed above. In Fig. 2.23 we reproduce the mean-field derived dispersion of a single hole from Ref. [19]. The open circles correspond to the experimental data of Ref. [143], the solid line denotes the spin-flux result and the dashed line the result for the conventional phase. The spin-flux phase reproduces the experimentally observed symmetry around  $(\pi/2, \pi/2)$  with respect to the two directions  $(0, 0) - (\pi, \pi)$  and  $(\pi, 0) - (0, \pi)$  very well. Unfortunately, the line shape has not been discussed.

Chubukov and Morr [223] argue that an explanation of both the dispersion and the line shape within a t - t' - t'' - J model necessitates a fine tuning of parameters which renders for example the isotropic mass around  $(\pi/2, \pi/2)$  completely accidental. They calculate the quasiparticle Green's function for a spin-density wave state in a self-consistent Born approximation, including a next-nearest neighbor hopping t' = -0.4J, and claim that the single particle dispersion strongly depends on the magnon propagator. They argue on the basis of Raman and neutron scattering data that zone boundary magnons are not free particles and introduce a *small* cut-off momentum  $q_c$  above which they *ignore* the magnetic excitations. This way they claim to be able to reproduce *all* features of the ARPES



Figure 2.24: Comparison of dispersion relations, reproduced from Ref. [258]. Open symbols: experimental data of insulating  $Sr_2CuO_2Cl_2$  of Ref. [143]; solid line: spinon dispersion; dashed line: result of the t-J model.

data of insulating  $\text{Sr}_2\text{CuO}_2\text{Cl}_2$  discussed above, in particular the dispersion, the isotropic mass around  $(\pi/2, \pi/2)$  and the band width. Most remarkably they find weakly damped excitations only in a small region around  $(\pi/2, \pi/2)$ , whereas excitations are overdamped at all other points, giving rise to broad maxima in the spectral function. In a sense this result is surprising since the key role dominating the single hole dynamics is played by the magnetic excitations, most likely the short wavelength ones; being able to describe the data by *ignoring* them is at least counterintuitive.

Laughlin [258] argues that the ARPES spectra imply that the quasiparticle indeed does not exist at those momenta where the spectra rather resemble a continuum than a peak. In his opinion the relevance of the t-J model is suggested by the experimental band width of approximately 0.3 eV at all doping levels, which fits the t-J model result of 2.2J regardless of the value of t [259]. Further, he argues that the isotropy of the dispersion around  $(\pi/2, \pi/2)$  demonstrates that the dispersion is controlled by the single parameter J and not by the coincidental interplay of different parameters. The non-integrity of quasiparticles is attributed to a decay into a spinon-holon pair but, contrary to the case of 1D, there remains an attractive force between the two. The quasiparticle-like peak is interpreted as a bound state of spinon and holon [258], and the momentum dependent width is attributed to the momentum dependence of the attractive force. For a large attraction the quasiparticle picture and the dispersion of the t-J model are recovered. The failure of the t-J model calculation in this scenario is to grossly overestimate the attraction between spinon and holon. Laughlin states that at present the reason for this failure cannot be identified, but proposes doping, modification of the Hamiltonian or the elevated temperature. He favored the latter, since at that time experimental data were only available





Figure 2.25: Spin correlations in the reference frame of the mobile hole at  $(\pi, 0)$  reproduced from Martins et al. [263]. The antiferromagnetic correlation strength is given by the width of the line. (a) J/t = 0.4, t' = t'' = 0, (b) J/t = 0.2, t'/t = -0.35, t''/t = 0.25.

Figure 2.26: Same as Fig. 2.25 but with two holes, reproduced from Ref. [263]. J/t = 0.4, t'/t = -0.35, t''/t = 0.25. (a) Projection with hole distance 2a. (b) Same as (a) but with hole distance a.

for 350 K [143]. The more recent data of Kim and co-workers reproduced in Fig. 2.20 were collected at 150 K, *i.e.*, far below the Néel temperature and show that temperature was *not* the cause for the failure. This, however, does not imply that the general reasoning was wrong. A more detailed study of the confinement of spinons and holons to a weakly or strongly bound state in the cuprates is clearly called for. For the moment, we have to compare the experimental dispersion (open symbols) of  $Sr_2CuO_2Cl_2$  measured by Wells *et al.* [143] with the spinon dispersion (solid line) in Fig. 2.24 [258]. The dashed line depicts the t-J model result. The spinon dispersion (as opposed to the holon dispersion) is the relevant one because it traces the edge of the very broad continuum, and the experimental dispersion was derived from this edge. The agreement is obvious. It is worth mentioning that according to Laughlin [258] the  $\pi$ -flux phase of Affleck and Marston [142], the spinon-holon scenario and other models yielding the same dispersion [260, 261] are mathematically equivalent. The flux order is only a way of describing the fractional particles spinon and holon in a conventional quasiparticle picture.

Several numerical studies indicate the composite nature of quasiparticles in the 2D t-J model. Béran, Poilblanc and Laughlin [262] argue that composite quasiparticles naturally

explain the two different energy scales found in numerical results, such as the dispersion being dominated by J and for example the Drude weight of the optical conductivity depending mainly on t [262]. Remarkably, they visualize this scenario using the string picture described above in connection with the spin bag. The composite quasiparticle is viewed as a heavy spinon and a light holon which are bound together by a long-range force that scales with J. The above mentioned rubber band of the string picture provides also the glue for spinons and holons. Martins, Eder and Dagotto [263] study the extended t-Jmodel and develop an intuitive understanding of the connection between distant-neighbor hopping terms and spin-charge separation. They find robust antiferromagnetic correlations between the spins separated by the hole, *i.e.*, "across-the-hole" correlations (see Fig. 2.25). These antiferromagnetic correlations connect spins of the same sublattice and generate dynamical 1D segments. The across-the-hole correlations are strongly promoted by next-nearest and next-next-nearest neighbor hoppings. At the same time these extra possibilities for the hole to hop result in a more severe scrambling of the antiferromagnetic spin background and drastically reduce Z at  $(\pi, 0)$ . In the opinion of the authors the across-thehole correlations suggest that the spin is spread over a larger region, leaving only a small spin in the vicinity of the hole, which indicates spin-charge separation at short distances. Evidence for a spreading of the spin caused by t' and t'' is given [263]. Martins, Eder and Dagotto propose that a picture using 1D segments surprisingly suits the 2D cuprates better than a RVB-like spin liquid. Most remarkably adding a second hole to the cluster produces a 1D metallic stripe with strong 1D antiferromagnetic correlations both within and *across* the stripe (see Fig. 2.26). The antiferromagnetic correlations across the stripe correspond to the experimental observation that stripes form anti-phase domain walls (see discussion of stripes in section 2.3.2; original ideas have been contributed by Zaanen and Gunnarsson [264] and Emery and Kivelson [265]).

We summarize this section by stating that in particular the line shape of the ARPES data measured on insulating cuprates points towards a flaw of a conventional quasiparticle scenario. Tendencies to spin-charge separation at least on short length or time scales have been found numerically, and confined spinon-holon pairs are very likely candidates to give an appropriate picture of the underlying physics. Considering the magnetic excitations by themselves, the two-magnon Raman line shape speaks the same language. Large efforts have greatly improved our understanding of Raman scattering in the insulating cuprates, in particular the variation of the spectrum with the laser frequency, but have nevertheless not been able to give a convincing answer to the puzzle of the large peak width and the strong high frequency spectral weight. A decay of magnons into spinons on short time or length scales might very well explain the width, and the "internal" excitations of a composite "spin wave" could possibly be the origin of the high frequency spectral weight. We are convinced that this is *not* at variance with the well defined magnon peak observed in inelastic neutron scattering at the Brillouin zone boundary, since the full line shape cannot be determined from the data, and an asymmetry or a "tail" of the peak can definitely not be excluded at this stage [266]. We emphasize that the considered "short-length-scale" deviations from conventional spin waves do *not* contradict the good agreement obtained between the 2D Heisenberg model and long-wavelength quantities such as the correlation length. Moreover we want to state that temperature induced fluctuations disturb the low-energy long-wavelength spin waves, but that the quantum fluctuations of a highly fascinating 2D S=1/2 system scramble the *short-wavelength* magnetic excitations. Finally we want to stress that the celebrated success of spin wave theory is misleading and hides a truly fascinating piece of physics.

# 2.3 Some Trends and Visions in High $T_c$ Superconductivity

Naturally, the central issue in the field of high  $T_c$  superconductivity is to find the mechanism giving rise to the superconducting instability. There is some agreement that any theory for being successful would have to describe the very unconventional properties observed experimentally in the normal state of the cuprates. The disagreement starts with the question which of the normal state properties has to be considered the central one, providing the key to high  $T_c$ . According to Anderson it is the large anisotropy of the resistivity and the strong temperature dependence of this anisotropy, indicating the twodimensional nature and confinement of the carriers. For Pines the low frequency magnetic response is the most unusual, showing nearly antiferromagnetic behavior even at optimal doping concentrations and, in his view, three distinct magnetic phases in all but the highly overdoped systems. Varma chooses the NMR results as well, but to him it is the difference in Cu and O response that counts, the  $(^{Cu}T_1T)^{-1}$  diverging with decreasing temperature, whereas  $(^{O}T_{1}T)^{-1}$  shows the conventional constant behavior, suggesting very different *local* magnetic fluctuations at Cu and O sites. In order to give an unbiased impression of current discussions in the field we will show several phase diagrams from the work of others, allowing the reader to condense the similarities and to notice the differences. The differences of theoretical predictions and the discrepancies among experimental results might guide the way for future experimental work.

In discussing the phase diagram we will touch upon the hot subject of the pseudogap, which has to be viewed as a partial gap, a reduced density of states. We will then discuss the related issue whether the normal state is a Fermi liquid or not. On the way we will mention several theoretical models, but it is clearly beyond the scope of this introduction to give an adequate description of all of them.

We will not discuss another unconventional property, which is the *d*-wave symmetry of the order parameter, as this problem has more or less been settled after some years of hot debates [33-35]. During those years, the primary importance of the symmetry of the order parameter for deciding about the correct theoretical model has been emphasized. However, many models have adapted very well to this challenge.

## 2.3.1 Phase Diagrams and Pseudogaps

During the last years the phase diagram in the temperature versus doping plane of the cuprates has become richer than what was reproduced in Fig. 2.3 on page 14. For aesthetical



Figure 2.27: Schematic phase diagram of  $(La, Nd, Sr)_2 CuO_4$  given by Aeppli et al. [267]. The new axis y denotes "chemical pressure" or Nd concentration, while x gives the Sr content as usual. SG denotes a spin-glass phase typical for the  $La_{2-x}Sr_xCuO_4$ system.

reasons we start our tour with a schematic phase diagram of  $(La,Nd,Sr)_2CuO_4$  given by Aeppli and co-workers in Fig. 2.27 [267]. Here, a third axis y has been added which represents "chemical pressure" or the concentration of the smaller  $Nd^{3+}$  ions, while x denotes the Sr content. Besides the superconducting and antiferromagnetic phases a spinglass (SG) phase is shown in the figure which is typical for the  $La_{2-x}Sr_xCuO_4$  system. The "lipstick"-like mountain drawn for  $x \approx 0.1$  at finite y values represents an ordered stripe phase (a long-period spin density wave, see below). The reappearance of superconductivity behind the stripe "mountain" for higher values of y is not to be taken seriously. The new state presented here, the ordered stripe phase, has been identified via incommensurate peaks in the static magnetic response measured by neutron diffraction [268]. These static stripes suppress superconductivity. However, related incommensurate magnetic peaks have been observed in the superconducting phase in the *dynamic* response [269]. The important claim of Aeppli and collaborators in Ref. [267] is that these incommensurate magnetic fluctuations are nearly singular, *i.e.*, the amplitudes increase like  $1/T^2$  with decreasing temperature and are believed to show a divergence for  $T \rightarrow 0$ , which however is only observable for  $T > T_c$ . This suggests a so-called quantum critical point [270], a point where a zero temperature quantum phase transition occurs (such a point is also present at low doping levels when the Néel temperature goes to zero, as discussed above). A quantum critical point calls for an ordered phase nearby in phase space. The nearly singular behavior of the *incommensurate* peaks observed in Ref. [267] suggests that the obvious choice of the antiferromagnetic state of the parent compounds is not the correct one, but that the ordered stripe phase represents a better candidate.

New features which appeared in the usually drawn T-x plane are several crossover temperatures. Several sketches derived (at least mostly) from experimental data by different theoreticians in the last years are given in Fig. 2.28. Let us begin with describing to which



(a) Phase diagram for the cuprates reproduced from Fukuyama and Kohno 1996 [148].  $\delta_M$ : optimal doping;  $T_{SG}$ : spingap;  $T^*$ : charge anomaly;  $T_H$ : start of anomalous T-dependence of the Hall coefficient.



(c) Phase diagram reproduced from Pines 1997 [272].



(b) Reproduced from Castellani et al. 1998 [271]. QCP: quantum critical point; ICDW: incommensurate charge density wave; SG: spin glass.



(d) Phase diagram on the basis of resistivity data as given by Varma 1997 [86].  $x_c$  represents both optimal doping and a quantum critical point.



(e) Phase diagram of  $YBa_2 Cu_3 O_x$  including the antiferromagnetic quantum critical point at an oxygen content of about 6.4 as given by Barzykin and Pines 1995 [273]. RC: renormalized classical; QC: quantum critical; QD: quantum disordered.



(f) Reproduced from Zaanen 1998 [274].  $x_{M-I}$ : metal-insulator quantum critical point.

Figure 2.28: (a) – (f) Generic schematic phase diagrams in the temperature versus doping plane of the cuprates as drawn by several theoreticians. In most diagrams the solid lines indicate the phase transition temperatures to the antiferromagnetic and the superconducting phases, whereas the broken lines denote crossover temperatures as described in the text. The definitions of the crossover temperatures are summarized in Table 2.7 below.

	ho	NMR	INS	ho deviates	INS
	insulating	max. $(^{Cu}T_1T)^{-1}$	gap in $\chi_0$	from $\propto T$	max. in $\chi_0$
(a) Fukuyama		$T_{SG}$		$T^*$	
(b) Castellani		$\mathrm{T}^*$	$\mathrm{T}^*$	$\mathrm{T}_{0}$	$T_0$
(c),(e) Pines		$T_*$	$T_*$	$T_*$	$T_{cr}$
(d) Varma	$4 \rightarrow 2$			$1 \rightarrow 4$	

Table 2.7: Definitions of crossover temperatures in the schematic phase diagrams of Fig. 2.28. INS: inelastic neutron scattering.



Figure 2.29: The T=0 phase diagram of the stripe phase quantum critical point scenario given by Zaanen in Ref. [274]. The parameter 1/g suppresses superconductivity.

data the crossovers correspond in the different diagrams (see Table 2.7). The first example (Fig. 2.28(a)) given by Fukuyama and Kohno in 1996 [148] brings in three additional temperatures:  $T_{SG}$  denotes the opening of a *spin*-gap as derived from the maxima of the NMR rate  $1/T_1T$ , whereas the second temperature T<sup>\*</sup> indicates anomalies of *charge* excitations. At T<sup>\*</sup>, the in-plane resistivity starts to deviate from its anomalous linear T-dependence. A low frequency suppression of the c-axis optical conductivity also sets in at  $T^*$ . An anomalous T-dependence of the Hall coefficient  $R_H \propto 1/T$  is found to start at the much higher temperature  $T_H$ , which is not discussed in the other plots. Castellani and co-workers [271] (diagram (b)) agree as to the definition of  $T_{SG}$  and  $T^*$ , but use a different notation (see Table 2.7). Diagram (c) drawn by Pines [272] shows a different interpretation. Here, the lower temperature ( $T_*$  in his case) corresponds not only to the maximum of the NMR rate, but is also identified with the onset of deviation from linear behavior in resistivity, which was the *higher* temperature in the two previous diagrams. Also in Varma's diagram, Fig. 2.28 (d), which is based on resistivity data, the higher temperature  $(1 \rightarrow 4)$  corresponds to the downturn of resistivity from linear behavior. In contrast to the other interpretations his second crossover is ascribed to the onset of insulating behavior in  $\rho_{ab}$ . The additional crossover in the overdoped regime between non-Fermi liquid (or anomalous metal) and Fermi liquid behavior is based on the Fermi liquid like  $T^2$  dependence of the resistivity recovered above optimal doping. One should note that the actual line drawn does not correspond to any particular temperature in experimental data. Diagram (e) by Barzykin and Pines [273] is based on data of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub>, (Y,Pr)Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> and YBa<sub>2</sub>Cu<sub>4</sub>O<sub>8</sub>. It was enclosed because it emphasizes the existence of an antiferromagnetic quantum critical point at an oxygen content y of about 6.4. Note that the superconducting phase is not shown in this diagram, and that optimal doping corresponds to  $y \approx 6.93$  in the figure. Finally, diagram (f) given by Zaanen is an interpretation of the one by Pines, but based on a zero temperature phase diagram (Fig. 2.29, see below).

Important is the disagreement between the different schools about the crossing point of the crossover lines and about where they hit  $T_c$ . In scenarios (a) and (c)/(e) both points fall together to a single one, but its location is at optimal doping for case (a) and in the overdoped regime for case (c)/(e). The other three diagrams display a quantum critical point scenario where the crossover lines meet in the (slightly) overdoped regime for



Figure 2.30: (a) Schematic phase diagram around a quantum critical point (in the absence of superconductivity) [275]. Dashed line: mean-field critical temperature. (b) Very schematic phase diagram indicating singlet pairing at  $T_{SP}$  and Bose-Einstein condensation at  $T_{BEC}$ . Superconductivity (SC) arises if phase coherence is established among the pairs, i.e., for  $T < \min\{T_{SP}, T_{BEC}\}$ .

T = 0 at the quantum critical point (QCP,  $x_c$  or  $x_{M-I}$ ). Obviously, the "interpretation" of experimental data is guided by the phase diagram which is predicted by the theoretical model to be advertized. This disagreement clearly has to be sorted out by experimental data.

Let us briefly discuss the underlying theoretical models. The schematic structure of the phase diagram in a quantum critical point scenario is displayed in Fig. 2.30 (a). It shows a quantum critical region, a quantum disordered phase and an ordered phase. Both superconductivity and the anomalous or non-Fermi liquid behavior observed in the cuprates at optimal (critical) doping are attributed to "criticality", the dominance of quantum fluctuations. In the regions away from the quantum critical point for temperatures below the crossover lines fluctuations are less important and more conventional phases are found. Within the quantum critical point scenario there is disagreement about the location and the origin of criticality. Pines [272] claims that the critical fluctuations are antiferromagnetic, since NMR measurements find strong antiferromagnetic fluctuations even at optimal doping. This is why in his diagram in Fig. 2.28 (c) the crossover  $T_*$  bends down again at low doping levels towards the antiferromagnetic quantum critical point. The points on the  $T_*$  (dashed) line in Fig. 2.28 (e) which indicate this bending down have been obtained by Barzykin and Pines [273] in an extensive study of experimental data. They claim that the crossover temperatures are "clearly visible" in the data, a point one could argue about (see the viewpoint of Tallon and co-workers in the discussion of NMR data below). All other scenarios claim the existence of another quantum critical point at higher doping levels. Both Castellani [271] and Zaanen [274] derive critical behavior in a stripe phase or incommensurate charge density wave scenario. Zaanen shows a T=0 phase diagram (see Fig. 2.29) which in a sense forms the basal plane for Aeppli's sketch shown in Fig. 2.27. The 1/q axis in Zaanen's diagram represents something that suppresses superconductivity, which may be a magnetic field or chemical pressure (Nd or Eu content) as in the case of Fig. 2.27. The novelty in this T = 0 phase diagram is the presence of *lines* of critical points





(a) Schematic temperature-density phase diagram [276].

(b) Experimental data of  $CePd_2Si_2$ , showing a  $T_c$  of 500 mK [276].

Figure 2.31: Superconductivity mediated via magnetic fluctuations as found recently by Lonzarich and co-workers [276] in heavy Fermion systems. Magnetic interactions are strong and long-range near the critical density. Fluctuations are thought to cause both the anomalous normal state and Cooper pairing.

as opposed to the isolated QCP of the other diagrams. According to Varma [86] criticality is driven by a charge-transfer instability with microscopic currents circulating within the unit cell.

At this point a short excursion to the field of heavy Fermion superconductivity is instructive. Lonzarich and collaborators [276] recently found superconductivity at high pressure in high-purity CePd<sub>2</sub>Si<sub>2</sub> and CeIn<sub>3</sub> and explained it by magnetic fluctuations. The relevant phase diagram is drawn in the temperature versus density plane, where the density is varied experimentally via applying pressure (see Fig. 2.31). The materials considered show an antiferromagnetic metallic state at low densities. With increasing pressure the Néel temperature tends to zero and superconductivity appears in a narrow window around the critical density. Above  $T_c$  an unconventional metallic state is deduced from the resistivity which varies as  $T^{1.2\pm0.1}$  over nearly two decades (see inset of Fig. 2.31 (b)). This anomalous exponent  $\alpha$ , with  $1 \leq \alpha \leq 1.5$ , has been attributed by Rosch to the interplay between isotropic impurity scattering and quantum critical antiferromagnetic fluctuations near the quantum critical point [277]. Lonzarich and co-workers mention that  $T_c$  could possibly be increased by going from narrow band f electrons to d electrons in a system with reduced dimensionality, *i.e.*, they suggest a possible relevance to the cuprates. However, one has to be aware that  $T_c$  is only about 500 mK and that a minute amount of impurities suppresses


(a) Phase diagram of the SU(2) conserving slave-boson mean-field theory reproduced from Wen and Lee [145].  $\pi F$ :  $\pi$ -flux phase; sF: staggered flux phase; uRVB: uniform RVB phase; FL: Fermi liquid; SC: d-wave superconducting phase; LS: localized spin phase.



(b) Slave-boson mean-field treatment of the extended t-J model by Fukuyama and Kohno [148]. AM: anomalous metal; SG: spin-gap; EL: electron Fermi liquid;  $T_{RVB}$ : formation of spinon singlet pairs;  $T_B$ : Bose condensation of holons;  $T_D$ : onset of coherent motion of spinons and holons.

Figure 2.32: Schematic phase diagrams which emphasize the existence of a singlet pairing temperature and Bose-Einstein condensation.

the superconducting phase.

Let us continue now with the discussion of the different phase diagrams proposed for the cuprates. We saw that a quantum critical point scenario predicts that the crossover temperatures coincide only for T = 0. A different viewpoint was expressed for example by Fukuyama and Kohno in plot (a) of Fig. 2.28. The slave-boson mean-field theories for the (extended) t-J model proposed by Fukuyama and co-workers [148, 278] and Wen and Lee [145], and the very different bipolaron theory of Mott and Alexandrov [279] all predict a phase diagram as sketched in Fig. 2.30 (b). Here,  $T_{SP}$  indicates a singlet pairing temperature, whereas a Bose-Einstein condensation takes place at  $T_{BEC}$ . Superconductivity occurs only when the singlet pairs condense and establish phase coherence, *i.e.*, for temperatures smaller than both  $T_{SP}$  and  $T_{BEC}$ . In the underdoped region above  $T_{BEC}$  and below  $T_{SP}$ the presence of preformed pairs is predicted. More sophisticated versions of this simple diagram are given in Fig. 2.32. As in the case of the quantum critical point scenarios, there are again fundamental differences in theoretical models which give rise to similar kinds of phase diagrams. According to Alexandrov's version of the bipolaron theory [279] the driving force for bipolaron formation is electron-phonon coupling, whereas Mott originally was advertizing bipolarons in the spin sector (see the contribution to Ref. [59]). For both Lee and Fukuyama it is the strong antiferromagnetic exchange which plays the dominant role. In this picture strong quantum fluctuations suppress magnetic ordering and stabilize spin liquid phases (see chapter 2.2). They disagree on the symmetry: Lee and co-workers preserve the SU(2) symmetry — which is an exact symmetry at half-filling only — for finite

values of doping, whereas in Fukuyamas treatment doping breaks the symmetry to U(1). Preservation of SU(2) symmetry clearly restricts the model to the underdoped region and causes shortcomings at higher doping levels. In Fig. 2.32 the "anomalous" or "strange" metallic behavior above  $T_{SP}$  and  $T_{BEC}$  is due to a uniform RVB state (uRVB or AM), where the coherent motion of spinons and holons determines the physics. The opening of a spin-gap at  $T_{SP}$  is due to spinon singlet pairing, whereas  $T_{BEC}$  corresponds to the Bose condensation of holons.<sup>\*\*</sup> For  $T_{SG} < T < T_{BEC}$  conventional Fermi liquid behavior is recovered. The superconducting phase has a *d*-wave order parameter. Interestingly, Wen and Lee [145] adopt the view that the spin gap below about 150 K is restricted to bilayer systems as proposed by Millis and Monien [106], and identify the crossover temperature from a uniform RVB phase to a staggered flux phase in their model with a *high* temperature reduction of the magnetic susceptibility observed at about 400 K (see references in Ref. [106]). The  $\pi$ -flux phase at zero to low doping is equivalent to the description of the 2D S = 1/2 Heisenberg antiferromagnet by Affleck and Marston [142] (see chapter 2.2). Another crossover is predicted at low doping levels: At high temperatures the models contain a localized spin phase (LS), with an onset temperature for the coherent motion of spinons and holons  $(T_D)$ .

#### Experimental Status Quo

At this point we finally should have a look at the experimental data concerning crossovers, spin-gaps and pseudogaps. It would be too easy to blame the theoreticians for an "overinterpretation" of the experimental data. In fact, determining a *crossover* temperature is much more uncertain compared to a real phase transition. A further uncertainty comes from the symmetry of the pseudogap opening below the crossover, which follows according to ARPES measurements [35, 281, 282] the *d*-wave  $|\cos k_x - \cos k_y|$  behavior as for the superconducting gap. As a consequence the pseudogap is not only opening partially but also gradually, making its precise determination a formidable task. An extensive review of experimental data covering different techniques has recently been published by Timusk and Statt [283].

The most direct observation of the pseudogap is possible in angle-resolved photoelectron spectroscopy. In ARPES data of the bilayer system  $Bi_2Sr_2CaCu_2O_{8+\delta}$  two energy scales have been resolved in underdoped samples: a gap in the leading edge of about 20 to 25 meV and a high energy hump (the maximum of the leading edge) of about 100 to 200 meV [284,285] both showing *d*-wave symmetry [249]. The leading edge pseudogap [281,282,284] presents itself as a continuation of the superconducting gap. With increasing temperature the leading edge gap does not close at  $T_c$ , but survives in the normal state with a similar magnitude and momentum dependence. However, there has to be some difference, and it is found in the line shape. The superconducting state is characterized by a sharp resolutionlimited peak [256, 257, 281, 282], indicating the existence of well-defined quasiparticles,

<sup>\*\*</sup>In an alternative scenario [280] one may consider a pair condensation of both spinons and holons. The enforcement of the slave boson constraint favors holon pairing with respect to a Bose-Einstein condensation.

whereas the normal state spectra are very broad. Due to this large width, spectral weight extends up to the Fermi energy in the normal state, which justifies the term pseudogap. The width even increases towards lower doping concentrations, which reminds us of the peak width mystery of the single hole in the insulator (see chapter 2.2.3). The particular importance of the sharp peak below  $T_c$  is that it tells us that the very large width in the normal state is indeed intrinsic and not an experimental artefact. And if we treat the sharp peak below  $T_c$  as an example of what a quasiparticle peak should look like, then it tells us that there are no quasiparticles in the normal state [256, 257].

With regards to the doping dependence, the onset temperature of the normal state gap approaches  $T_c$  around optimal doping, and no pseudogap is observed for overdoped samples [285]. Similar to the onset temperature, the magnitude of the normal state gap increases from optimal doping towards the underdoped region, and surprisingly the gap observed in the superconducting state does the same [286], the two gaps having about the same magnitude as stated above. As a consequence,  $2\Delta/k_BT_c$  is not constant, as  $\Delta$ increases while  $T_c$  decreases. Recently, a normal state gap was observed also in the single layer material Bi<sub>2</sub>Sr<sub>2-x</sub>La<sub>x</sub>CuO<sub>6+ $\delta$ </sub> [287].

A very interesting way of looking at ARPES data of the correlated insulating phase has recently been proposed by Ronning and collaborators [249]. In a metal the Fermi surface is defined by a step in the occupation number  $n(\mathbf{k})$  of electronic states with momentum  $\mathbf{k}$ , and the magnitude of the step is proportional to the strength of the quasiparticle pole. In a correlated Mott-Hubbard insulator there is no such step at half-filling, the slope of  $n(\mathbf{k})$  stays finite for all  $\mathbf{k}$  and the chemical potential lies within a gap. However, the authors of Ref. [249] claim that the profile of  $n(\mathbf{k})$  mimics the shape to be expected in the absence of correlations, and in analogy to a metal they define the point of steepest drop of  $n(\mathbf{k})$  as a "remnant" or "underlying" Fermi surface (see Fig. 2.33). The contour and its volume extracted this way from data of insulating  $Ca_2CuO_2Cl_2$  indeed resemble predictions of band structure calculations, which yield a metal for the half-filled case, as stated above. The term "remnant Fermi surface" has however to be taken with care, as this contour is far from being isoenergetic. In fact, the energy dispersion of this contour follows a  $d_{x^2-y^2}$  symmetry, with a difference as large as 320 meV between  $(\pi, 0)$  and  $(\pi/2, \pi/2)$ . This difference is called a "gap", which is again very misleading since both states are occupied. This name only becomes meaningful if one assumes that doping simply shifts the chemical potential through the potential mountains of the undoped compound shown in Fig. 2.33. Although definitely too simple, this scenario has the advantage of solving some problems. Moving the chemical potential into the "remnant Fermi surface" would give rise to segments of a "real" Fermi surface around  $(\pi/2, \pi/2)$  and a gap around  $(\pi, 0)$ at the same time. Shen and collaborators suggest that this insulating d-wave "gap" evolves into the broad hump at about 100 to 200 meV observed in underdoped samples [284, 285] and take the common *d*-wave symmetry of all the features as evidence for a common origin. However, whether the behavior of the undoped insulator develops smoothly towards the underdoped regime or whether instead a picture as given by Barzykin and Pines in Fig. 2.28 (e) on page 63 is appropriate remains to be studied in more detail.

As in the case of ARPES, the magnitude of the superconducting gap does not show a



Figure 2.33: A comparison of an insulator (A) and a slightly overdoped sample reproduced from Ronning et al. [249]. From bottom to top it shows the occupation number  $n(\mathbf{k})$ , the resultant (remnant) Fermi surface and the quasiparticle dispersion. Note that the "remnant Fermi surface" is far away from  $E_F$  and that the isoenergetic true Fermi surface of case (B) has turned into a "roller coaster" contour in the insulator, which Ronning et al. ascribe to strong correlations. The topmost part replots the dispersion from  $(\pi, 0)$  to  $(0, \pi)$  and shows the d-wave symmetry of both cases. Moreover, it explains the connotation of the term "gap" in Ref. [249].

temperature dependence in scanning tunnelling microscope (STM) spectra of the underdoped bilayer Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+ $\delta$ </sub> [288]. In particular it does not close at  $T_c$  but survives in the form of a conduction depression centered around zero bias. Even this normal state depression does not close up to room temperature but it merely fills in. And as in the ARPES data, the magnitude of the gap *increases* going from optimal doping to the underdoped phase, again also in the superconducting state [288, 289]. However, the STM pseudogap is found not only in underdoped compounds, but also in the overdoped regime [288].

The specific heat coefficient  $\gamma$  also shows a depression in the normal state in underdoped samples [292]. A very interesting observation was made around optimal doping. Here,  $T_c$ varies only slowly around the maximum but the condensation energy drops very rapidly and strongly towards the underdoped regime, whereas it follows the slow evolution of  $T_c$ towards overdoping [292]. An analysis of entropy as determined from the specific heat coefficient and magnetic susceptibility by Loram *et al.* shows that the normal state gap exists equally for spin and charge degrees of freedom [293], an observation that challenges models considering spin charge separation.

Historically, NMR data were the first to report a spin-gap in the cuprates. A gap is obvious from a reduction of the spin-lattice relaxation rate of the Cu nuclei  $1/^{63}T_1$  and from a reduction of the Knight shift  $K_s$  which is proportional to the real part of the susceptibility  $\chi'(\mathbf{q}=0,\omega)$  and measures the density of states at the Fermi energy. Both features are reported in the normal state of underdoped systems. The smooth continuation from the superconducting to the normal state observed in ARPES and STM data can for example be found in the Knight shift of  $YBa_2Cu_3O_{6.7}$ , which is drastically reduced in the normal state starting from far above  $T_c$  and does hardly indicate the superconducting transition [294]. The two different crossover temperatures mentioned above in the discussion of the phase diagrams of Fig. 2.28 are usually inferred from NMR data. A synoptical definition of these two crossover temperatures in terms of the behavior of spin-lattice relaxation rates, Knight shift and spin-spin relaxation rates has been given by Pines in Fig. 2 of Ref. [272]. In their review, Timusk and Statt suggest the possibility that the lower temperature might be related to magnetic phenomena and the upper one to the density of states [283]. They point out that only some compounds such as  $YBa_2Cu_4O_8$  show clear crossovers, whereas others exhibit a smooth evolution. A very different point of view is strongly emphasized by Williams, Tallon and Loram [291]. They claim that only one crossover exists which is best described by an energy scale, since no real kinks are present in a careful analysis of the data, be it for  $YBa_2Cu_4O_8$  or another cuprate. The appearance of the lower onset temperature is claimed to be an artefact due to the division of  $1/^{63}T_1$  by T. Moreover, they stress the absence of anomalies in the specific heat at the crossover temperatures.

Beautiful data on the suppression of  $T_c$  with Zn substitution in  $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ and  $(Y,Ca)Ba_2(Cu_{1-y}Zn_y)_3O_{7-\delta}$  have been presented by Tallon and co-workers [290] (see Fig. 2.34 (a)). Interestingly, the phase curves collapse in both cases with increasing Zn concentration y towards an overdoped hole concentration of p=0.19 for T=0, *i.e.*, not symmetrically around optimal doping. Similar data have been reported for the Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+\delta</sub> system [295]. The more rapid suppression  $dT_c/dy$  on the underdoped side is explained by the presence of the pseudogap. In the lower panel, the steep solid line hitting T=0 at



(a)  $T_c$  versus hole concentration p for Znconcentrations in % as indicated in the figure. Upper panel:  $La_{2-x}Sr_xCu_{1-y}Zn_yO_4$ , lower panel:  $(Y,Ca)Ba_2(Cu_{1-y}Zn_y)_3O_{7-\delta}$ . Steep solid line: pseudogap energy. Reproduced from Tallon et al. [290].



(c) Superconducting gap  $\Delta(0)$ , normal state gap  $\Gamma(110 \ K)$  and  $T_c$  in  $Y_{0.8} Ca_{0.2} Ba_2 Cu_3 O_{7-\delta}$  as a function of oxygen depletion  $\delta$ , after Loram et al. [292]. Note that the underdoped regime is on the right hand side in this plot.



(b) Pseudogap energy scale  $E_g$  determined from scaling of <sup>89</sup> Y NMR and heat capacity by Williams, Tallon and Loram [291] for  $(Y, Ca)Ba_2Cu_3O_{7-\delta}$  and  $YBa_2Cu_4O_8$ .



(d) Overview of the pseudogap magnitude in  $Bi_2 Sr_2 CaCu_2 O_{8+\delta}$  as collected by Timusk and Statt [283] from different techniques. Solid line:  $2\Delta = 9.5k_B T_c$ .

Figure 2.34: Different experimental views on the question whether the normal state pseudogap merges with the superconducting gap in the overdoped regime or whether the two are independent. p=0.19 depicts the pseudogap energy as determined for the same samples from a scaling analysis of <sup>89</sup>Y NMR data and heat capacity (the dashed line in the upper panel is the same line rescaled by  $T_{c,max}$ ). The experimental data points of this analysis emphasize the point of view of an energy scale passing right through  $T_c$  [291] (Fig. 2.34 (b)). However, a data point for p=0.18 at about  $T_{c,max}/2$  as predicted by a linear fit would definitely be enlightening. Most data points stem from Ref. [292] where the magnitudes of the normal state gap ( $\Gamma(110K)$ ) and of the superconducting gap ( $\Delta(0)$ ) were plotted together with  $T_c$ as a function of oxygen depletion  $\delta$  in  $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ , *i.e.*, the underdoped regime is on the right hand side of Fig. 2.34 (c). More evidence for the independence of the two gaps comes from susceptibility and <sup>89</sup>Y NMR measurements of YBa<sub>2</sub>Cu<sub>4</sub>O<sub>8</sub>, where an oxygen isotope effect is observed in  $T_c$  but absent in the normal state gap [296]. In summary, Tallon, Loram and co-workers take the point of view that the pseudogap *competes* with superconductivity and that it eats away the spectral weight and entropy in the underdoped regime, thereby strongly suppressing  $T_c$  in spite of the large gap value [296].

This has to be contrasted with the collection of data points reproduced from the review of Timusk and Statt [283] in Fig. 2.34 (d). It shows the magnitude of the (normal state) gap obtained on Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+ $\delta$ </sub> by various techniques and advertizes a smooth evolution of the pseudogap into the superconducting gap, which is shown in the figure via the empirical formula  $2\Delta = 9.5k_BT_c$  (solid line).

Another example underlining the importance of a particular slightly overdoped hole concentration is the study by Boebinger and co-workers [297] of the low temperature resistivity of  $La_{2-x}Sr_xCuO_4$ , which is measured by applying pulsed magnetic fields of 61 T to suppress superconductivity. It indicates a metal-insulator transition for  $p \simeq 0.16$  and  $T \rightarrow 0$ , placing a quantum critical point in the slightly overdoped regime. However, to what extent a system in a huge magnetic field represents the ground state in the absence of superconductivity is questionable.

The often cited "linear" T dependence of the in-plane resistivity  $\rho_{ab}$ , one of the main issues in the non-Fermi liquid discussion (see below), is found only in a narrow region around optimal doping. However, right *at* optimal doping the extremely broad range of validity of the linear behavior from 7 to 700 K in  $\text{Bi}_{2+x}\text{Sr}_{2-y}\text{CuO}_{6\pm\delta}$  [298] or 40 to 800 K in  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  [299] and the lack of any sign of saturation is truly impressive. Another striking observation at optimal doping is that the linear curves extrapolate to zero resistance at T=0. In underdoped samples  $\rho_{ab}$  is linear at high temperatures and becomes steeper for lower temperatures (see  $d\rho_{ab}/dT$  in Fig. 2.35). This suppression is interpreted as due to a reduced scattering caused by the opening of the pseudogap. Batlogg and co-workers [300] determined this crossover temperature T<sup>\*</sup> in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  over a broad doping range and find values of T<sup>\*</sup> ranging up to as high as 800 K for x=0.02.

One of the most unconventional<sup>††</sup> features of the cuprates is the temperature dependence of the resistivity anisotropy. In the same temperature range where the in-plane resistivity  $\rho_{ab}$  becomes non-linear the *c*-axis resistivity  $\rho_c$  starts to *increase* with decreasing temperature [301], *i.e.*, the anisotropy rises steeply, eventually arriving at values of up to

<sup>&</sup>lt;sup>††</sup>Apparently, we cannot escape from being involved in the race for the superlatives.

10<sup>5</sup> in  $\operatorname{Bi}_{2+x}\operatorname{Sr}_{2-y}\operatorname{CuO}_{6\pm\delta}$  [298]. This can possibly be explained by the momentum dependence of the *c*-axis hopping matrix element  $t_c(\mathbf{k})$ . Band structure calculations [302] indicate that (in a bilayer)  $t_c(\mathbf{k})$  vanishes along the Brillouin zone diagonals and has maxima for momenta parallel to  $(\pi, 0)$ , *i.e.*, it has the same functional form as both the normal state and the superconducting gap. As a consequence, the gap opens wherever  $t_c(\mathbf{k})$  is finite, and in the ungapped regions such as  $(\pi/2, \pi/2)$  the hopping parameter  $t_c(\mathbf{k})$  vanishes. Opening of the pseudogap hence causes  $\rho_c$  to increase. The same mechanism might be at least partially responsible for the generally very low values of the *c*-axis optical conductivity and the absence of a coherent quasiparticle peak in microwave data of the superconducting state [303]. However, this is only one of the numerous ideas competing for the valid solution of the *c*-axis mystery. We want to postpone a more detailed discussion to chapter 8 and refer the reader for the moment to the extensive reviews of Leggett [38] and Cooper and Gray [39].

Let us take this chance and move to optical spectroscopy, the technique chosen in this thesis. Measurements of the c-axis optical conductivity  $\sigma_c(\omega)$  of underdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> by Homes *et al.* [32] were the first spectroscopic indications of a normal state *charge* gap. They reported a suppression of  $\sigma_c(\omega)$  below 400 cm<sup>-1</sup> which started far above T<sub>c</sub> and followed the temperature dependent suppression of the Knight shift. This suppression of  $\sigma_c(\omega)$  agrees with the "semiconducting" increase of  $\rho_c$ . Once more, the magnitude of the gap does not show a temperature dependence in underdoped samples, it merely fills in with increasing temperature. Moreover, the magnitude of the gap decreases with increasing doping, and no normal state gap is observed in the overdoped region [304]. All observations agree favorably with ARPES data, and Bernhard and collaborators [304] claimed that  $\sigma_c(\omega)$ can be derived directly from ARPES data around  $(\pi, 0)$ . However, a note of caution has to be added. The suppression of  $\sigma_c(\omega)$  has so far only been reported convincingly in bilayer materials such as  $YBa_2Cu_3O_{7-\delta}$  [32,305],  $YBa_2Cu_4O_8$  [306] and  $Pb_2Sr_2(Y,Ca)Cu_3O_8$  [307]. All available studies of the single layer compound  $La_{2-x}Sr_xCuO_4$  do not show a well defined pseudogap but indications for a gradual suppression of  $\sigma_c(\omega)$  over a broad frequency range in the normal state [308–311] (see Fig. 8.13 on page 227). The very low values of  $\sigma_c(\omega)$ observed in  $La_{2-x}Sr_xCuO_4$  are clearly a challenge to the experimentalist and impede a definite verdict at this stage. Contrary to the commonly measured reflectance spectra we will show transmittance data of  $La_{2-x}Sr_xCuO_4$  in chapter 8.2 to clarify this point. In all bilayer materials studied so far, the suppression of  $\sigma_c(\omega)$  is accompanied by the rise of a "strange bump", as it was originally called. This bump is strongly suppressed by Zn impurities, which however do not influence the optical normal state gap [312]. Since Zn substitution is known to have a strong influence on the pseudogap, a relation between the bump and the pseudogap was claimed [312]. Timusk and Statt on the other hand drew parallels between the bump and the famous 41 meV resonance peak observed in neutron scattering spectroscopy. In this thesis, we will develop a simple model for the optical response of a layered structure and will show that the bump can be explained as an optical plasmon, a pure multilayer phenomenon [313]. A more detailed discussion of the c-axis physics will follow in chapter 8. At this point we want to emphasize that it is too easy, in the absence of a microscopic theory of the pseudogap, to attribute every

anomaly occurring in the normal state to it. The absence of a normal state gap in the NMR data of the single layer compound  $La_{2-x}Sr_xCuO_4$  had inspired Millis and Monien [106] to propose an interlayer exchange mechanism which treats the pseudogap as a pure bilayer phenomenon. Meanwhile normal state gaps have been seen in several single layer materials with distinct techniques and the NMR mystery of  $La_{2-x}Sr_xCuO_4$  is believed to be due to impurities giving rise to local moments. However, most of the samples studied in the pseudogap discussion are still multilayers, and the "strange bump" in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> is but one example that one should keep in mind.

Evidence for a normal state gap in the in-plane optical conductivity  $\sigma_{ab}(\omega)$  is more intricate. The original anomaly is the non-Drude behavior of the free particle contribution to  $\sigma_{ab}(\omega)$ . In a conventional metal,  $\sigma_{ab}(\omega)$  shows a  $1/\omega^2$  behavior, whereas a much broader peak falling off only like  $1/\omega$  is found in the cuprates. This is equivalent to the linear behavior of the resistivity. To account for this anomaly a frequency dependent scattering rate  $1/\tau(\omega)$  is assumed in the extended Drude model (see chapter 3). This  $1/\tau(\omega)$  shows a low frequency suppression in the normal state from high frequency linear behavior which is interpreted as a pseudogap [30,31,283]. The frequency below which the depression sets in is about 700 cm<sup>-1</sup> in all samples studied so far [30,283]. Contrary to all other examples given up to now, the magnitude of the normal state gap tends to *increase* slightly with increasing doping.

Although we are convinced that there are already too many different temperature scales floating around in this discussion, we finally want to focus the attention on another one, one that has been pointed out to us by Freimuth [315], but has to the best of our knowledge not been discussed in the literature yet. In Fig. 2.35 we reproduce the *derivative* of the inplane resistivity  $d\rho_{ab}/dT$  in La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> from the work of Takagi *et al.* [299]. The upper panel shows data from underdoped to optimally doped samples, whereas the lower panel continues towards the overdoped regime using an enlarged scale. Usually, two characteristic temperatures are inferred from the points where (i)  $\rho_{ab}$  drops below the linear behavior (*i.e.*, where  $d\rho_{ab}/dT$  becomes larger than 1), and where (ii)  $\rho_{ab}$  starts to increase with decreasing temperature and becomes semiconducting-like,  $d\rho_{ab}/dT < 0$ , which might be caused by localization. However, we argue that the onset of this tendency to localize can possibly be attributed to the maximum slope of  $\rho_{ab}$  and not to the zero crossing of  $d\rho_{ab}/dT$ . The maximum slope is most remarkably observed at 300 K for all samples up to the optimal doping concentration. The same value of 300 K plays also an important role in the inverse magnetic correlation length displayed in Fig. 2.36 from Keimer and collaborators [179], again for the  $La_{2-x}Sr_xCuO_4$  system. The inverse correlation length stays constant up to almost 300 K and increases linearly for higher temperatures.<sup>‡‡</sup> Keimer and collaborators interpreted their data in terms of the quantum non-linear  $\sigma$  model and treated doping

<sup>&</sup>lt;sup>‡‡</sup>Later measurements on insulating cuprates [180–182] extending to lower and higher temperatures do not show a linear behavior, but an exponential divergence of  $\xi$  in 1/T. For our discussion here the true high temperature behavior is however not that important, since for the moment we only focus on the *constant* behavior of  $\xi^{-1}$  at low temperatures. In fact, the finite and constant  $\xi^{-1}$  is even more confusing if the high temperature behavior shows the renormalized classical exponential behavior, for which  $\xi^{-1}$  should go to zero for low temperatures.



Figure 2.35: Temperature-derivative of the in-plane resistivity  $d\rho_{ab}/dT$ , reproduced from Takagi and collaborators [299]. A maximum at 300 K is clearly present for all doping concentrations up to optimal doping, x=0.15.



Figure 2.36: Inverse magnetic correlation length  $\xi^{-1}$  as given by Keimer and coworkers [179]. Up to almost 300 K,  $\xi^{-1}$ is constant in all samples. The solid lines are simply displaced vertically.

simply as an increase in the quantum coupling constant g. The linear increase at high temperatures is characteristic for the quantum critical regime. Since none of the curves shows linear behavior down to low temperatures, which is the behavior expected for the critical point, they conclude that x = 0 itself has to be the quantum critical point. In this scenario the presence of Néel order is due to a delicate balance between interlayer coupling and doping. However, their treatment of doping is clearly too crude. We want to argue that localization possibly can explain the data. If we assume that the doped quasiparticles are becoming localized below 300 K and scramble the antiferromagnetic background locally, then the magnetic correlation length is constant with a value determined by their average distance and hence proportional to  $a/\sqrt{x}$ . As soon as the quasiparticles are allowed to move they disturb the magnetic order more effectively and the inverse correlation length increases (see dotted lines in the schematic Fig. 2.37). Early measurements of the correlation length have been shown to fit the  $a/\sqrt{x}$  dependence very well (see lower data points in Fig. 2.38) [314]. Gooding and collaborators attributed both the experimental correlation length [234,235] and the transport properties [237] to chirality arising from the localization of holes around Sr impurities in  $La_{2-x}Sr_xCuO_4$ . Opposed to the simple model of static holes given above, this scenario predicts  $\xi \approx (a/2)/x$  (solid line in Fig. 2.38), which fits more recent data on (probably) cleaner samples. For a discussion of the two alternative scenarios and





Figure 2.37: Schematic temperature dependence of the inverse magnetic correlation length. Solid lines mimic results of the quantum non-linear  $\sigma$  model [127].  $g < g_c$ : renormalized classical for low T;  $g = g_c$ : quantum critical;  $g > g_c$ : quantum disordered for low T. For large T all curves are in the quantum critical limit. We suggest that the dotted lines represent  $\xi^{-1}$  in the presence of impurities and phonons, which together with electronic correlations cause localization below  $T_{loc}$ .

Figure 2.38: Magnetic correlation length, reproduced from Gooding et al. [235]. The solid line represents approximately (a/2)/x, where a is the lattice constant. The lower data points correspond to earlier measurements and had been shown to agree very well with  $a/\sqrt{x}$  [314]. See also Ref. [105].

the relation to the doping dependence of the spin glass temperature see Johnston [105]. The omnipresence of 300 K has however not been noted thus far. In chapter 7 we will present optical data which show that the doped carriers indeed are localized up to 300 K in the very low doping limit. We will argue that the interplay between electronic correlations, impurities and phonons is responsible for localization at this rather high temperature. Obviously, including all three components represents a major challenge to theory. It is tempting to speculate about an extrapolation of our low doping result to higher doping levels given the information contained in Figs. 2.35 and 2.36.

### 2.3.2 Fermi Liquid?

One of the major unresolved issues is whether Fermi liquid theory applies to the normal state of the cuprates. We have seen thus far that many normal state properties certainly do not follow canonical Fermi liquid behavior, which has inspired some exotic ideas. Let us briefly scan through some of them, moving from the non-Fermi liquid models to the more conventional ones. Anderson studied non-Fermi liquid behavior by applying onedimensional concepts to the 2D cuprates. In 1987 he suggested a resonating valence bond liquid of singlet pairs in analogy with a linear spin chain [20]. Over the years this turned into the idea of the occurrence of spin-charge separation also in two dimensions [55] (see chapter 2.2), mainly motivated by the highly anisotropic transport properties which suggest a 2D confinement of the carriers. This confinement is supposed to give rise to coherent behavior (of spinons and holons) in the  $CuO_2$  layers and incoherent behavior along the c-axis. Another unconventional aspect is the way superconductivity appears in this "interlayer tunnelling model": in a BCS superconductor the condensation energy stems from a reduction of potential energy, and the kinetic energy is actually rising. On the contrary, the driving force for pairing in the interlayer tunnelling model is the reduction of kinetic energy along the *c*-direction: holons are not allowed to tunnel between adjacent layers, but Cooper pairs are. Both aspects are emphasized in the *c*-axis optical conductivity spectra. The strong anisotropy is obvious from the strongly overdamped behavior along the *c*-axis in the normal state, and the relaxation of the confinement in the superconducting state reveals itself via the appearance of a sharp, undamped Josephson plasmon (see chapter 8). The idea of a reduction of kinetic energy has found support in an analysis of the spectral weight transfer observed in the *c*-axis optical conductivity in underdoped cuprates by Basov and co-workers [316]. However, the model predicted a particular relation between  $T_c$  and the penetration depth, and experimental tests with optical techniques of our group and SQUID measurements of Moler and collaborators show that this prediction is more than one order of magnitude off in the 90 K compound  $Tl_2Ba_2Cu0_6$  [41,42], which yields a contribution to the condensation energy of less than 1 %. But theories behave like Hydra, it is not enough to chop off one head, and accordingly Chakravarty [317] claims to be able to account for much of the discrepancy. Ioffe and Millis [318] argued that the temperature dependent anisotropy can be reconciled with a Fermi liquid scenario if one assumes that  $\rho_{ab}$  and  $\rho_c$  are controlled by different parts of the Fermi surface. This is a reasonable option since the c-axis hopping parameter  $t_c(\mathbf{k})$  vanishes along the zone diagonals [302], as stated above. A further discussion of the optical conductivity and the resistivity in this case has recently been given by van der Marel [319]. The "1D" ideas find some support in the observation of superconductivity at 12 K under pressure in the doped ladder compound  $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$  [177] which is supposed to be a spin liquid in the absence of doping. Related to Andersons ideas are the gauge field theories as proposed by, e.g., Nagaosa and Lee [320] and Fukuyama and Kohno [148], which introduce an auxiliary boson field.

We already encountered some other 1D-related objects, the so-called stripes, in the discussion of the phase diagram of  $(La,Nd,Sr)_2CuO_4$  on page 61 and of the phase diagrams of Figs. 2.28 (b) and (f) and 2.29. The original idea of Zaanen and Gunnarsson [264] goes back to 1989 and was born from a simple mean-field study of holes in an antiferromagnet using the Hubbard model. There it was found that a doped hole can significantly reduce its energy by reducing the magnitude of the spins, not only by disturbing the orientation of the spin background, and that several holes pile up to form a kind of soliton, a charged antiphase domain wall. A different route to a similar result was taken by Emery and Kivel-

son [265], who discussed the tendency of an antiferromagnet to expel doped holes, *i.e.*, to phase separate into hole-rich and hole-poor domains. They included the usually neglected competing long-range Coulomb repulsion, which results in frustrated phase separation and charge-ordered states. The charge-order then drives the spin-order, whereas stripe formation is spin-driven in the scenario of Zaanen and Gunnarsson. The self-organized charge structures lead to a variety of electronic phases and crossover phenomena, which is proposed as an explanation for the pseudogap [265]. More recently the appearance of domain walls was attributed to the interplay of the chiralities of impurity bound holes [235] or to an intrinsic chirality of the doped holes [19]. The first definite experimental confirmation of the existence of stripe order came from the observation of incommensurate peaks in neutron diffraction data of hole-doped  $La_2NiO_{4,125}$  [321]. Similar static stripe order was later found in  $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$  (with x=0.12, 0.15 and 0.20) [268] and also in certain manganates, which underscores the general importance of the concept. The key feature of the experiment is that there have to be two sets of peaks in the neutron data at different but correlated momenta, one for the spin order and one for the charge order (or better the associated lattice displacements). Both were indeed observed [268]. Recently, the occurrence of striped charge order in the cuprates has been confirmed by x-ray diffraction measurements of  $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$  (x = 0.12 and 0.15) [322, 323]. Static stripe order, however, competes with superconductivity, which explains one of the early mysteries of the cuprates, the "anomalous" suppression of  $T_c$  around a hole concentration of 1/8 [324], which seems to be the most desirable filling fraction for static stripes in the cuprates. Similar incommensurate peaks had been observed long before in *inelastic* neutron scattering [269], but they were only a posteriori taken as indication for dynamical stripes. These inelastic peaks suggest the coexistence of superconductivity and local antiferromagnetism, which is confirmed by NMR, NQR and  $\mu$ SR measurements (see references in Ref. [325]). The important finding of Aeppli and co-workers [267] that these incommensurate peaks behave nearly singular for  $T \rightarrow 0$  has been discussed above. One serious drawback was that this dynamical stripe order only seemed to occur in  $La_{2-x}Sr_xCuO_4$ , whereas  $YBa_2Cu_3O_{7-\delta}$  showed a *commensu*rate peak. This issue was recently resolved by Mook and co-workers [110, 113] who found consistency between the incommensurate low-energy spin fluctuations of  $La_{2-x}Sr_xCuO_4$ ,  $YBa_2Cu_3O_{7-\delta}$  and  $Bi_2Sr_2CaCu_2O_{8+\delta}$ . Most remarkable is that they also succeeded in finding the incommensurate dynamical *charge* fluctuations, which strongly points towards the presence of stripes in all cuprates. Experimentally, this field is developing very rapidly these days, and we refer the reader to the short discussion of recent results given in Ref. [325] and to the recent reviews of Tranquada [326].

Another exotic idea, the so-called SO(5) theory recently proposed by Zhang [327], reflects upon antiferromagnetism and superconductivity as just two faces of one and the same coin. The superconducting state has a well defined phase and hence breaks the gauge invariance or U(1) charge symmetry. The antiferromagnetic order parameter, on the other hand, breaks the rotational or SO(3) spin symmetry. Zhang proposes a five dimensional superspin as order parameter which contains the three entries from the staggered magnetization and two entries corresponding to the magnitude and phase of the former complex superconducting order parameter. In the thus defined five-dimensional space it becomes possible to find symmetry operations which "rotate" the antiferromagnetic into the superconducting d-wave state and vice versa. In a magnetic state these operations simply correspond to changing the direction of the (staggered) magnetization. In this model, the chemical potential breaks the SO(5) symmetry and the order parameter rotates from one state to the other just as the magnetic moment precesses in a uniform magnetic field. In this unified picture the high energy scale physics of the antiferromagnetic and the superconducting state are equal, and the pseudogap can be viewed as the formation of singlets that still have to decide whether they want to form a superconductor or an antiferromagnet. In other words, in the pseudogap region the 5D superspin has already acquired a finite magnitude, but no fixed orientation [328]. The model makes more direct contact with experiment in attributing a magnetic resonance peak found in superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> at 41 meV [108] to a Boson mode that corresponds to a modulation of the order parameter. We want to remark that the model in itself does not contain the phase diagram of the cuprates, additional symmetry breaking effects have to be added by hand to favor the antiferromagnetic state at low doping and the superconducting state at high doping concentrations.

The "nodal liquid" proposed by Fisher and collaborators [170] has been discussed on page 35 in the context of the magnetic insulating phase. In this scenario the underdoped phase is a disordered version of the *d*-wave superconductor. The Cooper pairs are quantum vortices, and the pseudogap phase is a (pinned) Wigner crystal of these vortices, analogous to the Abrikosov flux-lattice above  $H_{c1}$  in a type II superconductor. Here, the chemical potential  $\mu$  plays the role of the "magnetic field". Above " $\mu_{c2}$ " the Cooper pair "flux lattice" melts and they condense into a *d*-wave superconductor. Below  $\mu_{c2}$ , the Wigner crystal coexists with the nodal liquid, where the "nodons" are spin carrying and charge neutral Fermions, descendants of the quasiparticles living in the nodes of the *d*-wave gap in the superconducting state.

Varma and co-workers introduced the notion of a "marginal" Fermi liquid [329], which is on the verge of being a Fermi liquid. Those groups advertizing Fermi liquid behavior explain the anomalies by introducing an anomalous dependence of the self energy or the dynamical susceptibility  $\chi(\mathbf{q}, \omega)$  on the wave vector  $\mathbf{q}$ , the frequency  $\omega$  or the temperature, giving rise to "novel" or "extrapolated" Fermi liquid behavior [17]. Levin and co-workers claimed that the high transition temperature of the superconducting phase hides the true normal state behavior, and that above  $T_c$  the high temperature explains deviations from the canonical Fermi liquid, in analogy to observations in heavy fermion compounds [17]. The group of these "novel" Fermi liquids comprises the nearly antiferromagnetic [330], the nearly localized [17], the short range magnetically correlated [241] and the nested [331] Fermi liquids. Some support for these scenarios has been claimed to come from the recovery of Fermi liquid behavior in the overdoped regime.

## 2.4 Of Spin and Charge in the Cuprates

Thus far we seem to have collected excuses for not understanding the cuprate physics yet. We are dealing with low dimensionality, the "extreme quantum limit" of spin 1/2and strong interactions. Disorder is a serious issue, a point which particularly needs to be emphasized in two dimensions. This mixture attacks the very basis of our tools to describe systems containing  $10^{23}$  atoms, such as translational symmetry and well defined quasiparticles. Most likely the quasiparticle concept does not apply to the normal state of the metallic phase, but even in the insulator well defined magnons are not telling the full story, and a proper concept of the valid excitations is lacking. So how to proceed? In our opinion it is of major importance to establish the connection between the magnetic state at half-filling and the strange behavior present in underdoped samples. In the words of Laughlin [258] "the study of the insulator and the study of the spin gap are the same thing." The wide-spread use of the t-J model for finite doping is based on its applicability to the half-filled case. If it however fails to capture an important ingredient of the magnetic state and its excitations, then we still do not score, although we may be close to the goal. One can only hope to describe the *pairing* of two quasiparticles or, say, entities correctly after having understood the properties of a single quasiparticle as measured by ARPES. And in order to describe the "dressed" quasiparticle we first have to understand the excitations which are responsible for the dressing.

For the moment, let us play a bit with the main characters of our story, spins and doped holes, and let us imagine some funny things the two of them could do together. The effect of the antiferromagnetic spin background on the behavior of added carriers bears a similar fascination as the ability of strong correlations to drive the half-filled band into an insulating state in the first place. Instead of experiencing a bandwidth of 3 eV(8t) as expected in simple single-particle theory the doped holes are restricted to a much narrower band of width 0.3 eV (2.2J) (see chapter 2.2.3). Unlike the case of 1D, where spin and charge separate and the holon can move freely using the full bandwidth, in 2D it is the tedious neighbors with their determined opinions about spin directions that impede motion on the natural scale of t. There are two ways of looking at the problem. One is to say that the hole has to carry along the heavy load of "magnon" dressing which turns it into a heavy quasiparticle moving in a narrow band. The other is to realize that only the spin degrees of freedom allow the hole to move at all. If we assume for the moment that there was a gap in the spin excitation spectrum which cuts off spin fluctuations, then the doped hole would be chained to its site. One possible way for the holes to get rid of all those problems is to form pairs, singlets, and ignore the other spins further on. As stated above, Anderson proposed the very unconventional idea that opposed to the usual reduction of potential energy in BCS theory the pairing could be mediated via a reduction of *kinetic* energy: holons cannot hop between layers, but pairs do. In fact a similar mechanism might even work within the  $CuO_2$  planes. One amusing consequence is that the pairing into singlets in order to escape the spin sector takes away the burden for the other spins at the same time. Just as the singlets do not care about the spins any more, the remaining spins do not have to worry about the spins that form the singlet, and the two descriptions of singlets in a disordered

spin background or of spins in a singlet liquid may become equally valid. This might be related to the fact that no sharp quasiparticle peaks are seen in ARPES in the normal state, suggesting a totally incoherent spectrum, but that upon entry in the superconducting state a well defined and sharp quasiparticle peak develops [256, 257, 281, 282]. On these grounds Shen and Sawatzky [256] recently proposed that the superconducting transition may not only be due to the opening of a gap caused by some attractive interaction between welldefined quasiparticles, but that the quasiparticles themselves only develop when lowering the temperature below  $T_c$ . Time will tell how exotic *the* model really has to be, but from what we have seen so far our expectations should not be too low.

# Chapter 3

# **Optical Spectroscopy**

## 3.1 Linear Response

In this thesis we will be interested in low energy excitations. We choose to probe the charge response, or to be more precise the charge neutral dipole excitations, by applying a weak disturbance in the form of an external electric field. Assuming a linear response and using a macroscopic language the electric field  $\mathbf{E}$  is connected to the induced current density  $\mathbf{j}$  via the complex tensor of the optical conductivity  $\boldsymbol{\sigma}$  by

$$\mathbf{j}(\mathbf{q},\omega) = \boldsymbol{\sigma}(\mathbf{q},\omega) \cdot \mathbf{E}(\mathbf{q},\omega) , \qquad (3.1)$$

where  $\mathbf{q}$  and  $\omega$  denote the wave vector and the frequency, respectively. Since the wavelength of the electric field is very large compared to the lattice spacing we are restricted to the study of  $\mathbf{q} = 0$  phenomena. We have to be careful since  $\mathbf{E}$  designates the *total* electric field, *i.e.*, the applied external field and the induced local fields. Usually the quantities in the above equation are treated as averages over regions large compared to the lattice spacing. In the discussion of the optical response perpendicular to the CuO<sub>2</sub> layers in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> we will have to go beyond a continuum approach and include local field corrections. We will restrict ourselves to the study of tetragonal and orthorhombic systems, in which case only the diagonal elements of  $\boldsymbol{\sigma}$  are finite. These can be studied independently by using linearly polarized light, and hence we can neglect the tensor nature of  $\sigma(\omega)$  from now on.

In linear response theory the fluctuation-dissipation theorem relates the imaginary part of a susceptibility — the dissipation — to a correlation function, *i.e.*, the fluctuations. The response to the various external perturbations in terms of correlation functions is given by the so-called Kubo formulas [332, 333]. The optical conductivity is determined by the current-current correlation function.

## **3.2** Optical Conductivity and the Dielectric Function

An equivalent way of describing the optical response uses the dielectric function  $\epsilon(\omega)$ , which usually is described in terms of a density-density correlation function [334]. The

dielectric function or the dielectric susceptibility  $\chi_{\mathbf{e}}(\omega)$  can be transformed into the optical conductivity via the expression

$$\frac{4\pi i}{\omega}\sigma(\omega) = \epsilon(\omega) - 1 = 4\pi\chi_{\mathbf{e}}(\omega) . \qquad (3.2)$$

The relation between the electric field and the displacement field  $\mathbf{D}(\omega)$  or the polarization  $\mathbf{P}(\omega)$  is given by

$$\mathbf{D}(\omega) = \epsilon(\omega)\mathbf{E}(\omega) , \qquad \mathbf{P}(\omega) = \chi_{\mathbf{e}}(\omega)\mathbf{E}(\omega) . \tag{3.3}$$

For later use we introduce the refractive index  $n(\omega)$  and the extinction coefficient  $k(\omega)$  which form just another pair of variables that describe the optical properties of a material. The relation to  $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$  reads

$$\epsilon' = n^2 - k^2 , \quad \epsilon'' = 2nk . \tag{3.4}$$

In this thesis we will discuss the real parts of  $\epsilon(\omega)$  and  $\sigma(\omega)$ , the former describing displacement currents and the latter dissipative loss. We will use the terminology  $\Re\epsilon(\omega) \equiv \epsilon'(\omega)$ ,  $\Im\epsilon(\omega) \equiv \epsilon''(\omega)$  and  $\Re\sigma(\omega) \equiv \sigma(\omega)$ . Due to the requirement of causality the real and imaginary parts of a response function are not independent, they are related via the Kramers-Kronig relations, for example [335]

$$\epsilon'(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega' \epsilon''(\omega)}{{\omega'}^2 - \omega^2} d\omega' , \qquad (3.5)$$

where P refers to the principal value of the integral.

In order to study the material properties  $\sigma$  or  $\epsilon$  we still have to establish a relation to some sample properties that we can measure, in our case the reflectance R and transmittance T for near normal incidence of the light beam. This relation is provided by the Fresnel formulae, which yield for a semi-infinite sample under conditions of normal incidence

$$\sqrt{R(\omega)} e^{i\phi_r(\omega)} = \frac{1 - \sqrt{\epsilon(\omega)}}{1 + \sqrt{\epsilon(\omega)}}, \qquad (3.6)$$

where  $\phi_r(\omega)$  denotes the phase shift the light experiences during reflection from the sample surface. Both amplitude and phase of the reflected light can be determined using the technique of ellipsometry at a finite angle of incidence. However, high quality cuprate samples are often very small, particularly for the study of the *c*-axis properties, and therefore a reasonable signal-to-noise ratio at the necessary large angles of incidence can often only be achieved if a brilliant source such as a synchrotron is available. In the commonly used normal incidence reflectometry only the amplitude  $R(\omega)$  can be determined, but the phase can be obtained by performing a Kramers-Kronig analysis. Note that  $R(\omega)$  does not fulfill the criteria for a response function, and that the applicability of a Kramers-Kronig relation is not obvious. In practice, problems only arise at large angles of incidence. A Kramers-Kronig analysis requires a knowledge of  $R(\omega)$  for all frequencies from zero to  $\infty$ . Therefore the measured data have to be extrapolated to both low and high frequencies. Errors may in particular arise close to the borders of the measured frequency range. In all cases studied here the reflectivity has been experimentally determined over a sufficiently broad range to guarantee the necessary accuracy within the frequency windows shown in the plots. Details will be presented together with the measured data in the following chapters.

The uncertainties of a Kramers-Kronig analysis can be circumvented if a second "optical" quantity is accessible experimentally. In the case of weak absorption one can measure the transmittance of a thin platelet

$$T(\omega) = \frac{(1 - R(\omega))^2 \Phi}{1 - (R(\omega)\Phi)^2}, \quad \Phi = \exp\left(-4\pi k(\omega)d/\lambda\right), \quad (3.7)$$

where d denotes the sample thickness,  $\lambda$  the wavelength of light and  $k(\omega)$  the extinction coefficient. Note that as above  $R(\omega)$  denotes the single-bounce reflectance defined for a semi-infinite medium and not the actual reflectance measured on the thin platelet. In practice the Kramers-Kronig analysis of reflectance data and the measurement of the transmittance tend to be complementary rather than being true alternatives. Due to the exponential function in Eq. 3.7, the transmittance of a single crystalline sample is only finite in a measurable sense if absorption is weak; extraction of the corresponding small values of the optical conductivity are then beyond the limits of a Kramers-Kronig analysis of reflectivity data. In order to illustrate this point we plot in Fig. 3.1 a Drude-Lorentz simulation (see next section) of  $R(\omega)$ ,  $T(\omega)$ ,  $\sigma_1(\omega)$  and  $\epsilon'(\omega)$ . The simulation shows a weak metallic contribution<sup>\*</sup> at  $\omega = 0$ , a weak phonon at 500 cm<sup>-1</sup> and three very weak absorption features at 600, 700 and 900 cm<sup>-1</sup>. A sample thickness of  $d = 100 \mu m$  has been assumed. The relative strength of the excitations can easily be read from  $\sigma_1(\omega)$ . The metallic  $\omega = 0$ excitation and the phonon at 500 cm<sup>-1</sup> can be very well determined from  $R(\omega)$ , whereas  $T(\omega)$  is unmeasurably small at low frequencies. Exactly the opposite is true for the weaker features. Their fingerprint in  $R(\omega)$  is very vague and will be lost in the noise of a real experiment, but they are clearly visible in the  $T(\omega)$  spectrum. The high frequency region with larger values of transmittance is dominated by Fabry-Perot fringes, *i.e.*, interferences due to multiple reflection within the sample. Obviously the exponential function in Eq. 3.7 for  $T(\omega)$  requires a delicate balance between absorption strength and sample thickness.

### 3.2.1 Drude-Lorentz versus Asymmetric Models

For a quantitative and separate analysis of the various contributions to the optical conductivity or the dielectric function we have to choose a model. The case of independent

<sup>\*</sup>We will follow loose terminology in common use and call the angular frequency  $\omega$  in the text simply a frequency that will be given either in wave numbers (cm<sup>-1</sup>), *i.e.*, the inverse wave length of the light, or eV, where 8066 cm<sup>-1</sup>  $\approx$ 1 eV. The far-infrared roughly stretches from 1 to 100 meV, and the frequency range up to about 1 eV is called the mid-infrared.



Figure 3.1: Drude-Lorentz simulation of a weak metallic contribution at  $\omega = 0$ , a weak phonon at 500 cm<sup>-1</sup> and three very weak absorption features at 600, 700 and 900 cm<sup>-1</sup>. A sample thickness of  $d = 100 \,\mu$ m has been assumed. The full set of parameters ( $\omega_{0j}, \omega_{pj}, \gamma_j$ ) reads (0, 600, 50), (500, 200, 15), (600, 10, 5), (700, 20, 20), and (900, 10, 20). All units in cm<sup>-1</sup>.

harmonic oscillators is described by a sum of Lorentzian oscillators, the Drude-Lorentz or Helmholtz-Kettler model [335]

$$\epsilon(\omega) = 1 + 4\pi \sum_{j=1}^{n} \chi_j = 1 + \sum_{j=1}^{n} \frac{\omega_{p,j}^2}{\omega_{0,j}^2 - \omega^2 - i\gamma_j\omega} , \quad \omega_{p,j}^2 \equiv \frac{4\pi e^2 N f_j}{m} , \qquad (3.8)$$

where  $\omega_{0,j}$ ,  $\gamma_j$  and  $\omega_{p,j}$  denote the transverse eigenfrequency, damping and "plasma frequency" of the *j*-th oscillator, respectively, *e* designates the electronic charge, *m* the effective band mass and *N* the density of electrons. The sum runs over *all* contributions to  $\epsilon(\omega)$ . In most cases only excitations j = 1 to *m* up to a maximum frequency will be considered, which is possible if all higher frequency terms j = m + 1 to *n* can be summarized in a constant  $\epsilon_{\infty}$ , which then also contains the first term on the right hand side, the vacuum contribution equal to 1. The abbreviation  $\omega_{p,j}$  is called the *j*-th plasma frequency in analogy to the meaning it has in the Drude model where one only has the  $\omega_{0,j} = 0$  term

$$\epsilon(\omega) = 1 + 4\pi \chi_{Drude} = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} , \qquad (3.9)$$

which in the limit of zero damping vanishes for  $\omega = \omega_p$ , *i.e.*,  $\omega_p$  denotes the frequency of the longitudinal plasma oscillation of free carriers. A dimensionless oscillator strength S is defined by

$$S = (\Delta \epsilon')_j = \frac{\omega_{p,j}^2}{\omega_{0,j}^2} \,. \tag{3.10}$$

For the case that all other oscillators are sufficiently far away it indicates the contribution of mode j to  $\epsilon'$ , *i.e.*,  $\frac{1}{4\pi}(\Delta\epsilon')_j = \chi'_{ej}(\omega \to 0) - \chi'_{ej}(\omega \to \infty) = \chi'_{ej}(\omega \to 0)$ . The oscillator strength S is related to the splitting of longitudinal and transverse modes. The transverse oscillation of the photon electric field does not couple to longitudinal modes, at least not for propagation along the principal symmetry axes, since only there a strict distinction between the two kinds of modes can be made. The longitudinal eigenfrequencies  $\omega_{L,j}$  can nevertheless be determined with optical techniques, since the propagation of a longitudinal mode requires  $\epsilon(\omega_L) = 0$ . We assumed that all other modes are sufficiently far away, *i.e.*, the lower modes do not contribute to  $\epsilon$  in the range considered and the higher modes can be summarized in  $\epsilon_{\infty,j}$ . Neglecting damping we obtain

$$\epsilon(\omega_{L,j}) = \epsilon_{\infty,j} + (\Delta \epsilon')_j \frac{\omega_{0,j}^2}{\omega_{0,j}^2 - \omega_{L,j}^2} = 0 , \qquad (3.11)$$

which can be rewritten as

$$\frac{\omega_{L,j}^2 - \omega_{0,j}^2}{\omega_{0,j}^2} = \frac{(\Delta \epsilon')_j}{\epsilon_{\infty,j}} , \quad \text{or} \quad \frac{\omega_{L,j}^2}{\omega_{0,j}^2} = \frac{\epsilon_{0,j}}{\epsilon_{\infty,j}} , \quad (3.12)$$

the latter being the famous Lyddane-Sachs-Teller relation. Note that this interpretation is only valid in a single-mode approximation, *i.e.*, when all other modes are sufficiently far away. Otherwise different longitudinal modes will mix and the oscillator strengths will not be independent.

A sum of Lorentzians is equivalent to a classical model of a sum of uncoupled harmonic oscillators. Quantum mechanics enters via the oscillator strength S, which is proportional to the transition matrix element (see Eqs. 3.8 and 3.10). Another important correction arises from depolarization fields. In the situation where the local field is equal to the applied field the dielectric function is given by

$$\epsilon(\omega) = 1 + 4\pi\chi_e(\omega) = 1 + 4\pi N\alpha(\omega) , \qquad \alpha(\omega) = \frac{e^2}{m} \frac{1}{\omega_0'^2 - \omega^2 - i\gamma\omega} , \qquad (3.13)$$

where  $\alpha(\omega)$  denotes the polarizability. In a cubic material the depolarization field correction transforms this into the Clausius-Mosotti or Lorenz-Lorentz equation [336]

$$\frac{\epsilon(\omega) - 1}{\epsilon(\omega) + 2} = \frac{4\pi}{3} N\alpha(\omega) . \qquad (3.14)$$

For a dilute system with low density N the dielectric function  $\epsilon(\omega)$  is close to unity and the two expressions Eqs. 3.13 and 3.14 are equivalent. In a dense system where local field effects must be taken into account it is possible to recover the form of Eq. 3.13, however with a shifted eigenfrequency [336]

$$\omega_0^2 = {\omega_0'}^2 - \frac{4\pi N e^2}{3m} . \tag{3.15}$$

Similar expressions can be derived for symmetries other than cubic. This explains why the Drude-Lorentz formula is generally applicable to the description of solid state matter. This form of the depolarization field correction nevertheless still assumes a homogeneous material, where local field corrections on an atomic scale are not included.

In the Drude model of Eq. 3.9 we have  $\omega_p^2 = 4\pi N e^2/m$ . At sufficiently high frequencies, all electrons can be considered free and a comparison with Eq. 3.8 suggests the important f-sum rule [332, 335]

$$\sum_{j=1}^{n} f_j = 1 . (3.16)$$

In terms of the optical conductivity this sum rule reads

$$\int_0^\infty \sigma_1(\omega) d\omega = \frac{\omega_p^2}{8} = \frac{\pi N e^2}{2m} , \qquad (3.17)$$

which also serves as a definition for the frequency dependent effective number of carriers  $N_{eff}(\omega)$  involved in excitations up to  $\omega$ 

$$N_{eff}(\omega) = \frac{2m}{\pi e^2} \int_0^\omega \sigma_1(\omega') d\omega' . \qquad (3.18)$$

#### Extended Drude Model

The real part of the optical conductivity in the Drude model of Eq. 3.9 falls off like  $1/\omega^2$ 

$$\sigma_1(\omega) = \frac{1}{4\pi} \frac{\gamma \omega_p^2}{\gamma^2 + \omega^2} , \qquad (3.19)$$

whereas in the cuprates a more gradual  $1/\omega$  behavior is encountered [25–30]. The Drude model assumes an exponential decay of the current-current correlation function with a constant scattering rate  $\tau \equiv \gamma^{-1}$ . In order to account for the interactions between the carriers and some Bosonic degrees of freedom one can allow for a frequency dependence of the scattering rate [26–30, 337–342]. The scattering rate however turns out to be only the real part of the so-called memory function or the imaginary part of the complex self energy. Each fulfill Kramers-Kronig relations, which therefore necessitates a frequency dependent *complex* scattering rate. Equivalently, one can introduce a frequency dependence of both the (real) scattering rate and the effective mass

$$\sigma(\omega) = \frac{1}{4\pi} \frac{\omega_p^2}{\tau^{-1}(\omega) - \mathrm{i}\omega \frac{m^*(\omega)}{m}} \,. \tag{3.20}$$

At high frequencies the influence of the interactions has to vanish, whereas the zero frequency limit offers a measure for the interaction strength  $\lambda$ 

$$\lim_{\omega \to \infty} \frac{m^*(\omega)}{m} = 1 , \qquad \lim_{\omega \to 0} \frac{m^*(\omega)}{m} = 1 + \lambda . \qquad (3.21)$$

Both  $\tau(\omega)$  and  $m^*(\omega)$  can be calculated if the complex conductivity is known from a Kramers-Kronig analysis. A  $1/\omega$  behavior of  $\sigma_1(\omega)$  produces a linear increase in  $\tau^{-1}(\omega) \equiv \gamma(\omega)$  with increasing frequency (compare Eq. 3.19). A low frequency suppression of  $\tau^{-1}(\omega)$  below this linear behavior in underdoped samples is attributed to the opening of a pseudo-gap [30, 31, 283] (see chapter 2.3.1).

In the particular case of the cuprates, a  $\mathbf{k}$ -dependence of the scattering rate might play an essential role [318,319,343]. Ioffe and Millis postulated the form

$$\gamma(\mathbf{k}_{2D}) = 1/\tau + K\sin^2(2\Theta) , \qquad (3.22)$$

where  $\mathbf{k}_{2D}$  denotes the momentum in the 2D CuO<sub>2</sub> layers, and K describes the amplitude of the angular variation with  $0 \leq \Theta \leq 2\pi$ . The angle  $\Theta$  is given relative to the  $(\pi, \pi)$  direction. In a further analysis van der Marel derived an analytic expression for  $\sigma(\omega)$  which predicts a linear frequency dependence of the scattering rate for intermediate frequencies and crosses over to a constant scattering rate for  $\omega \to \infty$  [319]

$$\sigma(\omega) = \frac{\mathrm{i}\omega_p^2}{4\pi} \left[ (\omega + \mathrm{i}/\tau)^{1-2\alpha} \cdot (\omega + \mathrm{i}K)^{2\alpha} \right]^{-1} , \qquad (3.23)$$

where the parameter  $\alpha$  describes deviations from Fermi liquid behavior, which is recovered for  $\alpha \to 0$ .

#### Asymmetric Models

The assumption of independent harmonic oscillators is often too crude to describe the experimental spectra. In order to develop a more general model let us first recall the conditions on the behavior of the response functions  $\epsilon(\Omega)$  or equivalently  $\chi(\Omega)$  in the complex  $\Omega$  plane imposed by causality and energy conservation [344].

• 
$$\chi(-\Omega^*) = \chi^*(\Omega)$$

- $\chi(\Omega)$  does not have poles in the upper half-plane of  $\Omega$ .
- $\chi(\Omega)$  is real on the imaginary axis and purely imaginary on all other points of the upper half-plane.
- $\chi(\Omega) \to 0$  monotonically for  $\Omega \to \infty$  on the positive imaginary axis.

Recalling that the transverse and longitudinal eigenfrequencies are given by the poles and zeros of  $\epsilon(\Omega)$ , respectively, we can write down a factorized form that fulfills the above conditions [344,345]

$$\epsilon(\Omega) = \epsilon_{\infty} \prod_{j=1}^{n} \frac{\Omega_{L,j}^2 - \Omega^2 - i\gamma_{L,j}\Omega}{\Omega_{T,j}^2 - \Omega^2 - i\gamma_{T,j}\Omega} , \qquad (3.24)$$

where  $\Omega_{T,j}$  and  $\Omega_{L,j}$  denote the resonances in the system's response to external transverse or longitudinal perturbations, respectively, and the damping is allowed to be different at  $\Omega_{T,j}$  and  $\Omega_{L,j}$ . Care has to be taken if poles are present on the imaginary axis; for details see Ref. [344]. This has been called a generalized Lyddane-Sachs-Teller relation (see Eq. 3.12) [344].

Let us analyze the simple combination of one Drude plus one Lorentz term in the absence of damping in order to point out the important background behind the somewhat awkward definition of  $\Omega_{L,j}$  as a "resonance in the system's response". We start from

$$\epsilon(\omega) = 1 - \frac{\omega_{p,Dru}^2}{\omega^2} + \frac{\omega_{p,Lor}^2}{\omega_0^2 - \omega^2} \,. \tag{3.25}$$

The transverse and longitudinal modes for the individual terms are

$$\omega_{T,Dru} = 0 , \quad \omega_{L,Dru} = \omega_{p,Dru} \qquad \text{for} \quad \omega_{p,Lor} = 0 , \qquad (3.26)$$

$$\omega_{T,Lor} = \omega_0$$
,  $\omega_{L,Lor} = \sqrt{\omega_0^2 + \omega_{p,Lor}^2}$  for  $\omega_{p,Dru} = 0$ . (3.27)



Figure 3.2: Longitudinal plasmon-phonon coupling. Thick lines: the two longitudinal resonance frequencies  $\omega_{L1,L2}$  of the sum of one Drude and one Lorentz term as given in Eq. 3.29 as a function of the longitudinal frequency of the isolated Drude term, both in units of  $\omega_{L,Lor}$ . The thick solid (dashed) lines correspond to  $\omega_{T,Lor} = 0.8$  (0.97), as indicated by the respective thin lines. Straight dotted lines: longitudinal frequencies of the two individual terms.

In the case that both terms are non-zero the poles, i.e., the transverse resonance frequencies stay unaltered

$$\omega_{T1} = \omega_{T,Dru} = 0$$
,  $\omega_{T2} = \omega_{T,Lor} = \omega_0$ , (3.28)

but the zeros, *i.e.*, the longitudinal resonance frequencies of the system are mixed

$$\omega_{L1,L2} = \frac{1}{2} \left( \omega_{L,Lor}^2 + \omega_{L,Dru}^2 \right) \pm \frac{1}{2} \sqrt{ \left( \omega_{L,Lor}^2 - \omega_{L,Dru}^2 \right)^2 + 4\omega_{L,Dru}^2 \left( \omega_{L,Lor}^2 - \omega_{T,Lor}^2 \right)}$$
(3.29)

This equation describes the well known phenomenon of longitudinal plasmon-phonon coupling. For the influence of finite damping see Refs. [346,347]. We elaborate a bit on this point since understanding this coupling in the conventional Drude-Lorentz model will help in the discussion of the mixing of *transverse* modes in a layered structure in the next section. The two solutions of Eq. 3.29 are plotted as a function of  $\Omega_{L,Dru}$  in Fig. 3.2 in units of  $\Omega_{L,Lor}$  for  $\Omega_{T,Lor}/\Omega_{L,Lor} = 0.8$  (thick solid lines) and 0.97 (thick dashed lines). The influence of longitudinal plasmon-phonon coupling on optical spectra is depicted in Fig. 3.3. In the parameter range where the two individual longitudinal modes are close to each other a substantial phonon-plasmon mixing is obvious in both figures. This was our starting



Figure 3.3: The influence of longitudinal plasmon-phonon coupling on optical spectra. We plot  $R(\omega)$ ,  $\sigma_1(\omega)$  and  $\epsilon'(\omega)$  derived from Eq. 3.25 for parameter values as given in the figure, i.e., for a phonon and a Drude peak. The curves differ only in the value of  $\omega_{p,Dru}$ . The longitudinal coupling changes the reflectivity line shape drastically, eventually turning the phonon from a Reststrahlenband (a "peak") on low background to a dip in high background. The phonon appearing as a dip indicates that its longitudinal frequency is lower than the transverse one (see Fig. 3.2). A substantial longitudinal phonon-plasmon mixing occurs if the individual longitudinal frequencies of the two contributions are close to each other (dashed line in Fig. 3.2). The real part of the optical conductivity does not reflect longitudinal modes and is unimpressed by the mixing. It only shows the increasing oscillator strength of the Drude peak. In  $\epsilon'$  the mixing can be seen from the zero crossings. Note that the finite damping shifts the zeros away from the real axis in the complex  $\Omega$  plane.

point: we wanted to illustrate that the  $\Omega_{L,j}$  in the factorized model of Eq. 3.24 denote the resonance frequencies of the *total* system from which the properties of the individual constituents in general *cannot* easily be derived. The clear advantage of the factorized model is that the  $\Omega_{L,j}$  can in many cases be "read" by eye from the experimental data, contrary to the coupled oscillator strengths of the conventional Drude-Lorentz model.

Another remarkable point visualized in Fig. 3.2 concerns the order of longitudinal and transverse modes. For the sake of simplicity we still neglect damping. In a pole  $\epsilon'(\omega)$  changes sign, and therefore a zero crossing has to occur between two poles, *i.e.*, transverse and longitudinal modes will line up in alternate order on the frequency axis (see lower

panel of Fig. 3.3). For a single oscillator the transverse mode is always the lower of the two. However, if both modes of one oscillator, say A, are enclosed between the two modes of another oscillator B as is the case for large  $\omega_{L,Dru}$  at the right hand side of Fig. 3.2 or for the thick gray line in Fig. 3.3, then the order will be  $\omega_{T,B} < \omega_{L,A} < \omega_{T,A} < \omega_{L,B}$ , *i.e.*, for the enclosed oscillator A the longitudinal resonance frequency will be *lower* than the transverse one. In reflectivity the reversed order will produce a dip instead of a peak (see top panel of Fig. 3.3). This is a "built-in" feature of the Drude-Lorentz model, but in the factorized model we have to take care ourselves not to start from an unphysical set of parameters. This may sound very easy, but in the presence of damping and for a large number of partially overlapping modes a fit with the factorized model is in fact often not feasible. Therefore the factorized model can be a useful tool for the analysis of for example phonons, as will be discussed in the next chapter, but meets its limits if in the same frequency range both a metallic contribution and phonons have to be fitted simultaneously. As a remedy a sum of the factorized model and a generalized Drude term in the form of

$$\epsilon(\Omega) = \epsilon_{\infty} \prod_{j=1}^{n} \frac{\Omega_{L,j}^{2} - \Omega^{2} - i\gamma_{L,j}\Omega}{\Omega_{T,j}^{2} - \Omega^{2} - i\gamma_{T,j}\Omega} - \epsilon_{\infty} \frac{\Omega_{p}^{2} - i(\gamma_{p} - \gamma_{0})\Omega}{\Omega^{2} + i\gamma_{0}\Omega}$$
(3.30)

has been proposed [348]. The last term reduces to a conventional Drude term for  $\gamma_p = \gamma_0$ . However, one can obtain the longitudinal eigenfrequencies of the constituents from a Drude-Lorentz fit, and the longitudinal resonances of the total coupled system from a fit with the factorized model, but in the combined form none of the two applies and therefore none of the longitudinal parameters of Eq. 3.30 bears *any* physical significance.

Let us finally mention the big advantage of the factorized form in the study of for example phonons: the additional fourth parameter. The independent choice of the damping rates for the longitudinal and transverse modes,  $\gamma_L$  and  $\gamma_T$ , allows for the description of asymmetric line shapes. One could of course argue that an additional free parameter will always lead to a better fit, but the inherent assumption of the Drude-Lorentz model of a constant, frequency independent damping is often not justified. A frequency dependent scattering rate had been introduced in the extended Drude model. The disadvantage of the extended Drude model is that it can only be applied to a single mode, usually the Drude peak, whereas the factorized model is able to describe many modes. The price one has to pay is that the damping can only be chosen at two points,  $\omega_L$  and  $\omega_T$ , and in between an approximately quadratic frequency dependence is produced [348,349]. For  $\gamma_L/\gamma_T = 1$  the Drude-Lorentz model is recovered. The influence of  $\gamma_L/\gamma_T$  on the line shape is shown in Fig. 3.4. The two values  $\gamma_L$  and  $\gamma_T$  determine the slope of the reflectivity curve at the upper and lower edges, respectively. However, the factorized model does not guarantee a physical response, as stated above. In fact the curves for  $\gamma_L/\gamma_T = 4$  or 6 show an unphysical negative value of  $\sigma(\omega)$  on the low frequency side of the peak. It has been pointed out that the conditions  $\gamma_L \geq \gamma_T$  and  $\gamma_T/\gamma_L \geq (\omega_T/\omega_L)^2$  should be satisfied [350]. Lobo and collaborators claimed that the factorized model gives a good account of the non-Drude like in-plane optical conductivity in the cuprates [351]. This is equivalent to



Figure 3.4: An asymmetrical line shape of the optical conductivity arises in the factorized model of Eq. 3.24 for  $\gamma_L/\gamma_T \neq 1$ . The slope of the reflectivity curve at the upper and lower edges is determined by  $\gamma_L$  and  $\gamma_T$ , respectively. For  $\gamma_L/\gamma_T = 4$  and 6 the model produces an unphysical negative value of  $\sigma_1(\omega)$  on the low frequency side of the peak. A value of  $\epsilon_{\infty} = 3$ has been assumed in the figure.

saying that the factorized model is able to mimic the frequency dependence obtained in an extended Drude model analysis by fixing the scattering rate at only two points. Of course further information obtained from the memory function analysis such as the suppression of  $1/\tau(\omega)$  at low frequencies cannot be derived from a fit with the factorized model.

Asymmetrical phonon line shapes are very common in the cuprates, and we will present examples in both the insulating state and at optimal doping (for polarization along the caxis). In particular, in the discussion of the c-axis phonons another phenomenological route has been chosen in order to describe the asymmetric line shapes [32, 305, 307]. Deviations from the Lorentz model are described by multiplying with a complex phase factor [32, 305]

$$\epsilon(\omega) = 1 + \sum \frac{\omega_p^2 e^{i\pi\phi}}{\omega_0^2 - \omega^2 - i\gamma\omega} .$$
(3.31)

This model violates causality since it does not respect reflection symmetry of  $\Re \sigma(\omega)$  about zero frequency. This demonstrates a lack of time reversal symmetry. Moreover, it violates the sum rule for integration from zero to  $\infty$  because  $\sigma_1(\omega)$  is falling off too slowly. In practice it nevertheless can be very useful as long as the values of  $\phi$  are not too large. It bears two advantages: (i) it offers a smooth transition from a symmetric line shape for  $\phi = 0$  to asymmetry for finite values of  $\phi$ , and (ii) one can easily compare the oscillator strength of symmetric and slightly asymmetric modes. The microscopically motivated Fano model [352]

$$\Re\sigma(\omega) = \sigma_0 \frac{(x+q)^2}{1+x^2}, \qquad x = \frac{\omega - \omega_0}{\gamma}$$
(3.32)

approaches the Lorentzian line shape only in the limit  $|q| \to \infty$ , where 1/q is a measure of the asymmetry, and the constant  $\sigma_0$  denotes the magnitude. The Fano formula also violates reflection symmetry of  $\Re \sigma(\omega)$  about zero frequency. If one wants to make use of the model for fitting experimental data one has to remember that it is an approximation valid only close to resonance. Both expressions given in Eqs. 3.31 and 3.32 may be used to account for a locally (in frequency) asymmetric line shape, but care has to be taken if one, for example, subtracts the phonon contribution, fitted with the above formulas, from the measured optical conductivity in order to apply a sum rule to the electronic contribution only. An expression which is capable of describing asymmetric profiles but at the same time respects  $\sigma^*(\omega) = \sigma(-\omega)$  has been given by Damascelli and van der Marel [353]

$$\sigma(\omega) = \mathrm{i}\sigma_0 \left[ \frac{(q-\mathrm{i})^2}{\mathrm{i}+x} + \frac{\gamma q^2 \omega}{\omega_0^2} \right] , \qquad x = \frac{\omega^2 - \omega_0^2}{\gamma \omega} , \qquad (3.33)$$

where  $\sigma_0$  denotes the background and  $q(\omega) = \omega_q/\omega$  labels the dimensionless asymmetry parameter. A symmetric Lorentzian line shape is recovered for  $|q| \to \infty$ .

## 3.2.2 Dielectric Function of a Layered Structure

Thus far we have assumed a homogeneous medium. The "local" field  $E_{loc}$  was homogeneous as well and only determined by the applied field E and the macroscopic polarization P of the sample. Now we want to go one step further and discuss a toy model of an alternating stack of layers in the form  $ABAB \cdots$ . We will still treat the individual layers and the fields therein as homogeneous, but allow for different local dielectric functions  $\epsilon_A^{loc}(\omega)$  and  $\epsilon_B^{loc}(\omega)$ . We are only interested in the electromagnetic response along the stacking direction. The displacement field D stays unaltered by the neutral medium, and hence  $D \equiv D_A^{loc} \equiv D_B^{loc}$ . Locally, we have

$$D_{j}^{loc} = \epsilon_{j}^{loc} E_{j}^{loc} = E_{j}^{loc} + 4\pi P_{j}^{loc} , \qquad j \in \{A, B\}$$
(3.34)

where the index j denotes the local fields in sublayers A and B. For the whole stack the equation  $D = \epsilon E$  still holds, where E is the average field determined by

$$E = \sum_{j} x_j E_j^{loc} = \sum_{j} \frac{x_j}{\epsilon_j^{loc}} D , \quad j \in \{A, B\}$$
(3.35)

and  $x_j = d_j/d$  denotes the relative volume fraction, where  $d_j$  is the thickness of sublayer jand  $d_A + d_B = d$ . Up to now, the various contributions to the response have been additive in  $\epsilon$ , for example in the Drude-Lorentz model of Eq. 3.8, and behaved like parallel "conduction channels". Here, one has to add up the contributions to  $1/\epsilon$ 

$$\frac{1}{\epsilon} = \sum_{j} \frac{x_j}{\epsilon_j^{loc}} \, . \qquad j \in \{A, B\} \tag{3.36}$$

This expression was derived by van der Marel and Tsvetkov in the context of a stack of Josephson coupled layers [43]. Equation 3.36 has some important consequences, and therefore we want to strengthen the intuitive understanding by rephrasing the above argument in terms of the complex impedance  $\rho(\omega)$  defined as

$$\rho(\omega) = \frac{4\pi i}{\omega} \frac{1}{\epsilon(\omega)} . \qquad (3.37)$$

We can envisage the electromagnetic response of any medium, say sublayer A, in terms of equivalent electrical circuits. Resistors describe loss, a capacitance plus an inductance an oscillator at finite frequencies and the contribution of quasi-free carriers can be modelled by an inductance. In a homogeneous medium the various conduction channels work parallel to each other and we have to add up the inverse impedances

$$1/\rho = \sum_{i} 1/\rho_i ,$$
 (3.38)

where i labels the various parallel contributions. This corresponds to the Drude-Lorentz model of Eq. 3.8. However, gluing two materials together is equivalent to putting the impedances in *series*, which is precisely what we have done in Eq. 3.36.

In the past much work has focused on the effective medium theory, studying for example the properties of one or more materials randomly embedded in a host,<sup>†</sup> where the grain size is supposed to be much smaller than the wavelength of light. It is interesting to note that rigorous bounds for  $\epsilon(\omega)$  have been given within effective medium theory as [354–356]

$$\left(\sum_{j} \frac{x_j}{\epsilon_j}\right)^{-1} \le \epsilon \le \sum_{j} x_j \epsilon_j , \qquad (3.39)$$

where  $x_j$  denotes the volume fraction of phase j analogous to our treatment. Applied to two phases A and B this expression states that putting A and B in series or in parallel are the two limiting cases for the effective media that one can construct [356].

In order to understand the consequences of adding  $1/\epsilon_j$  it is helpful to reconsider the factorized form of  $\epsilon$  as given in Eq. 3.24. There, the parameters of the transverse modes

 $<sup>^\</sup>dagger {\rm Effective}$  medium theory is connected with the name of Bruggeman, who was a student at the University of Groningen.

determined the denominator, and the numerator was given by the longitudinal parameters. Obviously, the role of longitudinal and transverse modes in a layered structure is turned around in a certain sense. In the Drude-Lorentz model we described the mixing of longitudinal modes. Here we therefore have to expect mixed *transverse* modes, or in other terms, an *optical* branch. Let us simply consider a free carrier contribution in each of the two sublayers. Again we neglect damping for the sake of simplicity, but want to emphasize that weak damping, at least, does not change the physics qualitatively. On an intuitive level we can immediately understand that the new optical branch in the layered structure corresponds to the *out-of-phase* motion of the carriers in the two subsystems, *i.e.*, the superstructure has folded back a Brillouin zone boundary mode to  $\mathbf{k} = 0$ . Let us derive this mode explicitly. For  $\epsilon_j = 1 - \omega_{p,j}^2/\omega^2$  we find

$$\epsilon = \left(\frac{x_A}{\epsilon_A} + \frac{x_B}{\epsilon_B}\right)^{-1} = \frac{(\omega^2 - \omega_{p,A}^2) \cdot (\omega^2 - \omega_{p,B}^2)}{\omega^2 \cdot (\omega^2 - x_A \omega_{p,B}^2 - x_B \omega_{p,A}^2)}, \qquad (3.40)$$

with the following eigenmode frequencies (in ascending order for  $\omega_{p,A} < \omega_{p,B}$ )

$$\omega_{T1} = 0$$
,  $\omega_{L1} = \omega_{p,A}$ ,  $\omega_{T2} = \sqrt{x_A \omega_{p,B}^2 + x_B \omega_{p,A}^2}$ ,  $\omega_{L2} = \omega_{p,B}$ .  
(3.41)

The layered stack sustains the two different longitudinal plasmons of the individual layers and produces a transverse optical plasmon in between. We display the corresponding optical spectra in Fig. 3.5, where  $x_A = 0.72$  and  $x_B = 0.28$  appropriate for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> has been used. In general, the peak in  $\sigma(\omega)$  corresponds to the transverse mode and the peaks in  $\Re\rho(\omega)$  indicate the two longitudinal modes. Plotting  $\Re\rho(\omega)$  is therefore equivalent to displaying the loss-function  $\Im(-1/\epsilon)$ . For zero damping and in the absence of background conductivity, both  $\sigma(\omega)$  and  $\rho(\omega)$  only produce  $\delta$ -functions at finite frequencies, but nevertheless the optical plasmon is clearly visible in reflectivity. It appears as a sharp Reststrahlenband (thick line), *i.e.*, light cannot propagate in the sample for frequencies in the interval  $\omega_{T2} \leq \omega \leq \omega_{L2}$ . The same of course holds for the low frequency plasmon, and reflectivity equals unity for  $\omega_{T1} \leq \omega \leq \omega_{L1}$ . It is important to note that adding some damping to the original sublayer plasmon is only one of the possible ways to give a finite width to the lines in  $\sigma(\omega)$  or  $\rho(\omega)$ . Even the undamped plasmon acquires some width in the presence of a finite background conductivity (as shown in the figure), which may be due to for example phonons or quasiparticles. Note that in Fig. 3.5 the zero background spectra are plotted as thick black lines, and that all visible spectra in both  $\sigma(\omega)$  and  $\rho(\omega)$ correspond to a finite background.

The first account of an out-of-phase collective excitation of the relative phase was given by Leggett [357] in 1966 for a two-band superconductor. A comprehensive calculation of the **k**-dependent collective charge density fluctuation excitation spectrum of a superconducting bilayer was performed by Hwang and Das Sarma [358]. There, the inter-bilayer coupling was neglected, which shifts the lower longitudinal resonance in the *c*-axis spectrum to zero frequency. Other treatments of plasmons in superlattices can be found in Refs. [359–363].



Figure 3.5: Optical spectra of an alternating stack of sublayers A and B for polarization along the stacking direction derived from Eq. 3.40 for parameters as given in the figure. The transverse optical plasmon appears as a peak in  $\sigma(\omega)$ , and the two longitudinal modes are most easily recognized in  $\rho(\omega)$ . Note that the resonance frequencies are renormalized by a factor  $\sqrt{\epsilon_{\infty}}$ . The thick black line corresponds to zero background, whereas all other curves have been derived by adding a constant conductivity term, as indicated in the second panel from the top. A finite background results in a finite width of the plasmon peaks in both  $\sigma(\omega)$  and  $\rho(\omega)$ . Even for zero background the optical plasmon gives rise to a clearly observable Reststrahlenband, as light cannot propagate within the sample for  $\omega_{T1} \leq \omega \leq \omega_{L1}$ and  $\omega_{T2} \leq \omega \leq \omega_{L2}$ .

In chapter 8 we will argue that our toy model is able to describe the *c*-axis reflectivity spectra of the bilayer YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub>, where the sublayers *A* and *B* correspond to the intraand inter-bilayer subcells. We will identify a so far not understood feature — which is present also in other bilayer cuprates — with the optical plasmon. The implications of the applicability of this model on the microscopic bilayer scale for the physics of the cuprates will be discussed in chapter 8. In the following we only want to set the stage. In order to apply the model to real data we first have to incorporate the "background", *i.e.*, phonons, quasiparticles and high frequency excitations. In principle one has to calculate the response of mode *i* by taking into account the local charge displacement fields of all other modes. We are mainly interested in the optical plasmon itself and will therefore stick to our simple toy model, on the level of which there are several distinct possibilities. We could assume completely independent materials for sublayers *A* and *B*, in which case both  $\epsilon_A$  and  $\epsilon_B$ would have to be described with independent Drude-Lorentz models

$$\epsilon_j(\omega) = \epsilon_{\infty,j} - \frac{\omega_{s,j}^2}{\omega^2} - \frac{\omega_{n,j}^2}{\omega^2 + i\gamma_{n,j}\omega} + \sum_i \frac{\omega_{p,i,j}^2}{\omega_{0,i,j}^2 - \omega^2 - i\gamma_{i,j}\omega} , \quad j \in \{A, B\} ,$$
(3.42)

where j labels the sublayer, i is the mode index,  $\omega_{s,j}$  and  $\omega_{n,j}$  denote the undamped superconducting and damped normal plasma frequencies, respectively, and the sum runs over all phonons and mid-infrared excitations, whereas the high energy contributions are summarized in  $\epsilon_{\infty,j}$ . The assumption of completely independent phonons certainly does not apply to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub>. In a fit, this could be accomplished by choosing similar phonon parameters for the sublayers, but we prefer a model with less parameters. The other extreme would be to treat only the low energy electronic contributions  $\epsilon_{e,j}$  as inhomogeneous and neglect the layered structure for the vibrational response

$$\epsilon = \left(\frac{x_A}{\epsilon_{e,A}} + \frac{x_B}{\epsilon_{e,B}}\right)^{-1} + \epsilon_{\infty} + \sum_i \frac{\omega_{p,i}^2}{\omega_{0,i}^2 - \omega^2 - i\gamma_i\omega} .$$
(3.43)

We can bring this expression closer to reality by letting the still homogeneous phonons "feel" the inhomogeneous local fields

$$\frac{1}{\epsilon} = \frac{x_A}{\epsilon_{e,A} + \epsilon_{hom}} + \frac{x_B}{\epsilon_{e,B} + \epsilon_{hom}}, \quad \epsilon_{hom} = \epsilon_{\infty} + \sum_i \frac{\omega_{p,i}^2}{\omega_{0,i}^2 - \omega^2 - i\gamma_i\omega}.$$
(3.44)

Note that the model recovers the conventional Drude-Lorentz form if we either choose  $\epsilon_{e,A} = \epsilon_{e,B}$  or  $x_A = 1 - x_B = 0$ . This form of the model already captures the experimentally observed phonon asymmetries in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> to a certain extent, although the input consists of perfectly symmetric features. This is due to the creation of *additional* mixed modes, as will be discussed below, which appear as broad sidebands to the main peak. Although these additional modes might not correspond to true eigenmodes in the particular case of the cuprates, they provide a conceptually straightforward and convenient way to describe the experimentally observed asymmetries.

In some cases, such as for the apical oxygen or chain oxygen phonon modes in which the charge displacements are almost entirely restricted to the inter-bilayer subcell, it may even make sense to use a local phonon picture

$$\frac{1}{\epsilon} = \frac{x_A}{\epsilon_{e,A} + \epsilon_{phon,A} + \epsilon_{hom}} + \frac{x_B}{\epsilon_{e,B} + \epsilon_{phon,B} + \epsilon_{hom}}, \qquad (3.45)$$

where only a few selected modes are transferred with respect to Eq. 3.44 from  $\epsilon_{hom}$  to either  $\epsilon_{phon,A}$  or  $\epsilon_{phon,B}$ . This expression allows for a full description of the experimental data including all asymmetries. A more realistic microscopic interpretation of observed asymmetries, frequency shifts and spectral weight anomalies has recently been obtained by Munzar and collaborators [364] by a detailed analysis of the microscopic local fields. The latter analysis is in particular helpful in the case of the bond bending vibration along c of the planar oxygen ions, which sit right on the border of our subcells.

In order to gain some intuitive understanding of the unusual properties of the model we want to discuss optical spectra of two particular cases. Starting from the situation displayed in Fig. 3.5 for zero background, we first add one phonon homogeneously (Eq. 3.44) and then discuss what happens if the same phonon exists only locally in sublayer *B* (Eq. 3.45 for  $\epsilon_A = \epsilon_{hom} = 0$ ). The homogeneous phonon case is displayed in Fig. 3.6. The thick lines show the spectra if the plasmon is homogeneous as well,  $\omega_{p,A} = \omega_{p,B} = 300 \text{ cm}^{-1}$ , *i.e.*, the conventional Drude-Lorentz model. All other lines are obtained by tuning  $\omega_{p,B}$ from 300 to 3000 cm<sup>-1</sup>. The phonon and the lower plasmon stay rather unaffected by the changes of  $\omega_{p,B}$ , but surprisingly *two* new peaks appear in both  $\sigma(\omega)$  and  $\rho(\omega)$ . They all correspond to plasmon-phonon mixtures: the conventional sum within the sublayer mixes the longitudinal modes, and the inverse sum of sublayers then mixes the transverse ones. It seems paradoxical that we start with one homogeneous phonon and two local plasmons and end up with *four* modes, but the puzzle is solved if we realize that the phonon experiences different local fields in the two sublayers. The major part of the spectral weight shifts from the low frequency mixed mode to the high frequency one as  $\omega_{n,B}$  sweeps across the phonon.

It seems that we have created too many modes, particularly if we want to apply this model to the cuprates. We obtained *two* new poles by adding one phonon mode, whereas in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> every phonon mode of course corresponds to a single pole. However, for the description of our YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> data a background conductivity of about 100  $\Omega^{-1}$  cm<sup>-1</sup> has to be taken into account, which smears out the mixed modes considerably. The additional poles give rise to broad sidebands of the main peak and thereby mimic the experimentally observed asymmetry. Our toy model is definitely too crude to derive truly meaningful parameters for the phonons, but in fact it captures the correct mechanism responsible for the asymmetries, namely the inhomogeneity of the local fields. The model does not aim at an adequate description of the phonons, but is intended to show the existence of a second transverse plasma mode at finite frequencies. In contrast to the phonon case, the additional pole in the electronic response reflects a true new eigenmode of the physical system.

Intriguing spectra are being created if we only put the phonon locally, say in sublayer B (see Fig. 3.7). We use identical parameters as in the previous case of a homogeneous phonon. Again we start with homogeneous plasmon parameters,  $\omega_{p,A} = \omega_{p,B} = 300 \text{ cm}^{-1}$ .



Figure 3.6: Optical spectra for one undamped plasmon in each sublayer and a homogeneous phonon (Eq. 3.44). The thick solid lines correspond to  $\omega_{p,A} = \omega_{p,B} = 300 \text{ cm}^{-1}$ , in which case the Drude-Lorentz model is recovered. The mixed plasmon-phonon modes appearing for  $\omega_{p,A} \neq \omega_{p,B}$  are discussed in the text. Starting from the thick solid lines, the different line types correspond to  $\omega_{p,B} = 300$ , 500, 700, 900, 1100, 1300, 1500, 2000 and 3000 cm<sup>-1</sup>, respectively. The curves displaying  $\sigma_1(\omega)$  and  $\rho'(\omega)$  have been offset with respect to each other for clarity.



Figure 3.7: Same as Fig. 3.6 but with a local phonon in sublayer B instead of a homogeneous one. Note that in this case an optical plasmon is created even in the homogeneous case of  $\omega_{p,A} = \omega_{p,B} = 300 \text{ cm}^{-1}$  due to local differences in screening (thick lines). The mixed modes are similar to Fig. 3.6, but the pure phonon is not an eigenmode of the total system.
Since  $x_B$  amounts only to 0.28, the phonon oscillator strength is drastically reduced. The longitudinal eigenfrequency is however identical with the homogeneous phonon case, and the reduced oscillator strength shifts the *transverse* eigenfrequency up, although we kept  $\omega_0 = 500 \text{ cm}^{-1}$  fixed. At the same time, an optical plasmon is created at low frequencies, although we started from homogeneous plasmons! This is explained by the same argument as for the fourth peak in the homogeneous phonon case: here, the absence of the phonon in sublayer A reduces the local screening of the plasmon, the resonance in sublayer A shifts to higher frequencies, resulting in an optical plasmon. Note that in this case the transverse mode produced at about 140  $\rm cm^{-1}$  is very close to the longitudinal one. This close coincidence has indeed been observed by different groups [40,310,365,366] in c-axis spectra of single layer  $La_{2-x}Sr_xCuO_4$  (see section 8.2). For this case van der Marel and Tsvetkov [43] proposed treating the single layer with Sr impurities as an effective multilayer, where the local dielectric function is modulated by the Sr concentration. Assuming a Gaussian distribution for the effective interlayer coupling they obtained good fits of the experimental data [43]. Our treatment shares the same spirit and adds the possibility of explaining the modulation of the effective dielectric constant by local differences of the phonon spectrum, again due to the Sr impurities. The experimental observation of coinciding peaks in  $\sigma(\omega)$  and  $\rho(\omega)$  at several doping concentrations (see section 8.2) corroborates the physical significance of the additional poles which the toy model creates.

Increasing  $\omega_{p,B}$  in the present local phonon case yields a similar mixed mode spectrum as with a homogeneous phonon, but the pure phonon is no longer an eigenmode of the total system and with increasing  $\omega_{p,B}$  its spectral weight is "carried away" with the plasmonphonon mixed mode. Finally, we want to mention again that we only took a small damping of the phonon into account. A finite background or a damping of the electronic contributions will not change the physics qualitatively, at least not for small damping. However, the features discussed will become blurred and more difficult to observe experimentally.

### **3.3** Fourier Spectroscopy

Optical spectroscopy is conceptually straightforward: shine light on a sample and measure what is going through or what is coming back. In order to determine the absolute value one needs a reference, which is trivial in the case of transmission (the aperture the sample was attached to) and a bit more tricky for reflectance. In the frequency range of interest to us, the far- and mid-infrared, Au has a reflectivity very close to unity and is used as a standard. If the sample face to be measured is very small or irregular the absolute value is determined elegantly by evaporating Au *in situ* onto the sample. The real problem of infrared spectroscopy, particularly at low frequencies, is intensity. The emission of for example a black body source decreases rapidly towards low frequencies. Synchrotrons and far-infrared lasers are available these days, but Fourier spectroscopy offers the possibility of a home based solution. The technique is very well established, instruments are available commercially and a less fancy but more robust version is even in use at the conveyor belt level for the industrial recovery of the plastic left overs of society.<sup>‡</sup> Very detailed descriptions of Fourier spectroscopy have been published [367, 368], which allows us to be very brief.

Fourier spectroscopy is an interferometric technique. The initial white light beam is split into two parts which are rejoined after adding a linearly time dependent path difference via a scanning mirror. The measured quantity is the time dependent intensity which corresponds to the autocorrelation function of the electric field. Each individual frequency contributes a separate Fourier component to this intensity, and the frequency dependent spectrum can be recovered by a Fourier transform. This offers two main advantages in comparison with a dispersive measurement which makes use of a prism or grating monochromator. Since the whole spectrum is collected at once we can perform N independent measurements in the same time that a dispersive technique needs to build up the whole spectrum only once from N frequency intervals. This Fellgett or multiplex advantage thus improves the signal to noise ratio by a factor  $\sqrt{N}$ . At the same time, a dispersive technique has to utilize narrow slit apertures in order to reach a given frequency resolution, whereas large circular apertures can be used in an interferometer. This is the Jacquinot or throughput advantage. The frequency resolution of an interferometer is determined by the maximum path difference, since the length of the time interval (for a given scanner velocity) of the measured intensity available for the Fourier transform determines the width a  $\delta$ -function peak acquires by the Fourier transform. In principle the circular apertures also limit the resolution due to the path difference of central and outer rays, but for the frequency range and resolution interesting to us this is not a limitation yet. The high frequency resolution, the high frequency accuracy and the possibility of dealing with the low intensities in the far-infrared directly follow from the two advantages mentioned. Technically, a Fourier spectrometer needs a computer for the Fourier transform and a He-Ne laser in order to monitor the scanning mirror and thereby the path difference accurately. Both requirements have impeded a wide spread acceptance of the technique for many years, but nowadays a Fourier spectrometer is a standard apparatus in a physics and certainly in a chemistry laboratory.

<sup>&</sup>lt;sup>‡</sup>For the separation of the different plastics the characteristic mid-infrared absorption lines are used as fingerprints.

## Chapter 4

# Phonon-Polaritons in Oxygen Isotope Substituted $YBa_2Cu_3O_{6+u}$

The first decade of cuprate high  $T_c$  superconductivity has witnessed a strong interest in the lattice properties. This interest was partly driven by the role phonons play in conventional superconductors and the hope to find indications for strong electron-phonon coupling in order to explain the high values of  $T_c$ . The complexity of the new materials challenged experimental and theoretical tools to describe them. A large number of neutron scattering [369], Raman [370-372] and infrared [25,46,372] studies were performed. Meanwhile, the phonon dispersion of several compounds has been mapped throughout the entire Brillouin zone by neutron scattering experiments [369], and a satisfactory theoretical description of the dispersion has been reached [373]. Raman and infrared data allow a more precise determination of the resonance frequencies at the Brillouin zone center and reveal the line shapes, which are too narrow to be resolved by neutrons. Moreover, many more compounds and also the detailed temperature dependence have been studied with the technically less demanding optical techniques. Due to symmetry reasons, Raman and infrared spectroscopy offer complementary information on the phonons in the cuprates. In the early days, most infrared studies were carried out on powder or ceramic samples [372, 374–378], and many phonon modes of  $YBa_2Cu_3O_{6+y}$  were identified by substitution of Y with rare earth elements [374, 376–379] or by oxygen isotope substitution [378, 380, 381]. Infrared studies of oxygen isotope substituted polycrystalline material were reported for the insulating phase in Refs. [378,381] and for highly oxygenated samples in Refs. [378,380]. The latter revealed the isotope shifts of the *c*-axis modes, and the isotope shifts of the *ab*-plane phonons have been studied on Al contaminated highly doped single crystals by Bazhenov [382]. Single crystal reflectivity data of insulating YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> were published for both  $E \parallel ab$  and  $E \parallel c \mid 383-386 \mid$ , but only for room temperature. Bauer showed low temperature measurements for both polarization directions in his Ph.D. thesis [387], but only spectra of samples containing also impurity phases were published [388]. For high doping concentrations, the analysis of infrared data with  $E \parallel ab$  has focused on the dominant electronic contribution, and only little information has been extracted about phonons and electron-phonon coupling [46, 382, 389, 390]. Humlíček and co-workers have studied the infrared phonon spectrum of the highly oxygenated phase in non-superconducting  $PrBa_2Cu_3O_7$  [391] (see also Ref. [392]). Electron-phonon coupling effects have been studied more extensively for the *c*-axis polarization [46]. The *c*-axis phonons have been reported by many authors. A detailed analysis of the doping and temperature dependence of the *c*-axis phonons has been performed by Schützmann and collaborators [305] for oxygen concentrations in the range 6.1 < 6.9, and by Homes and co-workers [32] for 6.5 < 6.95.

In this chapter we analyze in detail the low temperature far-infrared spectra of high quality single crystals of antiferromagnetic  $YBa_2Cu_3O_6$  for polarizations parallel and perpendicular to the  $CuO_2$  layers. We studied samples with oxygen isotopes <sup>16</sup>O and <sup>18</sup>O, samples of different purity (grown in different crucibles), and a sample in which  $\approx 3\%$  of the Cu ions were substituted with Zn. We observed *all* eleven infrared active phonon modes. Our analysis focusses on the six modes of  $E_u$  symmetry  $(E \parallel ab)$ . The mode assignment and the temperature dependence will be discussed. The strong dependence of the in-plane Cu-O bond stretching mode on the lattice parameter, which is controlled by temperature. is compared to results obtained on other cuprates [384]. The vibration of this stretching mode modulates electronic parameters such as the hopping t, the charge transfer energy  $\Delta$  or the exchange constant J [224, 393–395]. The asymmetric high frequency tails of the planar oxygen modes and in particular of the stretching mode are tentatively attributed to a coupling to magnetic degrees of freedom. Interference fringes are used to determine the phonon-polariton dispersion, and the results agree with a Kramers-Kronig analysis of the data. The phonon spectra of superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> will be discussed briefly for both  $E \parallel ab$  and  $E \parallel c$ .

## 4.1 Phonons in $YBa_2Cu_3O_6$ and $YBa_2Cu_3O_7$

#### Sample Preparation

Single crystals of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> were grown in the recently developed BaZrO<sub>3</sub> crucibles (BZO) [117,118], which in contrast to other container materials do not pollute the resulting crystals. These samples therefore exhibit a superior purity (> 99.995 at. %; see Table 2.3 on page 24) [118]. For the highly doped samples, the oxygen concentration was fixed by annealing according to the calibration of Lindemer [396]. An oxygen content of x = 7 was obtained by annealing for 400 h at 300° C in 100 bar of high purity oxygen. Annealing in flowing oxygen at 517° C for 260 h produced x = 6.93. Measurements of the ac-susceptibility indicate  $T_c = 91$  K for x = 6.93 and 87 K for x = 7. The width of the transitions were 0.2 K and 1 K, respectively. In order to exchange the oxygen isotope, the crystals were annealed at 600°C in a sealed quartz ampoule containing a 99.5 % isotope pure <sup>18</sup>O atmosphere. The obtained weight gain corresponded to a complete exchange of the oxygen isotope. The oxygen content was fixed to a value very close to O6 by annealing the crystals in a flow of high purity Argon (99.998 %) at 750°C for about a week. Residual oxygen in the annealing atmosphere was eliminated using an oxygen absorption system. For comparison,

single crystals grown in Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub> crucibles (YSZ) [397] have been studied as well. In these samples, an oxygen content of O6 has been obtained by annealing them in ultra high vacuum at 700°C for several days. In the case of YBa<sub>2</sub>Cu<sub>3-y</sub>Zn<sub>y</sub>O<sub>6</sub> [398], the melt nominally contained 5% of Zn. After oxygenation a T<sub>c</sub> of 67 K was measured, and hence we obtain  $0.05 \le y \le 0.07$  [399]. Assuming that Zn prefers the planar Cu(2) sites this corresponds to a substitution of  $\approx 3\%$ . The reduction to insulating YBa<sub>2</sub>Cu<sub>3-y</sub>Zn<sub>y</sub>O<sub>6</sub> was performed as described above. The samples had typical dimensions of  $1 \times 1 \text{ mm}^2$  in the *ab*-plane.

#### 4.1.1 Phonon Assignment in $YBa_2Cu_3O_6$ (E || ab)

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> belongs to the symmetry group  $D_{2h}$  and is expected to show 11 infrared active phonons (5  $A_{2u}$  modes for  $E \parallel c$  and 6  $E_u$  modes for  $E \parallel ab$ ), 10 Raman active phonons  $(4A_{1g} + 1B_{1g} + 5E_g)$  and a silent mode  $(B_{2u})$ . Due to symmetry, the Y and the Cu(1) ions<sup>\*</sup> do not contribute to the Raman modes. In contrast, every ion can in principle contribute to all infrared active modes. Previous studies observed only five  $E_u$  modes, the sixth thus far escaped detection due to a very small oscillator strength.

The reflectivity spectra for  $E \parallel ab$  at T = 4 K of two single crystals of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> grown in a BaZrO<sub>3</sub> crucible are plotted in Fig. 4.1. The solid line corresponds to data of YBa<sub>2</sub>Cu<sub>3</sub><sup>16</sup>O<sub>6</sub>, the dotted line depicts data of YBa<sub>2</sub>Cu<sub>3</sub><sup>18</sup>O<sub>6</sub> (from now on: <sup>16</sup>O and <sup>18</sup>O). The <sup>16</sup>O data agree well with previous results [387, 388]. Data on single crystals of YBa<sub>2</sub>Cu<sub>3</sub><sup>18</sup>O<sub>6</sub> have not been reported in the literature thus far. Our results for the isotope shifts are similar to those obtained on polycrystalline material by Crawford and co-workers [378] and on embedded powders by Ye and collaborators [381]. However, their estimates of the resonance frequencies of the high frequency oxygen modes deviate from the single crystal results by up to 20 cm<sup>-1</sup>. The spectra of  $\sigma_1(\omega)$ ,  $\rho_1(\omega)$  and  $\epsilon'(\omega)$  plotted in the other panels of Fig. 4.1 were derived via a Kramers-Kronig analysis, for which measured data have been used up to 8000 cm<sup>-1</sup>. According to the definition given in chapter 3, a peak in the dynamical resistivity  $\rho_1(\omega)$  denotes a longitudinal eigenmode. The transverse resonance is given by a peak in the optical conductivity  $\sigma_1(\omega)$ . In Fig. 4.1 the background conductivity between the phonon resonances is very small and demonstrates that the samples are very close to the semiconducting limit.

In the following, we will first show all six modes in our spectra and then discuss the mode assignment. Five of the six  $E_u$  phonon modes are clearly resolved in Fig. 4.1. In the reflectance spectrum, the low absorption below 100 cm<sup>-1</sup> and between the lower phonon peaks gives rise to interferences caused by multiple internal reflections within the thin samples. This point is emphasized in Fig. 4.2, which focusses on the low frequency range. The lower panel of Fig. 4.2 depicts reflectivity spectra of the <sup>16</sup>O sample grown in BZO shown before, of a sample grown in YSZ and of a Zn-substituted sample ( $\approx 3\%$ ) [400]. From bottom to top the sample thickness decreases from 210 (BZO) via 100 (YSZ) to 35  $\mu$ m (Zn), and therefore both the amplitude of the interference fringes and their period increase.

<sup>\*</sup>The copper and oxygen sites will be labelled according to Fig. 2.1 on page 12.



Figure 4.1: In-plane reflectance spectra  $(E \parallel ab, \mathbf{k} \parallel c)$  of oxygen isotope substituted single crystals of  $YBa_2Cu_3O_6$  at T = 4 K. Solid lines: <sup>16</sup>O, dashed lines: <sup>18</sup>O. Following the discussion in chapter 3 spectra of the dynamical resistivity  $\rho_1(\omega)$  have been included. A peak in  $\rho_1(\omega)$  indicates a longitudinal mode.



Figure 4.2: Upper panel: Inplane far-infrared transmission spectrum of a  $YBa_2 Cu_3^{16}O_6$ single crystal at T = 4 K. Inset: Temperature dependence of the transmission (dashed line: 300 K). Lower panel: Reflectivity spectra at 4 K of a sample with a thickness of  $d=210 \ \mu m \ grown \ in \ a \ BaZrO_3$ crucible (BZO), of one grown in  $ZrO_2$  (YSZ) (d=100  $\mu m$ ) and of a sample containing about 3% of Zn  $(d=35 \ \mu m)$ |400|. Spectra have been translated vertically for clarity. With decreasing sample thickness both the amplitude and the period of the interference fringes increase. All spectra show signatures of the weak Ba phonon mode at 83  $cm^{-1}$ [401].

The top panel of Fig. 4.2 shows transmittance data of the sample grown in a YSZ crucible. In the transmission spectrum we can clearly identify the sixth phonon mode of symmetry  $E_u$  [401], which has a very small oscillator strength, with the absorption line disturbing the interference fringes at 83 cm<sup>-1</sup>. The same mode shows up in the reflectivity data of thin samples as a *suppression* of the interference spectrum. Therefore, this mode has to be identified with a dip (peak) in the reflectance if it is close to an interference maximum (minimum). Due to its very small oscillator strength, the sixth phonon mode does not leave any measurable signature in the bulk reflectivity of a thick sample. Previously, observation of the sixth mode has been claimed at 65 cm<sup>-1</sup> [385, 386] in a heavily Al-contaminated sample and at 210 cm<sup>-1</sup> [374] in a Sm-substituted ceramic sample. In ceramic samples, three further shoulders at 144 cm<sup>-1</sup> [378], 320 cm<sup>-1</sup> [381] and 625 cm<sup>-1</sup> [378] have been observed. Our data confirm a weak absorption feature at 140 cm<sup>-1</sup> (see the dip in the transmission spectrum in the upper panel of Fig. 4.2) and absorption at 625 cm<sup>-1</sup>, which will be discussed below.

Our results for the frequencies of all six modes agree very well with dispersion curves extracted from neutron scattering data [403] of symmetry  $\Delta_3$ , which depicts the transverse modes of symmetry  $E_u$  ( $\Delta_1$  gives the longitudinal modes). The modes are assigned as

follows. From a crystallographers point of view, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> has only two distinct oxygen sites, namely the planar O(2,3) sites and the apical O(4) site. However, light polarized along, say, the *a*-axis, distinguishes between "O(2)" and "O(3)" (see Fig. 2.1 on page 12), although crystallographically identical. The planar sites give rise to both a bond stretching mode ("O(2)") and a bond bending mode ("O(3)"). Since oxygen is the lightest element in the unit cell, the highest three  $E_u$  phonons are expected to show large oxygen contributions. This agrees with the oxygen isotope substitution results. Fits to the Drude-Lorentz model (see Table 4.2 below) on <sup>16</sup>O and <sup>18</sup>O show that the three high frequency modes all shift by about 5 to 5.3% (see Fig. 4.1), *i.e.*, the amount of oxygen contributing to the normal modes is about the same for all three modes. Among the oxygen  $E_u$  modes, the bond stretching vibration of the in-plane O(2,3) and Cu(2) ions shows the highest frequency (599 cm<sup>-1</sup> in  ${}^{16}$ O). The two peaks at 351 cm<sup>-1</sup> and 246 cm<sup>-1</sup> can be attributed to the bond bending modes of the O(2,3) ions and the apical oxygens O(4), respectively. In the past, there was some disagreement in the literature about which of the two bending modes is higher in frequency. In principle, measurements on samples with site selective isotope substitution [404] would be able to disentangle the two bending modes. This issue has, however, been settled by Tajima and collaborators [384], who compared infrared data of a series of insulating single and bi-layer cuprates. They observed a phonon mode at about 360  $cm^{-1}$  in all materials, *i.e.*, regardless of the presence of an apical oxygen ion, and attribute this peak to the bending mode of the in-plane oxygen. At the same time, the (weak) lower phonon peak which they assign to the apical mode in  $La_2CuO_4$  shifts drastically if the apical oxygen is replaced by Cl or Br, as in  $Sr_2CuO_2Cl_2$  and  $Sr_2CuO_2Br_2$  [384]. An analysis of neutron scattering data agrees with assigning the higher frequency to the planar bending mode. There, a longitudinal phonon branch at  $\approx 250 \text{ cm}^{-1}$  is attributed to the apical bending mode [373], whereas scattering around  $\approx 430 \text{ cm}^{-1}$  is identified with the so called O(2) scissor mode, *i.e.*, the bending mode in  $(\pi, \pi)$  direction [369].<sup>†</sup>

The two low frequency modes at  $188 \text{ cm}^{-1}$  and  $116 \text{ cm}^{-1}$  shift only by a small, but finite amount upon substitution of the oxygen isotope. This reflects that in principle all ions can contribute to every infrared active mode. The phonon peak at  $188 \text{ cm}^{-1}$  has been identified by substitution of rare earth elements as an Y mode [374, 376–379]. The eigenvectors calculated by Thomsen *et al.* show a small contribution of in-plane oxygen to this mode [376]. Experimentally, we obtain an oxygen isotope shift of about 1.1% from the fit parameters.

The phonon peak at 116 cm<sup>-1</sup> has been described as a Ba or Ba-Y-bending mode by most authors, arguing that the lowest frequency mode should be the Ba mode, as Ba is the heaviest ion in the system [376,378]. However, Thomsen and co-workers [376] pointed out that the shift of the Ba-Y-bending mode upon rare earth substitution should be larger than the experimentally observed shift of the 114 cm<sup>-1</sup> peak in their ceramic samples [376]. The detection of the weak sixth phonon mode at 83 cm<sup>-1</sup> brings us to the conclusion that the Ba mode has to be identified with the feature at 83 cm<sup>-1</sup>, whereas the phonon peak at 116 cm<sup>-1</sup> corresponds to a Cu(1) vibration. This assignment is supported by lattice

<sup>&</sup>lt;sup>†</sup>Usually the neutron data are plotted in units of THz, where 1 THz  $\approx 4.1 \text{ meV} \approx 33.4 \text{ cm}^{-1}$ .





Figure 4.3: Phonon dispersion as determined by neutron scattering [402]. The labels indicate the character at the zone boundary. Note that 1 THz  $\approx 33.4$  cm<sup>-1</sup>.

Figure 4.4: Simulation of the reflectivity around the Cu(1) mode. A sample thickness of  $d=31 \ \mu m$  has been assumed in order to match the interference pattern. Grey line: single mode at 114 cm<sup>-1</sup>, no peak splitting. Thick black line: a weak second mode at 119 cm<sup>-1</sup> produces the experimentally observed splitting. Parameters are given in more detail in Table 4.1. Curves have been translated vertically for clarity.

Table 4.1: Parameters used for the simulation of Fig. 4.4. Columns on the left correspond to the thick black line with a weak second mode at 119 cm<sup>-1</sup>, columns to the right produce the thick grey line. Oscillators at 83 and 137 cm<sup>-1</sup> are kept the same. The broad absorption feature at 137 cm<sup>-1</sup> is necessary to describe the experimentally observed suppression of the interference fringes just above the Cu(1) phonon mode.

$\omega_0$	$\mathbf{S}$	$\gamma$	$\omega_0$	$\mathbf{S}$	$\gamma$
$\mathrm{cm}^{-1}$		$\mathrm{cm}^{-1}$	$\mathrm{cm}^{-1}$		$\mathrm{cm}^{-1}$
114.2	4.62	2.5	114.2	5.16	3.1
119.4	0.25	2.5			
82.7	0.03	1.0	82.7	0.03	1.0
137.0	0.43	30	137	0.43	30

dynamical calculations [376, 388], which show a very small oscillator strength for the Ba mode. The normal mode calculations of Bates [405] predict the Ba mode as the lowest one at 88 cm<sup>-1</sup>. Experimentally, this assignment is supported by neutron scattering results (see Fig. 4.3 [402]). The zone center frequencies of Fig. 4.3 agree very well with our results. The assignment given in the figure refers to the Brillouin zone boundary. In the zone center, the order is the same and the character of a  $\mathbf{k} = 0$  excitation is equivalent to the one at the zone boundary with the same energy [406], *i.e.*, the  $\mathbf{k} = 0$  mode at 2.5 THz (83 cm<sup>-1</sup>) shows predominantly Ba character, and the one at 3.5 THz (116 cm<sup>-1</sup>) is the Cu(1) mode. Moreover, we observe a splitting of the Cu(1) mode at 114 cm<sup>-1</sup> in the Zn-substituted sample (see lower panel of Fig. 4.2) [400]. This can be explained by assuming that some of the Zn ions occupy Cu(1) chain sites. Note that this splitting cannot be attributed to interferences, which are fully suppressed at the resonance frequency. They dominate the spectrum only in the regions of low absorption. This is demonstrated by the simulations shown in Fig. 4.4. The corresponding parameters are given in Table 4.1.

In order to determine the amount of Ba and Cu in the two normal modes on a more quantitative basis, measurements on Ba and Cu isotope substituted samples would be necessary. Recently, such measurements have been reported [407,408] on ceramic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and show only a small mixing of Ba and Cu normal modes.

#### 4.1.2 Temperature Dependence

For a quantitative description of the phonon peaks we use the Drude-Lorentz model of the dielectric function (see Eq. 3.8 on page 87). The fit parameters for different temperatures are summarized in Table 4.2. In the table, the bold letter style denotes the six main modes, the other oscillators are sidebands of the oxygen modes which are necessary to describe the line shape correctly. This will be discussed more thoroughly in section 4.1.4 on page 122. In the following, we focus on the behavior of the resonance frequencies. The relative peak frequencies normalized with respect to the 4 K value are plotted in the left panels of Fig. 4.5 for the two different oxygen isotopes. In  $^{16}$ O, four of the modes behave very similar and show only a small shift with increasing temperature. The planar bending mode (open squares) is constant up to 200 K. The change in frequency of the  $599 \text{ cm}^{-1}$  stretching mode (full squares) is much larger. In <sup>18</sup>O, the redshift of all modes is smaller than in <sup>16</sup>O: three modes hardly show any softening at all; the planar O(2)bending mode at  $350 \text{ cm}^{-1}$  even hardens slightly with increasing temperature; and also the much stronger shift of the stretching mode (full squares) is reduced. The temperature dependence of  $R(\omega)$  and  $\sigma_1(\omega)$  of the planar bending and stretching modes are plotted on an expanded scale in Figs. 4.7 and 4.8. The spectra of  $\sigma_1(\omega)$  have been obtained from a Kramers-Kronig analysis. They agree with the fit parameters by showing a softening of the 350 cm<sup>-1</sup> bending mode in <sup>16</sup>O and a hardening of the same mode in <sup>18</sup>O (see Fig. 4.7). The apparent anomalies of the line shapes will be discussed below. At this point we only want to point out that although in reflectivity the anomalies at the high frequency sides of both modes look rather strong, they only produce small features in the tails in  $\sigma_1(\omega)$ . The anomalous line shapes nevertheless cause some uncertainty in the determination of

160											
			100 IZ			200 IZ			200 1/		
4 K	C		100 K	C		200 K	C		300 K	C	
$\omega_0$	<u>د</u>	$\frac{\gamma}{10}$	$\omega_0$	<u>د</u>	γ 1 F	$\omega_0$	د 0.01	$\frac{\gamma}{2}$	$\omega_0$	<u>ى</u>	$\frac{\gamma}{2}$
82.9	0.03	1.0	02.9	0.02	1.0 9 1	82.0 115 6	0.01	2.U 2 4	82.U	0.01 2 0	2.0 2.6
100 /	3.L 2.D	⊿.1 วา	100 5	2.9 1 0	3.1 2.0	1000	2.0 1 9	3.4 4 0	1079	4.0 1.7	3.0 ธา
246 1	2.0 1.5	2.2	245 0	1.9	2.9 2.0	2456	1.0	4.0	2446	1.1	J.4 65
240.1	1.J 0.6	⊿.U 15 1	240.9	1.4	<b>J.U</b> 17.9	240.0 252.7	<b>1.</b> 0 4	4 <b>.</b> 4 18.0	244.0 253-7	0.3	20.2
250.5	18	51	249.9 <b>351</b> 4	0.0 2 0	74	252.7 351 A	0.4 21	10.9 0 0	255.7 350 0	0.5 <b>9 1</b>	02.0 1∕11
357.6	1.0	53.6	379.7	<b>2.0</b>	553	380.3	<b>2.1</b> 0.3	<b>9.9</b> 49.6	382.7	<b>2.1</b>	1 <b>4.11</b> /0 0
599.3	0.5	68	598.0	0.5	7 1	593 7	0.5	49.0 <b>8 1</b>	587 1	0.2	14 5
624.5	0.00	6.5	624.2	0.003	54	603.2	0.04	19.4	604.3	0.02	47.6
621.8	0.000	32.5	616.5	0.000	38.1	615.5	0.01	37.4	614 4	0.02	38.6
	6.76	02.0	010.0	6.62	00.1	010.0	6.84	0111	011.1	6.49	00.0
- 00				0.0-			0.0 -			00	
<sup>18</sup> O											
<sup>18</sup> O 4 K			100 K			200 K			300 K		
$ \begin{array}{c} 18 \\ 4 \\ \omega_0 \end{array} $	S	γ	100  K $\omega_0$	S	γ	200  K $\omega_0$	S	γ	$300 \mathrm{K}$ $\omega_0$	S	γ
$ \begin{array}{r}     18 \\     4 \\     \hline     4 \\     \hline     6 \\     \hline     82.2 \end{array} $	S 0.03	$\frac{\gamma}{1.5}$	100  K $\omega_0$	S	<u>γ</u>	200  K $\omega_0$	S	<u>γ</u>	300  K $\omega_0$	S	γ
$     \begin{array}{r}             18 \\             4 \\             K \\           $	S 0.03 3.7	$rac{\gamma}{1.5}$	100 K $\omega_0$ 	S  3.7	γ  1.7	200 K ω <sub>0</sub> – 114.9	S  <b>3.6</b>	γ  <b>3.0</b>	$300 \text{ K}$ $\omega_0$ 114.8	S  3.2	γ  4.1
$     \begin{array}{r}         180 \\         4 K \\         \omega_0 \\         82.2 \\         114.9 \\         186.5 \\         \end{array} $	S 0.03 3.7 2.3	$rac{\gamma}{1.5} \\ 1.1 \\ 1.4$	100 K ω <sub>0</sub> 114.7 186.6	S  2.3	γ  1.7 1.7	200 K ω <sub>0</sub> 114.9 186.5	S  3.6 2.1	γ  3.0 3.7	300 K ω <sub>0</sub> 114.8 186.0	S  3.2 1.8	$\gamma$ 
$     \begin{array}{r}         180 \\         4 K \\         \omega_0 \\         82.2 \\         114.9 \\         186.5 \\         233.6 \\         \end{array} $	S 0.03 3.7 2.3 1.7	$\gamma \\ 1.5 \\ 1.1 \\ 1.4 \\ 1.1$	100 K ω <sub>0</sub> 	S — 3.7 2.3 1.8	$\gamma$ 	200 K $\omega_0$ 114.9 186.5 233.8	S 	$\gamma$ 3.0 3.7 3.9	$300 \text{ K} \\ \omega_0 \\ \\ 114.8 \\ 186.0 \\ 233.4 \\ \end{array}$	S — 3.2 1.8 1.6	$\gamma$ 4.1 5.8 6.8
$     \begin{array}{r}         180 \\         4 K \\         \omega_0 \\         82.2 \\         114.9 \\         186.5 \\         233.6 \\         228.5 \\         \end{array} $	S 0.03 3.7 2.3 1.7 0.5	$\gamma$ 1.5 1.1 1.4 1.1 32.2	100 K ω <sub>0</sub> <b>114.7</b> <b>186.6</b> <b>233.6</b> 228.6	S 3.7 2.3 1.8 0.7	γ <b>1.7</b> <b>1.7</b> <b>2.3</b> 72.6	200 K ω <sub>0</sub>  114.9 186.5 233.8 239.4	S 3.6 2.1 1.7 0.5	γ 3.0 3.7 3.9 46.4	300 K ω <sub>0</sub> <b>114.8</b> <b>186.0</b> <b>233.4</b> 249.2	S 3.2 1.8 1.6 0.2	$\gamma$ 4.1 5.8 6.8 39.6
$     \begin{array}{r}       18 \\       4 \\       K \\       \omega_0 \\       82.2 \\       114.9 \\       186.5 \\       233.6 \\       228.5 \\       334.4 \\     \end{array} $	S 0.03 3.7 2.3 1.7 0.5 2.2	γ <b>1.5</b> <b>1.1</b> <b>1.4</b> <b>1.1</b> 32.2 <b>4.8</b>	100 K ω <sub>0</sub> <b>114.7</b> <b>186.6</b> <b>233.6</b> 228.6 <b>334.5</b>	S 3.7 2.3 1.8 0.7 2.2	γ <b>1.7</b> <b>1.7</b> <b>2.3</b> 72.6 <b>6.2</b>	200 K ω <sub>0</sub> <b>114.9</b> <b>186.5</b> <b>233.8</b> 239.4 <b>336.0</b>	S 3.6 2.1 1.7 0.5 2.1	γ <b>3.0</b> <b>3.7</b> <b>3.9</b> 46.4 <b>8.3</b>	300 K ω <sub>0</sub> 	S 3.2 1.8 1.6 0.2 1.8	$\gamma$ 4.1 5.8 6.8 39.6 12.0
18           4 K           ω0           82.2           114.9           186.5           233.6           228.5           334.4           379.6	S 0.03 3.7 2.3 1.7 0.5 2.2 0.1	$\begin{array}{c} \gamma \\ \textbf{1.5} \\ \textbf{1.1} \\ \textbf{1.4} \\ \textbf{1.1} \\ 32.2 \\ \textbf{4.8} \\ 33.1 \end{array}$	100 K ω <sub>0</sub>  <b>114.7</b> <b>186.6</b> <b>233.6</b> 228.6 <b>334.5</b> 374.7	S 3.7 2.3 1.8 0.7 2.2 0.2	γ <b>1.7</b> <b>1.7</b> <b>2.3</b> 72.6 <b>6.2</b> 36.5	200 K ω <sub>0</sub> <b>114.9</b> <b>186.5</b> <b>233.8</b> 239.4 <b>336.0</b> 367.8	S 3.6 2.1 1.7 0.5 2.1 0.4	γ <b>3.0</b> <b>3.7</b> <b>3.9</b> 46.4 <b>8.3</b> 59.6	300 K ω <sub>0</sub>  114.8 186.0 233.4 249.2 336.3 362.4	S 3.2 1.8 1.6 0.2 1.8 0.5	γ 4.1 5.8 6.8 39.6 12.0 71.7
$18O \\ 4 K \\ \omega_0 \\ 82.2 \\ 114.9 \\ 186.5 \\ 233.6 \\ 228.5 \\ 334.4 \\ 379.6 \\ 569.7 \\ 18O \\ 569.7 \\ 18O \\$	S 0.03 3.7 2.3 1.7 0.5 2.2 0.1 0.7	γ <b>1.5</b> <b>1.1</b> <b>1.4</b> <b>1.1</b> 32.2 <b>4.8</b> 33.1 <b>6.2</b>	100 K ω <sub>0</sub> <b>114.7</b> <b>186.6</b> <b>233.6</b> 228.6 <b>334.5</b> 374.7 <b>569.4</b>	S 3.7 2.3 1.8 0.7 2.2 0.2 0.7	γ <b>1.7</b> <b>1.7</b> <b>2.3</b> 72.6 <b>6.2</b> 36.5 <b>6.5</b>	200 K ω <sub>0</sub> <b>114.9</b> <b>186.5</b> <b>233.8</b> 239.4 <b>336.0</b> 367.8 <b>566.4</b>	S 3.6 2.1 1.7 0.5 2.1 0.4 0.6	γ <b>3.0</b> <b>3.7</b> <b>3.9</b> 46.4 <b>8.3</b> 59.6 <b>8.6</b>	300 K $\omega_0$ 114.8 186.0 233.4 249.2 336.3 362.4 561.5	S  3.2 1.8 1.6 0.2 1.8 0.5 0.5	γ 4.1 5.8 6.8 39.6 12.0 71.7 11.4
$\begin{array}{r} 18 \\ 0 \\ 4 \\ k \\ \omega_0 \\ 82.2 \\ 114.9 \\ 186.5 \\ 233.6 \\ 228.5 \\ 334.4 \\ 379.6 \\ 569.7 \\ 599.6 \\ \end{array}$	S 0.03 3.7 2.3 1.7 0.5 2.2 0.1 0.7 0.01	γ <b>1.5</b> <b>1.1</b> <b>1.4</b> <b>1.1</b> 32.2 <b>4.8</b> 33.1 <b>6.2</b> 7.7	100 K $\omega_0$ 114.7 186.6 233.6 228.6 334.5 374.7 569.4 598.7	S 3.7 2.3 1.8 0.7 2.2 0.2 0.2 0.7 0.02	γ <b>1.7</b> <b>1.7</b> <b>2.3</b> 72.6 <b>6.2</b> 36.5 <b>6.5</b> 14.6	200 K $\omega_0$ <b>114.9</b> <b>186.5</b> <b>233.8</b> 239.4 <b>336.0</b> 367.8 <b>566.4</b> 594.9	S 3.6 2.1 1.7 0.5 2.1 0.4 0.6 0.02	γ <b>3.0</b> <b>3.7</b> <b>3.9</b> 46.4 <b>8.3</b> 59.6 <b>8.6</b> 16.7	$300 \text{ K}$ $\omega_0$ 114.8 186.0 233.4 249.2 336.3 362.4 561.5 594.9	S 3.2 1.8 1.6 0.2 1.8 0.5 0.5 0.5 0.02	γ 4.1 5.8 6.8 39.6 12.0 71.7 11.4 35.7
$\begin{array}{r} 18 \\ 0 \\ 4 \\ k \\ \omega_0 \\ \textbf{82.2} \\ \textbf{114.9} \\ \textbf{186.5} \\ \textbf{233.6} \\ 228.5 \\ \textbf{334.4} \\ 379.6 \\ \textbf{569.7} \\ 599.6 \\ 605.7 \\ \end{array}$	S 0.03 3.7 2.3 1.7 0.5 2.2 0.1 0.7 0.01 0.04	γ <b>1.5</b> <b>1.1</b> <b>1.4</b> <b>1.1</b> 32.2 <b>4.8</b> 33.1 <b>6.2</b> 7.7 33.7	100 K $\omega_0$ <b>114.7</b> <b>186.6</b> <b>233.6</b> 228.6 <b>334.5</b> 374.7 <b>569.4</b> 598.7 594.7	S 3.7 2.3 1.8 0.7 2.2 0.2 0.2 0.2 0.2 0.2 0.02 0.09	γ <b>1.7</b> <b>1.7</b> <b>2.3</b> 72.6 <b>6.2</b> 36.5 <b>6.5</b> 14.6 72.2	$200 \text{ K} \\ \omega_0 \\ \hline \\ 114.9 \\ 186.5 \\ 233.8 \\ 239.4 \\ 336.0 \\ 367.8 \\ 566.4 \\ 594.9 \\ 581.7 \\ \hline $	S 3.6 2.1 1.7 0.5 2.1 0.4 0.6 0.02 0.2	γ <b>3.0</b> <b>3.7</b> <b>3.9</b> 46.4 <b>8.3</b> 59.6 <b>8.6</b> 16.7 65.8	$\begin{array}{c} 300 \text{ K} \\ \hline \\ \omega_0 \\ \hline \\ 114.8 \\ 186.0 \\ 233.4 \\ 249.2 \\ 336.3 \\ 362.4 \\ 561.5 \\ 594.9 \\ 575.5 \\ \end{array}$	S 3.2 1.8 1.6 0.2 1.8 0.5 0.5 0.02 0.2	γ 4.1 5.8 6.8 39.6 12.0 71.7 11.4 35.7 53.3

Table 4.2: Parameters of the Drude-Lorentz fit for  $YBa_2 Cu_3{}^{16}O_6$  (upper half) and  $YBa_2 Cu_3{}^{18}O_6$ . The bold letter style denotes the six main modes, the other four oscillators are sidebands to the oxygen modes which are necessary to describe the line shape correctly. A discussion of the line shape follows in section 4.1.4 on page 122. Units of  $\omega_0$  and  $\gamma$  are cm<sup>-1</sup>, the oscillator strength S is dimensionless.



Figure 4.5: Relative frequency shifts of  $^{16}O$  (top) and  $^{18}O$  (bottom) as a function of the temperature (left panels) and of the lattice parameter a (right panels). The determination of a(T) from lattice expansion data of  $YBa_2 Cu_3 O_7 [409]$  is described in the text. For the grey symbols, a(T)has been derived from  $Sr_2 CuO_2 Cl_2 data [410].$ Due to the lack of better information the lattice parameter a of  $^{18}O$  is assumed to be the same as in  $^{16}O$ .

Figure 4.6: Left panel: linear fit of the stretching mode frequency in YBa<sub>2</sub>Cu<sub>3</sub><sup>16</sup>O<sub>6</sub> (grey line; squares). Triangles: estimates of the same mode in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.93</sub> for  $T > T_c$ , using an average of the a- and b-axis lattice parameters for a(T) (see text). Right panel: Comparison of the x = 6 data from the left panel with results of other groups. (i) Tajima et al. [384] (open circles; 300 K): different insulating cuprates (695 cm<sup>-1</sup>: La<sub>2</sub>CuO<sub>4</sub>; points above a = 3.96 Å:  $Sr_2$ CuO<sub>2</sub>Cl<sub>2</sub> and  $Sr_2$ CuO<sub>2</sub>Br<sub>2</sub>). (ii) and (iii) Crawford et al. [378] (+; 10 K) and Thomsen et al. [376] (×; 300 K): REBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> for RE=Er, Y, Ho, Gd, and Sm. The three large symbols denote YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> (x = 6.1 for Ref. [384]). (iv) Humlíček et al. [391] (diamond; 10 K): PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>. The lattice parameter has been estimated for the rare earth results of (ii), (iii) and (iv) by the corresponding average of a- and b of the x = 7phase [411] (neglecting the measurement temperature). The dashed line depicts  $\omega \propto a^{-7}$  as discussed in Ref. [384].

the resonance frequencies, which in particular could be responsible for the surprising "sign change" of the small temperature dependence of the bending mode.

In the right panels of Fig. 4.5 the relative frequency shifts are replotted, this time as a function of the lattice constant a. We did not succeed in finding temperature dependent measurements of a of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> in the literature. We fit data of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> [409] and insulating  $\operatorname{Sr}_2\operatorname{CuO}_2\operatorname{Cl}_2$  [410] with the expression  $a(T) = a_0 + a_1T + a_2T^2$ . The two materials yield similar results, which gives us some confidence that the *a*-axis lattice expansion is rather universal in the cuprates. An estimate of a(T) of  $YBa_2Cu_3O_6$  has then been obtained by using  $a_0 = 3.86$  Å typical for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>, and  $a_1 = 8.498 \times 10^{-6}$ Å/K and  $a_2 = 7.692 \times 10^{-8} \text{\AA}/\text{K}^2$  from the fit to the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> expansion data. Due to the lack of better information we applied the same values to <sup>18</sup>O. For the most interesting stretching mode (full squares) we also give the estimate calculated from the  $Sr_2CuO_2Cl_2$  data (grey squares). Remarkably, the stretching mode shows a *linear* dependence on a within the given uncertainties. In <sup>18</sup>O, the deviation from linearity for the 4 K point can at least partially be explained by the overestimation of the low temperature lattice expansion by using the <sup>16</sup>O data for the heavier isotope. In Fig. 4.6 we compare a linear fit to the <sup>16</sup>O data (thick grey line) with the results of other groups. The open circles depict room temperature results of Tajima and collaborators [384] for a series of different insulating cuprates. Other symbols denote results obtained on the 123 family by rare earth substitution (see caption of Fig. 4.6 for more details). The dashed line depicts the expression  $\omega_0 \propto a^{-7}$  as discussed by Tajima and collaborators [384], which gives a reasonable approximation of the data. The triangles in the left panel denote data points of  $YBa_2Cu_3O_{6.93}$  which will be discussed below.

Considering phonon anomalies, a large body of work has focused on the apical oxygen modes. Some authors find strong, others weak anharmonicity, and the existence of a double well potential has been discussed very controversially [402,412–417]. The strong dependence of the stretching mode frequency on the lattice constant a indicates that in fact this planar oxygen mode might be the most peculiar one. The in-plane bond stretching vibration modulates electronic parameters such as the hopping t and the charge transfer energy  $\Delta$ . At finite **k**-values, this strongly modulates the antiferromagnetic exchange coupling between adjacent Cu ions, which will play a major role in the context of bimagnon-plusphonon absorption in chapter 5. Tajima and collaborators [384] correlate the stretching mode anomaly to the dependence of the charge transfer energy  $\Delta$  on a [394]. In neutron scattering measurements, the observation of a drastic softening of this mode for  $\mathbf{k} \neq 0$  upon changing the oxygen content from x = 6 to x = 7 has been taken as indication for strong electron-phonon coupling [369,402,418].

The relative isotope shifts  $\omega_{0,j}({}^{16}\text{O})/\omega_{0,j}({}^{18}\text{O})$  of the various modes and their temperature dependence are depicted in Fig. 4.9. Remarkably, all isotope shifts become smaller with increasing temperature. The frequency of the weak lowest mode at 83 cm<sup>-1</sup> could only be determined at 4 K in  ${}^{18}\text{O}$ , and for the following analysis of the Teller-Redlich product rule [419] the shift of this mode is kept constant. The Teller-Redlich rule

$$\Omega = \frac{\omega_1 \omega_2 \dots \omega_n}{\omega'_1 \omega'_2 \dots \omega'_n} = \left(\frac{m'}{m}\right)^{\alpha/2} \tag{4.1}$$



Figure 4.7: Temperature dependence of the planar oxygen bending mode which softens slightly with increasing temperature in <sup>16</sup>O and hardens in <sup>18</sup>O. Similar to the stretching mode (see figure below), the reflectivity spectra show anomalies on the high frequency side, but in  $\sigma_1(\omega)$  these only produce small features in the tails.

Figure 4.8: Temperature dependence of the planar oxygen stretching mode. The large redshift with increasing temperature agrees with the strong dependence of the peak frequency on the lattice parameter a observed by other groups (see text).



Figure 4.9: Temperature dependence of the relative isotope shifts,  $\omega_0({}^{16}O)/\omega_0({}^{18}O)$ . The dashed horizontal line denotes the value of  $(18/16)^{1/2}$ , and the crosses give the result of the Teller-Redlich product rule [419],  $\Omega^{1/3}$ , as defined in Eq. 4.1.

offers an important check for our results on the oxygen isotope shifts. Here, m denotes the isotope mass and  $\omega_i$  designates the frequency of the *i*-th mode,  $i \in \{1, n\}$ . The primes indicate parameters of the isotope substituted sample and  $\alpha$  gives the number of distinct sites that have been substituted. For the case of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> with three distinct oxygen sites (see above) it states that the overall isotope shift of all six phonon modes has to be equal to the isotope shift three pure oxygen modes would show, *i.e.*, it predicts that the product of the relative isotope shifts of all modes (see Fig. 4.9) is equal to  $(18/16)^{3/2} = 1.1932$  (or 1.1905 for the composition of 98.24% <sup>18</sup>O, 0.76% <sup>17</sup>O and 1% <sup>16</sup>O given by the supplier of the gas). In Fig. 4.9 the dashed line corresponds to  $\sqrt{18/16}$ , and the crosses depict the experimental result of  $\Omega^{1/3}$ . At low temperatures both agree well, which shows that we observed all six modes and the correct isotope shifts. Moreover, this corroborates that the isotope substitution has been a complete one. At elevated temperatures, the Teller-Redlich product rule is not satisfied anymore. This is an indication for anharmonicity, which gives rise to thermal expansion. In comparison to <sup>16</sup>O, the heavier isotope <sup>18</sup>O shows a smaller amplitude of vibration, and hence probes a potential which is closer to the harmonic approximation. This yields a smaller shift with temperature. In an electronphonon coupling scenario for superconductivity, the small isotope shift of the phonon modes would for example give rise to a reduced isotope effect on  $T_c$  [420].

#### 4.1.3 Finite Doping and *c*-axis Modes

At finite doping concentrations, the optical conductivity reveals the intricate interplay of electronic and vibrational degrees of freedom. Far- and mid-infrared spectra at low doping concentrations will be discussed in chapter 7. At higher oxygen concentrations, the



Figure 4.10: Reflectivity spectrum of  $YBa_2 Cu_3 O_{6.93}$  for  $E \parallel ab$ . The grey lines depict fits from which the phonon frequencies have been determined (see Table 4.3). Note that the simple Drude-Lorentz model is not able to fully describe the electronic contribution in the superconducting state. It nevertheless offers a reasonable estimate of the phonon frequencies.



Table 4.3: Fit parameters for the stretching mode resonance frequency in  $YBa_2 Cu_3 O_{6.93}$  for  $E \parallel ab$ .



Figure 4.12: Comparison of the resonance frequency obtained from a fit (circles) and of the corresponding minimum in reflectivity (triangles) in  $YBa_2 Cu_3 O_{6.93}$  for  $E \parallel ab$ . A determination of only the minimum clearly fails to describe the correct temperature dependence. The dotted vertical line denotes  $T_c$ .

electronic contribution dominates the infrared spectra for  $E \parallel ab$ , making an examination of the phonon spectrum very difficult. In Fig. 4.10 we plot the far-infrared reflectivity of an optimally doped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.93</sub> single crystal for  $E \parallel ab$  between 4 and 300 K. The two planar oxygen phonon modes are clearly resolved. The thick grey lines depict fits of the data. Due to the large electronic absorption, an accurate determination of all phonon parameters requires knowledge of the spectrum on a much wider scale. For the fits, experimental data have been used up to 5000  $\rm cm^{-1}$ , which allows us to obtain reasonable estimates of the resonance frequencies (see Fig. 3.3 on page 92 for an example of the position of the dip in  $R(\omega)$  relative to the resonance frequency). The bending mode shows a value of  $363.5 \pm 1 \text{ cm}^{-1}$ , almost independent of temperature within the error bars. In contrast, the stretching mode experiences a strong redshift with increasing temperature  $(T > T_c)$ . similar to the case of the insulator discussed above (see left panel of Fig. 4.11; the fit parameters are given in Table 4.3). The figure reveals the influence of superconductivity on the phonon mode: below  $T_c$ , the temperature dependence of the stretching mode is reversed. The same behavior is observed for the *c*-axis apical stretching mode (right panel of Fig. 4.11). These changes upon opening of the superconducting gap reflect the influence of the electronic density of states on the phonon parameters [421, 422].

Thus far reports of the ab-plane phonon spectrum are scarce. In direct measurements of the absorptivity below 400 cm<sup>-1</sup> Pham and collaborators [389] observed absorption features at 142, 187, 332 and 351 cm<sup>-1</sup>, in reasonable agreement with the above given value of the bending mode of 363.5 cm<sup>-1</sup>. Renk and co-workers derived the phonon conductivity spectrum "from the fine structure of the reflectivity curve" [390]. This spectrum contains a multitude of peaks, of which features at about 275, 365 and 590 cm<sup>-1</sup> are attributed to the *a*-axis response, whereas the two highest structures of the *b*-axis are claimed to be at about 530 and 475 cm<sup>-1</sup> [390]. Bazhenov [382] performed an oxygen isotope substitution study on single crystals of YBa<sub>2</sub>Cu<sub>2.9</sub>Al<sub>0.1</sub>O<sub>6.9</sub> with 10% Al contamination on chain Cu sites. In this work, the resonance frequencies are erroneously identified with the *minima* in reflectivity at 189, 248, 353, 477 and 590 cm<sup>-1</sup> (we again refer to Fig. 3.3 on page 92), which in particular introduces errors in the determination of the temperature dependence. A *hardening* of the 353 cm<sup>-1</sup> resonance is claimed with decreasing temperature around



Figure 4.13: Reflectivity spectrum of  $YBa_2 Cu_3 O_7$  for  $E \parallel ab$ . The minimum at 475 cm<sup>-1</sup> observed for x = 6.93 (see Fig. 4.10) is absent in the fully oxygenated sample.

 $T_c$ , but this clearly reflects rather a sharpening of the feature than a real shift. The discrepancy between the frequency of the minimum and the resonance frequency obtained from a fit is emphasized in Fig. 4.12. The minima of both modes show a much stronger temperature dependence than the resonances themselves The hardening of the bending mode minimum observed in Ref. [382] is reproduced, although the resonance frequency stays constant. Bazhenov reported oxygen isotope shifts of 4.6% (353 cm<sup>-1</sup>), 2% (477  $cm^{-1}$ ) and 5.6% (590  $cm^{-1}$ ) [382]. The feature at 477  $cm^{-1}$  is attributed to the chains, and the Al contamination is suspected to cause the small isotope shift of this minimum. since Al binds the chain oxygen strongly and thereby might prevent the substitution [382]. Also in our data of  $YBa_2Cu_3O_{6.93}$  (see Fig. 4.10) a minimum at about 475 cm<sup>-1</sup> can be observed at low temperatures. The apparent onset of absorption at the same frequency at 4 K has been discussed controversially [28, 423]. We attribute the minimum at 475 cm<sup>-1</sup> in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.93</sub> to oxygen vacancies on chain sites. This is motivated by the absence of structure at this frequency in fully oxygenated  $YBa_2Cu_3O_7$  (see Fig. 4.13). We summarize the preceding two paragraphs by stating that the observation of the planar bending and stretching phonons at 363.5 and 595  $\rm cm^{-1}$  and of a chain vacancy mode at 475  $\rm cm^{-1}$  agrees with previous studies [382,389,390]. We, however, are the first to present the temperature dependence of the phonons for  $E \parallel ab$  of highly doped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> correctly.

For  $T > T_c$ , the resonance frequency of the planar stretching mode is plotted as a function of the (estimated) lattice constant in the left panel of Fig. 4.6 (triangles). As an



Figure 4.14: Reflectivity spectrum for  $E \parallel c$  of  $YBa_2 Cu_3 O_6$  (thin line: 4 K; thick grey line: fit),  $YBa_2 Cu_3 O_{6.93}$  (300 K; thin line) and  $YBa_2 Cu_3 O_7$  (300 K; thick line).

	$\omega_0 ~(\mathrm{cm}^{-1})$	104.3	144.8	214.3	363.0	636.9	
$4 \mathrm{K}$	S	2.8	7.2	0.7	3.8	0.5	
	$\gamma~({ m cm}^{-1})$	1.2	2.5	2.2	8.4	10.8	Table 4.4: Drude-Lorentz fit
	$\omega_0 ~(\mathrm{cm}^{-1})$	104.4	143.4	212.5	363.0	635.9	parameters of $YBa_2 Cu_3 O_6$
$300 \mathrm{K}$	S	2.0	6.3	0.5	3.4	0.4	for $E \parallel c \ at \ T = 4 \ K \ and \ 300$
	$\gamma~({\rm cm}^{-1})$	3.2	2.0	5.3	20.5	16.9	K.

estimate of a(0 K) an average of the *a*- and *b*-axis parameters, (3.813+3.881)/2 Å [409] has been used. The temperature dependence a(T) has been derived from the data of Ref. [409] as discussed above for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>. In fact, one might expect two very different resonance frequencies for the *a*- and the *b*-axis on the basis of the strong dependence of this mode on the lattice parameter. A naive extrapolation of the data given in Fig. 4.6 yields a difference of 50 to 100 cm<sup>-1</sup>. However, normal mode and lattice dynamical calculations predict only a small difference of order 10 [405] to 20 cm<sup>-1</sup> [391]. In a film of non-superconducting PrBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> Humlíček and co-workers attributed only a single resonance at 552 cm<sup>-1</sup> to the stretching mode. In untwined single crystals of the same compound, phonon absorption has been reported above 250 cm<sup>-1</sup> [392]. Peaks at about 350, 550 and 650 cm<sup>-1</sup> are observed for *both*  $E \parallel a$  and  $E \parallel b$ , but the latter polarization shows additional structure between 480 and 500 cm<sup>-1</sup>, which might be related to the chain vacancy mode discussed above.

The *c*-axis reflectivity spectra of single crystals of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> (4 K), YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.93</sub> (300

K) and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (300 K) are plotted in Fig. 4.14.<sup>‡</sup> The doping dependence of the c-axis phonons has been discussed in detail by Schützmann and collaborators [305] for oxygen concentrations in the range 6.1 < 6.9, and by Homes and co-workers [32] for 6.5 < 6.95. Due to the relatively small electronic background, the *c*-axis phonons can be determined accurately at all doping levels. In YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> we observe all five  $A_{2u}$  modes predicted by a group theoretical analysis. The two high frequency peaks correspond to oxygen stretching and bending modes, similar to the case of the *ab*-plane spectrum. Here, the apical oxygen gives rise to the stretching mode at  $637 \text{ cm}^{-1}$ , and the mode at  $363 \text{ cm}^{-1}$  is assigned to the out-of-plane bond bending vibration of the planar oxygen ions. The Drude-Lorentz fit parameters of  $YBa_2Cu_3O_6$  (see Table 4.4) agree with the results of Schützmann and collaborators [305] for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.1</sub>. Most remarkably, the c-axis stretching mode shifts by only  $1 \text{ cm}^{-1}$  from 4 to 300 K, in contrast to the 12 cm<sup>-1</sup> redshift of the stretching mode in the *ab*-plane. Also the shift with doping is very small, contrary to what Fig. 4.14 suggest at first sight. The different resonance frequencies of the c-axis stretching mode for x=6and 7 are due to the chain oxygen ions. The chain Cu ion, against which the apical oxygen vibrates, has either zero, one or two chain oxygen neighbors. Therefore, three different peaks are expected for intermediate oxygen concentrations, which indeed is the case for x = 6.93: most of the spectral weight is in the "full chain" mode at 571 cm<sup>-1</sup>, and small features are observed at 620 and 634  $\text{cm}^{-1}$  (at 4 K), *i.e.*, the "empty chain" mode has only shifted by 3 cm<sup>-1</sup> from x=6 to 6.93. The absence of these higher peaks in the x=7 data proves the stoichiometry of this sample. A more detailed discussion of the spectra for large doping concentrations will be presented in chapter 8.

#### 4.1.4 Phonon Line Shape in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>

In the in-plane reflectivity spectrum of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> the phonon line shapes deviate strongly from the predictions of the Drude-Lorentz model, in particular for the oxygen modes. This forms a strong contrast to the case of the *c*-axis spectrum (see Fig. 4.14), where every phonon peak is described rather nicely by a single oscillator. In the following, we will first discuss the line shape observed in  $R(\omega)$  and then analyze the consequences for  $\sigma_1(\omega)$ and  $\rho_1(\omega)$ . Various fits of the *ab*-plane reflectance are displayed in Fig. 4.15. In contrast to the *c*-axis modes, the slope of  $R(\omega)$  is very different on the high and low frequency sides of the peaks: although  $R(\omega)$  shows a typical Reststrahlen behavior on the latter by rising steeply for  $\omega < \omega_0$ , the drop on the high frequency side is very gradual, which indicates additional absorption. In Fig. 4.15, curves A-C represent Drude-Lorentz fits with 14, 7 and 3 oscillators between 200 and 700 cm<sup>-1</sup>, respectively. With a large number of oscillators, *i.e.*, parameters, the experimental spectrum obviously can be reproduced with high accuracy. A satisfactory fit quality is reached by using seven oscillators (curve B), two

<sup>&</sup>lt;sup>‡</sup>In the case of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>, the measurement has been performed using an aperture with a diameter of 0.5 mm and an Au mirror as reference. The x = 7 (6.93) data have been collected on a free standing sample face of  $0.5 \times 1.5 \text{ mm}^2$  ( $0.7 \times 2 \text{ mm}^2$ ), using *in-situ* Au evaporation for the reference measurement. The quality and reliability of the x = 7 and 6.93 data is therefore better than in the case of x = 6 in Fig. 4.14.



Figure 4.15: Various fits (grey lines) of the 4 K reflectance spectrum of  $YBa_2Cu_3{}^{16}O_6$  (E || ab). The number of oscillators used in the displayed frequency range is given in the figure. A-C: Drude-Lorentz model; D: asymmetric Drude-Lorentz model (see Eq. 3.31 on page 94); E: factorized model (see Eq. 3.24 on page 90).

for every phonon plus one for the dip at  $625 \text{ cm}^{-1}$ . The second mode per peak describes the absorption on the high frequency side (see below). A single Lorentz mode per peak (curve C) is clearly not sufficient to describe the data. Assuming an asymmetric line shape (see chapter 3; Eq. 3.31 for curve D and Eq. 3.24 for curve E) allows to approximate the basic line shape with a single oscillator per peak (four parameters each).

From now on we concentrate on the most interesting stretching mode. In Fig. 4.16 we compare the spectra of  $\sigma_1(\omega)$  and  $\rho_1(\omega)$  derived from the various fits with the Kramers-Kronig result, for which measured data have been used up to 8000 cm<sup>-1</sup>. The  $\sigma_1(\omega)$  and  $\rho_1(\omega)$  spectra obtained via the Kramers-Kronig analysis are almost indistinguishable from the ones of the most accurate fit A of  $R(\omega)$ . Also fit B using 3 oscillators in the range plotted in Fig. 4.16 yields an acceptable result. Note that the apparent deviation of the peak frequency in  $\sigma_1(\omega)$  amounts to less than 2 cm<sup>-1</sup>. All three fits (C-E) assuming a single mode per peak give a poor description. This had to be expected for curve C, but the failure of the asymmetric models (D and E) in particular to describe  $\rho_1(\omega)$  is surprising. Note that part of the motivation to apply an asymmetric model is to prevent from using several oscillators per mode. Therefore it is unreasonable to describe one peak with more than one *asymmetric* modes, in particular since already two *symmetric* oscillators (B) per peak do the job.



Figure 4.16: Comparison of  $\sigma_1(\omega)$  and  $\rho_1(\omega)$  as derived from the fits displayed in Fig. 4.15 (grey lines) with a Kramers-Kronig result. The number of oscillators used in the displayed frequency range is given in the figure. A-C: Drude-Lorentz model; D: asymmetric Drude-Lorentz model (see Eq. 3.31 on page 94); E: factorized model (see Eq. 3.24 on page 90).



Figure 4.17: Line shape details of the stretching phonon mode. Thick black line: Kramers-Kronig result; grey line: fit A of Figs. 4.15 and 4.16; other lines: individual contributions to the fit.

Figure 4.18: Comparison of the planar stretching mode line shape for different samples of  $YBa_2 Cu_3^{16}O_6$ . From bottom to top: sample grown in a  $BaZrO_3$  crucible; grown in a  $ZrO_2$  crucible; sample with  $\approx 3\%$  of Zn substitution.

Thus far we established that only a multi-oscillator fit yields a reasonable description of the data. Let us now try to ascribe some physical significance to the line shape. In Fig. 4.17 we resolve the individual contributions to  $\sigma_1(\omega)$  of fit A. Note that a similar analysis is not possible for  $\rho_1(\omega)$ , since the various oscillators are not additive there. Most of the spectral weight is carried by a single symmetric oscillator, the other modes are necessary to describe the slow fall-off at high frequencies. In  $\sigma_1(\omega)$  the sidebands are less spectacular than what one might have expected on the basis of the reflectance data. The pronounced dip in  $R(\omega)$  at 625 cm<sup>-1</sup> produces only a small feature in  $\sigma_1(\omega)$ . This dip is the only one of the sidebands to which possibly an *individual* physical significance can be ascribed. Remarkably, the isotope shift of the dip is only about 4% or  $25 \text{ cm}^{-1}$  (from 624.5  $cm^{-1}$  in <sup>16</sup>O to 599.6  $cm^{-1}$  in <sup>18</sup>O; see Table 4.2), which indicates that it might be due to a multi-phonon with an oxygen-mode contribution of 450 to 500 cm<sup>-1</sup>. This dip gives a fingerprint of the crucible the sample has been grown in. In Fig. 4.18 the lowest line depicts a very pure sample grown in a BaZrO<sub>3</sub>-crucible. There, the side peak at  $625 \text{ cm}^{-1}$  is very pronounced. In the sample grown in a  $ZrO_2$ -crucible the dip is washed out, and there are some smaller wiggles just above the maximum (between 600 and 640  $\rm cm^{-1}$ ). We attribute these to the larger amount of impurities in this sample. The intentional addition of Zn (top line; grown in an  $ZrO_2$ -crucible) emphasizes the wiggles a lot, e.g., at 608 cm<sup>-1</sup> and hides the side peak further. Note that the structures below  $550 \text{ cm}^{-1}$  are interferences, which cannot explain the irregularities around the peak maximum, where absorption is high and interferences are not measurable (see also Fig. 4.4). A shoulder at  $625 \text{ cm}^{-1}$  (603 cm<sup>-1</sup>) had been observed in ceramic samples of  $YBa_2Cu_3^{16}O_6$  (<sup>18</sup>O<sub>6</sub>) [378], and it is also present in the only low temperature single crystal data of  $YBa_2Cu_3O_6$  published thus far [387].

Disregarding the 625 cm<sup>-1</sup> feature, all other sidebands do not have an individual significance but mimic a *continuum* of absorption on the high frequency side of the resonance. One possible source for this could be a coupling between vibrational and magnetic degrees of freedom. This coupling is most pronounced for the in-plane oxygen stretching mode: the change of the Cu-O bond length modulates the electronic parameters such as the hopping t, the charge transfer energy  $\Delta$  or the exchange constant J [224, 393–395]. In the mid-infrared, this coupling gives rise to bimagnon-plus-phonon absorption [224] (see chapter 5). Here, we tentatively ascribe the high frequency tails to the simultaneous excitation of a phonon and low-energy magnons of the acoustic spin-wave branch. We summarize the experimental observations in order to motivate this claim: (a) The asymmetries are by far strongest for those phonon modes which modulate the exchange constant, *i.e.*, the planar oxygen ions at 350 and 600 cm<sup>-1</sup>. (b) No asymmetries are observed in the *c*-axis spectrum of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>. (c) Additional absorption is only observed at the high frequency side of the resonances, whereas for example multi-phonon absorption should not be restricted to this range, given the multitude of phonon bands in this complicated structure.

Thomas and co-workers [424] reported a similar asymmetry in undoped and lightly doped Nd<sub>2</sub>CuO<sub>4-x</sub> and proposed a tilting of the Cu-O unit as origin, with the absorption frequency being lower where the tilting is larger (see Fig. 4.19). Doping induces a broad side peak at the *low* frequency side of the in-plane stretching mode (lower panel). This mode also arises in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+y</sub> upon doping and will be discussed in chapter 7.



Figure 4.19: Optical conductivity of the planar stretching mode in undoped and slightly doped  $Nd_2 CuO_{4-x}$  as given by Thomas et al. [424]. A similar asymmetry as in  $YBa_2 Cu_3 O_6$  is observed. Thick lines; Kramers-Kronig resymbols: Lorentzian fit; sult: other lines: individual contributions to the fit. The doping induced mode shown in the lower panel arises in  $YBa_2 Cu_3 O_{6+y}$ with doping as well. It will be discussed in chapter 7.

Similar line shapes can be explained for excitations at much higher frequencies by the spatial dispersion in **k**-space of the resonance to which the photon couples (see chapter 6 of Ref. [336] and references therein). The part of the Brillouin zone that one probes with infrared light is, however, so small that dispersion is most probably completely negligible (see the following section).

### 4.2 Phonon-Polariton Dispersion in $YBa_2Cu_3O_6$

Inside the sample, the photon mixes with phonons, forming a phonon-polariton [425]. Due to the large velocity c of light, the vacuum wave vector  $k_v = \omega/c$  is very small for infrared frequencies, and we are used to think of infrared spectroscopy as measuring a single point at  $k \approx 0$  of a given dispersion branch. However, there are means to follow the dispersion, and some of these we want to present here.

The mid-infrared reflectivity of a thin YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> single crystal is plotted in Fig. 4.20, part of the far-infrared spectrum is shown in the inset. In the frequency ranges of low absorption, strong interferences are observed. The absorption process which modulates the amplitude of the interferences in the mid-infrared will be discussed in chapter 5. Here, we are only interested in the *position* of interference extrema. Due to a phase shift of  $\pi$ upon reflection on the sample surface, an interference minimum occurs in reflectivity for  $m\lambda = 2d$ , where  $\lambda$  denotes the wavelength of light *in* the sample, *d* measures the sample



Figure 4.20: Mid-infrared interference spectrum of a thin  $YBa_2 Cu_3 O_6$  single crystal. Inset: Far-infrared data of the same sample, which corresponds to the curves labelled YSZ in Fig. 4.2.

thickness and m is an integer number. A maximum corresponds to  $(m + 1/2)\lambda = 2d$ . With these expressions one can relate the *frequency* of an extremum with a wave vector, if the thickness d and the order m are known. In an insulator, the polariton dispersion for  $\omega \to 0$  is linear with  $\omega(q) = q/\sqrt{\epsilon_0}$ , where  $\omega$  and q are both measured in units of  $\mathrm{cm}^{-1}$ , and  $\epsilon_0 = \epsilon'(\omega = 0)$ . In practice, one can determine the slope from the interferences at low frequencies and adjust the order m to guarantee  $\omega(q = 0) = 0$ . In Fig. 4.21 we plot the thus obtained polariton dispersion at low frequencies for two different samples. The linear dispersion for  $\omega \to 0$  and the mixing with the phonons (hatched areas indicate  $\omega_{T,j} < \omega < \omega_{L,j}$ ) are nicely resolved. The grey line and the grey symbols show data of the same sample, where the grey line has been derived via  $\omega^2(q) = q^2/\epsilon'(\omega)$ . Here,  $\epsilon'(\omega)$  is the Kramers-Kronig result plotted above in Fig. 4.1. The agreement with the polariton dispersion derived from the interferences is excellent. For frequencies above the phonon resonance at 115 cm<sup>-1</sup> the order m of the interferences has been adapted to fit the grey line. Note that this procedure only allows to translate the full set of symbols horizontally.

The dashed line indicates the resonance frequency of the weak sixth phonon at  $83 \text{ cm}^{-1}$ . We focus on this frequency range in Fig. 4.22. Mixing with the polariton occurs only in a very narrow frequency window, which is due to the very small oscillator strength of this phonon mode. The data sets of both samples nevertheless resolve a clear kink in the



Figure 4.21: Phonon-polariton dispersion as derived from the extrema of the interference pattern (symbols) or from  $\omega^2(q) = q^2/\epsilon'(\omega)$  (grey line), where  $\epsilon'(\omega)$  is the Kramers-Kronig result displayed in Fig. 4.1. Grey symbols and the grey line show data of the same sample. The hatched areas denote the phonon "stop bands" with  $\omega_{T,j} < \omega < \omega_{L,j}$ , and the dashed line indicates the weak phonon at 83 cm<sup>-1</sup>.



Figure 4.22: Enlarged view of Fig. 4.21 around the weak phonon mode at 83 cm<sup>-1</sup>, which gives rise to a kink in the polariton dispersion. Every grey symbol corresponds to one of the interference "wiggles" in the grey line.

dispersion at the resonance frequency. On this enlarged scale it is also possible to correlate every grey symbol with one of the "wiggles" of the grey line, which correspond to the interferences in the original reflectivity data.

Finally, we plot the polariton dispersion at higher frequencies and wave vectors in Fig. 4.23. Hatched areas denote the phonon "stop bands". The inset shows data points up to  $\omega = 3600 \text{ cm}^{-1}$  and  $q \approx 9000 \text{ cm}^{-1}$  that have been derived from the spectrum of Fig. 4.20. Note that the displayed range corresponds to about  $10^{-4}$  of a reciprocal lattice vector.



Figure 4.23: Polariton-dispersion for larger frequencies and wave vectors. The data points shown in the inset correspond to the black symbols in the main panel and have been derived from the interference pattern plotted in Fig. 4.20.

## Chapter 5

# Magnetic Mid-Infrared Absorption in Antiferromagnetic $YBa_2Cu_3O_6$ : Failure of Spin Wave Theory in Undoped Cuprates?

In this chapter the optical conductivity  $\sigma(\omega)$  of undoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> is studied in detail in the mid-infrared range. Substitutions on all but the Ba site are used to identify the prominent absorption processes at 2800 and 3800 cm<sup>-1</sup>. Experimental evidence for bimagnonplus-phonon absorption is collected. Other scenarios such as d-d exciton and charge transfer exciton absorption are discussed and rejected. However, a more critical analysis of the line shape and the spectral weight reveals the limits of the bimagnon-plus-phonon approach: only the main peak at 2800 cm<sup>-1</sup> is well described, but the large amount of spectral weight at 3800 cm<sup>-1</sup> and above remains puzzling, a situation very similar to the case of two-magnon Raman scattering. Taking into account an interaction between phonons and magnons in terms of phonon-two-magnon multiple scattering seems to reproduce the line shape, but the necessary coupling is unrealistically large. The strong increase of high frequency spectral weight with increasing temperature makes the failure of spin-wave theory even more evident.\*

## 5.1 Bimagnon-plus-Phonon Absorption

The undoped parent compounds of the high  $T_c$  cuprates are regarded as an almost ideal realization of a two-dimensional (2D) spin 1/2 Heisenberg antiferromagnet (see chapter 2.2). Despite the low dimensionality and the low spin the excitations are thought to be spin-waves with a well-defined dispersion [126], as opposed to e.g. 1D systems, where a

<sup>\*</sup>Parts of this chapter are to be published by M. Grüninger, D. van der Marel, A. Damascelli, A. Erb, Th. Wolf, T. Nunner, and T. Kopp [225]. More details of the theoretical calculations will be published by T. Nunner, T. Kopp, M. Grüninger, and D. van der Marel [426].

spinon continuum is observed in neutron scattering [199]. In the cuprates, a spin-wave dispersion has been extracted throughout the whole Brillouin zone from the maxima in neutron scattering intensities (see page 40), but energies are rather high, large backgrounds are observed and the magnitude of quantum corrections is unclear [190] (see Table 2.6 on page 39). The peculiarities of the ARPES spectra of undoped cuprates have been discussed in chapter 2.2.3. These have been taken as evidence for the existence of spinons also in two dimensions by Laughlin [258] (see Fig. 2.24 on page 57). Also in a self-consistent Born approximation approach by Chubukov and Morr [223] the key point in the description of the ARPES data was the assumption that magnons are not well-defined particles at the Brillouin zone boundary. Two-magnon Raman scattering shows several anomalies in the cuprates, in particular a very broad line shape, spectral weight at high energies and a finite signal in  $A_{1q}$  geometry [202] (see page 43). A large body of theoretical work has been dedicated to this problem, and the importance of resonance phenomena [203, 220, 222] was emphasized. For a discussion of non-resonant treatments such as including the interaction with phonons and extensions of the Heisenberg model we refer the reader to page 43. Certainly, the strong influence of the charge transfer resonance on the Raman spectra complicates the problem significantly.

Optical spectroscopy probes the magnetic excitations more directly. The main peak in mid-infrared absorption (MIR) spectra of La<sub>2</sub>CuO<sub>4</sub> and other single layer cuprates [226] has been interpreted by Lorenzana and Sawatzky [224] in terms of bimagnon-plus-phonon (BIMP) absorption.<sup>†</sup> A similar feature was reported in the bilayer system YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> (YBCO<sub>6</sub>) [114, 400, 401, 429], in 2D S = 1 La<sub>2</sub>NiO<sub>4</sub> [224, 228] and in 1D S = 1/2 Sr<sub>2</sub>CuO<sub>3</sub> [430, 431]. Good agreement between observed and calculated spectra is achieved in 1D [431] because quantum fluctuations are included *ab initio*, and for the 2D S = 1 nickelates [224] because fluctuations beyond spin-wave theory are small even for S = 1. However, a large amount of spectral weight is observed above the bimagnon-plus-phonon peak. Interpretations in terms of multi-magnon-plus-phonon absorption [224], *d-d* transitions [228] and charge transfer excitons [432] have been proposed. We challenge these approaches and suggest that a full account of our mid-infrared data in the undoped cuprates has to include quantum fluctuations beyond spin-wave theory. This might provide an important feedback to the Raman experiment and the basic picture of the undoped cuprates.

#### Experimental Evidence for Bimagnon-plus-Phonon Absorption

We measured the mid-infrared reflectance and transmittance spectra of single crystals of  $YBa_2Cu_3O_6$ . The samples were grown in either  $BaZrO_3$  (BZO) or  $Y_2O_3$  stabilized  $ZrO_2$  (YSZ) crucibles. Details of the sample preparation and of the oxygen isotope and Zn substitution are described on page 106. In this chapter we additionally discuss the substitution of Y with Pr and Gd. A finite amount of Y in the single crystals of  $RE_{0.8}Y_{0.2}Ba_2Cu_3O_6$ 

<sup>&</sup>lt;sup>†</sup>The early roots of this topic date back to optical measurements of Newman and Chrenko on NiO in 1959 [427]. A there observed absorption band at 0.24 eV was interpreted in terms of combined absorption of two magnons and one phonon by Mizuno and Koide [428] in the early days of Anderson's superexchange theory [70].

(RE=Pr, Gd) studied here is due to the  $Y_2O_3$  in the ZrO<sub>2</sub> crucibles. We calculated  $\sigma(\omega)$  by inverting the Fresnel equations for the experimentally measured transmission and reflection data. Measurements were carried out with the electric field vector polarized both parallel and perpendicular to the *ab*-plane. The small remnants of interference fringes in some of the calculated spectra of  $\sigma(\omega)$  are artefacts caused by deviations of the measured data from the assumed ideal case of absolutely flat and plane parallel surfaces.

The mid-infrared reflectance and transmittance spectra of a sample grown in a BZO crucible are displayed in Fig. 5.1 together with the resultant optical conductivity spectrum. For the orientation of the reader, the plotted frequency range includes the Cu-O stretching phonon mode at  $600 \text{ cm}^{-1}$ . Above, the reflectivity is constant within the noise level, which indicates the low level of absorption in the insulator below the charge transfer gap. The very rich structure of the conductivity spectrum is only revealed in a transmission experiment (compare Fig. 3.1 on page 86). An even lower value of absorption could be obtained by annealing in ultra-high vacuum, as described on page 106. In this case, the sample was transparent up to the onset of charge transfer absorption at about  $11000 \,\mathrm{cm}^{-1}$ (see Fig. 5.2). Both reflectance and transmittance are dominated by interference fringes, from which the polariton dispersion had been derived in chapter 4.2. The suppression of the amplitude of the interference fringes above  $2000 \,\mathrm{cm}^{-1}$  in reflectivity corresponds to the lower values of transmission. The reflectance above  $3600 \,\mathrm{cm}^{-1}$  has been measured with a prism spectrometer [433], and the experimental resolution is not sufficient to resolve the fringes. The corresponding optical conductivity spectrum is displayed in Fig. 5.3, where the phonons in the far-infrared range have been included for a direct comparison of the absorption strength. In the mid-infrared, the values of  $\sigma(\omega)$  plotted in Fig. 5.3 are two (four) orders of magnitude lower than for  $YBCO_{6,1}$  (YBCO<sub>7</sub>) in this frequency range.

Similar absorption features have been reported by Perkins and collaborators [89, 226– 228] in the single layer cuprates  $La_2CuO_4$  (upper panel of Fig. 5.4),  $Sr_2CuO_2Cl_2$ ,  $Nd_2CuO_4$ and  $Pr_2CuO_4$ . Data on  $Sr_2CuO_2Cl_2$  has also been published by Zibold and co-workers [434]. The main peak (2800 cm<sup>-1</sup> in YBCO<sub>6</sub>) has been interpreted successfully by Lorenzana and Sawatzky [224] in terms of bimagnon-plus-phonon absorption (dashed line in Fig. 5.4). Direct two-magnon absorption is not infrared active in the cuprates due to inversion symmetry. It only becomes weakly allowed by symmetry breaking effects such as impurities or the combination with a phonon. Among the latter, the in-plane Cu-O bond stretching phonon is the most effective. The success of this theory is underlined by the correct reproduction of the absorption line shape in the case of S = 1 in 2D [224,227,228] (La<sub>2</sub>NiO<sub>4</sub>; lower panel of Fig. 5.4). In 1D the corresponding bispinon-plus-phonon scenario describes the spectrum of S = 1/2 Sr<sub>2</sub>CuO<sub>3</sub> correctly [430, 431] (see Fig. 5.5). Note that in all three cases depicted in Figs. 5.4 and 5.5 a linearly increasing background was subtracted from the experimental data. The theoretical line shapes for different spin values in a 2D single layer material are reproduced from Ref. [224] in Fig. 5.6. This plot offers an intuitive understanding of the line shape. In the classical non-interacting case of  $S = \infty$  the twomagnon absorption reproduces the line shape of the density of states and diverges at the upper cut-off  $2E_m$ , where  $E_m = zSJ(1+Z_c/2S)$  is the zone boundary magnon energy. Here, z=4 denotes the number of nearest neighbors, and  $Z_c$  is the Oguchi correction (see Table



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Figure 5.1: Mid-infrared spectra of insulating  $YBa_2 Cu_3 O_6$  grown in a  $BaZrO_3$  crucible. Experimentally, the rich absorption structure is only revealed in the transmission spectrum, which has been measured on a  $85\mu$ m thick single crystal. In the reflectance spectrum measured on a thicker sample the corresponding structures are below the (low) noise level. For the orientation of the reader, the displayed frequency range extends down to the Cu-O stretching phonon mode.



Figure 5.3: Optical conductivity spectrum of a  $YBa_2Cu_3O_6$  sample annealed in ultra-high vacuum. In those frequency ranges where the transmission is finite,  $\sigma_1(\omega)$  has been derived from  $R(\omega)$  and  $T(\omega)$  (solid line). The thick grey line was derived from a fit of reflectivity data (see chapter 4).

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Figure 5.4: Bimagnon-plus-phonon absorption spectra (solid lines) of the 2D single layer compounds  $La_2 CuO_4$  (S=1/2) and  $La_2 NiO_4$  (S=1) at T = 10K as measured by Perkins et al. [226– 228]. Dashed lines: theoretical results of Lorenzana and Sawatzky [224], which in panel (a) are scaled to fit the experiment (see below). In panel (b) the dashed line refers to the right axis.

Figure 5.6: Bimagnon-plus-phonon absorption line shape for different spin values in 2D single layer materials, reproduced from Ref. [224]. The dashed line depicts a particular approximation in the case of S = 1/2. The second peak at lower frequencies is an artefact of the approximation used. The energy scale is given in units of the zone boundary magnon energy  $E_m$  (including the Oguchi correction), which corresponds to 2.32 J for S = 1/2.



Figure 5.5: Absorption spectrum of the 1D S = 1/2 compound  $Sr_2 CuO_3$ at T = 32K (solid line) as reported by Suzuura et al. [430]. Dashed line: theoretical curve of phononassisted spinon absorption as given by Lorenzana and Eder [431], yielding J = 246 meV and  $\omega_{ph} = 80$  meV.

Note that a linearly increasing background has been subtracted from the experimental data in all three cases shown in Figs. 5.4 and 5.5.



2.4 on page 30). With  $Z_c = 1.158$  we obtain  $E_m = 2.32J$  for S = 1/2 on a 2D square lattice. For a comparison with the experimental bimagnon-plus-phonon peak frequency, the bimagnon absorption spectra displayed in Fig. 5.6 have to be shifted by the phonon frequency. Attractive quantum magnon-magnon interactions are switched on by reducing the spin value. The spectral weight is pulled down and a resonance peak is formed inside the absorption continuum. Increasing the interaction strength, *i.e.*, reducing the spin value further, pulls the resonance to frequencies where the background is very small. Thereby the resonance peak sharpens, and for the limiting case of S = 1/2 it can be viewed as a nearly bound state of two magnons, *i.e.*, a bimagnon.



Figure 5.7: Solid lines: Acoustic and optical branches of the single magnon dispersion in units of q (for  $J_{12}/J = 0.1$ ). Gray area: two-magnon continuum in units of  $q_1 + q_2$ . Zone boundary contributions dominate the bimagnon-plus-phonon line shape due to the gap in the two-magnon continuum.

Bimagnons with a combined wave vector Q = $q_1+q_2=(\pi,0)$  show the longest life time [224] and form the most important contribution to the line shape. This is due to a gap in the two-magnon density of states at the zone boundary, as depicted in Fig. 5.7. The solid lines in Fig. 5.7 indicate the single magnon dispersion in a bilayer (in units of the single magnon q), and the gray area corresponds to the two-magnon continuum (in units of the *combined* wave vector  $Q = q_1 + q_2$ ). At Q = 0 the continuum extends from 0 to  $2E_m$ , *i.e.*, independent of the magnon-magnon interaction strength the peak of the Q = 0 contribution to the two-magnon resonance will always reside in a finite background and therefore it will be rather broad. However, at  $Q = (\pi, 0)$  there is a gap in the two-magnon continuum at  $E_m$ . The spectral weight is pulled down very close to the gap (see Fig. 5.6) and a rather sharp resonance peak is formed, justifying the notion of nearly-bound "bimagnons". Below this gap, a true bimagnon bound state can be formed: since one cannot find two single magnon states that conserve both momentum and energy, a bimagnon within the gap cannot decay into two magnons. In Ref. [224] a high energy approximation was used which is in-

appropriate for zone center excitations. The RPA results for two interacting magnons given below show that the high energy approximation reproduces the line shape rather well. Both RPA and the high energy approximation produce two-magnon bound states with a strong dispersion in momentum space. However, the peak at the low energy side of the bimagnon-plus-phonon resonance in Fig. 5.6 which is strongly enhanced in the dashed curve is an artefact of the high energy approximation which is removed in RPA.

The agreement between theory and experiment is obviously excellent for S = 1 in 2D (La<sub>2</sub>NiO<sub>4</sub>), and also for the 1D S = 1/2 case of Sr<sub>2</sub>CuO<sub>3</sub>. However, in the 2D S = 1/2

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cuprates the bimagnon-plus-phonon theory only reproduces the lowest peak, the spectral weight at higher frequencies remains unexplained. This deserves our major interest and will be discussed below in detail. Here, we first collect experimental evidence for the applicability of a magnon-phonon interpretation of the main resonance at  $2800 \text{ cm}^{-1}$  in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>. Let us compare the experimental data with predictions of bimagnon-plusphonon theory on a qualitative basis. Substitution of Y with Pr or Gd leads to a significant frequency shift of the main peak [400] (upper panel of Fig. 5.8; see also Fig. 5.10 and Table 5.1). Similar shifts were observed in two-magnon Raman scattering [39, 435] and were explained by the dependence of the exchange constant J on the lattice parameter a. A magnetic origin of the main peak is also favored by recent measurements of the pressure dependence of the mid-infrared and Raman spectrum of  $Sr_2CuO_2Cl_2$  [437]. A finite phonon contribution to the bimagnon-plus-phonon peak is evident from the frequency shift induced by oxygen isotope substitution in  $YBa_2Cu_3O_6$  (see Fig. 5.9). The measured isotope shift of  $28 \pm 8 \,\mathrm{cm}^{-1}$  is consistent with the bimagnon-plus-phonon interpretation, assuming that the longitudinal Cu-O stretching phonon of approximately  $550 - 600 \,\mathrm{cm}^{-1}$  is excited. The same phonon frequency can be inferred from the result obtained by Zn substitution (mid panel of


Table 5.1: Experimental bimagnon-plus-phonon resonance frequency for Zn and specific rare earth substitutions in  $YBa_2 Cu_3 O_6$  [400]. \*: the last two entries have been obtained in collaboration with Zibold and co-workers [439] (see Fig. 5.10).

Fig. 5.8). Similar to the phonons, the Zn impurities have a symmetry breaking effect in the  $CuO_2$  planes, and therefore it should be possible to observe *direct* bimagnon absorption. But phonons are not only breaking the symmetry, they also contribute momentum. Only the combined  $\vec{q} = \vec{q}_{phonon} + \vec{q}_{bimagnon}$  has to be zero in order to be infrared active. Hence the infrared bimagnon-plus-phonon spectrum is a weighted average over the Brillouin zone. In the case of a localized impurity, we have to integrate over the whole Brillouin zone, only with a slightly different form factor. Therefore the peak frequency of charged bimagnon absorption can be estimated by subtracting the appropriate phonon frequency from the bimagnon-plus-phonon peak. The broad absorption feature at  $2200 - 2250 \,\mathrm{cm}^{-1}$  present only in the Zn substituted sample (see arrow in Fig. 5.8) corroborates the above given value for the phonon frequency of  $550 - 600 \,\mathrm{cm}^{-1}$ . Recently, similar 'charged magnons' have been observed in our group in the 2-leg ladder compound  $\alpha'$ -NaV<sub>2</sub>O<sub>5</sub> [353, 438]. Another effect of the Zn impurities is to broaden the  $2800 \,\mathrm{cm}^{-1}$  peak drastically. A similar broadening is caused by the disorder on the Y site after substitution of 80% of Pr or Gd. Finally, the  $2800 \,\mathrm{cm^{-1}}$  peak is not observed if the electric field is applied parallel to the c axis (bottom panel of Fig. 5.8), in agreement with the single layer data [226].

 $Pr^*$ 

2560



Figure 5.11: Temperature dependence of the optical conductivity for specific substitutions of  $YBa_2 Cu_3 O_6$ .

3000

Frequency  $(\text{ cm}^{-1})$ 

200K4K

2000

0

1000

Pr<sub>0.8</sub>Y<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>

5000

4000



Figure 5.12: Main fit parameters of  $YBa_2Cu_3O_6$  (open (full) symbols: grown in  $ZrO_2$ (BaZrO<sub>3</sub>) crucible; circles denote the 2800 cm<sup>-1</sup> peak). Left panel: the BIMP peak shows a strong temperature dependence. For comparison the in-plane Cu-O stretching phonon mode is displayed as well (full squares). Mid panel: the width  $\gamma$  of the BIMP resonance is reduced in the cleaner sample. Right panel: the high frequency spectral weight with a peak at 3800 cm<sup>-1</sup> (diamonds) increases drastically with increasing temperature (see also Fig. 5.13). In this panel, the circles (diamonds) denote the sum of the circles (up and down triangles) of the corresponding panel of Fig. 5.13.



Figure 5.13: Fit parameters of 4 oscillators of  $YBa_2 Cu_3 O_6$  (top row; open (full) symbols: grown in  $ZrO_2$  ( $BaZrO_3$ ) crucible) and  $Gd_{0.8} Y_{0.2}Ba_2 Cu_3 O_6$  (bottom row; note the larger temperature scale). The circles denote the Lorentzian at  $\approx 2800 \text{ cm}^{-1}$  and the broad Gaussian at  $\approx 3300 \text{ cm}^{-1}$  which together mimic the theoretically predicted BIMP line shape. Also the high frequency part needs 2 oscillators (up and down triangles). These two peaks at about 3800 and 4300 cm<sup>-1</sup> are most easily distinguished in the sample grown in  $BaZrO_3$ (see bottom panel of Fig. 5.1). See text for a more detailed discussion.

The temperature dependence of the optical conductivity of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> and the effect of oxygen isotope, rare earth and Zn substitution thereon are displayed in Fig. 5.11. In the spectrum of the oxygen isotope substituted sample shown in panel (b) the background conductivity is larger than in the other cases. Note that panel (b) is the only one which does not extend down to zero conductivity. This background causes the broad feature centered around 1400  $\rm cm^{-1}$  at low temperatures, which will be discussed in connection with doping in chapter 7. Possibly, the background is also responsible for other differences in the line shape. However, the peak frequency of the bimagnon-plus-phonon resonance is not influenced by these low values of the background (see chapter 7). For a quantitative analysis we used the following fitting procedure: first, the theoretical bimagnon-plus-phonon line shape (see dashed line in upper panel of Fig. 5.4 and below) has been fitted using a Lorentzian for the main peak and a broad Gaussian for the tail of the theoretical curve up to the twomagnon cut-off. For the fits of the experimental spectra at *finite* temperatures, for which the precise theoretical line shape is unknown, the difference in frequency of the Lorentzian and the Gaussian was kept roughly constant. Also the width of the Gaussian, which mainly mimics the two-magnon cut-off, was assumed to be constant. The experimentally observed high frequency peaks which deviate from the theoretical prediction were fitted by additional Lorentzian oscillators. The spikes on top of the main resonance of the sample grown in  $BaZrO_3$  (see Fig. 5.1) and the other sharp features have not yet been identified. A relation to bimagnon-plus-phonon absorption is unlikely, as their position is identical in the rare earth substituted samples (see chapter 6 for a more detailed discussion). We fitted these sharp structures separately. The main parameters for  $YBa_2Cu_3^{16}O_6$  are given in Fig. 5.12. The full circles refer to data of the sample grown in a BaZrO<sub>3</sub> crucible displayed in Fig. 5.1, the open symbols depict a sample grown in a  $ZrO_2$  crucible (panel (a) in Fig. 5.11). The strong temperature dependence of the bimagnon-plus-phonon peak frequency (left panel of Fig. 5.12) is most likely due to the reduction of spin stiffness with increasing temperature. For comparison we included the temperature dependence of the in-plane Cu-O stretching phonon mode (full squares), which shows by far the strongest softening of all infrared active phonons (see Fig. 4.5). The reduced width  $\gamma$  of the bimagnon-plus-phonon resonance in the cleaner sample grown in a  $BaZrO_3$  crucible possibly reflects the not negligible influence of impurity scattering on the line shape, which we already discussed above in the cases of Zn substitution and disorder on the Y site.

Most remarkable is the strong increase by more than a factor of two of the spectral weight around  $3800 \text{ cm}^{-1}$  with increasing temperature (right panel of Fig. 5.12), although the spectral weight of the lower bimagnon-plus-phonon resonance stays more or less constant. A qualitatively similar behavior can be detected in the temperature dependence of  $\sigma(\omega)$  of Sr<sub>2</sub>CuO<sub>2</sub>Cl<sub>2</sub> [227, 434]. We consider this high frequency weight and in particular its temperature dependence as a central issue for the correct microscopical description of the mid-infrared data. Therefore we discuss the experimental data concerning this point in more detail. In Fig. 5.13 we compare the fit results for the resonance frequencies and oscillator strengths of three different samples (open (full) symbols: YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> grown in ZrO<sub>2</sub> (BaZrO<sub>3</sub>); grey symbols: Gd<sub>0.8</sub>Y<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>). In each case four oscillators have been used in the considered frequency range: the circles denote the Lorentzian ( $\approx 2800 \text{ cm}^{-1}$ ) and





Figure 5.14: Mid-infrared absorption in  $La_2 CuO_4$  as reported by Perkins and coworkers [227]. Top panel: measured data of the in-plane (" $\sigma$ ") and c-axis (" $\pi$ ") response of two different samples. The distinct polarizations are defined in the sketch, where the dashed axes lie in the  $CuO_2$  plane. Bottom panel: Data after subtracting the linearly increasing background.

Figure 5.15: In samples of  $YBa_2 Cu_3 O_6$ which have been annealed in UHV only a very small background absorption is observed, as indicated by the low value of  $\sigma(\omega)$  at about 8000 cm<sup>-1</sup>. Therefore the strong increase of spectral weight from 4 to 300 K around 4000 cm<sup>-1</sup> has to be attributed to magnetic excitations, not to a background.

Gaussian ( $\approx 3300 \text{ cm}^{-1}$ ) which mimic the theoretical bimagnon-plus-phonon line shape as described above. Two additional Lorentzians have been used at higher frequencies. The existence of *two* independent peaks in this range is most clearly observable in the spectrum of the sample grown in BaZrO<sub>3</sub> depicted in Fig. 5.1. The corresponding oscillator strengths are displayed in the other three panels for each sample independently. In the case of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> sample grown in ZrO<sub>2</sub> this figure reports the data of the above discussed right panel of Fig. 5.12 in more detail: there, the circles (diamonds) correspond to the *sum* of the circles (up and down triangles) of the corresponding panel of Fig. 5.13. In all three samples the spectral weight of the main bimagnon-plus-phonon resonance (sum of the circles) is more or less independent of temperature. The only exception is at 485 K in the Gd sample. At this temperature all contributions have broadened that much that a reliable distinction between peaks is not possible any more. Furthermore, all three samples show the dramatic increase by more than a factor of two of the high frequency spectral weight between 4 and 300 K. The data disagree on other details such as the absolute value of spectral weight at high frequencies. Since a *unique* distinction between the two high frequency contributions is not always possible, the data also disagree on the distribution of spectral weight into the two different high frequency contributions and the temperature dependence of the peak positions at high frequencies. These discrepancies reveal the rather large experimental uncertainties of the quantitative analysis, but the central issue, the strong increase of high frequency spectral weight with increasing temperature is nevertheless firmly established. As far as the absolute value of spectral weight is concerned it is important to note that it is common use in the literature [226-228, 430] to subtract a linearly increasing background from the measured data. Perkins and collaborators [226, 227] motivate this subtraction with the form of the c-axis spectrum (see  $\pi$  polarization in upper panel of Fig. 5.14; the spectra with background subtracted are shown in the lower panel). We do not follow this procedure. In particular in the spectra of samples annealed in ultra high vacuum (see Fig. 5.3) no such background is present in our data. Therefore, the above discussed increase of spectral weight with increasing temperature cannot be attributed to a background (see Fig. 5.15). For a discussion of the dependence of the spectral weight on the doping level we refer the reader to chapter 7.

Before addressing the microscopic theory, we complete the discussion of experimental data with a plot of the temperature dependence of the onset of charge transfer absorption (see Fig. 5.16) of two different samples of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> annealed in ultra high vacuum. Both data sets agree very well with each other. The inset shows the temperature dependence of  $\omega_{CT}$ , which has been defined for this purpose as  $\sigma(\omega_{CT}) = 4\Omega^{-1}$ cm<sup>-1</sup>. A 10% change is observed between 4 and 300 K. This shift is much larger both in absolute and relative units than the shifts of the magnetic excitations discussed above.

For a more detailed comparison of theory and experiment we have to extend the bimagnon-plus-phonon theory to the bilayer case.<sup>‡</sup> In order to obtain the coupling to light we start from a Heisenberg Hamiltonian which takes into account a dependence of the in- and inter-plane exchange constants J and  $J_{12}$  on the external electric field  $\mathbf{E}$  and the phonon coordinates:

$$H = \sum_{L=1,2} \sum_{\langle i,j \rangle} J(\mathbf{E}, \mathbf{u}) \, \mathbf{S}_{L,i} \cdot \mathbf{S}_{L,j} + \sum_{i} J_{12}(\mathbf{E}, \mathbf{u}) \, \mathbf{S}_{1,i} \cdot \mathbf{S}_{2,i}$$
(5.1)

where i and j label nearest neighbor Cu sites in a 2D square lattice, L labels the two planes in a single bilayer, and **u** denotes the displacements of O ions. Only Einstein phonons are considered. The different phonons modulate the exchange coupling constants via modulations of the intersite hopping t and of the on-site energies on both Cu and O sites. The site energies additionally contain the coupling to the electric field. These modulations produce contributions to J and  $J_{12}$  which are proportional to the electric field

<sup>&</sup>lt;sup>‡</sup>This calculation has been performed by T. Nunner and T. Kopp, details will be published elsewhere [426].



Figure 5.16: Temperature dependence of the onset of charge transfer absorption in two different samples of  $YBa_2 Cu_3 O_6$  (open and full symbols; both annealed in UHV). A 10% change is observed between 4 and 300 K.

 $\mathbf{E}_{ab}$  (polarized in the CuO<sub>2</sub> plane), and they give rise to the actual coupling term

$$H_1 = \sum q_{eff} \mathbf{E}_{ab} \cdot \mathbf{u} \mathbf{S} \cdot \mathbf{S} = \sum \mathbf{E}_{ab} \mathbf{P}_{S \cdot S} \quad , \qquad (5.2)$$

where  $\mathbf{P}_{S \cdot S}$  is a spin-dependent dipole moment,  $q_{eff}$  denotes an effective charge and  $\mathbf{u}$ a phonon displacement. A more detailed analytic discussion of the modulations and of the coupling term is given in Appendix 5B. In the bimagnon-plus-phonon treatment of Lorenzana and Sawatzky [224] modulations are taken into account to first order in  $\mathbf{E}_{ab}$  and **u**, as indicated in Eq. 5.2. Phonons and magnons are decoupled and treated independently. The effect of the phonons can then be summarized in the following points: (a) the magnetic excitations gain a finite oscillator strength in the form of magneto-elastic absorption; (b) the energy scale of the latter is shifted by  $\hbar \omega_{phonon}$  with respect to the pure magnetic excitations (assuming a k-independent Einstein mode), but the line shape is not affected; (c) the phonon provides the momentum  $k_{ph}$ , which compensates the bimagnon momentum  $k_{bim} = -k_{ph}$  for the infrared absorption process. Therefore the bimagnon response has to be calculated throughout the entire Brillouin zone. Here, we take the modulations into account to second order since we also included *multiple* phonon-bimagnon scattering processes in a refined approach (see below). Multiple phonon-bimagnon scattering describes the interactions between magnons and phonons, *i.e.*, the two kinds of elementary excitations are coupled (see Fig. 5.19 for the relevant diagrams).

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Figure 5.17: Left panel: calculated two-magnon Raman and infrared bimagnon frequencies as a function of  $J_{12}/J$ . To the latter the phonon frequency has to be added for comparison with experimental data. Right panel: the two experimentally measured parameters (twomagnon Raman and infrared bimagnon-plus-phonon peak positions in YBa<sub>2</sub> Cu<sub>3</sub> O<sub>6</sub>) are not sufficient to determine the three unknown parameters J,  $J_{12}/J$  and  $\omega_{ph}$ . If one of the parameters is given, the two others can be determined from this plot [225, 426].



Figure 5.18: Calculated optical conductivity spectrum of bimagnon-plus-phonon excitations in a bilayer with parameters as indicated in the figure for different values of the magnonphonon coupling constant  $\lambda_{p2m}$  [426]. Circles: inter-layer contribution for  $\lambda_{p2m} = 0$ . All other curves depict the in-plane contribution. Filled area: zero coupling result. A repulsive magnon-phonon coupling ( $\lambda_{p2m} < 0$ ) shifts spectral weight to higher frequencies.



Figure 5.19: Relevant diagrams of phonon-bimagnon scattering. Zig-zag lines: photons; wiggly lines: phonons; thin solid lines: magnons; thick solid lines: bimagnons. (a) Diagram describing the coupling of light to bimagnon-plus-phonons. Magnon-phonon coupling is taken into account via the multiple phonon-bimagnon scattering processes defined in (b). (c) Magnon-magnon scattering diagrams which define a bimagnon.

First we use the experimentally observed bimagnon-plus-phonon peak position (2795 cm<sup>-1</sup> at T = 4 K) and the two-magnon Raman result (2720 ±10 cm<sup>-1</sup> at T = 4 K [202]), both for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>, for the determination of the model parameters. Both the Raman and infrared bimagnon peak frequencies were calculated as a function of  $J_{12}/J$  (left panel of Fig. 5.17; the Oguchi correction has been included). In the infrared case, the phonon frequency  $\hbar\omega_{ph}$  still has to be added. The two experimentally measured parameters are not sufficient to determine the three parameters J,  $J_{12}/J$  and  $\hbar\omega_{ph}$ . If one of the unknown parameters is given, the two others can be determined from the right panel of Fig. 5.17, in which the values of J and  $\hbar\omega_{ph}$  are given as a function of  $J_{12}/J$ . A LDA+U study [440] predicts  $J_{12} = 160$  cm<sup>-1</sup>. Neutron scattering suggests  $J_{12}/J = 0.1 - 0.15$  [115, 116] and  $\hbar\omega_{ph} \approx 550 - 600$  cm<sup>-1</sup> [373] for the relevant longitudinal stretching phonon mode. We hence obtain  $J = 790 \pm 10$  cm<sup>-1</sup> and  $J_{12}/J = 0.08 \pm 0.04$ . However, taking into account a finite next-nearest neighbor coupling J' will shift the values of J and  $J_{12}$  considerably [153].

The calculated optical conductivity spectrum of bimagnon-plus-phonon excitations in a bilayer material with  $J = 780 \text{ cm}^{-1}$ ,  $J_{12}/J = 0.1$  and  $\hbar \omega_{ph} = 530 \text{ cm}^{-1}$  are shown in Fig. 5.18 (momentum-resolved curves are displayed in Fig. 5.20). The bimagnon-plus-phonon line shape depends on the value of the dimensionless magnon-phonon coupling constant  $\lambda_{p2m}$  for multiple phonon-bimagnon scattering (see Fig. 5.19), which is defined as

$$\lambda_{p2m} = \frac{1}{2J} \langle \frac{d^2 J}{du^2} \rangle \langle u^2 \rangle \quad . \tag{5.3}$$

This is very similar to the purely magnetic response, where the line shape depends on the magnon-magnon interaction, *i.e.*, on the value of the spin (see Fig. 5.6). In a bilayer one has to distinguish two contributions to  $\sigma(\omega)$ : a photon can flip two spins (i) in the same layer (lines; in-plane contribution) or (ii) in adjacent layers (circles; inter-plane contribution for



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Figure 5.20: Solid lines: momentum-resolved contributions to the bimagnon spectrum for momenta from (0,0) (thick lines) to  $(\pi, 0)$  and from (0,0) to  $(\pi, \pi)$  [426]. Circles: momentum-integrated spectra with structure factors as appropriate for the in-plane Cu-O bond stretching phonon. The bottom scale uses units of the k=0 value of the optical magnon branch,  $E_{op} = 4S\sqrt{\tilde{J}\tilde{J}_12}$ ; the top scale gives values in terms of  $\tilde{J}$  (the tilde indicates  $\tilde{J} = Z_c J$ , where  $Z_c$  denotes the Oguchi correction). Here,  $\lambda_{p2m}$  is assumed to be zero. Offsets have been added for clarity.



Figure 5.21: The small damping necessary for the numerical evaluation [426] is further reduced in this plot, which reveals that a bound state is formed in the inter-plane contribution just below the step-like onset of absorption at  $2E_{op}$ . Note the extremely blown up energy scale. For larger values of damping the bound state overlaps with the continuum and decays into a resonance.

 $\lambda_{p2m} = 0$ ). For (i) a rough estimate of the binding energy of two magnons in the Ising limit is J for S = 1/2 on a 2D square lattice. This implies that the bimagnon energy at the zone boundary is of order J below the upper cut-off of the two-magnon spectrum, which approximately corresponds to the bimagnon-plus-phonon peak position of the inplane contribution for  $\lambda_{p2m} = 0$  in Fig. 5.18 (filled area). Similarly, the binding energy is  $J_{12}$  for the inter-layer case (ii) which explains why the absolute maximum of the calculated inter-plane conductivity lies just below the two-magnon cut-off. The inter-layer response also includes processes in which magnons switch the CuO<sub>2</sub> layer and form pairs in the same plane, resulting in a small peak which approximately coincides with the maximum of the in-plane contribution. The estimated relative spectral weight of inter- and in-plane coupling constant  $J_{12}$  in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> the spectra are not very different from the single layer results. Therefore the experimentally observed large amount high frequency spectral weight remains a puzzle in the bilayer as well.

Let us compare the calculated and measured oscillator strengths and line shapes of the bimagnon-plus-phonon peak. The calculated bimagnon-plus-phonon absorption for J=780 cm<sup>-1</sup>,  $J_{12}/J = 0.1$  and  $\hbar \omega_{ph} = 530$  cm<sup>-1</sup> is plotted together with the experimental 4 K curve in Fig. 5.22. An offset of  $0.1 \ \Omega^{-1}$ cm<sup>-1</sup> has been used for the calculated curves. The perturbatively estimated spectral weight is a factor of 4-7 too small compared to experiment [426] (for  $\lambda_{p2m}=0$ ). The deviation is somewhat larger than given in Ref. [224], since a realistic estimate of  $q_{eff}/e \approx -6JU_{pd}/\Delta^2$  (where e is the electron charge and  $q_{eff}$  is the spin-dependent effective charge of Eq. 5.2; see Appendix 5B and Ref. [224]) yields  $q_{eff}/e \approx -0.025 \cdots -0.08$  for both La<sub>2</sub>CuO<sub>4</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>, whereas  $q_{eff}/e \approx -0.1$  was assumed in Ref. [224]. Within the given uncertainties, this result is nevertheless corroborating the bimagnon-plus-phonon interpretation.

Regarding the line shape the calculated curve is sharper than the experimental one, but

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Figure 5.22: Solid line:  $\sigma(\omega)$  of  $YBa_2 Cu_3 O_6$  at 4 K. Circles: calculated in-plane bimagnonplus-phonon spectrum for  $J = 780 \text{ cm}^{-1}$ ,  $J_{12}/J = 0.1$ ; full circles: contribution of the inplane Cu-O stretching phonon for the theoretical case of a coupling constant of  $\lambda_{p2m} = -0.2$ ; open circles: contribution of the apical stretching phonon mode, for which  $\lambda_{p2m} = 0$ ; grey circles: sum of the two [225, 426].

the width of the bimagnon-plus-phonon peak is sample dependent, as stated above. As in the single layer cuprates, the real problem is obviously at higher frequencies: the strong peak at 3800 cm<sup>-1</sup> remains unexplained. It is likely that the high energy anomaly has the same origin in mid-infrared and Raman spectra. This is substantiated by the absence of the anomaly in both spectroscopies in  $S = 1 \text{ La}_2\text{NiO}_4$  [204, 228]. In several cuprates, the frequency ratio of the two dominant mid-infrared peaks is about 0.73 (see Table 5.2), strongly suggesting a common magnetic origin. In other terms, the second peak in both single and bilayers is close to the two-magnon cut-off. It is possible to shift spectral weight towards the two-magnon cut-off by considering a repulsive phonon-bimagnon interaction, which translates into a negative value of  $\lambda_{p2m}$ . Large negative values of  $\lambda_{p2m}$  produce a distinct second peak close to the two-magnon cut-off (see Fig. 5.18). For even larger coupling strengths a sharp anti-bound state is formed beyond the two-magnon cut-off. The sharpness of this anti-bound state and the abrupt edge at the two-magnon cut-off are, to a certain degree, artefacts of the calculation which will be removed by considering also higher multi-magnon contributions.

From Harrison's  $t_{pd}(u) \approx t \cdot (1+u/a_{pd})^{7/2}$  [441] and modulations of the on-site potentials we estimate the coupling constant to be  $\lambda_{p2m} \approx -0.02 \cdots + 0.01$  for the planar Cu-O stretching phonon mode (see Appendix 5B). A way to test the reliability of our estimate of  $\lambda_{p2m}$  is to compare the *linear* coupling dJ/du with the experimental pressure dependence

	peak A	peak B	A/B	two-magnon cut-off
$egin{array}{c} YBa_2Cu_3O_6\ La_2CuO_4\ Sr_2CuO_2Cl_2 \end{array}$	$2800 \\ 3300^* \\ 2900^*$	$3800 \\ 4500^* \\ 4000^*$	$0.74 \\ 0.73 \\ 0.73$	3700 = 4.72J 4500 = 4.63J 4000 = 4.63J

Table 5.2: Measured frequencies of the two main mid-infrared absorption peaks, their ratio, and the two-magnon cut-off (all frequencies in  $cm^{-1}$ ). \* taken from Ref. [226].

of J [442]. There, our estimate is 1-2 times smaller. However, an excellent fit to our infrared data (grey symbols in Fig. 5.22) is obtained only if we assume  $\lambda_{p2m} = -0.2$  for the in-plane stretching phonon (black circles) and add the bimagnon-plus-phonon contribution of the apical stretching phonon. The apical contribution is expected to have a 5 times smaller weight and a negligible phonon-bimagnon coupling (open circles). This large value of  $\lambda_{p2m}$  required to obtain a good fit makes such a scenario very unlikely. Phonon-magnon scattering processes have also been considered for the explanation of the width of the two-magnon Raman resonance [209-215, 219] (see discussion on page 45). Contrary to our dynamic treatment, most approaches simply enhance the width of the main peak, e.q., by considering magnon damping by phonons or by modelling static disorder. This does not result in a second resonance. However, Lee and Min [214] reported a shoulder at the experimentally observed second peak position of 4J, if the magnon-phonon interaction in the form of an effective magnon-magnon scattering through virtual phonons is taken into account explicitly. We conclude that phonon-magnon interaction processes cannot explain the magnetic mid-infrared and Raman anomalies, if a reasonable value of the phononmagnon coupling strength is used.

A severe constraint for any interpretation of the high frequency spectral weight is the observed increase of the oscillator strength by a factor of more than two from 4 to 300 K (see Figs. 5.12 and 5.13). We propose that these findings support the notion of a strong local deviation from the Néel state which is even more pronounced at 300 K. Whereas the broken symmetry of the antiferromagnetic state will still support long wavelength spin-wave excitations, the character of the short wavelength magnetic excitations reflects the strong quantum fluctuations and consequently they are insufficiently represented by spin-waves. Both Raman and mid-infrared spectra are dominated by short wavelength magnetic excitations which makes their evaluation within spin-wave theory less reliable. We emphasize that this interpretation does not contradict the good agreement of neutron scattering results with spin-wave theory for small momenta (see discussion on page 40). Note that even in 1D the inapplicability of a spin-wave picture to neutron data was not realized for many years [200].

Exact diagonalization should serve to identify the weight of magnetic excitations. However, only clusters of up to  $\sqrt{20} \times \sqrt{20}$  were investigated and produced a minor contribution to mid-infrared absorption at high frequencies [443]. Since this cluster size is still comparable to the size of the considered high frequency excitations, a finite size scaling analysis would be a serious test whether the Heisenberg model or an extension in the form of a cyclic four-spin exchange term [216–219] of it can generate the measured high frequency weight. A study of the infrared absorption using other techniques such as series expansion or quantum Monte Carlo would be very valuable.

In the absence of doping, the only alternative to a magnetic origin of the anomaly are excitons. Perkins and co-workers [226] originally suggested that the main peak has to be attributed to a localized transition in the open d shell, a ligand field d-d exciton. The spectral weight at higher frequencies was explained as due to magnon and/or phonon sidebands of the exciton absorption peak. After the bimagnon-plus-phonon explanation of Lorenzana and Sawatzky [224] and after measuring  $La_2NiO_4$ , Perkins and collaborators insisted on an excitonic absorption band in the cuprates, which they now identified with the puzzling high frequency peak at about 4000 cm<sup>-1</sup> [227, 228]. Already in 1988 the observation of a d-d transition was claimed at about 5000 cm<sup>-1</sup> in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> by Geserich and collaborators [453]. An excitonic state at such low frequency would be of major importance for the physical properties of the cuprates. In the ground state, the hole is in a  $d_{x^2-y^2}$  state, which for the given symmetry allows for three distinct local d-dexcitations to the  $d_{3z^2-r^2}$ , the  $d_{xy}$  and the degenerate  $d_{xz}$  and  $d_{yz}$  orbitals. The  $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$  states belong to the  $e_q$  manifold, and the other three states form the  $t_{2q}$  one. The crystal-field d-d excitations are optically forbidden, but one may expect that they gain a finite oscillator strength by coupling to phonons, which lift the inversion symmetry at the Cu site. Semi-empirical [444] and *ab initio* [445–447] cluster calculations predict all d-d excitations between 0.64 and 2.3 eV in the cuprates<sup>§</sup> (see Table 5.3). Due to the very localized nature of the d-d excitations a cluster approach is a reasonable choice. This is emphasized by de Graaf [446], who calculated the local transitions within the open d shell of NiO, CoO,  $La_2CuO_4$  and  $La_2NiO_4$ . We reproduce a comparison with the experimental results of Perkins and co-workers [228] for the case of  $La_2NiO_4$  in Table 5.5. The typical accuracy is about 0.15 eV [446]. A similar accuracy has been obtained in the case of the insulating cuprates, for which the following experimental results were reported (see also Table 5.4: in Raman scattering experiments [448, 449] the  $d_{x^2-y^2} \rightarrow d_{xy}$  transition has been observed at about 1.5 eV (1.7) in  $Gd_2CuO_4$  (La<sub>2</sub>CuO<sub>4</sub>). Electric-field induced transitions at 1.4 and 1.6 eV which were observed in electroreflectance measurements of  $La_2CuO_4$  [450] have been attributed to the  $d_{x^2-y^2} \rightarrow d_{xy}$  and  $d_{x^2-y^2} \rightarrow d_{xz}$ ,  $d_{yz}$  excitons. Recently, Kuiper and co-workers [452] studied the x-ray Raman spectrum of  $Sr_2CuO_2Cl_2$  and reported the transitions to the  $d_{xy}$  and  $d_{xz,yz}$  states at 1.35 and 1.8 eV, respectively. They also deduced an energy of 1.6 eV for the  $d_{x^2-y^2} \rightarrow d_{3z^2-r^2}$  excitation from the data. Before the work of Kuiper and collaborators, the transition to the  $d_{3z^2-r^2}$  orbital had not been observed in the above mentioned experiments, which motivated Perkins and collaborators to identify it with the absorption band at about 0.5 eV. Note that the spread in the theoretical

<sup>&</sup>lt;sup>§</sup>We apologize for shifting from units of  $cm^{-1}$  used by spectroscopists to units of eV commonly used in the discussion of electronic parameters. Note that  $1 eV \approx 8065 cm^{-1}$ .

Cuprates		Eskes $[444]$	Martin [445]		de Graaf $[446]$		Grant $[447]$	
		semi-empir.	SCF	CI1	CI2	CASSCF	CASSPT2	$\operatorname{CI}$
$d_{3z^2 - r^2}$	$(A_{1g})$	1.3	1.64	1.82	1.89	0.99	0.85	0.64
$d_{xy}$	$(B_{2g})$	1.4	1.54	1.74	1.82	1.26	1.31	
$d_{xz}, d_{yz}$	$(E_g)$	1.5	1.98	2.20	2.28	1.55	1.60	

Table 5.3: Theoretical predictions of the optically forbidden d-d transitions in the cuprates based on cluster calculations. SCF: self-consistent field; CI: configuration interaction; CASSCF: complete active space self-consistent field; CASSPT2: complete active space second-order perturbation theory. All values are given in eV.

Cuprates	Liu [448, 449]		Falck [450]	Falck [451]	Kuiper [452]
	Raman		electroreflect.	reflectivity	x-ray Raman
	$La_2CuO_4$	$\mathrm{YBCO}_{6.1}$	$\rm La_2CuO_4$	${ m La_2CuO_4}$	$\mathrm{Sr}_2\mathrm{CuO}_2\mathrm{Cl}_2$
$ \begin{array}{c} d_{3z^2-r^2} & (A_{1g}) \\ d_{xy} & (B_{2g}) \\ d_{xz},  d_{yz} & (E_g) \\ \text{unspecified} \end{array} $	1.7	1.55	$\begin{array}{c} 1.4 \\ 1.6 \end{array}$	1.75	$1.6 \\ 1.35 \\ 1.8$

Table 5.4: Experimental values of the ligand field d-d transitions in the insulating cuprates. Differences between the various compounds reflect the dependence on the Cu-O bond length [449]. Raman results for other rare earth ions in  $RE_2 CuO_4$  can be found in Ref. [449]. All values are given in eV.

$\mathbf{La}_{2}\mathbf{NiO}_{4}$	de Graaf [446]		Perkins [228]		Ni/Cu	Ni/Cu
	CASSCF	CASSPT2	optics		to	to
					$O_{\text{plane}}$	$O_{apex}$
$a^3 E_g$	1.00	1.07	1.05			
$a^3B_{2g}$	1.26	1.21	1.25			
$b^3B_{2g}$	1.73	1.50	1.60	${ m La_2NiO_4}$	1.93	2.26
$b^3 E_g$	2.06	1.77	1.75	$\rm La_2CuO_4$	1.91	2.40

Table 5.5: Theoretical and experimental values of some of the ligand field d-d transitions in  $La_2NiO_4$ . All values are given in eV. CASSCF, CASSPT2: see Table 5.3.

Table 5.6: Structural parameters of  $La_2NiO_4$  and  $La_2CuO_4$ . All values given in units of Å.

predictions is largest for this  $d_{x^2-y^2} \rightarrow d_{3z^2-r^2}$  excitation. Perkins and collaborators [227] point out that the experimentally observed anisotropies of the gyromagnetic Landé factor  $g_L$  and of the Van Vleck susceptibility are consistent with values of about 1.5 eV for the  $d_{x^2-y^2} \rightarrow d_{xy}$  and  $d_{x^2-y^2} \rightarrow d_{xz}$ ,  $d_{yz}$  excitations. These anisotropies do in principle not restrict the value of the  $d_{x^2-y^2} \rightarrow d_{3z^2-r^2}$  transition [454]. However, de Graaf points out that the similarities in local geometries and transition metal to oxygen distances between NiO, CoO,  $La_2NiO_4$  and  $La_2CuO_4$  (see Table 5.6) do not reveal any reason for an excitation energy as low as 0.5 eV in the cuprates, *i.e.*, more than 0.5 eV lower than in the other compounds mentioned [446]. In fact, the distance from the transition metal ion to the planar oxygen ions is smaller and the one to the apical oxygen is larger in  $La_2CuO_4$  as compared to La<sub>2</sub>NiO<sub>4</sub> (see Table 5.6), which both *increase* the  $d_{x^2-y^2} - d_{3z^2-r^2}$  splitting. Kuiper and collaborators [452] also argue against a low lying excitonic excitation by pointing out that the splitting of the  $e_q$  states should be at least 2 or 3 times larger than the one of the  $t_{2q}$ manifold in  $d_{xy}$  and  $d_{xz,yz}$ , which they observe to be about 0.45 eV. They claim that the  $d_{3z^2-r^2}$  level lies at 1.6 eV, which they can only derive indirectly from their data, since in their x-ray Raman experiment it is shifted upward by a further 0.2 eV by a spin flip excitation and therefore coincides with the  $d_{xz,yz}$  peak in the spectrum [452]. Note that the interpretation of Kuiper and co-workers is supported by the calculations of Martin and Hay [445], who also report the  $d_{3z^2-r^2}$  state to be higher in energy than the  $d_{xy}$  level. They explain the near degeneracy of  $d_{3z^2-r^2}$  and  $d_{xy}$  by the Jahn-Teller distortion, *i.e.*, the compression of the planar Cu-O bonds and the elongation of the apical bond. This distortion shifts the  $d_{3z^2-r^2}$  orbital to higher and the  $d_{xy}$  orbital to lower energies (in hole notation), and the amplitude of the distortion is large enough to compensate the original  $e_q - t_{2q}$  splitting [445]. We conclude that there is no theoretical justification for the assumption of a d-d excitation as low as 0.5 eV.

Wang et al. [432] predict a charge transfer exciton at 0.8 eV ( $6500 \text{ cm}^{-1}$ ) from fits to electron energy loss spectroscopy (EELS) data between 2.5 and 4 eV. We consider the Coulomb attraction necessary to pull this exciton down to 3800 cm<sup>-1</sup> (0.47 eV) – far below the charge transfer gap – as unrealistically large (see also Refs. [455] and [456] for a theoretical discussion of exciton energies). Furthermore, a charge transfer exciton should follow the strong redshift of the onset of charge transfer absorption with increasing temperature (11300 to 10200 cm<sup>-1</sup>, see Fig. 5.16), which is not observed.

Both exciton models fail to describe the strong increase of spectral weight with temperature. Hence the exciton interpretation is an unlikely scenario for the considered resonance (see also chapter 6 for a discussion of exciton energies).

Our initial idea involved direct excitation of two magnons in bilayers via spin-orbit coupling [114] to reproduce the mid-infrared line shape in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> up to 4000 cm<sup>-1</sup>. However, a spin exchange of  $J_{12} \approx 0.5J$  had to be assumed, which is not anymore consistent with neutron scattering results [115, 116]. This scenario is described in more detail in Appendix 5A.

We conclude that present day understanding of magnetic excitations in undoped cuprates is not sufficient to explain both mid-infrared and Raman data. The appearance of a large amount of spectral weight at high frequencies in the infrared spectrum agrees with the conclusion on page 47 that taking into account resonance phenomena is necessary but not sufficient to fully describe the Raman data of the insulating cuprates. Only a more appropriate treatment of the short wavelength excitations will explain the anomalies observed with both spectroscopies. We are convinced that an understanding of the short wavelength magnetic excitations will also be of central importance for the description of the ARPES line shape observed in insulating and underdoped cuprates (see discussion in section 2.2.3, in particular on page 53 and thereafter). Tendencies to spin-charge separation in the cuprates at least on short length or time scales have been discussed in the literature (see section 2.2.3). A decay of magnons in spinons on short time or length scales might very well explain the width, and the "internal" excitations of a composite "spin wave" possibly could be the origin of the high frequency spectral weight. We are convinced that this is *not* at variance with the well defined magnon peak observed in inelastic neutron scattering at the Brillouin zone boundary, since the full line shape cannot be determined from the data, and an asymmetry or a "tail" of the peak can definitely not be excluded at this stage [266]. We emphasize that the considered "short-length-scale" deviations from conventional spin waves do not contradict the good agreement obtained between the 2D Heisenberg model and long-wavelength quantities such as the correlation length.

# Appendix 5A The Initial Idea: Direct Magnon Absorption

Over the years, our understanding of the mid-infrared absorption spectrum of the insulating cuprates has evolved in several stages, connected to experimental and theoretical progress. This appendix is devoted to the description of our initial idea and starting point for the microscopic interpretation: the direct absorption of magnons [114]. Although this interpretation has been proven wrong for the cuprates by other experimental results, in particular neutron scattering [115, 116], we still consider it worth an appendix. Moreover, the misleadingly good agreement achieved between the experimental spectrum and the calculated magnon absorption curve is instructive by reminding us how difficult it is to decide about the correct microscopic model in a complex physical system. In the second part we describe an experimental test of our interpretation which was performed in high magnetic fields [401].

## 5A.1 Single and Two-Magnon Absorption

Our first measurements [457] of the mid-infrared absorption of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> date back to early 1993, *i.e.*, prior to the publication of the single layer data by Perkins and co-workers in September of 1993 [226] and the bimagnon-plus-phonon interpretation of Lorenzana and Sawatzky published in March 1995 [224]. At that time, the optical magnon branch of the bilayer YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> had not been observed yet in neutron scattering experiments, and the latest lower bound for the zone center optical magnon gap equaled 480 cm<sup>-1</sup> [458,459], suggesting a bilayer coupling of  $J_{12} \gtrsim 65$  cm<sup>-1</sup>. No further information was available on the

inter-layer exchange constant  $J_{12}$ , whereas values of the in-plane exchange constant J as large as  $840 \pm 140 \text{ cm}^{-1}$  [458] and  $1200 \text{ cm}^{-1}$  [460] had been reported (both for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.15</sub>; the Oguchi quantum corrections are included). From the frequency range of the dominant mid-infrared absorption we concluded a magnetic origin. Our attention was attracted by the peculiar sharp line at  $1436 \text{ cm}^{-1}$  observed in the transmission spectrum (see Fig. 5.2). The frequency of this feature is too high to be attributed to two-phonon excitations, which are relevant below  $1350 \text{ cm}^{-1}$  (see chapter 6 for a more detailed discussion). We noticed that this line was at about half the frequency of the main peak at  $2795 \text{ cm}^{-1}$ and therefore interpreted the sharp line as due to the excitation of *single* magnons of the optical branch, *i.e.*,  $E_{op} = 1436$  cm<sup>-1</sup> (see Fig. 5.23). The two stronger bands at 2795 cm<sup>-1</sup> ( $E_{2a} \approx 1.946 E_{op}$ ) and 3800 cm<sup>-1</sup> ( $E_{2b} \approx 2.6 E_{op}$ ) both were assumed to belong to the two-magnon spectrum. The broad high energy tail of the spectrum was ascribed to higher multi-magnon excitations. In this scenario, good agreement between linear spin wave theory and the measured spectrum was achieved for  $J = 970 \text{ cm}^{-1}$  and  $J_{12} \approx 0.5 J$ . The coupling  $J_{12}$  between spins on adjacent planes of a bilayer is an important parameter since a sizable value of it would influence the spin excitation spectrum as well as the nature of the ground state (see section 2.2). For  $YBa_2Cu_3O_{6.6}$  a singlet pairing of spins in adjacent  $CuO_2$  planes with strong antiferromagnetic fluctuations within a plane had been proposed [106, 461, 462]. Such a scenario seems to require an unrealistically large  $J_{12} \gtrsim 2.5J$  [162]. However it was argued that, for finite doping, the itinerant carriers destroy the antiferromagnetism of the insulating phase and, therefore, much smaller values of  $J_{12}$  will produce a singlet interplane pairing in the conducting phase of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub>.

In order to interpret the assumed magnon spectrum displayed in Fig. 5.23, we used spin wave theory including magnon-magnon interactions up to O(1/S) to gain the excitation spectrum of localized spins on a bilayered square lattice.<sup>¶</sup> A Heisenberg Hamiltonian accounts for these low energy excitations for zero doping:

$$H = J \sum_{a=1,2} \sum_{\langle i,j \rangle} \mathbf{S}_{a,i} \mathbf{S}_{a,j} + J_{12} \sum_{i} \mathbf{S}_{1,i} \mathbf{S}_{2,i}$$
(5.4)

where *i* and *j* label nearest neighbor sites in a two-dimensional square lattice and  $a \in \{1, 2\}$  labels the two different planes in a single bilayer. Each bond is counted once. Spin-orbit effects are relatively small [131] and were neglected in Eq. (5.4). However, a finite spin-orbit coupling is needed to couple the external electric field to a single magnon. In this case, the allowed processes involve a dipole transition to the oxygen *p*-orbitals and a spin-orbit interaction on the Cu sites, which finally flips the spin. Spin-orbit coupling in combination with the buckling of the CuO<sub>2</sub> layers is furthermore necessary in order to make direct two-magnon absorption possible for the considered crystal symmetry [463]. The two-magnon absorption was calculated with a coupling Hamiltonian of the form

$$H_1 = D \sum_{a,b} \sum_{\langle i,j \rangle} \mathbf{E} \cdot \left[ (\mathbf{S}_{a,i} \times \mathbf{S}_{b,j}) \times \boldsymbol{\pi}_{a,i;b,j} \right]$$
(5.5)

<sup>&</sup>lt;sup>¶</sup>This calculation was performed by T. Kopp [114].



Figure 5.23: Thin black line: Optical conductivity for  $\mathbf{k} \parallel c$ ; thick grey line: Linear spinwave result for T = 0 fitted to the experimental two-magnon absorption for  $\tilde{J}_{12}/\tilde{J} = 0.58$ and a two-magnon decay rate of  $0.09E_{op}$ . Inset: Peak positions of the lower ( $E_{2a}$ ; thick line) and upper ( $E_{2b}$ ; thin line) two-magnon resonances in units of  $E_{op}$  for negligible broadening. Arrows indicate the experimental values. The tilde indicates  $\tilde{J} = Z_c J$ , where  $Z_c$  is the Oguchi correction.

where  $\pi_{a,i;b,j}$  points in the direction of the vector joining the pair  $\langle a, i; b, j \rangle$  and **E** is the electric field vector [464]. This is the only coupling allowed by crystal symmetry for a nearest neighbor two-magnon generation.  $D\pi$  was found from a perturbation series in the nearest neighbor exchange interaction and spin-orbit interaction [463]. Since we restrict ourselves to  $\mathbf{k} \parallel c$ , the two-magnon coupling is proportional to  $E^y \pi_{1,i;2,i}^z \cdot (S_{1,i}^- S_{2,i}^+ - S_{1,i}^+ S_{2,i}^-)$  which creates a singlet pair of magnons on adjacent planes. This type of magnon pair generation is a consequence of the spin alignment in the *xy*-plane in the Néel ground state.

The convoluted density of states of two magnons shows a step at the optical twomagnon edge,  $2E_{\rm op}$ . Similar to the case of the main resonance in a single layer compound, the interaction between two-magnons will reduce the frustration produced by the two spinflips and allow two optical magnons to form nearly bound states or resonances. If such a state is located *below*  $2E_{\rm op}$  it is justified to call it a *bound* state. However, due to some admixture of acoustic magnons the bound state shows up as a resonance. We identified the  $E_{2a}$ -peak at  $1.946E_{\rm op}$  with this resonance. The  $E_{2b}$ -band corresponds to the density of states peak at the upper cut-off. Even for a value of the inter-layer coupling as small as  $J_{12}/J = 0.1$  considered in the main part of this chapter both peaks are pronounced in the *inter-plane* contribution for k = (0,0) (see Fig. 5.20). However, the peak below  $2E_{\rm op}$  is negligible in the in-plane spectrum for such small values of  $J_{12}$ .

The exact positions of both peaks depend upon the ratio  $\tilde{J}_{12}/\tilde{J}$ , as displayed in the inset of Fig. 5.23. The tilde indicates  $\tilde{J} = Z_c J$ , where  $Z_c = 1.143$  is the Oguchi correction in the case of  $J_{12}/J = 0.5$ . For comparison with the experiment we introduced an additional decay rate for the two-magnon excited state of about  $0.09E_{\rm op}$  to gain an optimal fit. Due to this additional broadening we obtain a value of approximately 0.58 for  $\tilde{J}_{12}/\tilde{J}$ , slightly higher than marked in the inset of Fig. 5.23. With  $E_{\rm op} = 1436 \,\mathrm{cm}^{-1}$  we obtain  $\tilde{J} \approx 944 \,\mathrm{cm}^{-1}$  and  $\tilde{J}_{12} \approx 548 \,\mathrm{cm}^{-1}$ , *i.e.*,  $J \approx 826 \,\mathrm{cm}^{-1}$  and  $J_{12} \approx 480 \,\mathrm{cm}^{-1}$ . This was in excellent agreement with a value of  $J_{12} \approx 450 \,\mathrm{cm}^{-1}$  that had been derived in perturbation theory by Barriquand and Sawatzky [465], whereas a LDA+U study by Andersen and collaborators [440] predicted  $J_{12} = 160 \,\mathrm{cm}^{-1}$ . We point out that the two-magnon spectrum is not necessary to determine J and  $J_{12}$ . It is sufficient to know the slope of the acoustic magnon branch from neutron scattering and the position of the one-magnon peak to deduce the value of  $J_{12}$ . In this flow of logic the knowledge of the positions of the  $E_{2a}$ - and  $E_{2b}$ -peaks is not necessary to fix the coupling parameters but they rather seem to confirm the interpretation that both peaks are to be identified with the two-magnon resonance.

With the publication of the single layer data [226] it appeared that the shape of the absorption spectrum was quite similar in monolayer cuprates, and the question arose if the bimagnon-plus-phonon interpretation of Lorenzana and Sawatzky [224] also holds for the bilayer YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>. With the large values of J reported in the literature at that time it seemed that the 2795 cm<sup>-1</sup>  $E_{2a}$ -peak may not be explained as a phonon-assisted bimagnon absorption process because the energy of this resonance is too low for a bimagnon plus the appropriate phonon. We expected an energy of roughly  $2.73 J+J_{12}+\hbar\omega_{ph} \approx (2.73\cdot826+480+600 \text{ cm}^{-1} \approx 3335 \text{ cm}^{-1}$  for this process (for  $J_{12}/J \simeq 0.58$ ) and concluded that bimagnon-plus-phonon absorption might well account for part of the high frequency spectral weight above the main peak.

The scenario of direct absorption of magnons had several attractive points: it gave a clear interpretation of the peculiar sharp feature at 1436 cm<sup>-1</sup> (single optical magnon excitation) and reproduced the two-magnon absorption line shape and both peak positions of the two-magnon curve nicely without any free parameter, with J given from neutron scattering and  $J_{12}$  from 1436 cm<sup>-1</sup> =  $2\sqrt{\tilde{J}\tilde{J}_{12}}$ . Moreover, the obtained value of  $J_{12}$  agreed favorably with the theoretical result of Barriquand and Sawatzky [465]. Nevertheless the model was proven not to apply for the cuprates: in 1996 Reznik and co-workers [115] and Hayden and collaborators [116] reported neutron scattering data of the optical magnon branch in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> with x = 6.2 and 6.15, respectively. There, the gap of the optical mode was determined to be  $540 \pm 40$  and  $600 \pm 40$  cm<sup>-1</sup>, respectively, resulting in  $J_{12}/J \approx 0.1$ .





### 5A.2 Magnetic Field Dependence

In order to test our interpretation of direct magnon absorption and to disentangle the magnetic excitations in the mid-infrared from, *e.g.*, higher order phonon excitations, we performed measurements in high magnetic fields in the High Field Magnet Laboratory of the University of Nijmegen.<sup>||</sup> These experiments were carried out before neutron scattering data of the optical magnon branch were available [115, 116] and also before the isotope substitution measurements described in the main part of this chapter.

The far- and mid-infrared spectrum of antiferromagnetic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> was investigated by infrared transmission measurements ( $\mathbf{k} \parallel c, E \parallel ab$ ) in high magnetic fields up to 16.5 Tesla at T = 1 K. The external magnetic field was applied either parallel or perpendicular to the CuO<sub>2</sub> layers. The peak at 1436 cm<sup>-1</sup> which previously was assigned to the excitation of single optical magnons did not show a measurable shift with magnetic field. In the farinfrared, no signature of acoustic magnon absorption has been observed in the magneto transmittance. These results agree with a study of the mid-infrared magneto transmittance of Y<sub>1-x</sub>Pr<sub>x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> [439].

Measuring the Zeeman splitting in magnetic field should be the ultimate test for a single magnon interpretation. On the other hand, the insulating parent compounds are expected to undergo a transition to a spin-flop phase [466], in which all spins are mainly oriented *perpendicular* to the external field and only canted by a small angle in the direction of the field. In this situation much smaller effects have to be expected. The shift with magnetic field<sup>\*\*</sup> of an hypothetical optical magnon at 1436 cm<sup>-1</sup> in the spin-flop phase is depicted in Fig. 5.24. Note the narrow range of the energy scale. Due to the in-plane/out-of-plane anisotropy of the exchange constant J, the magnon branch is split into two different modes already for zero field. The upper mode contains 70% (30%) of out-of-plane (in-plane)

<sup>&</sup>lt;sup>||</sup>We gratefully acknowledge the experimental support of P.J.M. can Bentum and the hospitality of the High Field Magnet Laboratory.

<sup>\*\*</sup>Calculations of the magnetic field dependence were carried out by T. Kopp [401].

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Figure 5.25: Top panel: calculated transmittance ratios (zero field/16.5 Tesla) in the spinflop phase for coupling to the in-plane (two upper curves) or out-of-plane (lower curves) mode. Bottom panel: dotted line: measured transmittance; other lines: ratios of measured transmittance. In both panels the solid (dashed) lines denote  $B \parallel ab$  (c). The measurements are only reliable outside the hatched area, inside they are dominated by noise due to the very low signal (note the ratio of two measurements at zero field; dashed-dotted line).

character. The solid lines in Fig. 5.24 show the behavior of the modes in an external magnetic field for  $B \parallel ab$ , while the dashed lines are valid for  $B \parallel c$ . The size of the splitting  $\Delta E$  can be obtained from the value of the gapped acoustic mode at  $\mathbf{k} = 0$ , which is known to be  $E_{ac} = 36 \text{ cm}^{-1}$  from neutron scattering [459]. With  $\Delta E = E_{ac}^2/2 * E_{op}$  the splitting turns out to be  $0.45 \text{ cm}^{-1}$ , much too small to be observable due to the line width of about  $8 \text{ cm}^{-1}$ .

Nevertheless one may hope to observe even such a small *shift* in a high magnetic field. The original transmission data around  $E_{op} = 1436 \text{ cm}^{-1}$  at T = 1 K is depicted by the dotted line in the bottom panel of Fig. 5.25. The curves in the top panel of the figure show *calculated* transmittance ratios (zero field/16.5 Tesla) which have been obtained by distributing the measured spectral weight into the two modes (in-plane/out-of-plane) and



Figure 5.26: Ratios of measured transmittance at T = 1 K. The structure at 1436 cm<sup>-1</sup> is a spike as indicated in Fig. 5.25.

shifting them according to Fig. 5.24. The predicted changes are very small for any orientation of the external magnetic field. The upper two curves show the case where the infrared light couples only to the in-plane spin-wave excitations, while the lower two curves are valid for a coupling to out-of-plane excitations. The actual measurements are depicted in the bottom panel of Fig. 5.25. The lowest (dashed-dotted) curve shows the ratio of two different measurements obtained at zero field. It shows that the ratios are only reliable *outside* the frequency range indicated by the hatched area because the measured transmittance in this range — around the absorption maximum — almost goes to zero. Outside the hatched area, the calculated curves (top panel) show only small effects. Nevertheless, in the case of coupling to in-plane (out-of-plane) excitations these should be observed at least for  $B \parallel ab \ (B \parallel c)$ . However, the ratios of the spectra measured at zero field and at 16.5 Tesla (the two upper curves in the bottom panel) do not show any measurable effect of the magnetic field for both orientations of the sample. This result seriously questions the single magnon interpretation.

Transmittance ratios for different orientations and different values of the external field are plotted over a broad frequency range in Fig. 5.26. The finite slope of the curves is due to a field dependence of the detector, which was placed inside the magnet directly behind the sample. We cannot detect any field dependence for  $YBa_2Cu_3O_6$  in the whole frequency range. The spikes at  $1436 \text{ cm}^{-1}$  are due to the very low signal around the peak frequency, as mentioned above.

In neutron scattering experiments on YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> (x = 6.2 and 6.15), the optical magnon branch at k = 0 was observed at 540 ± 40 [115] and 600 ± 40 cm<sup>-1</sup> [116], respectively. In the infrared spectrum, this frequency range is dominated by strong phonon

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Figure 5.27: Ratios of measured transmittance at T = 1 K for  $B \parallel c$ . Due to the strong phonon absorption in this frequency range, the transmitted intensity is very small and the spectra are very noisy. Only data in the window from 450 to  $550 \text{ cm}^{-1}$  may be considered as reliable.



Figure 5.28: Top panel: farinfrared transmittance at T = 4K, dominated by interference fringes. Arrows indicate phonon absorption lines. Inset: Magnetic field dependence of the acoustic magnon modes in the spin-flop phase (Solid lines:  $B \parallel ab$ , dashed line:  $B \parallel c$ ). Bottom panel: ratios of measured transmittance at T = 1 K for  $B \parallel c$  (thin line: zero field/zero field, thick line: zero field/16.5 Tesla).

absorption, and hence transmission measurements are only possible in narrow windows in between the phonon bands. The experimentally not accessible range is indicated by the strong noise in the ratio of two zero field spectra given in Fig. 5.27 for  $B \parallel c$  at T = 1 K. Convincing evidence for magnetic absorption in this frequency range cannot be derived from the 16.5 Tesla data (see Fig. 5.27).

The far-infrared transmittance measurements are displayed in Fig. 5.28. The top panel shows the zero field transmittance which is dominated by interference fringes and two phonon bands. In neutron scattering measurements the gapped acoustic magnon mode at  $\mathbf{k} = 0$  has been observed at  $E_{ac} = 36 \text{ cm}^{-1}$  [459]. The absolute intensity of the infrared signal at such low frequencies is quite small and the spectrum becomes noisy. On the other hand, if there is finite absorption due to acoustic magnons, this should be easily detectable as a change in the magneto-transmittance for  $B \parallel c$ , since the gapped acoustic magnon mode is expected to shift about  $3.5 \text{ cm}^{-1}$  (for  $B_{max} = 16.5$  Tesla, see inset of Fig. 5.28) even in the spin-flop phase. But the lower panel of Fig. 5.28 indicates that there is no magnetic field dependence, thus we are probably not coupling to acoustic magnons. The change in absolute value is due to the field dependence of the detector; and the structure in the transmittance ratios at  $83 \text{ cm}^{-1}$  which is already present in the ratio of two different zero field measurements (thin line) can be explained as noise due to the small intensity of the signal at the phonon frequency.

To conclude, we were not able to detect any signature of single magnon absorption neither in the far- nor in the mid-infrared magneto-transmittance of single crystal YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> for values of the external magnetic field up to 16.5 Tesla both with  $B \parallel ab$  and  $B \parallel c$ . This puts a severe experimental constraint on the magnon interpretation of the peak at 1436 cm<sup>-1</sup>. Note that to first order no effect of the magnetic field on the *two*-magnon absorption spectrum is expected.

## Appendix 5B Various Superexchange and Coupling Constants

Antiferromagnetic order in the ground state of the insulating cuprates arises due to the finite hybridization between the localized spins. For a three site cation-anion-cation cluster (Cu-O-Cu) with two spins the superexchange energy equals the energy difference between singlet and triplet states. A theory for the indirect superexchange mediated via the intervening anions was developed in 1959 by Anderson [70], with original ideas of Kramers [467] and Anderson [468] dating back to 1934 and 1950, respectively. A recent review has been given by Geertsma [469]. Here, we need a theoretical estimate of the superexchange constants J and  $J_{12}$  and of their dependence on lattice displacements and external electric fields for a quantitative comparison of the bimagnon-plus-phonon interpretation with experiment. We follow Lorenzana and Sawatzky [224] and expand J and  $J_{12}$  to first order in

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Figure 5.29: The four steps of the Anderson contribution to superexchange for a three site cluster.



Figure 5.30: The four distinct paths which constitute the Geertsma contribution to superexchange for a three site cluster.

E and second order in u,

$$J(u,E) = J_0 + J_u + J_{u^2} + J_{E,u} + \dots, \ J_{12}(u,E) = J_{12,0} + J_{12,u} + J_{12,u^2} + J_{12,E,u} + \dots,$$
(5.6)

where for example  $J_u = (dJ/du) \cdot u$ . The expansion is valid for  $t \ll \Delta$ ,  $\varepsilon$ ,  $U_d$ . The values of J calculated perturbatively are known to be not reliable [71], in particular since the expansion converges only slowly, which in principle requires a correct treatment of higher order terms. The major advantage of a perturbative approach is that it allows to visualize the various contributions to the exchange process, and that it may allow to select the important ones. Moreover, our main interest are not  $J_0$  and  $J_{12,0}$ , since these can be derived from the peak *positions* of the infrared spectrum in combination with the Raman and neutron scattering results (see the main part of this chapter). In fact, we are rather interested in  $J_{E,u} = q_{eff}Eu$ — where  $q_{eff}$  is an effective charge — and  $\lambda_{p2m} = J_{u^2}/J_0$ , which determine the spectral weight of bimagnon-plus-phonon absorption and its *line shape*, respectively. Although the perturbative calculation of these values has to be viewed with caution, we may hope that the relative trends such as  $J_{u^2}/J_0$  are reproduced more reliably than  $J_0$  itself, *i.e.*, we may still expect to achieve a correct estimate of the order of magnitude of the phononbimagnon coupling constant  $\lambda_{p2m}$  (see below and the main part of this chapter). This can be tested by comparing with experimental results for the pressure dependence of J. Note that the absolute value of  $J_0$  is strongly influenced by the Madelung potential, which gives an additional uncertainty in the calculation of  $J_0$  but not for  $J_u/J_0$ , where the change of

Δ	$U_d$	$U_p$	$U_{pd}$	$t_{pd}$	$t_{pp}$	$t_{pp,12}$
3.5	8.8	6.0	0.5 - 1	1.3	0.65	0.3

Table 5.7: Standard parameter set in units of eV [63, 471].

the Madelung potential is taken into account. The influence of the Madelung potential for example produces a larger exchange constant in the 1D cuprates as compared to their 2D counterparts [470], and yields a difference in the material dependence of J [394] and its pressure dependence.

Let us describe the procedure for the case of  $J_0$  in a Cu-O-Cu cluster with two spins. The first non-vanishing term is of fourth order in the hopping  $t_{pd}$  and contains intermediate states with double occupancy on either an O or a Cu site. The latter has been considered by Anderson in 1959 [70] and will be called the Anderson contribution. The virtual hopping processes of this term and the corresponding intermediate state energies are depicted in Fig. 5.29, from which one can easily read the following expression,

$$J_{0,Anderson} = 4 \frac{t_{pd}^4}{\Delta^2 U_d} \quad (\text{for } U_{pd} = 0).$$
 (5.7)

The prefactor can be determined from the number of distinct paths contributing, which is 2 in this case (start with the first hop either on the left or on the right Cu site). Another factor of 2 originates in the way the Heisenberg Hamiltonian is usually written,

$$J\mathbf{S}_{i}\mathbf{S}_{j} = JS_{i}^{z}S_{j}^{z} + \frac{J}{2}\left(S_{i}^{-}S_{j}^{+} + S_{i}^{+}S_{j}^{-}\right) , \qquad (5.8)$$

from which we have only considered the second part with the prefactor J/2 thus far. Using the standard parameter set of Table 5.7 we obtain  $J_{0,Anderson} = 106$  meV.

The term with double occupancy on the O site has been described by Geertsma [469],

$$J_{0,Geertsma} = 8 \frac{t_{pd}^4}{\Delta^2 (2\Delta + U_p)} \quad \text{(for } U_{pd} = 0\text{)}.$$
 (5.9)

The four paths which constitute this term are depicted in Fig. 5.30. The contribution of this term to superexchange amounts with the standard parameter set to  $J_{0,Geertsma} = 143$  meV. Thus far our estimate of  $J_0 = J_{0,Anderson} + J_{0,Geertsma} = 249$  meV is a factor of two too large. Taking into account a finite value of  $U_{pd}$  helps to improve the result.

Barriquand and Sawatzky [465] have pointed out the importance of *empty* O orbitals for the exchange process. Stechel and Jennison [473] described a second-order *ferromagnetic* contribution which arises from the exchange between a hole on an O site and one on a Cu site. This further reduces the theoretical value. Despite the fact that the absolute value of the estimated J does not deserve too much confidence, the above considered exchange processes nevertheless capture an important part of the physics. Zaanen and Sawatzky [472] have shown that the experimentally observed evolution of the Néel temperature within the

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Figure 5.31: A fifth-order antiferromagnetic contribution to superexchange as described by Eskes and Jefferson [71]. Double occupancy is omitted for the order of steps given in the figure via involving O-O hopping.

transition-metal monoxides can be described by taking both  $J_{Anderson}$  and  $J_{Geertsma}$  into account.

Eskes and Jefferson [71] pointed out that the fifth-order contribution, which includes the O-O hopping  $t_{pp}$ , is even larger than the fourth-order processes described thus far. In fifth-order a new kind of process becomes possible which omits double occupancy via O-O hopping (see Fig. 5.31). Whether this contribution is ferro- or antiferromagnetic is not clear right away. All processes involving doubly occupied sites obviously are only allowed for the singlet, not for the triplet, and thereby lower the energy of the singlet state. In case of the new process the sign of the exchange constant depends on the sign of  $t_{pp}$  [71], *i.e.*, on the topology of the crystal. For the 2D cuprates, this topological or Eskes-Jefferson contribution is antiferromagnetic. The considerable size of this process is due to the reduced energy denominators (omitting U terms). In general, the perturbation expansion is only slowly convergent because the higher order terms have large prefactors due to the many different paths that contribute. A finite  $t_{pp}$  also gives rise to a next-nearest neighbor coupling J', which in principle should be included if these higher order processes are taken into account. This can have a rather large effect on the value of J derived from experimental data (see Table 2.5).

The inter-layer exchange constant  $J_{12}$  of the bilayer YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> has been calculated perturbatively by Barriquand and Sawatzky [465]. The lowest non-vanishing contribution is of order six in the hopping  $(t_{pd}^4 t_{pp,12}^2)$ ; see Fig. 5.32). Similar to the case of J in a single layer, there is an Anderson and a Geertsma contribution involving double occupancy of Cu and O sites, respectively, and the ferromagnetic Stechel-Jennison term. In a bilayer, however, the two spins can avoid each more easily because there are four equivalent pairs of O ions connecting Cu<sub>1</sub> and Cu<sub>2</sub>. The lowest non-vanishing topological term omitting doubly occupied sites is therefore of the *same* order as the Anderson and Geertsma terms (see Fig. 5.32). It favors an antiferromagnetic alignment. One finds

$$J_{12,0,Anderson} = 64 t_{pd}^4 t_{pp}^2 / (\Delta^4 U_d) \approx 12 \text{ meV}$$
(5.10)

$$J_{12,0,Geertsma} = 64 t_{pd}^4 t_{pp}^2 / (\Delta^4 \varepsilon) \approx 7 \text{ meV}$$
(5.11)

$$J_{12,0,Eskes-Jefferson} = 96 t_{pd}^4 t_{pp}^2 / \Delta^5 \approx 47 \text{ meV} ,$$
 (5.12)

where the abbreviation  $\varepsilon = 2\Delta + U_p$  has been used. Note the large prefactor and the relatively small denominator of the Eskes-Jefferson term, which makes it the dominant contribution. As in the calculation of J, the Anderson contribution on its own occasionally



Figure 5.32: A sixth-order exchange path of the topological, antiferromagnetic contribution described by Barriquand and Sawatzky [465]. Double occupancy is omitted for the order of steps given in the figure.



Figure 5.33: Barriquand and Sawatzky [465] argued that the effective layerto-layer Geertsma contribution (the two spins meet on an O site) averages to zero because the coupling between a spin on site I of layer 1 and (a) a spin on site II of layer 2 directly above or (b) one of its neighbors (site II') is identical.

gives a reasonable estimate of the experimentally observed value. Barriquand and Sawatzky argued that taking into account more distant neighbors produces an average effective layerto-layer coupling of both the Geertsma and the Stechel-Jennison terms which tends to zero (see Fig. 5.33). Their estimate of  $J_{intrabilayer, effective} = 56 \text{ meV}$  is solely based on the Anderson and Eskes-Jefferson terms, where the prefactor of 48 instead of 64 had been used for the former, which again reflects the presence of next-nearest neighbor spins. Strictly speaking, a next-nearest neighbor inter-layer coupling has to be introduced into the Hamiltonian via an extra  $J'_{12}$  term. Our definition of  $J_{12}$  (see Eq. 2.10 on page 27) only incorporates the nearest-neighbor interlayer coupling. Since we are only interested in an estimate of the correct order of magnitude, we restricted ourselves to the calculation of the nearestneighbor coupling  $J_{12}$  and neglected more distant neighbors and in-plane O-O hopping via  $t_{pp}$ , which both increase the number of paths to be considered tremendously.

For the calculation of J(u, E) and  $J_{12}(u, E)$  we assume that only the O ions move, whereas the heavier Cu ions are immobile. We work in the adiabatic limit. The ionic displacements modulate the Cu-O hopping and the inter-layer O-O hopping as

$$\tilde{t}_{pd} = t_{pd} \pm (2-\lambda)\alpha u \pm \frac{\alpha}{\lambda a_{pd}} u^2 , \quad \tilde{t}_{pp,12} = t_{pp,12} \pm (2-\lambda)\alpha_{12} u \pm \frac{\alpha_{12}}{\lambda a_{pp,12}} u^2 , \quad (5.18)$$

where  $a_{pd}$  ( $a_{pp,12}$ ) is the planar Cu-O (inter-layer O-O) distance, and  $\lambda = 1$  if u is in the direction of the considered bond (as for the stretching mode and, in the case of  $J_{12}$ , also for the out-of-plane bending mode), and  $\lambda = 2$  if u is perpendicular to the bond (as for the inplane bending phonon). A shrinking bond corresponds to an increasing hopping amplitude.

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Figure 5.34: The  $Cu_2 O_7$  unit and the labelling of ions used in the calculation of J(u, E). The displayed configuration corresponds to the Cu-O stretching phonon mode at  $(\pi, 0)$  with  $u_0 = -u_2 = -u_5$ . A positive  $u_0$  denotes a displacement of the central O ion to the right / top / positive z-direction for the stretching/in-plane bending / out-of-plane phonon mode.



Figure 5.35: Labelling of apical O ions in a single layer compound. A positive  $u_{Ai}$ denotes a displacement in the positive z direction.

#### Single layer:

in-plane stretching mode:

$$u_L = u_1 + u_2 - u_3 \qquad (5.13)$$
  
$$u_R = u_4 + u_5 - u_6$$

all modes:

$$u_{LL}^{2} = u_{0}^{2} + u_{1}^{2} + u_{2}^{2} + u_{3}^{2}$$
 (5.14)  
$$u_{RR}^{2} = u_{0}^{2} + u_{4}^{2} + u_{5}^{2} + u_{6}^{2}$$



Figure 5.36: The  $Cu_2 O_8$  unit and the labelling of ions used in the calculation of  $J_{12}(u, E)$ . The displacement pattern shows the Cu-O stretching phonon mode at  $(\pi, 0)$   $(-u_1=u_2=u_3=-u_4)$ , the same as in Fig. 5.34. Here, the out-of-phase version of the displacements in the two layers is given. A positive  $u_1$  denotes a displacement of O ion 1 to the right / back / top for the stretching / in-plane bending / out-of-plane bending phonon mode.

#### **Bilayer**:

in-plane modes(stretching and bending):

$$u_B = u_1 - u_3 - u_5 + u_7 \qquad (5.15)$$
$$u_T = u_2 - u_4 - u_6 + u_8$$

out-of-plane bending mode:

$$u_B = u_1 + u_3 + u_5 + u_7 \qquad (5.16)$$
$$u_T = u_2 + u_4 + u_6 + u_8$$

all modes:

$$\begin{aligned} u_{BB}^2 &= u_1^2 + u_3^2 + u_5^2 + u_7^2 & (5.17) \\ u_{TT}^2 &= u_2^2 + u_4^2 + u_6^2 + u_8^2 \end{aligned}$$

Theoretical estimates of the parameters  $\alpha$  and  $\alpha_{12}$  have been given by Harrison [441],

$$\frac{\alpha \ a_{pd}}{t_{pd}} = \frac{7}{2} \ , \quad \frac{\alpha_{12} \ a_{pp,12}}{t_{pp,12}} = 2 \ . \tag{5.19}$$

The Cu and O site energies  $E_d$  and  $E_p$  are modulated by the electric field and the change of the Madelung potential due to the ionic displacements

$$\tilde{\mathbf{E}}_n = \mathbf{E}_n + \beta \sum \left( \pm u_i \pm \frac{\mu}{a} u_i^2 \right) + e \mathbf{E} \mathbf{r}_n , \qquad (5.20)$$

where a denotes the bond length and  $\mathbf{r}_n$  the position of ion n. The dimensionless factor  $\mu$  depends on geometry. For the Cu ions, the (hole) site energy increases if a bond becomes longer. A point charge estimate  $E_{Cu} = E_d - Ze/(a_{pd} \pm u)$  yields  $\beta a_{pd} \approx 2U_{pd}$ , where Z = 2 is the charge on an O site. The amplitude of the ionic displacements is obtained from the zero point motion  $\langle u \rangle = \hbar (2M\hbar\omega_{ph})^{1/2} = 4 \dots 6 \cdot 10^{-2}$  Å, where M is the oxygen atomic mass.

Expressions for J(u, E) and  $J_{12}(u, E)$  are given on the following pages for the different phonon modes. We indicate the Anderson, Geertsma and Eskes-Jefferson contributions independently. In the case of  $J_{12,u^2}$  we show only one example, the Anderson contribution to the in-plane stretching phonon mode, since the results for  $J_{12,u^2}$  are rather lengthy and since we only considered the effect of the *in-plane* phonon-bimagnon coupling  $\lambda_{p2m} = J_{u^2}/J_0$ in the main part of this chapter. For details of the phonon-magnon coupling we refer the reader to Ref. [426].

We determine the spectral weight of the in-plane contribution from  $J_{E,u,Anderson}$ . We follow Lorenzana and Sawatzky and consider only the dominant  $1/\Delta^2$  term with the structure factor  $2u_0 - u_L - u_R$ , which yields

$$\frac{q_{eff}}{e} \approx \frac{3J_0\beta a_{pd}}{\Delta^2} \approx \frac{6J_0U_{pd}}{\Delta^2} \approx -0.025\dots - 0.08 .$$
(5.21)

This is a factor of 4-7 too small compared with experiment, which we consider an excellent result within the given uncertainties.

Using the standard parameter set we derive  $\lambda_{p2m} = J_{u^2}/J_0 \approx -0.02 \cdots + 0.01$ . In order to test our result we consider magnetostriction,

$$J_{MS,Anderson} = J_0 \cdot \left[ 1 + \left( 2 \frac{\alpha}{t_{pd}} - 6 \frac{\beta}{\Delta} \right) \cdot u \right] , \qquad (5.22)$$

where u is the pressure induced change of the lattice constant. We obtain  $(dJ/du)/J \approx 1.8$ ... 2.6 Å<sup>-1</sup>. The experimental result of the pressure dependence of J yields  $(dJ/du)/J \approx 3$ ... 3.8 Å<sup>-1</sup> [442], *i.e.*, our estimate is 1 – 2 times too small.

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## (I) J(u,E), single layer

## • in-plane stretching

$$J_{u,Anderson} = -4 \frac{t_{pd}^4 \beta}{\Delta^3 U_d} (u_L - u_R)$$
(5.23)

$$J_{u,Geertsma} = -8 \frac{t_{pd}^4 \beta}{\Delta^2 \varepsilon} \left(\frac{1}{\Delta} + \frac{1}{\varepsilon}\right) (u_L - u_R)$$
(5.24)

$$J_{E,u,Anderson} = -eE \frac{4t_{pd}^4}{\Delta^2 U_d} \left\{ \beta a_{pd} \left( \frac{3}{\Delta^2} + \frac{4}{\Delta U_d} + \frac{4}{U_d^2} \right) (2u_0 - u_L - u_R) + \frac{2}{\Delta} u_0 \right\}$$
(5.25)

$$J_{E,u,Geertsma} = -eE \frac{16t_{pd}^{*}}{\Delta^{2}\varepsilon} \left\{ \beta a_{pd} \frac{1}{\Delta^{2}} (2u_{0} - u_{L} - u_{R}) + \left(\frac{1}{\Delta} + \frac{1}{\varepsilon}\right) u_{0} \right\}$$
(5.26)

$$J_{u^{2},Anderson} = 2 \frac{t_{pd}^{4}}{\Delta^{2} U_{d}} \left\{ \frac{3\beta^{2}}{\Delta^{2}} \left[ (u_{0} - u_{L})^{2} + (u_{0} - u_{R})^{2} \right] \right.$$
(5.27)

$$+\frac{2\beta^2}{U}\left(\frac{1}{\Delta}+\frac{1}{U}\right)(2u_0-u_L-u_R)^2-\frac{2\beta}{\Delta a_{pd}}(4u_0^2+u_{LL}^2+u_{RR}^2)-\frac{4\alpha}{t_{pd}}\left(\frac{\alpha}{t_{pd}}-\frac{2}{a_{pd}}\right)u_0^2\right\}$$

$$J_{u^2,Geertsma} = 2 \frac{t_{pd}^4}{\Delta^2 \varepsilon} \left\{ \frac{\beta^2}{\Delta^2} \left[ 5(u_L - u_R)^2 + 8(u_0 - u_L)(u_0 - u_R) \right] \right\}$$
(5.28)

$$+\frac{4\beta^2}{\varepsilon}\left(\frac{1}{\Delta}+\frac{1}{\varepsilon}\right)(u_L-u_R)^2-\frac{4\beta}{a_{pd}}\left(\frac{1}{\Delta}+\frac{1}{\varepsilon}\right)(4u_0^2+u_{LL}^2+u_{RR}^2)-8\frac{\alpha}{t_{pd}}\left(\frac{\alpha}{t_{pd}}-\frac{2}{a_{pd}}\right)u_0^2\right\}$$

• in- and out-of-plane bending

$$J_{u,Anderson} = J_{u,Geertsma} = 0 \tag{5.29}$$

$$J_{E,u,Anderson} = -8eE \frac{t_{pd}^*}{\Delta^3 U_d} u_0 \tag{5.30}$$

$$J_{E,u,Geertsma} = -16eE \frac{t_{pd}^4}{\Delta^2 \varepsilon} \left(\frac{1}{\Delta} + \frac{1}{\varepsilon}\right) u_0$$
(5.31)

$$J_{u^{2},Anderson} = 2\frac{t_{pd}^{4}}{\Delta^{2}U_{d}} \left\{ \frac{\beta}{\Delta a_{pd}} (4u_{0}^{2} + u_{LL}^{2} + u_{RR}^{2}) - \frac{4\alpha}{t_{pd}a_{pd}} u_{0}^{2} \right\}$$
(5.32)

$$J_{u^2,Geertsma} = 4 \frac{t_{pd}^4}{\Delta^2 \varepsilon} \left\{ \frac{\beta}{a_{pd}} \left( \frac{1}{\Delta} + \frac{1}{\varepsilon} \right) \left( 4u_0^2 + u_{LL}^2 + u_{RR}^2 \right) - \frac{4\alpha}{t_{pd}a_{pd}} u_0^2 \right\}$$
(5.33)

• apical stretching

$$J_{u,Anderson} = 4 \frac{t_{pd}^4 \beta_A}{\Delta^3 U_d} (u_{A1} - u_{A2} + u_{A3} - u_{A4})$$
(5.34)

$$J_{u,Geertsma} = 8 \frac{t_{pd}^4 \beta_A}{\Delta^2 \varepsilon} \left( \frac{1}{\Delta} + \frac{1}{\varepsilon} \right) \left( u_{A1} - u_{A2} + u_{A3} - u_{A4} \right)$$
(5.35)

$$J_{E,u,Anderson} = -4eE \frac{t_{pd}^4 \beta_A a_A}{\Delta^2 U_d} \left( \frac{3}{\Delta^2} + \frac{4}{\Delta U_d} + \frac{4}{U_d^2} \right) (u_{A1} - u_{A2} - u_{A3} + u_{A4}) (5.36)$$
  
$$J_{E,u,Geertsma} = -16eE \frac{t_{pd}^4 \beta_A a_A}{\Delta^4 \varepsilon} (u_{A1} - u_{A2} - u_{A3} + u_{A4})$$
(5.37)

$$J_{u^{2},Anderson} = 2 \frac{t_{pd}^{4}}{\Delta^{2} U_{d}} \left\{ \beta_{A}^{2} \left( \frac{3}{\Delta^{2}} + \frac{2}{\Delta U_{d}} + \frac{2}{U_{d}^{2}} \right) \left[ (u_{A1} - u_{A2})^{2} + (u_{A3} - u_{A4})^{2} \right] - \frac{4\beta_{A}^{2}}{U_{d}} \left( \frac{1}{\Delta} + \frac{1}{U_{d}} \right) (u_{A1} - u_{A2})(u_{A3} - u_{A4}) - \frac{2\beta_{A}}{\Delta} (u_{A1}^{2} + u_{A2}^{2} + u_{A3}^{2} + u_{A4}^{2}) \right\}$$

$$(5.38)$$

$$U_{d} \left( \Delta^{+} U_{d} \right)^{(a_{A1} - a_{A2})(a_{A3} - a_{A4})} \Delta a_{A}^{(a_{A1} + a_{A2} + a_{A3} + a_{A4})} \int J_{u^{2},Geertsma} = 2 \frac{t_{pd}^{4}}{\Delta^{2} \varepsilon} \left\{ \beta_{A}^{2} \left( \frac{5}{\Delta^{2}} + \frac{4}{\Delta \varepsilon} + \frac{4}{\varepsilon^{2}} \right) \left[ (u_{A1} - u_{A2})^{2} + (u_{A3} - u_{A4})^{2} \right]$$
(5.39)

$$+\beta_{A}^{2}\left(\frac{2}{\Delta^{2}}+\frac{8}{\Delta\varepsilon}+\frac{8}{\varepsilon^{2}}\right)(u_{A1}-u_{A2})(u_{A3}-u_{A4})-\frac{4\beta_{A}}{a_{A}}\left(\frac{1}{\Delta}+\frac{1}{\varepsilon}\right)(u_{A1}^{2}+u_{A2}^{2}+u_{A3}^{2}+u_{A4}^{2})\right\}$$

• apical bending

$$J_{u,Anderson} = J_{E,u,Anderson} = J_{u,Geertsma} = J_{E,u,Geertsma} = 0$$
(5.40)

$$J_{u^{2},Anderson} = 2 \frac{t_{pd}^{4} \beta_{A}}{\Delta^{3} U_{d} a_{A}} (u_{A1}^{2} + u_{A2}^{2} + u_{A3}^{2} + u_{A4}^{2})$$
(5.41)

$$J_{u^2,Geertsma} = 4 \frac{t_{pd}^4 \beta_A}{\Delta^2 \varepsilon a_A} \left(\frac{1}{\Delta} + \frac{1}{\varepsilon}\right) \left(u_{A1}^2 + u_{A2}^2 + u_{A3}^2 + u_{A4}^2\right)$$
(5.42)

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(II)  $J_{12}(u, E)$ ,  $E \parallel a$ , Bilayer

## • in-plane stretching

$$J_{12,u,Anderson} = 32 \frac{t_{pd}^4 t_{pp}^2}{\Delta^4 U_d} \left(\frac{\alpha}{t_{pd}} - \frac{4\beta}{\Delta}\right) (u_B + u_T)$$
(5.43)

$$J_{12,u,Geertsma} = 32 \frac{t_{pd}^4 t_{pp}^2}{\Delta^4 \varepsilon} \left( \frac{\alpha}{t_{pd}} - 2\beta \left[ \frac{2}{\Delta} + \frac{1}{\varepsilon} \right] \right) (u_B + u_T)$$
(5.44)

$$J_{12,u,Eskes-Jefferson} = 48 \frac{t_{pd}^4 t_{pp}^2}{\Delta^5} \left(\frac{\alpha}{t_{pd}} - \frac{5\beta}{\Delta}\right) (u_B + u_T)$$
(5.45)

$$J_{12,E,u,Anderson} = -32eE \frac{t_{pd}^4 t_{pp}^2}{\Delta^5 U_d} \left(1 - 2\frac{\alpha a_{pd}}{t_{pd}}\right) (u_1 + u_2 + u_3 + u_4)$$
(5.46)

$$J_{12,E,u,Geertsma} = -16eE\frac{t_{pd}^4 t_{pp}^2}{\Delta^4 \varepsilon} \left(\frac{2}{\Delta} + \frac{1}{\varepsilon}\right) \left(1 - 4\frac{\alpha a_{pd}}{t_{pd}}\right) (u_1 + u_2 + u_3 + u_4) \quad (5.47)$$

$$J_{12,E,u,Eskes-Jefferson} = -20eE \frac{t_{pd}^4 t_{pp}^2}{\Delta^6} \left(3 - 4\frac{\alpha a_{pd}}{t_{pd}}\right) (u_1 + u_2 + u_3 + u_4)$$
(5.48)

$$J_{12,u^2,Anderson} = 4 \frac{t_{pd}^4 t_{pp}^2}{\Delta^4 U_d} \left\{ 80 \frac{\beta^2}{\Delta^2} (u_B^2 + u_T^2) - 16 \frac{\alpha\beta}{\Delta t_{pd}} (u_B + u_T)^2 \right\}$$
(5.49)

$$+16\frac{\beta^2}{U_d}\left(\frac{2}{\Delta}+\frac{1}{U_d}\right)\left(u_B^2-u_T^2\right)+\frac{\alpha^2}{t_{pd}^2}\left[\left(u_B+u_T\right)^2+8\left(u_1u_2+u_3u_4+u_5u_6+u_7u_8\right)\right]\\+8\left(\frac{\alpha}{t_{pd}a_{pd}}-\frac{6\beta}{\Delta a_{pd}}\right)\left(u_{BB}^2+u_{TT}^2\right)-\frac{4\alpha_{\perp}}{t_{pp}a_{\perp}}\left[\left(u_1-u_2\right)^2+\left(u_3-u_4\right)^2+\left(u_5-u_6\right)^2+\left(u_7-u_8\right)^2\right]\right\}$$

## • in-plane bending

$$J_{12,u,Anderson} = J_{12,u,Geertsma} = J_{12,u,Eskes-Jefferson} = 0 \qquad (5.50)$$

$$J_{12,E,u,Anderson} = -32eE \frac{l_{pd} l_{pp}}{\Delta^5 U_d} (u_5 + u_6 + u_7 + u_8)$$
(5.51)

$$J_{12,E,u,Geertsma} = -16eE \frac{t_{pd}^{4}t_{pp}^{2}}{\Delta^{4}\varepsilon} \left(\frac{2}{\Delta} + \frac{1}{\varepsilon}\right) (u_{5} + u_{6} + u_{7} + u_{8}) \qquad (5.52)$$

$$J_{12,E,u,Eskes-Jefferson} = -60eE \frac{t_{pd}^{*} t_{pp}^{*}}{\Delta^{6}} (u_{5} + u_{6} + u_{7} + u_{8})$$
(5.53)

• out-of-plane bending

$$J_{12,u,Anderson} = 32 \frac{t_{pd}^4 t_{pp}^2}{\Delta^4 U_d} \left( \frac{\alpha_{12}}{t_{pp,12}} + \frac{2\beta_{12}}{\Delta} \right) (u_B - u_T)$$
(5.54)

$$J_{12,u,Geertsma} = 32 \frac{t_{pd}^4 t_{pp}^2}{\Delta^4 \varepsilon} \left( \frac{\alpha_{12}}{t_{pp,12}} + \beta_{12} \left[ \frac{2}{\Delta} + \frac{1}{\varepsilon} \right] \right) (u_B - u_T)$$
(5.55)

$$J_{12,u,Eskes-Jefferson} = 24 \frac{t_{pd}^{4} t_{pp}^{2}}{\Delta^{5}} \left( \frac{2\alpha_{12}}{t_{pp,12}} + \frac{5\beta_{12}}{\Delta} \right) (u_{B} - u_{T})$$
(5.56)

$$J_{12,E,u,Anderson} = 64eEa_{pd} \frac{t_{pd}^4 t_{pp}^2}{\Delta^5 U_d} \left(\frac{\alpha_{12}}{t_{pp,12}} + \frac{3\beta_{12}}{\Delta}\right) (u_1 - u_2 - u_3 + u_4)$$
(5.57)

$$J_{12,Geertsma} = 64eEa_{pd} \frac{t_{pd}^4 t_{pp}^2}{\Delta^4 \varepsilon} \left( \frac{\alpha_{12}}{t_{pp,12}} \left[ \frac{2}{\Delta} + \frac{1}{\varepsilon} \right] \right)$$
(5.58)

$$+\beta_{12} \left[ \frac{3}{\Delta^2} + \frac{1}{\Delta\varepsilon} + \frac{2}{\varepsilon^2} \right] \left( u_1 - u_2 - u_3 + u_4 \right)$$

$$J_{12,E,u,Eskes-Jefferson} = 16eEa_{pd} \frac{t_{pd}^4 t_{pp}^2}{\Delta^6} \left( \frac{5\alpha_{12}}{t_{pp,12}} + \frac{21\beta_{12}}{\Delta} \right) \left( u_1 - u_2 - u_3 + u_4 \right) \quad (5.59)$$

• apical stretching

$$J_{12,u,Anderson} = -128 \frac{t_{pd}^4 t_{pp}^2 \beta}{\Delta^5 U_d} (u_{A1} - u_{A3})$$
(5.60)

$$J_{12,u,Geertsma} = -64 \frac{t_{pd}^4 t_{pp}^2 \beta}{\Delta^4 \varepsilon} \left(\frac{2}{\Delta} + \frac{1}{\varepsilon}\right) (u_{A1} - u_{A3})$$
(5.61)

$$J_{12,u,Eskes-Jefferson} = -240 \frac{t_{pd}^4 t_{pp}^2 \beta}{\Delta^6} (u_{A1} - u_{A3})$$
(5.62)

$$J_{12,E,u,Anderson} = J_{12,E,u,Geertsma} = J_{12,E,u,Eskes-Jefferson} = 0 \qquad (5.63)$$

• apical bending

$$J_{12,u,Anderson} = J_{12,u,Geertsma} = J_{12,u,Eskes-Jefferson} = 0$$
(5.64)

$$J_{12,E,u,Anderson} = J_{12,E,u,Geertsma} = J_{12,E,u,Eskes-Jefferson} = 0$$
(5.65)
### Chapter 6

# Sharp Mid-Infrared Peaks of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>: Low-Lying Electronic States?

In chapter 5 we have discussed the broad magnetic absorption bands which dominate the mid-infrared spectrum of undoped  $YBa_2Cu_3O_6$ . The present chapter is devoted to the multitude of sharp features which have been observed in the same frequency range. Up to about  $1360 \text{ cm}^{-1}$  these can be attributed to two-phonon excitations. However, at frequencies as high as  $2860 \text{ cm}^{-1}$  a multi-phonon interpretation is very unlikely, and we have to consider, e.g., a magnetic or a distinct electronic origin, and the possible influence of impurities. In the first part of this chapter we will study the experimental spectra in detail. In the second part we calculate the energy levels of one possible sort of impurities, excess oxygen ions on chain sites.

### 6.1 Experimental Results

#### 6.1.1 Multi-Phonons

Phonons are the only absorption processes below the charge transfer gap which are strong enough to be observed in reflectivity measurements of the antiferromagnetic cuprates. The fundamental phonon spectrum has been described in chapter 4. The infrared active phonons with the highest frequency, the in-plane  $(E \parallel ab)$  and apical  $(E \parallel c)$  Cu-O bond stretching modes, were observed at about 600 cm<sup>-1</sup>. Neutron scattering experiments [373,402] indicate that the highest phonon branch of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> reaches 680 cm<sup>-1</sup> at the Brillouin zone boundary at room temperature. In chapter 5 we have demonstrated that, next to the phonons, many other interesting features can be found in the transmission spectra of thin single crystalline platelets. We have described the mid-infrared conductivity spectrum of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> and its dependence on temperature, specific substitutions, impurities and magnetic fields. Here, we first concentrate on the frequency range just above



Figure 6.1: The dependence of the multi-phonon spectrum of  $YBa_2 Cu_3 O_6$  on specific substitutions for E || ab. The different absolute values of the broad background are due to doping (see chapter 7). Differences in spectral weight of multi-phonon absorption are caused by impurities (see text). Panel F displays the spectrum for E || c. The largest measurable value of  $\sigma(\omega)$  depends on the sample thickness; higher values of  $\sigma(\omega)$  can be determined by using a thinner sample. A cut-off peak indicates that  $T(\omega)$  has dropped below the noise level due to strong absorption.

the phonons (see Fig. 6.1). From the above cited maximum single phonon frequency of 680  $\rm cm^{-1}$  we derive an upper cut-off for two-phonon excitations of 1360 cm<sup>-1</sup>. The detailed shape of the multi-phonon peaks is strongly sample dependent, but the experimental spectra with  $E \parallel ab$  reveal three main bands or groups of bands at about 700-800 cm<sup>-1</sup>, 850-950  $cm^{-1}$  and 1050-1200  $cm^{-1}$  in all samples (see Fig. 6.1). The most probable contributions to these bands are combinations of two Cu-O bond bending modes, of an Cu-O bending and an Cu-O stretching mode and of two Cu-O stretching modes, respectively. The lowest band could also be due to a combination of an Cu-O stretching and a rare earth mode. For a more detailed assignment one of course would have to take the dispersion, symmetry and also the infrared forbidden fundamental modes into account. However, the strong sample dependence of the exact shape of the three bands leads us to the conclusion that most of these absorption features are infrared forbidden and only weakly allowed due to the presence of some impurities. A comparison of the strength of the multi-phonon absorption in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> (panels B, C and D) and in YBa<sub>2</sub>Cu<sub>2.94</sub>Zn<sub>0.06</sub>O<sub>6</sub> (panel E) supports this view, since the spectral weight of especially the second and third band increases considerably by Zn substitution. Note that the scale is identical in all panels and that the differences in the absolute value of the broad background are due to doping, which will be addressed in chapter 7. A similar increase in the spectral weight of multi-phonons was observed upon substitution of several percent of Cu by Co [474]. Here, we also find a dependence of the multi-phonon spectral weight on the crucible material used for the crystal growth. The reduced absorption strength observed in samples grown in  $BaZrO_3$  (panel C) as compared to the ones grown in  $ZrO_2$  (panel B) demonstrates the very low amount of impurities in the former (compare Table 2.3 on page 24). Note that the conductivity spectrum of  $YBa_2Cu_3^{16}O_6$  grown in  $BaZrO_3$  is very similar in both shape and spectral weight to the one of the sample grown in  $SnO_2$  (panel D). Crystals grown in  $SnO_2$  crucibles are available for a long time already and are known to be of high purity [475]. These crucibles however do not allow the growth of *large* single crystals, which explains why they are not more commonly used. In the light of the strong dependence of the multi-phonon spectra on impurities the excellent agreement between the two samples grown in  $BaZrO_3$  and  $SnO_2$  is stunning and indicates that the features observed in these samples are intrinsic to  $YBa_2Cu_3O_6$ .

The Zn impurities give rise to a surprising temperature dependence of the absorption band between 1050 and 1200 cm<sup>-1</sup> (see Figs. 6.2 and 6.3). In YBa<sub>2</sub>Cu<sub>2.94</sub>Zn<sub>0.06</sub>O<sub>6</sub> this band consists at T = 300 K of two main peaks at about 1060 cm<sup>-1</sup> and 1155 cm<sup>-1</sup>, which both split at lower temperatures. However, at intermediate temperatures we observe a *superposition* of the 300 K and the 4 K data (see the spectrum of 125 K (100 K) for the peak at 1060 cm<sup>-1</sup> (1155)). The spectra of REBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> displayed in Fig. 6.3 show the same splitting at about 1150 cm<sup>-1</sup> at low temperature, but the peaks remain split at all temperatures presented here. However, the 200 K and 300 K curves of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> resemble the 100 K and 125 K data of the Zn-substituted sample. Possibly, this reflects the difference in the Néel temperature T<sub>N</sub>. In the case of YBa<sub>2</sub>(Cu<sub>0.9725</sub>Zn<sub>0.0275</sub>)<sub>3</sub>O<sub>6.1</sub> a Néel temperature of T<sub>N</sub> = 355 K has been determined from neutron scattering data [476], whereas values up to 500 K [477] have been reported for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>. A reduction of the Néel temperature caused by Zn substitution also agrees with the temperature dependence of the bimagnon-



Figure 6.2: Temperature dependence of absorption bands in  $YBa_2 Cu_{2.94} Zn_{0.06} O_6$  for  $E \parallel ab$ . Note that spectra at intermediate temperatures (100 K, 125 K) contain the structures of both high and low temperature spectra at the same time.

Figure 6.3: Same as Fig. 6.2 for samples of  $REBa_2Cu_3O_6$ . Contrary to the case of  $YBa_2Cu_{2.94}Zn_{0.06}O_6$ , all three panels show two separate peaks at about 1150  $cm^{-1}$  for all temperatures presented here.

plus-phonon peak at about  $2800 \text{ cm}^{-1}$  (compare the 485 K data of  $(\text{Gd}, \text{Y})\text{Ba}_2\text{Cu}_3\text{O}_6$  and the 300 K curve of  $\text{YBa}_2\text{Cu}_{2.94}\text{Zn}_{0.06}\text{O}_6$  in Fig. 5.11). Therefore the splitting of this absorption band could be related to spin-lattice interactions. The features at about 1060 cm<sup>-1</sup> are unique to  $\text{YBa}_2(\text{Cu},\text{Zn})_3\text{O}_6$ .

#### 6.1.2 Sharp Features at Higher Frequencies

The oscillator strength of multi-phonon absorption decreases drastically with the number of phonons involved, which makes a multi-phonon interpretation of peaks above  $1360 \,\mathrm{cm}^{-1}$  very unlikely. Common to all compounds is the sharp peak at  $1436 \,\mathrm{cm}^{-1}$ . An intriguing image of this feature is given in Fig. 5.2 on page 135. Our initial interpretation as a



Figure 6.4: Comparison of two different samples of  $YBa_2 Cu_3 O_6$  (E||ab) grown in a  $BaZrO_3$  crucible, with thicknesses of 85 and 250µm. The sharp features are very well reproduced.



Figure 6.5: The effect of the sample thickness d is eliminated by plotting  $-(\ln T(\omega))/d$ . The frequency range in which the transmittance of the 250µm thick sample (thick line) is lower than 0.5% is indicated by the light grey line. These low values of  $T(\omega)$  do not allow to determine  $\sigma(\omega)$  accurately.



Figure 6.6: All features present in a sample of  $YBa_2 Cu_3 O_6$  grown in a  $BaZrO_3$  crucible are reproduced in a sample grown in a  $SnO_2$  crucible. Both container materials are known to produce samples of high purity.

direct excitation of single magnons of the optical branch is described in Appendix 5A. Sharp features at even higher frequencies appear in the clean samples grown in BaZrO<sub>3</sub> (compare Figs. 5.1 and 5.11). In order to demonstrate the reproducibility of these features we compare the transmission spectra of two different samples grown in BaZrO<sub>3</sub> in Fig. 6.4. All structures are identical in the two samples, the different absolute values are due to the difference in thickness. We can eliminate the effect of the sample thickness d by plotting  $-(\ln T(\omega))/d$  (see Fig. 6.5), which represents  $\sigma(\omega)$  very well due to the constant reflectance in this frequency range (see Eq. 3.7 on page 85 and Fig. 5.1). The figure demonstrates the excellent agreement of the two spectra in the frequency range where the measured transmittance is larger than 0.5%. Lower values of  $T(\omega)$  are not sufficient to determine  $\sigma(\omega)$  correctly, which we indicate with the light grey line in Fig. 6.5.

The sharp features are not only well reproduced in samples grown in BaZrO<sub>3</sub>, but also in the sample grown in a SnO<sub>2</sub> crucible (see Fig. 6.6). Excellent agreement is in particular observed at higher frequencies, for the sharp structures on top of the bimagnon-plus-phonon peak at 2800 cm<sup>-1</sup> (see inset; the sharp peaks are cut-off by the too low values of  $T(\omega)$ ) and for all the features above. Even the small feature at 3400 cm<sup>-1</sup>, *i.e.*, approximately  $600 \text{ cm}^{-1}$  above the main bimagnon-plus-phonon peak, is reproduced. This difference of  $600 \text{ cm}^{-1}$  suggests a bimagnon-plus-*two*-phonon origin, which agrees with the vanishingly small oscillator strength.



Figure 6.7: Temperature dependence of some sharp structures in the mid-infrared range.

Figure 6.8: Temperature dependence of the structures on top of the main bimagnonplus-phonon band at  $2800 \text{ cm}^{-1}$ .

In the previous section, excellent agreement between the multi-phonon spectra of samples grown in BaZrO<sub>3</sub> and SnO<sub>2</sub> crucibles has been observed. In combination with the small spectral weight of multi-phonon absorption in these samples this had been interpreted as a signature of high purity. Here, at higher frequencies, we encounter the opposite trend: some of the sharp features are only present in the pure samples (see Fig. 5.11), and they are washed out by disorder in samples with larger impurity concentrations. This claim is corroborated by the appearance of the same features in samples grown in ZrO<sub>2</sub> crucibles if starting material of higher purity is used in the sample growth [478]. A possible strong effect of disorder can also be derived from the temperature dependence (see Figs. 6.7 and 6.8): these sharp peaks broaden rapidly with increasing temperature, which possibly is related to the temperature-induced disorder. The structures on top of the main bimagnon-plus-phonon band at  $2800 \,\mathrm{cm}^{-1}$  disappear already at  $125 \,\mathrm{K}$  (see Fig. 6.8).

In the following we concentrate on the peak at  $1436 \text{ cm}^{-1}$ , which is common to all samples. The effect of oxygen isotope or rare earth substitution and the polarization dependence of this feature are summarized in Fig. 6.9. The main peak shows an oxygen isotope shift of  $21 \text{ cm}^{-1}$  or 1.5% down to  $1415 \text{ cm}^{-1}$  in YBa<sub>2</sub>Cu<sub>3</sub><sup>18</sup>O<sub>6</sub>. Substitution of 80% of Y by Pr (Gd) yields shifts of merely 4 (1.5) cm<sup>-1</sup>. An overview of the peak frequencies of the different samples is given in Table 6.1. The rather small frequency shifts are puzzling;



Figure 6.9: Enlarged view of  $\sigma_1(\omega)$  of the sharp 1436 cm<sup>-1</sup> peak in different samples.

$\operatorname{compound}$	$Y(^{16}O)$	$Y(^{16}O)$	$Y(^{18}O)$	Zn (3%)	$\mathrm{Gd}_{0.8}\mathrm{Y}_{0.2}$	$\mathrm{Pr}_{0.8}\mathrm{Y}_{0.2}$	${\rm Pr}_{0.4}{\rm Y}_{0.6}{}^{*}$
crucible	$ m ZrO_2$	${ m BaZrO_3}$	${ m BaZrO_3}$	$ m ZrO_2$	$ m ZrO_2$	$ m ZrO_2$	$ m ZrO_2$
$\omega \ ({\rm cm}^{-1})$	1436.2	1435.4	1414.8	1435.5	1434.8	1432.4	1434.0

Table 6.1: Effect of specific substitutions of  $YBa_2 Cu_3 O_6$  on the frequency of the 1436  $cm^{-1}$  peak at T=4 K. \*: the last entry has been obtained in collaboration with Zibold and co-workers [439].

they show that this peak is not a multi-phonon. Substituting Gd and in particular Pr for Y enlarges the unit cell, which yields both smaller phonon frequencies (for example a redshift of the in-plane Cu-O stretching phonon mode of about 70 cm<sup>-1</sup> for Y $\rightarrow$ Pr) and a reduction of the exchange constant J. In the case of the bimagnon-plus-phonon peak at 2795 cm<sup>-1</sup> this explains the almost 10% decrease of the peak frequency down to 2520 cm<sup>-1</sup> upon substitution of 80% Pr (see Table 5.1 on page 139). For the 1436 cm<sup>-1</sup> peak, we merely observe a shift of 0.25%, a stunning result. This is confirmed by the data of 40% substitution of Pr, which show only half of the shift as compared to 80% substitution. Moreover, the shift upon Gd substitution is about a factor of 3 to 4 smaller, similar to the case of the bimagnon-plus-phonon peak.

Also the oxygen isotope shift is rather small. In chapter 4 we had reported oxygen isotope shifts of the 250 to  $600 \,\mathrm{cm}^{-1}$  phonon modes of about 5.3%, which definitely rules out a multi-phonon interpretation of the  $1436 \,\mathrm{cm}^{-1}$  absorption. If we neglect the different line shapes, we can estimate a maximum (oxygen) phonon contribution of  $400 \,\mathrm{cm}^{-1}$  from the experimental isotope shift of  $21 \text{ cm}^{-1}$ . A contribution to the isotope shift from a dependence of the exchange constant J on the oxygen isotope mass is most probably small. One would expect that the lattice parameter a is smaller in samples substituted with <sup>18</sup>O due to the reduced zero point fluctuations. This should give rise to a larger overlap and an *increase* of J. However, measurements of the Néel temperature  $T_N$  of La<sub>2</sub>CuO<sub>4</sub> (T-phase) show a lower  $T_N$  in samples substituted with <sup>18</sup>O, with  $-\Delta T_N/T_N = 0.0058$  [479]. No influence of the oxygen isotope on  $T_N$  was found in the T'-phase  $\mathrm{Gd}_2\mathrm{CuO}_4$  [479]. Hanzawa has argued [480] that this is caused by an increase of the Cu-O tilt angle in samples with the heavier oxygen isotope, and this larger tilt angle increases the Cu-O distance. This effect is absent in the flat, untilted T'-phase material. Hubina and Sadiek [481] propose a coupling to the apical oxygen as origin for the isotope shift of  $T_N$ . Here the absence of apical oxygens in the T'-phase would explain the observed difference. However, the sensitivity of  $T_N$  to excess oxygen and the necessity of repeated annealing for the isotope exchange put a question mark on the reliability of the experimental result. Nevertheless, if we assume  $\Delta T_N/T_N = c\Delta J/J$  with c being constant and close to unity, then applying  $-\Delta J/J = 0.0058$  to the peak frequency of 1436 cm<sup>-1</sup> yields a redshift of 8.3 cm<sup>-1</sup>, which



Figure 6.10: Temperature dependence of the  $1436 \text{ cm}^{-1}$  band. The symbols denote the first moment of the band integrated over the displayed range for each temperature.



Figure 6.12: Lorentzian fits (thick grey lines) of the experimental spectra of  $YBa_2 Cu_3 O_6$  (see Fig. 6.10).



Figure 6.11: Temperature dependence of the  $1436 \text{ cm}^{-1}$  band in  $YBa_2 Cu_3{}^{18}O_6$ .



Figure 6.13: The temperature dependence for  $E \parallel c$  is very similar to the one for  $E \parallel ab$ . With increasing temperature the spectral weight is transferred from the satellites at the upper and lower edges towards the center of the absorption band.



Figure 6.14: Replicas of the  $1436 \text{ cm}^{-1}$  peak are found at twice the frequency. The upper (lower) curves in each panel correspond to the upper (lower) scale.

is a factor of 2.5 smaller than observed.

The temperature dependence of the  $1436 \text{ cm}^{-1}$  absorption band is depicted in Figs. 6.10 and 6.11 for samples with different oxygen isotopes. At low temperatures, a large part of the spectral weight is contained in the two sharp peaks at the lower and upper edges (see Fig. 6.10; a Lorentzian fit resolving the different contributions is shown in Fig. 6.12). With increasing temperature both satellites loose spectral weight, which is transferred to a broad feature in the middle of the band. The first moment or center of mass, indicated by the squares in Fig. 6.10, shifts only by 0.25% from 4 to 300 K. The basic behavior is not affected by oxygen isotope substitution, and the same transfer of spectral weight from the satellites to the center is also observed for  $E \parallel c$  (see Fig. 6.13). In section 6.1.1 we have described a very similar behavior of the 1150 cm<sup>-1</sup> band in the case of Zn substitution (see Fig. 6.2).

Finally, we point out a connection between the  $1436 \text{ cm}^{-1}$  band and the sharp features at 2800 cm<sup>-1</sup> on top of the bimagnon-plus-phonon peak. We compare the two structures in Fig. 6.14 by using two frequency axes which differ by a factor of two. The agreement is stunning. This is in particular true for the case of Pr substitution (lower panel), which shifts the bimagnon-plus-phonon peak to lower frequencies. The structure on top, however, is not shifted, but reproduces the change of line shape of the 1436 cm<sup>-1</sup> band. In  $Pr_{0.8}Y_{0.2}Ba_2Cu_3O_6$  at 200 K (dashed lines), the spectral weight has shifted towards the center of the bands at 1400 and 2800 cm<sup>-1</sup>. Note that also the 1150 cm<sup>-1</sup> structure, which shows the same intriguing temperature dependence (see Figs. 6.2 and 6.3), has its equiva-



Figure 6.15: Mid-infrared transmittance spectrum of insulating  $EuSr_2 GaCu_2 O_7$  at 4 K. Note the logarithmic scale.

lent at twice the frequency in  $Pr_{0.8}Y_{0.2}Ba_2Cu_3O_6$ .

We conclude that neither a vibrational nor a magnetic interpretation seems to be appropriate for the observed absorption features, which in the present case leaves only two alternatives: a low-lying electronic excitation or impurities. The vanishingly small effect of rare earth substitution on the peak frequencies is putting severe restrictions on a possible interpretation. The change of the lattice parameter upon Pr substitution produces not only a change of the exchange constant J, but also of many other electronic parameters. One possible candidate for an electronic excitation, a crystal field exciton or inter-multiplet transition, would be strongly affected by the change of interatomic distances. As far as impurities are concerned, it is difficult to understand that the 1436  $\rm cm^{-1}$  shows only a small sample dependence and that the sharp structures at higher frequencies appear only in samples which are believed to contain *less* impurity contamination. The most likely explanation to us at the present stage are excess oxygen ions on chain sites, which are the only "impurities" present in our samples of  $YBa_2Cu_3O_{6+x}$  in an appreciable amount. These oxygen ions can be randomly distributed or can form cluster or chain fragments, and the extend to which they will prefer one or the other arrangement will certainly depend on the purity of the sample. Other impurities such as Al are known to capture excess oxygen ions, and it is very likely that cleaner samples promote the formation of chain fragments (the oxygen ordering kinetics have been studied both experimentally [482, 483] and theoretically [484-486]). At the same time, the surrounding of the Cu(1) chain sites is the least changing in the elementary cell under rare earth substitution. The very short bond of 1.8 Å between the apical oxygen ion and the Cu(1) ion is mainly determined by the hybridization of their orbitals. The same short bond is found in other materials containing  $Cu^{1+}$ , e.g., in Cu<sub>2</sub>O [50, 487]. Mixing of  $3d^{10}$ ,  $3d^94s^1$  and  $3d^84s^2$  occurs. In the case of a single oxygen impurity its two Cu(1) neighbors will be  $3d^9$  or  $3d^84s^1$ . In the case of  $3d^9$  the two spins on the two Cu sites form a singlet. However, the short bonds are still towards the apical oxygen ions, and hence the overlap between the wave functions of the two spins is rather small, yielding a singlet-triplet splitting of the order of 1/10 of the in plane exchange J. The unusual threefold coordination of a Cu(1) ion next to a single excess oxygen ion or at the end of a chain fragment distorts the *d*-orbitals further from spherical symmetry, which possibly gives rise to low lying *d*-*d* transitions and relaxes optical selection rules. The electronic excitations in the neighborhood of Cu(1) are thus a good candidate for the explanation of the observed sharp structures. We present a calculation of the *d*-*d* excitations on a chain Cu site next to an oxygen impurity in the following section. In preliminary transmission measurements up to  $1600 \,\mathrm{cm}^{-1}$  on pellets of insulating RESr<sub>2</sub>GaCu<sub>2</sub>O<sub>7</sub> we did not find any sharp feature above  $950 \,\mathrm{cm}^{-1}$  (see Fig. 6.15). Structurally, RESr<sub>2</sub>GaCu<sub>2</sub>O<sub>7</sub> is very similar to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, but the Cu-O chains are replaced by Ga-O tetrahedra [488–490].

Also in Raman data the interpretation of some peaks in the 1200 to  $1600 \text{ cm}^{-1}$  range is ambiguous. One peak at  $1250 \text{ cm}^{-1}$  in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> has been clearly identified by oxygen isotope substitution as a multi-phonon feature, showing an isotope shift of 5% [491]. Rübhausen and co-workers [492] observed excitations at 730 and 1170 cm<sup>-1</sup> in PrBa<sub>2</sub>Cu<sub>2.7</sub>Al<sub>0.3</sub>O<sub>7</sub> which show a resonance behavior similar to the one of the two-magnon Raman scattering peak, whereas Liu and collaborators [493] pointed out that a peak at 1290 cm<sup>-1</sup> resonates at both the resonant energies of the fundamental phonons *and* of the two-magnon scattering. A possible relation of these observations to the mid-infrared absorption features studied here remains to be clarified.

#### 6.2 Exact Diagonalization

In this section we discuss the electronic excitations of short chain fragments in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub>. Studies of the electronic structure and of electron-phonon coupling effects related to the chains and apical O ions have been given in Refs. [484–486, 494–496]. We start by briefly recalling the crystal field splitting on a planar Cu(2) ion in the insulator YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>. In a CuO<sub>4</sub> cluster, the ground state wave function takes the form [63, 497]

$$|0\rangle = \sqrt{n_d} |d^9\rangle + \sqrt{1 - n_d} |d^{10}\underline{L}\rangle = \sqrt{0.7} |d^9_{x^2 - y^2}\rangle + \frac{\sqrt{0.3}}{2} \left(|p_{1\sigma}\rangle + |p_{2\sigma}\rangle + |p_{3\sigma}\rangle + |p_{4\sigma}\rangle\right) ,$$

$$(6.1)$$

where  $\underline{L}$  denotes a ligand hole which is distributed among the four surrounding O  $2p_{i\sigma}$  orbitals. In the ground state, both the *d* orbital and the linear combination of the *p* orbitals on the right hand side have  $x^2 - y^2$  symmetry. The hole strongly favors the  $d_{x^2-y^2}$  orbital due to its large overlap with the neighboring negatively charged O ions. All other *d* orbitals hardly mix with the O orbitals, and therefore their energetic positions are rather unaffected by hybridization. As a result, the lowest *d*-*d* excitation is of order 1.5 eV (see tables on page 153). The large overlap is also responsible for the large value of the exchange constant *J*. The occupation probability  $n_d \approx 0.7$  of the  $3d_{x^2-y^2}$  orbital has been determined by Eskes and Sawatzky [63,497] by fitting spectroscopical data.

Now we consider a Cu chain site. We distinguish three cases: next to the two apical O neighbors, a Cu(1) ion can have zero, one or two chain O neighbors in a partly filled chain.



Figure 6.16: Sketch of a single excess oxygen ion on a chain site and of a short chain fragment. Only ions lying within the same bc-face of the crystal are shown. For the calculation of the crystal field splitting of the Cu 3d levels the  $CuO_3$  unit enclosed by the dashed line was used.

The first case corresponds to a filled d shell, which is not of interest to us. The last case with two chain O neighbors is at first sight rather similar to the fourfold coordination within the CuO<sub>2</sub> plane. The  $d_{y^2-z^2}$  orbital will strongly contribute to the ground state. Here, it is important to note that the distance between the Cu(1) site and the apical O site of 1.795Å (1.846) in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>) is much shorter than the one to the chain site with  $a/2 = 1.93 \text{ Å} (b/2 = 1.942 \text{ Å} \text{ in YBa}_2 \text{Cu}_3 \text{O}_7)$  [51]. A recent study by Krüger and collaborators [498] reports an even shorter Cu(1) – apical O bond length, decreasing linearly from 1.80Å in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> to 1.72Å in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub>. Therefore the admixture of  $d_{3x^2-r^2}$  character in the ground state will not be negligible. The technically equivalent description in terms of  $d_{3z^2-r^2}$  and  $d_{x^2-r^2}$  orbitals turns out to be even more appropriate, with a dominating admixture of  $d_{3z^2-r^2}$  character. This is particularly important because the overlap of the  $d_{3z^2-r^2}$  orbital with the chain O  $p_y$  state is a factor of  $\sqrt{3}$  smaller than the  $d_{x^2-y^2} - p_y$ overlap. This is enough to reduce the antiferromagnetic exchange, which is proportional to  $t_{pd}^4$ , for the  $d_{3z^2-r^2}$  orbital by a factor of 9. In other words, one can basically neglect the contribution from the  $d_{3z^2-r^2}$  level to superexchange. As a consequence, the apical stretching phonon, which strongly modulates the symmetry character of the electronic state, will also considerably modulate the exchange constant  $J_{chain}$  within the chain. We expect that some interesting physics may be revealed by a detailed analysis of a chain fragment. However, such an analysis is complicated by the presence of *delocalized* holes within a chain. In a situation as drawn on the right hand side of Fig. 6.16 with two oxygen impurities and three Cu sites one finds *four* spins, which can be viewed as a very high doping level. It is by no means obvious in which way the holes of a short chain fragment are distributed among the CuO chain and the  $CuO_2$  planes. The two planes of a bilayer receive their holes from a single CuO chain. Fully oxygenated YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> is slightly overdoped, *i.e.*, it corresponds to a doping level of 15 to 20% per CuO<sub>2</sub> plane,

which corresponds to an average doping level of 60 to 70% within the chains.

For the sake of simplicity we restrict ourselves to the case of a single excess O impurity, where two holes are shared by the two neighboring Cu ions. The two spins form a singlet. As stated above, the singlet-triplet splitting  $J_{chain}$  is smaller than within the CuO<sub>2</sub> layers since the ground state wave function is a mixture of both  $d_{3z^2-r^2}$  and  $d_{x^2-y^2}$ , where the former is further promoted by the asymmetry of the CuO<sub>3</sub> cluster (see Fig. 6.17 and dashed line in Fig. 6.16). We also mentioned already above that this singlet-triplet splitting  $J_{chain}$ is strongly modulated by a displacement of O ions. In combination with the excitation of a phonon, such a singlet-triplet transition around a single O impurity is therefore a good candidate for the interpretation of one of the sharp peaks in the mid-infrared spectrum. We nevertheless will concentrate on the crystal field level splitting in order to figure out whether it is realistic to expect an electronic transition at a few tenths of 1 eV.



Figure 6.17: Sketch of the  $CuO_3$  cluster used for the calculation of the crystal field levels. The Cu-O distances are assumed to be 1.795Å to the apical O ion and 1.94Å to the chain O ion.

For the calculation of the crystal field level splitting it is sufficient to consider a  $CuO_3$  cluster containing a single hole (see Fig. 6.17). The small occupation probability of a planar hole on the apical O ions is neglected. Most probably the lattice of  $YBa_2Cu_3O_6$  is distorted around a single O impurity. An appreciable effect on the energy levels is however only obtained for unrealistically large spatial deviations, and therefore we assume an undistorted lattice. We furthermore neglect a possible mixing with 4s orbitals such as  $3d^9 \rightarrow$  $3d^84s^1$ . The relevant orbitals are  $3d_{3z^2-r^2}$ and  $3d_{x^2-y^2}$  on Cu(1),  $2p_{y\sigma}$  on the chain O site and the linear combination  $(2p_{z\sigma,apex1})$ - $(2p_{z\sigma,apex2})/\sqrt{2}$  on apical O sites. We neglect the  $(2p_{y\pi,apex1}+2p_{y\pi,apex2})/\sqrt{2}$  orbitals since  $t_{pp} = 0$  is assumed. All other levels are not affected by Cu-O hybridization. The on-site energy  $E_{p,apex}$  on an apical O site is chosen as zero of energy, resulting in  $E_d = -\Delta$ and  $E_{p,chain} = \epsilon$ , where  $\epsilon$  denotes the difference of the Madelung potentials of the distinct O sites, and  $\Delta = 3.5 \text{ eV}$  is the charge transfer energy. The interatomic matrix elements are given by Slater and Koster integrals [441], *e.g.*,

$$t_{pd}(y, x^2 - y^2) = -\frac{\sqrt{3}}{2} V_{pd\sigma} , \quad t_{pd}(z, x^2 - y^2) = 0 , \qquad (6.2)$$

$$t_{pd}(y, 3z^2 - r^2) = -\frac{1}{2} V_{pd\sigma} , \quad t_{pd}(z, 3z^2 - r^2) = V_{pd\sigma} , \qquad (6.3)$$

$$V_{pd\sigma} = V_{pd\sigma}^0 \left(\frac{1.9 \text{\AA}}{d}\right)^{1/2} \quad , \quad V_{pd\sigma}^0 = 1.5 \,\text{eV} \quad , \tag{6.4}$$

where d denotes the Cu-O distance. The ground state, the excited states and their energies can be calculated by diagonalizing the matrix

$$\begin{pmatrix} -\Delta & 0 & t_{13} & \sqrt{2} t_{14} \\ 0 & -\Delta & t_{23} & \sqrt{2} t_{24} \\ t_{13} & t_{23} & \epsilon & 0 \\ \sqrt{2} t_{14} & \sqrt{2} t_{24} & 0 & 0 \end{pmatrix} \begin{pmatrix} d_{3z^2 - r^2} \\ d_{x^2 - y^2} \\ p_{y\sigma,chain} \\ \frac{1}{\sqrt{2}} \left( p_{z\sigma,apex1} - p_{z\sigma,apex2} \right) \end{cases}$$
(6.5)

where the hopping matrix elements  $t_{ij}$  can be obtained from Eqs. 6.2 – 6.4. The resulting energy for the transition from the ground state to the first excited state is displayed in Fig. 6.18 as a function of the Cu(1) – apical O distance (left panel) and of the difference in Madelung potentials of the chain and apical O ions (right panel). The corresponding orbital occupancies in the ground state are plotted in Fig. 6.19. The excitation energy is of the order 1 eV for a reasonable choice of Cu-O distances. The Madelung potential on O sites clearly does not play an important role. In order to obtain a much smaller splitting one has to assume an unrealistically large Cu(1) – apical O bond length. Hence we can reject a scenario involving a low-lying d-d transition for the interpretation of the experimentally observed sharp features in the mid-infrared spectrum.

We conclude that the simplified picture of the electronic structure of short chain fragments described here does not support the identification of the experimentally observed mid-infrared feature with a crystal field transition. What remains as a possible candidate are spin excitations within a chain fragment. For a more detailed study of the spin dynamics within the chains the Cu 3d-4s hybridization might have to be taken into account.

Finally, we point out that a magnetic excitation of about 130 meV has been observed in NQR measurements [499] of La<sub>2</sub>Cu<sub>0.5</sub>Li<sub>0.5</sub>O<sub>4</sub>. In this compound, two holes are *localized* on every CuO<sub>4</sub> plaquette in the plane. Band structure calculations predict that the two holes form a local Zhang-Rice singlet [500], with both holes occupying orbitals of  $x^2 - y^2$ symmetry. A modest reduction of the large planar Cu – apical O distance is found to promote a triplet state, in which the holes occupy a  $d_{x^2-y^2}$  and a  $d_{3z^2-r^2}$  orbital, and the excitation of this triplet state has been proposed as an explanation for the NQR data [500]. It is possible that a similar excitation exists also in a low doped, "conventional" CuO<sub>2</sub> plane in the absence of Li, if a doped hole is localized by, *e.g.*, the potential distortion of an excess oxygen ion in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub>.



Figure 6.18: Exact diagonalization result for the transition from the ground state to the first excited state of a  $CuO_3$  cluster as given in Fig. 6.17. The left panel depicts the dependence on the Cu(1) – apical O bond length (the dashed line indicates a realistic choice), the right panel shows the small effect of a different Madelung potential on apical and chain O sites.



Figure 6.19: Occupation probabilities of  $Cu \ d$  and  $O \ p$  orbitals in the ground state of a  $CuO_3$  cluster as given in Fig. 6.17. The short Cu(1) – apical O distance clearly favors the  $d_{3z^2-r^2}$  state.

### Chapter 7

# Magneto-Elastic Polarons in Low Doped $YBa_2Cu_3O_{6+\delta}$

After having analyzed the optical conductivity spectrum of undoped  $YBa_2 Cu_3 O_6$  in the preceding chapters, we now turn to the study of low doped  $YBa_2 Cu_3 O_x$  ( $6.0 \le x \le 6.2$ ) in the far- and mid-infrared frequency range. We observe that very light chemical doping with oxygen introduces localized charge carriers in the form of magneto-elastic polarons, i.e., holes which are strongly coupled both to the vibrational and magnetic degrees of freedom.

#### 7.1 Introduction

The important question, whether the Hubbard model or its low energy version, the t-J model, capture the physics relevant to obtain a high  $T_c$  superconductor is still open. The low energy dynamics and in particular the optical conductivity  $\sigma(\omega)$  of holes doped into a 2D S = 1/2 square-lattice antiferromagnet have been the subject of intensive theoretical investigations [60-62, 242, 243, 502]. We reproduce an exact diagonalization result for  $\sigma(\omega)$ from Eder, Wróbel and Ohta [242] in Fig. 7.1. Strong interactions with the antiferromagnetic background renormalize the bandwidth drastically. The Drude weight is suppressed and a large part of the spectral weight is transferred to incoherent excitations, smeared out over a wide frequency range (up to about 6t in Fig. 7.1). Good agreement has been obtained between these exact diagonalization studies of the t-J model [242] and analytical calculations for spin-bag quasiparticles [243]. There, the very broad incoherent contribution is identified with internal excitations of spin-bags or spin polarons. The hole moves incoherently on an energy scale  $\sim t$  within a region of reduced staggered magnetization (see Fig. 2.19 on page 51). The hole plus the defect region move *coherently* on the lower energy scale  $\sim J$ , which is possible due to quantum spin fluctuations. In 1D, a robust Drude peak is obtained in exact diagonalization studies [503], but only a negligible amount of spectral weight is found at finite frequencies [503], contrary to the 2D case. The quasiparticles decay into spinons and holons in 1D and hence there is no "dressing" of the holons with





Figure 7.1: Exact diagonalization result of Figure 7.2: Doping dependence of  $\sigma(\omega)$  of the optical conductivity spectrum of one or  $La_{2-x}Sr_xCuO_4$  at 300 K, reproduced from two holes doped into a cluster of size N for the t-J model, reproduced from Eder, Wróbel and Ohta [242]. The relevant parameter set for the cuprates is J = 0.25t. The thin solid line denotes  $\omega = 1.7J$ .

Uchida et al. [65].

spin excitations, which supports the view that the incoherent excitations of the dressing are strongly related to the mid-infrared absorption in 2D [60]. However, one has to keep in mind that a photon creates an electron-hole excitation, *i.e.*, it does not couple directly to holons, and that the energy and the momentum of the electron-hole pair can be distributed among holons and spinons.

Experimentally,  $\sigma(\omega)$  deviates from the free electron Drude form at all doping levels in all 2D cuprates [25, 44, 65]. Spectra of  $\sigma(\omega)$  over a wide doping range are summarized in Figs. 7.2 and 7.3 for  $La_{2-x}Sr_xCuO_4$  [65] and  $YBa_2Cu_3O_{6+y}$  [29]. Note that the sample temperature is 300 K in both figures. In the metallic regime, the non-Drude behavior has been approached in a microscopically meaningful way by extracting the frequency dependent self-energy (usually in the form of scattering rate and effective mass) from the experimental spectra. It has been claimed [60–62] that the t-J model describes  $\sigma(\omega)$  in the metallic regime well. The experimental data of the low doped insulating state were



Figure 7.3: Doping dependence of  $\sigma(\omega)$  of  $YBa_2 Cu_3 O_{6+y}$  at 300 K, reproduced from Cooper et al. [29].



Figure 7.4: Top: reflectivity spectra of undoped (y=0) and low doped (y=0.014) La<sub>2</sub> CuO<sub>4+y</sub>. Bottom: temperature dependence of  $\epsilon''(\omega)$  for  $E \parallel CuO_2$  and y=0.014. Reproduced from Falck et al. [45].



Figure 7.5: Spectra of  $\sigma(\omega)$  of different low doped cuprates, reproduced from Thomas et al. [504]. Note that the sample temperatures are 300 K for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+y</sub> and 4 K for the others.



Figure 7.6: Low temperature photo-induced absorption spectra of powder samples, reproduced from Li, Kim and Cheong [506].

discussed in more conventional terms, neglecting the electronic correlations. Two distinct peaks at about 1200 and 5000 – 6000 cm<sup>-1</sup> have been found in various low doped cuprates in both reflectance spectra of chemically doped single crystals [45, 504] (see Figs. 7.4 and 7.5) and photo-induced absorption data (photo doping) [505, 506]. Different studies of photo-induced absorption disagree on the spectral weight of the two peaks, showing, *e.g.*, predominantly the lower (upper) peak in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+y</sub> (La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>) [507], which has led to some confusion concerning the assignment [507]. Recently, the simultaneous presence of both peaks in photo-induced absorption data has been demonstrated by Li, Kim and Cheong [506] in various cuprates (see Fig. 7.6).

For both doping induced peaks interpretations in terms of impurities and lattice degrees of freedom were proposed. Falck and co-workers [45] (see Fig. 7.4) interpreted the lower peak in La<sub>2</sub>CuO<sub>4.014</sub> as a photo-ionization process of holes bound to oxygen impurities forming polaronic impurities, *i.e.*, involving a lattice relaxation. Thomas and collaborators [504] (see Fig. 7.5) attributed the *higher* peak at about 5000 – 6000 cm<sup>-1</sup> to an impurity ionization process, and suggested a magnetic excitation of a carrier bound to an impurity as origin for the 1200 cm<sup>-1</sup> peak because its frequency is close to the exchange constant J. However, the theoretical oscillator strength of this excitation is too small compared to experiment [509]. These assignments seem to indicate that at low doping levels the hole dynamics are dominated by impurities and a coupling to the lattice, with the amusing consequence that the theoretically widely studied case of a "single hole in an antiferromagnet" only seems to apply to experimental data at higher doping levels [60–62].

So far, there have been no detailed experimental studies of  $\sigma(\omega)$  in the very low doping regime. We present low temperature spectra of eight different samples of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> with x < 6.1, corresponding to an effective carrier density  $\leq 5 \cdot 10^{19}$  cm<sup>-3</sup>. This allows us to draw the doping dependence of  $\sigma(\omega)$  on a logarithmic scale in Fig. 7.7. Data for  $x \geq 6.1$ have been reproduced from Münzel [501]. The x = 6.3 data agree favorably with the results of Thomas and co-workers [504] (see Fig. 7.5; note the different temperatures). Here, we concentrate on the low doping regime which is indicated by the grey area. Compared to the undoped case, the low doping level of our samples hardly affects the far-infrared spectrum, where a Drude contribution can only be inferred indirectly (see below). Yet, we observe drastic changes in the mid-infrared frequency range (see Fig. 7.8). A broad background arises which is attributed to the incoherent internal excitations of spin polarons. A strongly temperature dependent peak at  $1050 \text{ cm}^{-1}$  is interpreted as a photo-ionization process of a localized magneto-elastic polaron, *i.e.*, not of a bare hole, but of a quasiparticle dressed by phonons and magnons. The evolution of these features with doping is studied for x=6.1, 6.2 and 6.3.

#### Sample Preparation

Single crystals of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> were grown in Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub> (YSZ) crucibles as described elsewhere [397]. In order to reduce the oxygen content the samples were annealed (i) in ultra high vacuum at 700°C (undoped case), (ii) between 2 and 5 days in a flow of high purity Argon (99.998 %) at 750°C (x < 6.1), or (iii) according to the calibration of



Figure 7.7: Doping dependence of  $\sigma(\omega)$  of  $YBa_2 Cu_3 O_x$  at 4 K (100 K for the superconducting samples with x = 6.4 and 6.92). Data for  $x \ge 6.1$  are reproduced from Münzel [501]. The x = 6.3 data agree favorably with the results of Thomas and co-workers [504] (see Fig. 7.5; note the different temperatures). Here, we focus on the low doping regime indicated by the grey area.



Figure 7.8: Mid-infrared  $\sigma(\omega)$  spectra of  $YBa_2 Cu_3 O_x$  in the low doping regime x < 6.1 at 4 K. Note the very low values of  $\sigma(\omega)$ . Top panel: samples grown in  $ZrO_2$  crucibles; bottom panel: oxygen isotope substituted sample of  $YBa_2 Cu_3^{18}O_6$  grown in a  $BaZrO_3$  crucible.



Figure 7.9: Doping induced changes in  $\sigma(\omega)$  of  $YBa_2 Cu_3 O_x$  with x < 6.1 at 4 K. These curves have been obtained by subtracting the lowest spectrum in the top panel of Fig. 7.8 from all the others. The arrows indicate that it is not obvious whether the spectra show one or two doping induced peaks between 1000 and 1500 cm<sup>-1</sup>. Part of the structure at 1000 cm<sup>-1</sup> can be due to differences in spectral weight of multi-phonon absorption.

Lindemer and co-workers [396] (6.1  $\leq x \leq$  6.3). The full exchange of the oxygen isotope in a sample grown in a BaZrO<sub>3</sub> (BZO) crucible [117] was described on page 106. Reflection and transmission measurements were carried out between 30 cm<sup>-1</sup> and 12000 cm<sup>-1</sup> for temperatures ranging from 4 to 300 K. We calculated  $\sigma(\omega)$  either by (a) inverting the Fresnel equations for the experimentally measured transmission and reflection data, or (b) in the case of strong absorption ( $\sigma(\omega) \geq 20 \,\Omega^{-1}$ cm<sup>-1</sup>) by using a Kramers-Kronig analysis of reflectivity data measured up to 6 eV [433]. The small remnants of interference fringes in some of the calculated spectra of  $\sigma(\omega)$  are artefacts caused by deviations of the measured data from the in (a) assumed ideal case of absolutely flat and plane parallel surfaces.

### 7.2 Discussion

In the absence of doping  $\sigma(\omega)$  of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.0</sub> shows phonons below 650 cm<sup>-1</sup> and the charge transfer gap at about 12000 cm<sup>-1</sup> (see preceding chapters). The electronic low energy excitations are magnetic for zero doping, and they produce spectral weight in the gap





above 2000 cm<sup>-1</sup> in the form of bimagnon-plus-phonon absorption [224, 225] (see chapter 5). Experimentally, the undoped case is realized in the sample annealed in ultra high vacuum (lowest curve in the top panel of Fig. 7.8). All other curves in Fig. 7.8 represent the influence of very low doping on  $\sigma(\omega)$  (top/bottom panel: samples with O isotope  ${}^{16}\text{O}/{}^{18}\text{O}$ ). Note that all samples are still very close to the undoped limit YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.0</sub>, as  $\sigma(\omega)$  in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.1</sub> already amounts to 25 – 100  $\Omega^{-1}\text{cm}^{-1}$  (see Fig. 7.7). In order to focus on the doping induced *changes*, we subtracted the  $\sigma(\omega)$  spectrum of the undoped sample from the data of the others (see Fig. 7.9). Most prominent are: (a) a very broad, flat background, (b) a strong peak at about 1050 cm<sup>-1</sup>, and (c) an increase in oscillator strength of bimagnon-plus-phonon absorption. These data agree with the above mentioned results of previous studies of higher doping levels, which concentrate on peaks at about 1300 ± 250 and 5000 ± 400 cm<sup>-1</sup> (values for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+y</sub>) [45,504] (see Figs. 7.4 and 7.5). At the same time, our spectra reveal a strong contribution of the broad background, which is observed for the first time.

Let us first address the magnetic excitations. In the cuprates, direct magnon absorption is not allowed for symmetry reasons. This selection rule can be relaxed by either exciting a phonon simultaneously [224, 225] or by adding impurities as, e.g., Zn [429] (see Fig. 5.8 on



Figure 7.11: Photo-induced absorption spectra of powder samples of  $YBa_2Cu_3O_x$  mixed with CsI for temperatures in the range from 7 to 27 K, reproduced from Ye et al. [381]. Note the photo-induced bimagnon-plus-phonon absorption peak at 2800 cm<sup>-1</sup> for x > 6. The data agree very well with our results for chemical doping, see Fig. 7.9.

page 138). However, neither the O impurities located about 4 Å away from the spins of the  $CuO_2$  layers nor the holes doped into these layers do the same: we do not find any indication for direct bimagnon absorption below the bimagnon-plus-phonon peak. Unexpectedly, the spectral weight of *bimagnon-plus-phonon* excitations increases with doping, which cannot be explained by symmetry breaking effects. In chapter 5 a strong increase of spectral weight of magnetic excitations with increasing temperature was observed and attributed to enhanced spin fluctuations. It is hence tempting to speculate about a similar origin here, namely an enhancement of spin fluctuations caused by the doped holes.

Bimagnon-plus-phonon absorption can also be detected in low doping data of other authors. We identify a so far not understood weak peak in low doped Nd<sub>2</sub>CuO<sub>4- $\delta$ </sub> at 2750 cm<sup>-1</sup> [504] (see Fig. 7.5) with the bimagnon-plus-phonon peak observed at the same frequency by Perkins and co-workers [226] in Nd<sub>2</sub>CuO<sub>4</sub>. In Fig. 7.11 we reproduce photoinduced absorption spectra of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> from Ye and collaborators [381], which are in excellent agreement with our results. Note the different scales of the four panels. All spectra with x > 6 show an enhancement of bimagnon-plus-phonon absorption around 2800 cm<sup>-1</sup>, which had not been realized thus far. The photo-induced absorption spectra further agree with our results by showing a peak *above* 1250 cm<sup>-1</sup> at doping levels very close to the insulating state (upper left panel of Fig. 7.11) and a peak around  $1000 \text{ cm}^{-1}$  for higher doping concentrations. A similar behavior is apparent in Fig. 7.8; note also the arrows in Fig. 7.9. Ye and collaborators [381] had attributed this absorption to excitations within the Cu-O chains. However, the observation of a peak at this frequency in *all* low doped cuprates (see Figs. 7.4 and 7.5) identifies it as an intrinsic feature of the carriers doped into the CuO<sub>2</sub> planes.

At higher frequencies, our results indicate an increase of spectral weight at about 4000 cm<sup>-1</sup> which can be traced back to the features at 3825 and  $4325 \text{ cm}^{-1}$  in undoped samples (see Fig. 7.10). However, the above mentioned feature at  $5000 \pm 400 \text{ cm}^{-1}$  [504] does not coincide with any magnetic peak in the undoped compounds. This is particularly clear in the case of Nd<sub>2</sub>CuO<sub>4-y</sub>, in which the bimagnon-plus-phonon peaks are observed at a lower frequency than in La<sub>2</sub>CuO<sub>4</sub> [226,227], whereas the doping induced peak is much higher in frequency than in La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> [504] (see Fig. 7.5).

The doping induced broad background reflects the strongly correlated nature of the doped carriers. In an ordinary semiconductor doping gives rise to an impurity band with a well defined peak frequency within the semiconducting gap. Our data show that already low doping produces spectral weight in the *whole* frequency range below the charge transfer gap in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.0\delta</sub>. This can only be explained by strong correlations. The *t-J* model for example shows incoherent excitations for frequencies up to 6t [242] (see Fig. 7.1).

The key to the interpretation of the  $1050\,\mathrm{cm}^{-1}$  peak can be found in its temperature dependence (see Fig. 7.12; note the different absolute values of the three panels). The spectral weight of the  $1050 \text{ cm}^{-1}$  peak decreases strongly with increasing temperature, and at 300 K only the broad background is left. The spectral weight is transferred to  $\omega=0$ , which can only be shown indirectly. Due to the very low doping level, no Drude peak is observed in the measured frequency range down to  $30 \text{ cm}^{-1}$ . Absorption is low and the samples are transparent at all temperatures. This allows to observe and analyze interference fringes which occur due to multiple reflectance on the sample surfaces (see Fig. (7.13). The position of a given interference minimum is proportional to 1/nd (neglecting absorption), where n is the refractive index and d the sample thickness. Neglecting small changes in d with temperature, we can deduce the temperature dependence of n from the shift of an interference minimum (the arrows in Fig. 7.13 are guides to the eye). In the undoped case x = 6.0 (left panel) the minimum shifts to lower frequencies with increasing temperature, *i.e.*, *n* increases. For finite doping (mid panel, <sup>18</sup>O) n first increases from 4 to 100 K as in the undoped case, but for higher temperatures it starts to decrease. At a doping level corresponding to the highest curve in Fig. 7.8 n decreases with increasing temperature (right panel of Fig. 7.13). This claim can be substantiated by analyzing the full interference spectrum. As discussed in chapter 4 it is possible to determine the phonon-polariton dispersion from the interference spectrum. For the two samples of the left and mid panel of Fig. 7.13 the result is displayed in Fig. 7.14. The large period of the interferences in the higher doped sample (right panel of Fig. 7.13) prohibited such an analysis. We recall that the slope of the dispersion is given by  $(\epsilon')^{-1/2}$ . In the undoped sample, the 300 K dispersion curve is lying below the 4 K data, most likely due to the redshift of the phonon at  $115 \text{ cm}^{-1}$  with increasing temperature. The same is true for



Figure 7.12: Temperature dependence of  $\sigma(\omega)$  of  $YBa_2 Cu_3 O_x$  for different low doping concentrations. Note the different absolute values of  $\sigma(\omega)$  in the three panels. Bottom panel: data of  $YBa_2 Cu_3^{18}O_{6.0\delta}$ . Data in mid panel correspond to the highest curve in Fig. 7.8. The curve for x = 6.1 (top panel) is reproduced from Münzel [501] and was obtained via a Kramers-Kronig analysis of reflectance data, whereas data in the lower panels were calculated from transmittance and reflectance measurements.

the lightly doped sample between  $\omega = 85 - 100 \text{ cm}^{-1}$ , but at lower frequencies and wave vectors the opposite is the case, indicating a smaller value of  $\epsilon'$ . This decrease of n or  $\epsilon'$  with increasing temperature in the doped samples can be attributed to the negative contribution of the Drude peak to the real part of the dielectric constant. This is corroborated by the simulation plotted in the right panel of Fig. 7.14. Here, the solid line has been derived from a fit of the 4 K reflectivity data of an undoped sample. The dashed line is obtained by adding a small Drude term with  $\omega_0 = 0$ ,  $\omega_p = 100 \text{ cm}^{-1}$  and  $\gamma = 25 \text{ cm}^{-1}$  to the fit, and by using the experimental 4 to 300 K redshift of  $0.9 \text{ cm}^{-1}$  for the 115 cm<sup>-1</sup> phonon. The simulation agrees very well with the experimental data of the doped sample. Hence we conclude that spectral weight is transferred from the mid-infrared to  $\omega=0$ . In Ref. [45] the same conclusion was drawn from an analysis of the temperature dependence of the Hall coefficient.

The spectral weight transfer to  $\omega = 0$  points towards a photo-ionization process of a polaronic impurity [45]. Let us describe this process in more detail. We start by recalling that the scale for the coherent motion of a spin polaron is set to J by the strong interactions of a doped hole with the antiferromagnetic spin background. As this motion is slow, already a moderate coupling  $\lambda$  to the lattice is sufficient to distort the lattice around the spin polaron, *i.e.*, to form a *magneto-elastic* polaron. The doped hole now has to drag along a cloud of both magnetic and vibrational excitations, which makes it so heavy that it can be trapped easily by impurities. The polaronic impurity hence denotes an impurity-bound state of a hole, around which both the lattice and the spin background have relaxed. The above mentioned optical photo-ionization peak observed at  $1050 \,\mathrm{cm}^{-1}$ corresponds to a process, in which the bare hole is kicked off the impurity before the lattice can react. On contrary, thermal ionization is an adiabatic process, and therefore the thermal activation energy is much smaller: the presence of thermally activated phonons at elevated temperatures washes out the potential well of the lattice part of the polaron, and the peak vanishes already at 300 K. In photo-induced absorption measurements [505, 506, 508 the decrease of spectral weight with increasing temperature of the 1200 cm<sup>-1</sup> peak starts already at much lower temperatures, suggesting a smaller binding energy for photo-carriers [45] as compared to chemical doping. At first sight one might expect that the frequency of the photo-ionization process varies strongly among different cuprates due to, e.g., the differences in distance of the impurity to the  $CuO_2$  layers. However, the peak frequency is mainly determined by the relaxation of the lattice, especially of the O phonon modes of the  $CuO_2$  layers, which are similar among different cuprates. In an LDA+Ucalculation on a  $2 \times 2$  supercell of  $La_{2-x}Sr_xCuO_4$  Anisimov and collaborators [510] found an effective dielectric constant of  $\epsilon^* = 11$  and an impurity ionization energy of  $\approx 800 \,\mathrm{cm}^{-1}$ .

It is important to note that the broad background, *i.e.*, the incoherent *spin* polaron contribution to  $\sigma(\omega)$ , does not show an appreciable temperature dependence. Whether the quasiparticles are localized by impurities (4 K) or not (300 K) does not influence the spin polaron absorption. This reveals the nature of the bound particle: it is not a bare hole, but a spin-polaron.

The simultaneous coupling of the doped carriers to both spin and lattice degrees of freedom raises a chicken-or-egg question. Electron-phonon coupling and electron-spin coupling



Figure 7.13: Temperature dependent position of interference minima. The doping concentration increases from the left to the right panel. Data in the latter correspond to the highest curve in Fig. 7.8. The behavior observed in the right panel indicates a transfer of spectral weight to  $\omega = 0$  with increasing temperature (see Fig. 7.14 below and main text). Inset: 4 K spectra of the samples shown in the left and mid panels on an expanded scale.



Figure 7.14: Polariton dispersion at 4 and 300 K derived from the interference extrema of the same samples as shown in the inset and the left and mid panels of Fig. 7.13 above. The simulation in the right panel refers to the transfer of spectral weight in the low doped case. The solid line was derived from a fit of 4 K data of an undoped sample; the dashed line was obtained by (i) adding a small Drude peak with  $\omega_0 = 0$ ,  $\omega_p = 100 \text{ cm}^{-1}$  and  $\gamma = 25 \text{ cm}^{-1}$ , and (ii) shifting the  $115 \text{ cm}^{-1}$  phonon by  $0.9 \text{ cm}^{-1}$  to the lower 300 K position. For the dash-dotted line we used  $\omega_p = 200 \text{ cm}^{-1}$  and a phonon redshift of  $5 \text{ cm}^{-1}$ .



Figure 7.15: Absorption spectrum of the planar Cu-O stretching phonon mode for the case of one doped hole as calculated by Yonemitsu, Bishop and Lorenzana [502] in the three-band Peierls-Hubbard model. A moderate electron-phonon coupling constant of  $\lambda = 0.5$  is assumed, which produces a peak on the low frequency side of the phonon.

reinforce each other [511]. The electronic correlations renormalize the bandwidth, *i.e.*, the kinetic energy of the holes is no longer large compared to the lattice polaron binding energy. Without the coupling to the spin background in the first place the electron-phonon coupling would not be strong enough in the cuprates to trap the doped holes. On the other hand, a further increase of the electron-spin coupling makes the electron-phonon interaction even more effective, as observed in the S = 1 nickelates [512]. If  $\lambda$  were large on its own, then already the *bare* hole would be trapped by the lattice and the contribution of the magnetic polaron to  $\sigma(\omega)$  would be suppressed. In terms of  $\sigma(\omega)$  this means that both electron-spin and electron-phonon interaction suppress the Drude contribution centered at  $\omega=0$  and shift spectral weight to finite frequencies. With increasing temperature the electron-phonon part of this spectral weight transfer is neutralized, but this hardly affects the broad background.

A further indication for a lattice contribution to the absorption process at  $1050 \text{ cm}^{-1}$  is given by the different behavior of the oxygen isotope substituted YBa<sub>2</sub>Cu<sub>3</sub><sup>18</sup>O<sub>6+y</sub> sample. There, the temperature dependence (Fig. 7.12) is similar above the peak frequency, but more complicated below, where  $\sigma(\omega)$  is *higher* at 100 K than at 4K. Also the peak frequency seems to depend on the oxygen isotope, shifting from about  $1050 \text{ cm}^{-1}$  in YBa<sub>2</sub>Cu<sub>3</sub><sup>16</sup>O<sub>6+y</sub> to  $1450 \text{ cm}^{-1}$  in YBa<sub>2</sub>Cu<sub>3</sub><sup>18</sup>O<sub>6+y</sub>. However, it is possible that the feature in YBa<sub>2</sub>Cu<sub>3</sub><sup>16</sup>O<sub>6+y</sub> consists of *two* peaks, one at  $1050 \text{ cm}^{-1}$  and one at  $1450 \text{ cm}^{-1}$ , and the latter one dominates at lower doping levels (see arrows in Fig. 7.9; note also Fig. 7.11). Speculating about a possible origin for a distinct peak at  $1450 \text{ cm}^{-1}$  we note that an exact diagonalization study of the *t*-*J* model shows a peak in  $\sigma(\omega)$  at 1.7J [242] (see thin solid line in Fig. 7.1), corresponding to  $\approx 1350 \text{ cm}^{-1}$  in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>.

Based on a Hartree-Fock study Yonemitsu and co-workers [502] proposed that already for moderate values of electron-phonon coupling the relaxation of the lattice around a magnetic polaron will give rise to a local phonon mode (see Fig. 7.15). We identify this local mode with the side peak of the in-plane Cu-O bond stretching phonon mode at 500 cm<sup>-1</sup> for x=6.1, 6.2 and 6.3 (see Fig. 7.16). The temperature dependence of this side peak is identical to the one of the magneto-elastic polaron peak at 1050 cm<sup>-1</sup> (compare top panel of Fig. 7.12), which corroborates the assignment. A similar behavior was observed in Nd<sub>2</sub>CuO<sub>4- $\delta$ </sub> [424, 513] (see Fig. 4.19 on page 127 for the 4 K data).

All absorption processes described here can also be observed at higher doping levels (see



Figure 7.16: Temperature dependence of  $\sigma(\omega)$  of  $YBa_2 Cu_3 O_x$  at intermediate doping concentrations. Data for  $x \ge 6.1$  are reproduced from Münzel [501]. The broad peak at about 1000 cm<sup>-1</sup>, the peak at 500 cm<sup>-1</sup> (see Fig. 7.15) and the shoulder on the high frequency side of the stretching phonon mode at  $600 \text{ cm}^{-1}$  (see discussion in chapter 4) are all present at all doping levels at low temperatures.

Fig. 7.16). With increasing doping a strong increase of the broad background occurs. All samples show the photo-ionization peak of the magneto-elastic polaron and its suppression at higher temperatures. A Drude-like peak develops only for  $x \ge 6.3$ .

In conclusion, we have observed that very low doping of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> produces spectral weight at all frequencies below the charge transfer gap, as expected for an insulating correlated electron system. We have shown that the interactions of the doped carriers with both spin and lattice degrees of freedom are crucial to understand  $\sigma(\omega)$  in low doped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>.

### Chapter 8

## c-axis Electrodynamics in the Superconducting Phase

### 8.1 Observation of Out-of-Phase Bilayer Plasmons in $YBa_2Cu_3O_x$

The temperature dependence of the c-axis optical conductivity  $\sigma(\omega)$  of optimally and overdoped YBa<sub>2</sub> Cu<sub>3</sub> O<sub>x</sub> (x=6.93 and 7) is reported in the far- and mid-infrared range. Below  $T_c$  we observe a transfer of spectral weight from the far-infrared not only to the condensate at  $\omega = 0$ , but also to a new peak in the mid-infrared. This peak is naturally explained as a transverse out-of-phase bilayer plasmon by a model for  $\sigma(\omega)$  which takes the layered crystal structure into account. With decreasing doping the plasmon shifts to lower frequencies and can be identified with the surprising and so far not understood far-infrared feature reported in underdoped bilayer cuprates.

After many years the discussion about the charge dynamics perpendicular to the CuO<sub>2</sub> layers of the high T<sub>c</sub> cuprates is still very controversial. The role attributed to interlayer hopping ranges from negligible to being the very origin of high T<sub>c</sub> superconductivity [39]. There is no agreement about the relevant excitations nor about the dominant scattering mechanism. The *c*-axis resistivity  $\rho_c$  is much larger than predicted by band structure calculations. The anisotropy  $\rho_c/\rho_{ab}$  can be as large as 10<sup>5</sup> and shows a strong temperature dependence, especially in the underdoped regime, which has been interpreted as an indication for non-Fermi liquid behavior and confinement [55]. This strong temperature dependence is due to two different regimes with  $d\rho_c/dT < 0$  for  $T_c < T < T'$  and  $d\rho_c/dT > 0$  for T > T', with a crossover temperature T' that decreases with increasing doping (see phase diagram Fig. 2.28(d) on page 62). There is some agreement as to the phenomenology that  $\rho_c$  is described by a *series* of resistors [55,514,515], *i.e.*, that different temperature dependence of the competing contributions. Overdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> is often regarded as a remarkable exception, as  $\rho_c/\rho_{ab}$  is only about 50, and  $d\rho_c/dT > 0$  for all T > T<sub>c</sub>. It

is an important issue whether a sign change in  $d\rho_c/dT$  at low T is really absent or only hidden by  $T_c$  being larger than a possible T', *i.e.*, whether overdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> follows anisotropic three dimensional (3D) or rather 2D behavior.

The c-axis optical conductivity  $\sigma_1(\omega)$  of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> shows several remarkable features [32, 58, 304, 305, 312]: (1) It's very low value compared to band structure calculations, reflecting the large  $\rho_c$ . (2) A suppression of spectral weight at low frequencies already above  $T_c$  in underdoped samples referred to as the opening of a "pseudogap" (which agrees with the upturn in  $\rho_c$ ). We will elaborate the aspect of a pseudogap in the single layer compound La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> in the following section 8.2. (3) The appearance of an intriguing broad "bump" in the far-infrared at low temperatures in underdoped samples (see Fig. 8.6 below). (4) In overdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>, the spectral weight of the superconducting condensate is overestimated from  $\sigma_1(\omega)$  as compared to microwave techniques [516].

In this chapter we suggest that most of the above mentioned issues can be clarified by modelling the cuprates or in particular YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> as a stack of coupled CuO<sub>2</sub> layers with alternating weaker and stronger links. A similar model was proposed for the superconducting state by van der Marel and Tsvetkov [43]. A *transverse* optical plasmon was predicted in Josephson coupled bilayer cuprates. This model has been verified in SmLa<sub>0.8</sub>Sr<sub>0.2</sub>CuO<sub>4- $\delta$ </sub> by Shibata and Yamada [517]. We report the observation of this mode in the infrared spectrum of optimally and overdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> and propose a common origin with the above mentioned "bump" in underdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>. The multilayer model in the form introduced in section 3.2.2 fits the measured data at all doping levels and at all temperatures. Our observations can be regarded as a realization of the "excitons" first considered by Leggett [357], which involve the relative phase fluctuations of the condensates formed in two different bands crossing the Fermi surface.

Single crystals of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> were grown using the recently developed BaZrO<sub>3</sub> crucibles [117]. We studied two samples with x=6.93 and 7 with superconducting transition temperatures of 91 and 87 K, respectively, corresponding to the optimally doped and overdoped regimes. Details of the sample preparation are given on page 106. Polarized reflection measurements were carried out between 50 and 3000 cm<sup>-1</sup> for temperatures between 4 and 300 K. As a reference we used an *in-situ* evaporated Au film. Above 2000 cm<sup>-1</sup> the spectra are almost temperature independent. The optical conductivity  $\sigma_1(\omega)$  was calculated via a Kramers-Kronig analysis.

The measured *c*-axis reflectivity spectra are displayed in Fig. 8.1. The data show a weak free carrier contribution in the normal state. Upon cooling below  $T_c$  a sharp reflectivity edge develops at about  $250 - 300 \text{ cm}^{-1}$ . This had been identified as a Josephson plasmon, a collective mode in a stack of Josephson coupled 2D superconducting layers. Simultaneously, the optical out-of-phase bilayer plasmon peak forms at about  $800 - 900 \text{ cm}^{-1}$ . Due to the relatively small electronic background, the *c*-axis phonons can be determined accurately even at these high doping levels. The chain Cu - apical O bond stretching phonon is a sensitive indicator of the O concentration. This mode is located at  $574 \text{ cm}^{-1}$  for x =7 and at  $637 \text{ cm}^{-1}$  in the insulating phase with x = 6 (see chapter 4). The different resonance frequencies are due to the absence or presence of chain O ions. At intermediate O concentrations, the chain Cu ion, against which the apical O vibrates, has either zero,


Figure 8.1: Temperature dependence of the c-axis reflectivity of optimally (x = 6.93) and overdoped (x = 7) YBa<sub>2</sub> Cu<sub>3</sub> O<sub>x</sub>. The Josephson plasmon reflectivity edge at about 250 – 300 cm<sup>-1</sup> and the optical bilayer plasmon peak at about 800 – 900 cm<sup>-1</sup> form simultaneously upon cooling below T<sub>c</sub>.





one or two chain O neighbors. Therefore, three different peaks are expected for x = 6.93, which indeed is the case: most of the spectral weight is in the "full chain" mode at 571 cm<sup>-1</sup>, and small features are observed at 620 and 634 cm<sup>-1</sup>. The absence of these higher peaks in the x = 7 data proves the stoichiometry of this sample. The same conclusion can be drawn from the lowest phonon at  $155 \text{ cm}^{-1}$  (see Fig. 8.2). At 4 K, a sharp dip is observed for x = 7, whereas an O deficiency induced side band appears at  $147 \text{ cm}^{-1}$  for x = 6.93. The phonon parameters deduced from a Lorentzian fit of the 4 and 100 K data are summarized in Table 8.1.

The 4 and 100 K c-axis reflectivity and  $\sigma_1(\omega)$  derived from it are plotted in Fig. 8.3 (solid and dashed black lines). Disregarding the phonons,  $\sigma_1(\omega)$  shows an almost constant value of about 200  $\Omega^{-1}$  cm<sup>-1</sup>. A Drude-like upturn is only observed at low frequencies in the overdoped case x = 7. The gradual suppression of  $\sigma_1(\omega)$  below about 700 cm<sup>-1</sup> can be attributed to the opening of the superconducting gap. The finiteness of  $\sigma_1(\omega)$  at all

	x = 7						x=6.93					
	$4\mathrm{K}$			100K			4K			100K		
	$(\omega_{\varepsilon})$	$, \omega_n, \gamma$	(n)			elect	ronic					
A	1526	1171	700	0	1814	142	1311	0	0	0	2146	563
В	3461	1182	600	0	3389	150	3480	0	0	0	3677	498
	$(\omega_0,  \omega_p,  \gamma)$											
MIR	796	1511	633	629	2837	1343	525	1131	762	906	3818	4078
				Phonons								
	$(\omega_0,  \omega_p,  \gamma)$						147	203	14	146	80	3.7
	155	272	1.2	154	301	2.0	155	338	2.4	155	396	3.4
	194	121	4.3	195	109	5.0	193	133	4.0	194	113	5.2
	278	256	13	280	300	22	279	271	13	280	272	13
	312	382	4.3	315	372	7.4	313	453	4.6	316	526	10
	573	333	9.2	573	315	12	568	428	12	569	403	16
							618	92	7.3	618	116	10
							630	56	4.2	630	77	6.0

Table 8.1: Parameters (in  $cm^{-1}$ ) used in the two-layer model fit of the 4 K and 100 K reflectivity data. The electronic contribution in the mid-infrared (MIR) describes the broad incoherent background in the normal state and mimics the gap in the superconducting state. Contributions above 10000 cm<sup>-1</sup> describing the high frequency spectrum are not given in the table.

frequencies reflects the *d*-wave symmetry of the gap. The *increase* of  $\sigma_1(\omega)$  between 700 and 1500 cm<sup>-1</sup> from 100 to 4 K is a central issue in our discussion. The superconducting phase transition obeys case II coherence factors for electromagnetic absorption [518]. In the dirty limit relevant for *c*-axis transport this means that only a *suppression* of  $\sigma_1(\omega)$  is expected for frequencies not too close to 0. The difference of spectral weight above and below  $T_c$  defined as (for  $T < T_c$ ):

$$\omega_{\Delta}^{2}(\mathbf{T},\omega) = 8 \int_{0^{+}}^{\omega} \left[ \sigma_{1}(100\mathbf{K},\omega') - \sigma_{1}(\mathbf{T},\omega') \right] \mathrm{d}\omega'$$
(8.1)

is expected to rise monotonically with increasing frequency to a constant value for frequencies much larger than the gap. It is common practice to determine the spectral weight of the superconducting condensate from this constant value. Our data clearly indicate a non-monotonic behavior of  $\omega_{\Delta}(\omega)$  (Fig. 8.4, see also Ref. [305]) and a spectral weight transfer from low frequencies to a new peak above the phonons. This can naturally be explained by the following model for  $\sigma_1(\omega)$  which takes into account the layered structure of the cuprates (see section 3.2.2 for a more detailed discussion).

We divide the unit cell of  $YBa_2Cu_3O_x$  into the intra- and inter-bilayer subcells A and B. Let us imagine, that a time dependent current is induced along the c-direction, the



Figure 8.3: The c-axis reflectivity  $R(\omega)$  and  $\sigma_1(\omega)$  above (dashed lines) and below  $T_c$  (solid lines). The thick gray lines depict fits of  $R(\omega)$  using the multilayer model and, in  $\sigma(\omega)$ , the normal carrier electronic contribution  $\sigma_{en}(\omega)$  derived from it. The filled areas denote the 4 K out-of-phase contribution of superconducting carriers  $\sigma_{es}(\omega)$  as defined in the text.



Figure 8.4:  $\omega_{\Delta}(T,\omega)$  as defined in Eq. 8.1. Note the change of scale indicated by the dotted lines. The high frequency extrapolation of  $\omega_{\Delta}$  gives the value of the superconducting plasma frequency. The overshoot at intermediate frequencies is due to the formation of the out-of-phase bilayer plasmon.

time derivative of which is  $(dJ_c/dt)$ . We define  $(dV_j/dt)$  as the time derivative of the voltage between two neighboring CuO<sub>2</sub> layers, *i.e.*, across subcell *j*. Our multilayer model corresponds to the approximation, that the ratio  $(dV_j/dt)/(dJ_c/dt)$  is provided by a *local* linear response function  $\rho_j$  corresponding to the complex impedance which depends only on the voltage variations on the neighboring CuO<sub>2</sub> layers, and not on the voltages on layers further away. Microscopically this corresponds to the condition, that the mean free path along *c* must be shorter in the normal state than the distance between the layers,  $l_j$ . In the superconducting state this should be supplemented with the same condition for the coherence length along *c*. In this sense, the multilayer model reflects the confinement of carriers in the 2D CuO<sub>2</sub> layers. Let us treat the current as the parameter controlled by applying an external field. Since the current between the layers is now uniform and is independent of the subcell index *j*, the electric field average over the unit cell is a linear superposition of the voltages over all subcells within the unit cell. This effectively

corresponds to putting the complex impedances  $\rho_i$  of subcells in series,

$$\rho(\omega) = x_A \rho_A(\omega) + x_B \rho_B(\omega) \quad , \tag{8.2}$$

where the  $x_j = l_j/l_c$  are the relative volume fractions of the two subcells,  $l_A + l_B = l_c$ , and  $\rho_j(\omega)$  are the *local* impedance functions within subcells A and B. This sum for

$$\rho(\omega) = \frac{1}{\sigma(\omega) + \frac{\omega}{4\pi i}}$$
(8.3)

is very different from the case of a homogeneous medium, where different contributions are additive in  $\sigma(\omega) = \Sigma \sigma_j(\omega)$ , which corresponds to putting the various conducting channels of the medium *in parallel*. To illustrate this, let us adopt the Drude model for the complex interlayer impedance. In parallel conduction the sum of, *e.g.*, two Drude peaks yields

$$\frac{4\pi i/\omega}{\rho(\omega)} = 1 - \frac{\omega_{p,A}^2}{\omega^2 + i\gamma_A\omega} - \frac{\omega_{p,B}^2}{\omega^2 + i\gamma_B\omega}$$
(8.4)

where  $\omega_{p,j}$  denotes the plasma frequency, and  $\gamma_j$  labels the damping. This results in a single plasma resonance at a frequency  $\omega_p^2 = \omega_{p,A}^2 + \omega_{p,B}^2$ , *i.e.*, only one longitudinal mode (the zero) survives which is shifted with respect to the zeros of the individual components. The transverse mode (the pole at  $\omega = 0$ ) is identical. Putting two Drude oscillators in series in the multilayer model, *i.e.*, using  $\Sigma x_j \rho_j$  has a surprising consequence.

$$\frac{\rho(\omega)}{4\pi i/\omega} = \frac{x_A}{1 - \frac{\omega_{p,A}^2}{\omega^2 + i\gamma_A \omega}} + \frac{x_B}{1 - \frac{\omega_{p,B}^2}{\omega^2 + i\gamma_B \omega}}$$
(8.5)

Now both longitudinal modes (poles of  $\rho_j$ ) are unaffected, and in between a new transverse mode arises. This transverse optical plasmon can be regarded as an out-of-phase oscillation of the two individual components. This mode has been predicted in Ref. [43] for the case of a multilayer of Josephson coupled 2D superconducting layers. The existence of two longitudinal modes was confirmed experimentally in SmLa<sub>0.8</sub>Sr<sub>0.2</sub>CuO<sub>4- $\delta$ </sub> [517]. Note that superconductivity is not a necessary ingredient, the optical plasmon appears regardless of the damping of the individual components.

In order to apply the model to the measured reflectivity data we have to include the phonons, for which a separation into subcells is not generally justified, e.g., for the *c*-axis bending mode of the planar O ions, located on the border between subcells A and B. Therefore we adopt the following model impedance

$$\rho(\omega) = \sum_{j} \frac{x_j}{\sigma_j + \sigma_{ph} + \sigma_M + \omega/4\pi i}, \quad j \in \{A, B\}$$
(8.6)

where  $x_A = 0.28$ , and  $x_B = 1 - x_A$  for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>. Note that this model reduces to the conventional expression for a homogeneous medium commonly used for high T<sub>c</sub> superconductors if we either set  $x_A = 0$  or  $\sigma_A = \sigma_B$ . The  $\sigma_{A,B}(\omega)$  contain the purely electronic

contributions with eigenfrequency  $\omega_0 = 0$  within each subcell,

$$4\pi\sigma_j(\omega) = \frac{\mathrm{i}\omega_{s,j}^2}{\omega} + \frac{\mathrm{i}\omega_{n,j}^2}{\omega + \mathrm{i}\gamma_j}, \quad j \in \{A, B\}$$
(8.7)

where  $\omega_{s,j}$  and  $\omega_{n,j}$  label the plasma frequencies of superconducting and normal carriers, respectively. All other contributions (phonons, mid-infrared oscillators, etc.) are assumed to be identical in the two subcells and are included in a sum of Lorentz oscillators,

$$\frac{4\pi i}{\omega}[\sigma_{ph} + \sigma_M] = \sum \frac{\omega_{p,j}^2}{\omega_{0,j}^2 - \omega^2 - i\gamma_j\omega}$$
(8.8)

where  $\omega_{0,j}$  denotes the *j*-th peak frequency. The electronic contribution in the mid-infrared  $\sigma_M$  describes the broad incoherent background in the normal state and mimics the gap in the superconducting state. The parameters used in the fit are given in Table 8.1 for 4 and 100 K. In the superconducting state, the electronic response is modelled with 9 adjustable parameters in our approach, namely the plasma frequencies of superconducting and normal carriers  $\omega_{s,A}$ ,  $\omega_{s,B}$ ,  $\omega_{n,A}$  and  $\omega_{n,B}$ , the damping of the normal carriers  $\gamma_{n,A}$  and  $\gamma_{n,B}$  and the three parameters of the mid-infrared oscillator which mimics the gap. Note that the resonance frequency  $\omega_0 = 0$  of the normal and superconducting free carrier contributions is not adjustable. The same number of parameters is necessary in a conventional multi-oscillator fit using a Drude term ( $\omega_n$  and  $\gamma_n$ ), a London term ( $\omega_s$ ), the same mid-infrared oscillator and an additional, microscopically unmotivated oscillator which describes the "bump" itself. The agreement between the measured reflectivity data and fits using the multilayer model is very good at all temperatures (thick grey lines in Fig. 8.3). The strong mid-infrared peak of the optical plasmon caused by the out-of-phase oscillation of the superconducting carriers in the two subcells is very well reproduced.

In Fig. 8.5 we plot the real part of the dynamical resistivity  $\rho(\omega)$ . The thick grey line was obtained from the full fit parameters for T = 4 K and agrees with the Kramers-Kronig result. The solid line depicts the electronic contribution  $\rho_e(\omega)$ , which was obtained by leaving out the phonon part  $\sigma_{ph}(\omega)$  from the fit parameters in Eq. 8.6. In the multilayer model  $\rho_e(\omega)$  is the sum of the subcell contributions  $x_j \rho_{ej} = x_j / (\sigma_j + \sigma_M + \omega/4\pi i)$  ( $j \in \{A, B\}$ , dashed lines), which shows that  $\rho_e(\omega)$  is a linear superposition of the two plasmon peaks in the two subcells. This separation into subcell plasmon peaks works very well in particular for optimal doping and also underdoped samples (see Fig. 8.6 below).

Contrary to the conventional Drude-Lorentz model, the different contributions are not strictly additive in  $\sigma_1(\omega)$  due to the inverse summation in Eq. 8.6. Nevertheless we can calculate an estimate of the electronic contribution  $\sigma_e(\omega)$  from the fit parameters in the same way as done for  $\rho_e$ . An estimate of only the normal electronic contribution  $\sigma_{en}(\omega)$  is obtained by leaving out the London terms  $\propto \omega_{s,j}^2$  together with  $\sigma_{ph}$ . The part arising from the presence of superconducting carriers is then defined as  $\sigma_{es}(\omega) = \sigma_e(\omega) - \sigma_{en}(\omega)$  (see Fig. 8.3). The unfamiliar contribution of superconducting carriers to  $\sigma_1(\omega)$  at finite frequencies is caused by the out-of-phase motion of these carriers in the two subcells.

With decreasing doping level the absolute value of  $\sigma_1(\omega)$  decreases and therefore the optical plasmon peak becomes sharper. At the same time, all plasma frequencies and hence



Figure 8.5: Real part of the dynamical resistivity  $\rho(\omega)$  as obtained from the multilayer model (thick gray line). The solid line depicts the electronic contribution only, and the dashed lines the subcell contributions  $\rho_{eA}(\omega)$  and  $\rho_{eB}(\omega)$  to it. Insets: temperature dependence of  $\rho_{eA}(\omega)$  and  $\rho_{eB}(\omega)$ .

also the optical plasma mode shift to lower frequencies. This scenario explains the strong far-infrared "bump" reported in underdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> [32, 305]. Similar bumps have been observed in other bilayer cuprates [306,307], but never in a single layer material. This bump has hindered an unambiguous separation of electronic and phononic contributions to  $\sigma_1(\omega)$ . In Fig. 8.6 we show reflectivity spectra of underdoped samples of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> taken from Refs. [32,305] together with fits using the multilayer model. Again good agreement with the model is obtained. The strong phonon asymmetries present in the underdoped samples called for a fine tuning of the model: the two apical O stretching phonon modes at about 600 cm<sup>-1</sup> were described by *local* oscillators in the inter-bilayer subcell *B*, *i.e.*, they moved in Eq. 8.6 from  $\sigma_{ph}(\omega)$  to  $\sigma_B(\omega)$ . The figure demonstrates that this reproduces the asymmetry of the experimental phonon line shape well, although a Lorentz oscillator was used (see section 3.2.2 for a more detailed discussion). Similar fine tuning has only



Figure 8.6: Reflectivity data at 4 K as taken from Refs. [32, 305] and fits using the multilayer model. In all panels the thick grey lines show the fit result. The mid panels show  $\sigma_1(\omega)$  and the different electronic contributions to it ( $\sigma_{es}(\omega)$ : filled area;  $\sigma_{en}(\omega)$ : dashed line). The solid lines in the bottom panels show the electronic contributions to  $\rho(\omega)$  and the separation into subcells A and B (dashed lines).

a minor effect on the quality of the fit for the data presented in Fig. 8.3. Comparing the various doping levels shows that both the bending  $(350 \text{ cm}^{-1})$  and the stretching  $(600 \text{ cm}^{-1})$  phonon modes show strong asymmetries whenever they overlap with the transverse plasma mode, but that both modes are symmetric if the transverse plasmon is far enough away, as, *e.g.*, in the case of x=7. Very recently, Munzar and collaborators [364] showed that the phonon anomalies can be naturally explained by changes of the local fields acting on the ions arising from the onset of inter- and intra-bilayer Josephson effects. Their treatment shares the multi-layer spirit of our approach. Previously it was argued that the phonon spectral weight is only conserved for different temperatures if the bump is interpreted as a phonon [32]. However, a sum rule exists only for the total  $\sigma_1(\omega)$ , not for the phonon part separately. Moreover, in this scenario the width of the bump, its temperature and doping dependence and the phonon asymmetries remained unexplained.

Both the low frequency Josephson plasmon and the bump are suppressed simultaneously by Zn substitution [312], which supports our assignment that both peaks are plasma modes. An increase of spectral weight of the bump with decreasing temperature was reported to start far above  $T_c$  [32,305], but a distinct peak is only observed below  $T_c$ . We obtained good fits for all temperatures (not shown). As mentioned above, superconductivity is not a necessary ingredient of the multilayer model, an out-of-phase motion of normal carriers will give rise to a peak at finite frequencies, too. Upon cooling below  $T_c$ , the reduction of the underlying electronic conductivity due to the opening of a gap and the reduced damping produce a distinct peak.

Our results imply that the c-axis transport of quasi-particles is incoherent even between the two layers of a bilayer, which agrees with the absence of a bilayer bonding-antibonding transition in our spectra. Using photo electron spectroscopy [519] a bonding-antibonding splitting of about  $3000 \,\mathrm{cm}^{-1}$  was reported. The anomalous broad photoemission line shape may explain the absence thereof in the optical data.

In conclusion, we observed the out-of-phase bilayer plasmon predicted by the multilayer model. The good agreement of the optical data with the multilayer model at all temperatures and doping levels shows that  $YBa_2Cu_3O_x$  can be modelled by local electrodynamics along the *c*-axis in both the normal and the superconducting state. This applies even to overdoped  $YBa_2Cu_3O_x$ , one of the least anisotropic cuprates. Our results strongly point towards a non-Fermi liquid picture and confinement of carriers to single  $CuO_2$  layers.

### 8.2 Pseudogap in $La_{2-x}Sr_xCuO_4$

In this final section we address the *c*-axis optical conductivity of  $La_{2-x}Sr_xCuO_4$  in the optimally and underdoped regime.<sup>\*</sup> Our prime interest is to establish whether there is a "pseudogap", *i.e.*, a low frequency suppression of  $\sigma(\omega)$  above  $T_c$  in underdoped samples of this mono-layer compound. To this end we performed transmission measurements of single crystalline samples of  $La_{2-x}Sr_xCuO_4$  with x=0.10, 0.12 and 0.15, which have been provided to us by S. Uchida. Details concerning the sample growth by the traveling-solvent-floating-zone method and sample characterization have been given in Refs. [520,521]. These single crystals have large *ac* faces with diameters of 10 mm. In order to obtain sufficient intensity in transmission measurements, we reduced the sample thickness to  $60\mu m$  ( $20\mu m$ ) for x=0.10 (0.15) by polishing with diamond paste. Before, the brittle samples were glued to a Si substrate in order to prevent them from breaking.

With the obvious exception of the out-of-phase bilayer plasmon, the general features of the c-axis optical conductivity spectrum of  $La_{2-x}Sr_xCuO_4$  are similar to the case of  $YBa_2Cu_3O_{7-\delta}$  which we have described in the preceding section. The resistivity anisotropy  $\rho_c/\rho_{ab}$  of underdoped and optimally doped La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> is larger than in the case of  $YBa_2Cu_3O_{7-\delta}$ , and hence the main characteristics are even more emphasized. The electronic contribution to  $\sigma(\omega)$  is mainly incoherent and very small. In the normal state, a slight Drude upturn is only present at the lowest frequencies measured even for optimal doping with x = 0.15 (see Fig. 8.7). Phonons dominate the spectrum. A sharp Josephson plasma edge appears in the reflectivity spectrum at low frequencies upon cooling below  $T_c$ . Due to the lower electronic background conductivity and the absence of phonons at low frequencies, the plasma edge is more easily discernible in  $La_{2-x}Sr_xCuO_4$  than in highly doped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub>. With decreasing doping concentration the plasma edge shifts to lower frequencies (see Fig. 8.8). Note that  $T_c$  of the x=0.12 sample is lower than for x=0.10due to the 1/8 anomaly [309]. Nevertheless the Josephson plasma frequency is larger for x = 0.12 than for x = 0.10, and the plasma edge is just dropping below our measurement range in the latter (see left panel of Fig. 8.8). In this case we deduced a screened plasma frequency of  $\omega_{p,s} = 18 \text{ cm}^{-1}$  by an analysis of the minima and maxima of the interference fringes of the measured transmittance (see below), from which we derived the polariton dispersion as described in section 4.2 (see Fig. 8.9). The slope of the dispersion in the normal state at 70 K yields n = 4.99 (dashed line). Using  $\omega^2 = \omega_{p,s}^2 + q^2/n^2$  the value of  $\omega_{p,s}$  at 4 K can be derived from every single data point independently (see inset). The solid line gives the dispersion for  $\omega_{p,s} = 18 \,\mathrm{cm}^{-1}$ . This is in good agreement with the result of a Lorentzian fit of the reflectivity data, which yields  $\omega_p = n\omega_{p,s} = 106 \text{ cm}^{-1}$ . A similar analysis of the plasmon-polariton dispersion was performed by Uchida and Tamasaku [523] on reflectivity data of thin samples with x = 0.15.

Lorentzian fits of the 4 K reflectivity data of four different doping levels with  $0.10 \leq x \leq 0.15$  are displayed in Fig. 8.10. The curve with  $\omega_{p,s} \approx 40 \text{ cm}^{-1}$  was taken from Kim and collaborators [40]. Two fits are shown for each doping concentration, one including a

<sup>\*</sup>This project was performed in close collaboration with H.J.A. Molegraaf.



Figure 8.7: Reflectivity of optimally doped  $La_{1.85} Sr_{0.15} CuO_4$  for  $E \parallel c$ . Below  $T_c$ , a sharp Josephson plasma edge appears at low frequencies. The solid grey line depicts a Lorentzian fit of the 4 K data. The dotted grey line has been derived from the same fit by subtracting the highest phonon mode. It shows that the transverse frequency  $\omega_0 = 493 \text{ cm}^{-1}$  of the highest phonon is very close to the longitudinal frequency of the strongest mode, which explains the strong mixing of the two phonons and the strange line shape of the 493 cm<sup>-1</sup> mode.

small absorption peak in  $\sigma(\omega)$  close to the screened plasma frequency (thick grey lines), one without (dashed lines). The two lower panels depict the corresponding spectra of  $\sigma(\omega)$  and of the dynamical resistivity  $\rho(\omega)$ , which show the transverse and longitudinal excitations, respectively, as discussed in chapter 3. For all four doping concentrations, the small absorption peak in  $\sigma(\omega)$  is located just above the longitudinal plasma frequency, which can be derived from the peak in  $\rho(\omega)$ . This close coincidence has been observed by different groups [40, 310, 365, 366] in the c-axis reflectivity spectra of  $La_{2-x}Sr_xCuO_4$ . Recently, a small absorption peak in  $\sigma(\omega)$  has been seen in direct absorption measurements with x = 0.13 [524] at  $\omega = 10$  cm<sup>-1</sup>, *i.e.*, below the plasma edge of about 50 cm<sup>-1</sup>. However, the data also indicate a small hump at the plasma frequency itself [524]. As we have already discussed in chapter 3.2.2, van der Marel and Tsvetkov [43] proposed to envisage the single layer compound with Sr impurities as an effective multilayer, where the local dielectric function is modulated by the Sr concentration. Assuming a Gaussian distribution for the effective interlayer coupling they obtained good fits of the experimental data [43]. This interpretation of the small absorption peak in  $La_{2-x}Sr_xCuO_4$  corroborates our identification of the out-of-phase bilayer plasmon in  $YBa_2Cu_3O_{7-\delta}$ .



Figure 8.8: Doping and temperature dependence of the Josephson plasma edge in the reflectivity spectra of  $La_{2-x}Sr_xCuO_4$ . The curves in the right panel correspond to 4, 15, 24, 27, 30, 33, 36 and 45 K.



Figure 8.9: Polariton dispersion above and below  $T_c$  in underdoped  $La_{1.9}Sr_{0.10}CuO_4$  as derived from the minima and maxima of the interference fringes of the measured transmittance. The slope of the 70 K data yields n=4.99 (dashed line). At 4 K, the value of the screened Josephson plasma frequency  $\omega_{p,s}$  can be derived from every single data point independently by using  $\omega^2 = \omega_{p,s}^2 + q^2/n^2$ . The inset depicts  $\omega_{p,s}$  derived from the lowest four points. The solid line gives the dispersion for  $\omega_{p,s} = 18 \text{ cm}^{-1}$ .



Figure 8.10: Doping dependence of the Josephson plasma edge in  $La_{2-x}Sr_xCuO_4$  with  $0.10 \le x \le 0.15$ . The curve with  $\omega_{p,s} \approx 40 \text{ cm}^{-1}$  was taken from Kim et al. [40]. Two fits are shown for each doping concentration, one including a small absorption peak in  $\sigma_1(\omega)$  close to the plasma frequency (thick grey lines), one without (dashed lines).



Figure 8.11: Optical conductivity spectrum of optimally doped  $La_{1.85}Sr_{0.15}CuO_4$  at 4 K. Solid line: Lorentzian fit result corresponding to the thick grey line in Fig. 8.7. Dashed line: electronic contribution to the fit. Dotted line: result of a Kramers-Kronig analysis of the reflectivity data.

For x = 0.15, the result for  $\sigma(\omega)$  of the 4 K reflectivity fit is replotted on a broader scale in Fig. 8.11 (solid line). The dashed line denotes the electronic contribution to the fit, which shows the gradual opening of a gap below about 400 cm<sup>-1</sup>. The dotted line depicts  $\sigma(\omega)$  as derived via a Kramers-Kronig analysis of the 4 K reflectivity data, which agrees rather well with the fit result. Note in particular the good agreement concerning the small absorption peak at 60 cm<sup>-1</sup>. However, as discussed in relation with the mid-infrared spectrum of insulating YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> in chapter 5, measuring reflectivity is in most cases not appropriate in order to determine very small values of  $\sigma(\omega)$ . In the present case, it is probably a minute error in  $R(\omega)$  between 100 and 150 cm<sup>-1</sup> (compare the measurement with the fit in Fig. 8.7) which turns  $\sigma(\omega)$  even slightly negative at 100 cm<sup>-1</sup>. This sensitivity of the Kramers-Kronig analysis and the dominant phonon contribution impede a reliable determination of the electronic  $\sigma(\omega)$  within the gap.

However, we can try to observe a trend in the reflectivity data directly. Within the Reststrahlenband, *i.e.*, above the transverse and below the longitudinal frequency of the strongest phonon mode, reflectivity is close to unity and absorption is low (see Fig. 8.11). Assuming  $T(\omega) = 0$ , the amount of absorption A can be derived from A = 1 - R. The temperature dependence of  $R(\omega_0 = 280 \text{ cm}^{-1})$  of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  is given in Fig. 8.12. The opening of the superconducting gap below  $T_c$  (dashed line) is evident in the optimally doped sample with x = 0.15. The reduced conductivity corresponds to a sudden increase



Figure 8.12: Temperature dependence of the reflectivity at  $\omega = 280 \text{ cm}^{-1}$  of underdoped (x = 0.10 and 0.12) and optimally doped  $(x = 0.15) \text{ La}_{2-x} Sr_x CuO_4$ . At this frequency, which lies within the strong Reststrahlenband, absorption is low (see Fig. 8.11) and  $R(\omega)$  is close to unity. Assuming  $T(\omega) = 0$ , the amount of absorption can be derived from A = 1 - R.

of  $R(\omega)$  just below  $T_c$ . An increase of  $R(\omega)$  is also observed in the underdoped samples below  $T_c$ , however, this increase is much more gradual. The most prominent feature for all doping levels, the decrease of  $R(\omega)$  with increasing temperature in the normal state, is most likely due to a broadening of the phonon. Therefore the data do not allow any definite statement about the existence of a pseudogap.

Several authors claimed the observation of a pseudogap in  $La_{2-x}Sr_xCuO_4$  on the basis of reflectivity data. A suppression of the low frequency conductivity at temperatures far above  $T_c$  was reported not only in the underdoped regime  $(x=0.12 \ [309] \ and x=0.13 \ [308,311])$ , but also for an optimally doped sample with  $x = 0.15 \ [310]$  (see Fig. 8.13). In section 2.3.1 we have discussed several phase diagrams that have been proposed for the cuprates. The major difference between these phase diagrams is the precise location of the crossover to a state showing a pseudogap, and the interpretation of this pseudogap. It is therefore of utmost importance to clarify whether there really is a pseudogap in optimally doped  $La_{2-x}Sr_xCuO_4$ , and if so, at which temperature it opens up.

Due to the very low value of the electronic contribution to the optical conductivity, a transmission measurement offers a precise tool to answer this question. The temperature dependence of the low frequency transmittance of underdoped (x = 0.10) and optimally doped (x = 0.15) La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> is displayed in Figs. 8.14 and 8.15, respectively.<sup>†</sup> The

<sup>&</sup>lt;sup>†</sup>After dividing the sample-plus-substrate data by the Si substrate reference measurement, the spectra still showed remnants of substrate interference fringes. These have then been removed from the interferogram, which can affect the *shape* of narrow lines. Therefore the transmittance drops erroneously below zero at the 134 cm<sup>-1</sup> phonon in Fig. 8.14. The overall absolute value of the spectrum is not affected by this procedure.



(a) Data for x = 0.12 in the underdoped regime, reproduced from Uchida, Tamasaku and Tajima [309].



(c) Data of underdoped x = 0.13 and overdoped x = 0.20 samples, reproduced from Uchida et al. [308]. No pseudogap is observed in the overdoped sample.



(b) Data of an underdoped sample with x = 0.13, reproduced from Startseva et al. [311].



(d) Top: data of an optimally doped sample with x = 0.15, reproduced from Basov et al. [310]. Bottom:  $\sigma(\omega)$  of the bilayer compound YBa<sub>2</sub>Cu<sub>4</sub>O<sub>8</sub>. Phonons have been subtracted. Dashed areas indicate the spectral weight contained in the condensate.

Figure 8.13: Optical conductivity spectra of  $La_{2-x}Sr_xCuO_4$  for  $E \parallel c$  as derived from reflectivity data by different authors.



Figure 8.14: Temperature dependence of the transmittance spectrum of underdoped  $La_{1.9}Sr_{0.10}CuO_4$  for  $E \parallel c$ . The curves correspond to sample temperatures of 4, 20, 27, 33, 50, 70, 100, 150, 200, 250, and 300 K, respectively.



Figure 8.15: Temperature dependence of the transmittance spectrum of optimally doped  $La_{1.85}Sr_{0.15}CuO_4$  for  $E \parallel c$ .



Figure 8.16: Temperature dependence of  $ln(T(\omega_0))$  of underdoped  $La_{1.9}Sr_{0.10}CuO_4$  normalized to the 4 K value. A plot of the temperature dependence of the normalized optical conductivity would look very similar. The behavior is strikingly different from the optimally doped case depicted in Fig. 8.17 below. The opening of the pseudogap causes the gradual decrease at temperatures much higher than  $T_c$ .



Figure 8.17: Temperature dependence of  $ln(T(\omega_0))$  of optimally doped  $La_{1.85}Sr_{0.15}CuO_4$ normalized to the 4 K value.

observed behavior is strikingly different for the two doping concentrations. The transmittance of the optimally doped sample with x = 0.15 hardly changes between 200 K and  $T_c$ , but increases rapidly below  $T_c$  due to the opening of the superconducting gap. In the underdoped sample with x = 0.10, a significant increase of  $T(\omega)$  is already observed between the two highest measured temperatures of 300 and 250 K. We choose three different frequencies, namely  $\omega_0 = 75$ , 100 and  $175 \,\mathrm{cm}^{-1}$ , and plot the temperature dependence at these frequencies in Figs. 8.16 (x=0.10) and 8.17 (x=0.15). Plotting  $\ln(T(\omega_0))$  normalized to the 4 K value gives a reliable estimate of the temperature dependence of the normalized optical conductivity. The general behavior does not depend on the chosen value of  $\omega_0$ . These graphs make the remarkable difference between the optimally and underdoped samples even more evident. In the underdoped sample with x = 0.10, a strong suppression of  $\sigma(\omega)$  is observed between 300 K and T<sub>c</sub>, which can be interpreted as the gradual opening of the pseudogap. This suppression is completely absent in the optimally doped sample, at least between 300 and 50 K. Possibly, the small decrease between 50 K and  $T_c$ reflects a remnant of the pseudogap behavior for x = 0.15. The opening temperature of the superconducting gap is very well defined only in the optimally doped sample.

We conclude that a gradual suppression of the low frequency  $\sigma(\omega)$  is observed in underdoped La<sub>1.9</sub>Sr<sub>0.10</sub>CuO<sub>4</sub> between room temperature and T<sub>c</sub>, in agreement with the results of reflectivity measurements for  $0.12 \le x \le 0.13$  [308,309,311]. The data of optimally doped La<sub>1.85</sub>Sr<sub>0.15</sub>CuO<sub>4</sub> are strikingly different. Here, a suppression of  $\sigma(\omega)$  can definitely be restricted to temperatures between 50 K and T<sub>c</sub>=37 K for x=0.15. It is tempting to identify the behavior observed in the underdoped compound with the opening of a pseudogap. However, one has to keep in mind that the concept of a gap is completely undefined if the conductivity remains finite at all frequencies. Also the absence of a distinct temperature below which the pseudogap opens is disturbing. In a semiconductor picture, the presence (not necessarily the opening) of a gap causes a similar suppression of  $\sigma(\omega)$  with decreasing temperature. One possible explanation for the data presented above is the opening of a gap in a restricted region of k-space. However, our k-averaging probe does not allow to decide whether this is indeed the correct scenario for La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub>.

# Samenvatting

Centraal in dit proefschrift staan de elektronische eigenschappen van de cupraten, waarbij we zowel spinexcitaties als ladingsexcitaties bestuderen. De cupraten zijn voornamelijk bekend vanwege hun metallische fase met buitengewoon hoge overgangstemperaturen naar de supergeleidende toestand, maar de magnetische eigenschappen van de isolerende fase zijn niet minder interessant. Onze voornaamste interesse is het verband tussen magnetisme en supergeleiding. Eerst geven we een uitgebreid overzicht van de stand van zaken in de wetenschappelijke discussie over de cupraten. Dit overzicht vormt de achtergrond waarin we onze eigen resultaten plaatsen.

De oorsprong van het complexe gedrag van deze materialen ligt in de tweedimensionale  $CuO_2$  vlakken, die in alle cupraten aanwezig zijn. Verantwoordelijk voor de interessante fysica is de gedeeltelijk gevulde 3d schil van de koper ionen samen met de grote elektronelektron repulsie in deze 3d schil. Als gevolg van de sterke interactie tussen de elektronen levert het eenvoudige beeld van onafhankelijke elektronen, zoals men dat in vaste stof fysica leerboeken voor de beschrijving van simpele materialen kan vinden, verkeerde resultaten. Er moet daarentegen een veel-deeltjes model toegepast worden, dat de "correlaties" tussen de elektronen beschrijft. Daarmee zijn de cupraten deel van een grotere klasse van "gecorreleerde elektronsystemen", die nog veel meer fascinerende fenomenen kent, zoals de kolossale magneto-weerstand, "zware fermionen" of metaal-isolator overgangen. Een ander indrukwekkend voorbeeld van de correlatie effecten is de isolerende of halfgeleidende fase van de cupraten, waarbij zich één gat in de 3d schil per CuO<sub>2</sub> eenheid bevindt. Bij een model met onafhankelijke elektronen volgt daaruit dat de bovenste elektronische band met koper-oxide karakter half gevuld is en men verwacht derhalve metallisch gedrag. Maar door de sterke onderlinge repulsie zijn de elektronen in de grondtoestand ieder in hun eentje op een koper-oxide plaquette gelokaliseerd, wat in plaats van een metaal een isolator met magnetische orde van spin 1/2 deeltjes oplevert, zoals dat in de experimenten gezien wordt. De complexe oorsprong van deze niet geleidende toestand wordt duidelijk als men materialen bestudeert die vanwege dotering met elektronen dan wel gaten een niet precies half gevulde band hebben. De gevonden verschijnselen zijn erg verschillend van wat men in de gedoteerde toestand van een eenvoudige halfgeleider als bijvoorbeeld silicium vindt.

De interacties tussen de magnetische achtergrond en de gedoteerde ladingsdragers zijn erg groot. Enkele procenten dotering heffen de magnetische orde op, en het materiaal wordt een slecht metaal. Bij ongeveer 5% dotering vindt dan de metamorfose van de rups naar de vlinder plaats: het slechte metaal wordt een supergeleider met een buitengewoon hoge overgangstemperatuur. In dit proefschrift worden monsters van de antiferromagnetische isolator, van de licht gedoteerde fase en van de supergeleider met behulp van optische metingen in het infrarood en zichtbaar frequentie gebied bestudeerd. Een van de belangrijkste vragen voor ons is in hoeverre de zo verschillende fenomenen samen hangen; de zoektocht naar een gemeenschappelijke microscopische motor. We zijn er van overtuigd dat de studie van het gedrag van *enkele* elektronen, gedoteerd in de antiferromagnetische achtergrond, de sleutel kan opleveren voor het begrijpen van de interactie tussen magnetisme en supergeleiding. Het uitgangspunt voor de studie van deze interactie moet de magnetische toestand en zijn excitatie spectrum zijn, die beide vaak als goed begrepen beschouwd worden. We proberen echter te laten zien dat dit maar ten dele waar is, en dat de interessantste fysica in de afwijkingen tussen de experimenten en de gebruikelijke theoretische modellen gezocht moet worden. Alleen als we het juiste model voor de magnetische fase gevonden hebben, kunnen we hopelijk ook de gedoteerde toestand begrijpen. We laten zien dat de sleutel voor deze puzzel bij de correcte beschrijving van spin 1/2 deeltjes in twee dimensies ligt. vergelijkbaar met het goed bestudeerde eendimensionale geval. Dezelfde aanpak passen we vervolgens op de supergeleidende fase toe. Ook hier zijn we geïnteresseerd in de afwijkingen van wat men als "normaal" en goed begrepen beschouwt. We voeren bewijzen aan dat de cupraten eerder als een stapel van tweedimensionale vlakken beschreven moeten worden dan als een sterk anisotroop driedimensionaal materiaal.

#### De cupraten: magnetisme en supergeleiding

Het eerste bericht van cuprate supergeleiding boven 30 K in 1986 (en zelfs boven de 90 K kort daarna) heeft een ongelofelijke stroom van wetenschappelijk onderzoek veroorzaakt. Nog steeds staat de hoge temperatuur supergeleiding in de kinderschoenen, maar toch zijn er al tienduizenden publicaties op dit gebied verschenen. Dit proefschrift probeert de actuele stand van zaken in de discussie over de cupraten kritisch en uitgebreid uit te leggen. We concentreren ons daarbij in het eerste deel op de discussie van de antiferromagnetische toestand. We introduceren verschillende theoretische modellen voor spin 1/2 deeltjes op een vierkant rooster, zoals het tweedimensionale Heisenberg model en alternatieve modellen die van een spin vloeistof uitgaan. Het verband met de fysica van eendimensionale spin ketens en spin ladders wordt behandeld. De experimentele resultaten voor de magnetische fase van neutronen en Raman verstrooiing en van foto-emissie spectroscopie worden uitgebreid besproken in verband met verschillende theoretische interpretaties. We beweren dat de antiferromagnetische Néel toestand en de excitaties daarvan, de spin golven, niet voldoende zijn voor de correcte beschrijving van de metingen.

Daarna wordt het gedrag van één gat, dat in de antiferromagneet gedoteerd wordt, behandeld. Het te kort schieten van een quasi-deeltjes Fermi vloeistof beeld wordt ook hier aan een experiment gekoppeld, in dit geval aan de hoek-opgeloste foto-emissie spectroscopie. Enkele trends en gezichtspunten op het gebied van hoge temperatuur supergeleiding worden daarna besproken door 12 gelijkwaardige maar toch verschillende fasediagrammen, gepresenteerd door verschillende auteurs, voor te stellen. Een oorzaak voor de verschillen zijn de uiteenlopende definities van cross-over temperaturen in de ondergedoteerde fase, dat wil zeggen voor waarden van dotering tussen de isolator en de supergeleider met de hoogste overgangstemperatuur. Deze cross-over temperaturen hangen samen met één van de vandaag de dag centrale onderwerpen in dit gebied, de "pseudogap". Dit is een onvolledige kloof in het excitatiespectrum, een reductie van mogelijke toestanden aan het Fermi oppervlak met dalende temperatuur die al ver boven de supergeleidende overgangstemperatuur kan beginnen, maar er is geen goede, eenduidige definitie voor dit begrip. Experimentele resultaten die een pseudogap aantonen worden besproken.

#### Fonon-polaritonen

De eerste soort van excitaties die we experimenteel bestuderen zijn roostertrillingen of fononen. We laten alle fononen zien van de isolerende fase van één van de goed bestudeerde cupraten,  $YBa_2Cu_3O_{6+x}$ . We onderzoeken het karakter van de verschillende fonon modes met behulp van zuurstof isotoop substitutie. De lijnvorm van bepaalde modes wijkt af van de gewone Lorentz oscillator, en een verband met een koppeling aan magnetische excitaties wordt behandeld. In de supergeleidende fase van  $YBa_2Cu_3O_{6+x}$  onderzoeken we de temperatuurafhankelijkheid van de fononfrequenties en vinden dat bepaalde fonon modes in de supergeleidende toestand naar lagere frequenties verschuiven.

In feite vormen tijdens de meting de fotonen en de fononen in de vaste stof een gecombineerde excitatie, een fonon-polariton. Door een analyse van het gemeten interferentie spectrum wordt de dispersie van de fonon-polaritonen in de Brillouin zone bepaald. Uiteraard zijn we hier op een  $10^{-4}$ -de deel van de Brillouin zone beperkt, maar dat is net genoeg om het mengen van fotonen en fononen te kunnen zien.

#### Het magnetische excitatie spectrum in de isolerende fase

De magnetische excitaties in de isolerende fase worden vaak als spin golven (magnonen) beschouwd. In de optische spectroscopie kunnen alleen processen bestudeerd worden waarbij de spin behouden is, bijvoorbeeld twee-magnon excitaties. Deze hebben echter in de cupraten vanwege de symmetrie geen dipoolmoment en zijn daarom niet infrarood actief. De situatie verandert als we aan de excitatie van tegelijkertijd twee magnonen en een roostertrilling (fonon) denken. Het fonon breekt de symmetrie en het combineerde twee-magnon-plus-fonon proces is infrarood actief. Dit fenomeen is inmiddels in meerdere laag dimensionale systemen met spin 1/2 of 1 geobserveerd, en de gemeten lijnvorm van het optische spectrum komt goed overeen met de theoretische verwachting. Ook in de cupraten is twee-magnon-plus-fonon absorptie al eerder gezien. In dit proefschrift laten we de eerste data zien van een materiaal met twee  $CuO_2$  lagen per eenheidscel,  $YBa_2Cu_3O_6$ . Met behulp van verschillende substituties tonen we aan dat de geobserveerde excitaties inderdaad magnetisch en vibrationeel zijn. Echter, de twee-magnon-plus-fonon interpretatie is in staat slechts een deel van het absorptie spectrum te verklaren. We laten zien dat de gemeten afwijkingen van de theoretische verwachting niet beschreven kunnen worden door de theorie uit te breiden met de wisselwerkingen tussen magnonen en fononen. Andere, niet-magnetische interpretaties van het spectrum worden besproken en als niet van

toepassing beschouwd. We concluderen dat het hele spectrum een magnetische oorsprong heeft, en dat de theorie te kort schiet omdat het excitatie spectrum van spin 1/2 deeltjes in twee dimensies niet goed door spin golven beschreven wordt.

#### Het absorptie spectrum van enkele gaten in de antiferromagneet

Het absorptie spectrum van enkele gaten in de antiferromagnetische achtergrond van de halfgeleidende fase verschilt erg van wat men bij een vergelijkbare dotering van een eenvoudige halfgeleider als bij voorbeeld silicium vindt. Door de sterke elektron-elektron interacties is een groot deel van het excitatie spectrum incoherent en het materiaal absorbeert licht bij *alle* frequenties beneden de halfgeleidende energiekloof. Door verschillende waarden van lage dotering en de temperatuurafhankelijkheid van de spectra te vergelijken kunnen we de absorptie als excitaties van spin-polaronen en rooster-polaronen interpreteren. Een spin (rooster) polaron is een excitatie van een gedoteerd gat waarbij ook nog een hele groep van spin (rooster) excitaties wordt aangeslagen. De observatie van een roosterpolaron werd in de literatuur soms als indicatie beschouwd voor de grote rol van fononen bij de hoge temperatuur supergeleiding. Onze data zijn de eerste die naast rooster-polaronen ook spin-polaronen laten zien. Daardoor wordt duidelijk dat er weliswaar een koppeling tussen fononen en gaten bestaat, maar dat deze alleen van belang is omdat de elektronen al sterk onderling gekoppeld zijn.

#### Anti-fase plasmonen in meerlagige systemen

Voor de supergeleidende fase concentreren zich de experimenten in dit proefschrift op metingen waar het elektrisch veld van het licht loodrecht op de  $\text{CuO}_2$  vlakken gepolariseerd is, dat wil zeggen langs de zogenaamde *c*-as. In materialen waarin de afstand tussen de  $\text{CuO}_2$  vlakken varieert (bij voorbeeld  $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ ) werd in eerdere metingen voor deze polarisatie een rare piek gezien. We stellen hier een model voor van de dielektrische constante dat rekening houd met het verschil in lokale elektrische velden veroorzaakt door de verschillende afstanden tussen de vlakken. In dit model zijn excitaties mogelijk waar de elektronen tussen de vlakken 1 en 2 in de tegenover gestelde richting bewegen als de elektronen tussen de vlakken 2 en 3 (anti-fase plasmonen). Dit model komt goed overeen met onze metingen en de eerder gepubliceerde data. Een consequentie van dit model is dan ook dat het elektronentransport tussen twee vlakken incoherent is, dat wil zeggen dat we de cupraten eerder als een stapel van aparte tweedimensionale werelden (CuO<sub>2</sub> vlakken) moeten beschouwen dan als een sterk anisotroop driedimensional materiaal. Daarmee kan het karakter van de fysica in een vlak erg verschillen van wat we uit drie dimensies kennen, equivalent met het eerder besproken geval van magnetische excitaties.

Tenslotte presenteren wij resultaten voor de supergeleidende fase van  $La_{2-x}Sr_xCuO_4$ , weer voor polarisatie langs de *c*-as. Deze metingen geven een duidelijk voorbeeld van de pseudogap in de ondergedoteerde fase.

## References

- [1] D.C. Mattis, The Theory of Magnetism I (Springer, Berlin, 1981).
- [2] H.B.G. Casimir, after-dinner speech at the International Euroconference on Magnetic Correlations, Metal-Insulator Transitions and Superconductivity in Novel Materials (Groningen, 1995).
- [3] H.K. Onnes, Proc. Royal Acad. (Akad. van Wetenschappen, Amsterdam) 14, 818 (1911) (equivalent with Leiden Comm. 124c); see also Leiden Comm. 119, 120b (1911) and Proc. Royal Acad. (Akad. van Wetenschappen, Amsterdam) 14, 113 (1911) (equivalent with Leiden Comm. 122b).
- [4] A. Schilling, M. Cantoni, J.D. Guo, and H.R. Ott, Nature **363**, 56 (1993).
- [5] M. Lagues, X.M. Xie, H. Tebbji, X.Z. Xu, V. Mairet, C. Hatterer, C.F. Beuran. and C. Deville-Cavellin, Science 262, 1850 (1993).
- [6] J. Bardeen, L.N. Cooper, and J.R. Schrieffer, Phys. Rev. 108, 1175 (1957).
- [7] J.G. Bednorz, and K.A. Müller, Z. Phys. B 64, 189 (1986).
- [8] M. Cyrot, and D. Pavuna, Introduction to Superconductivity and High-T<sub>c</sub> Materials (World Scientific, Singapore, 1992).
- [9] L.D. Landau, Sov. Phys. JETP 3, 920 (1957); *ibid.* 5, 101 (1957); *ibid.* 8, 70 (1958).
- [10] F. Bloch, Z. Phys. 57, 545 (1929); A.H. Wilson, Proc. R. Soc. London, Ser. A 133, 458 (1931), *ibid.* 134, 277 (1931).
- [11] H.J. de Boer, and E.J.W. Verwey, Proc. Phys. Soc. A 49, 59 (1937).
- [12] N.F. Mott, Metal-Insulator Transitions (Taylor and Francis, London, 1974 and 1990).
- [13] G.A. Sawatzky, Proceedings ICTP Spring College in Condensed Matter on Superconductivity (Trieste, 1992) in Superconductivity: From Basic Physics to the Latest Development, edited by P.N. Butcher, and Yu Lu (World Scientific, Singapore, 1995) p. 145 - 197.
- [14] S. Tomonaga, Prog. Theor. Phys. 5, 349 (1950).
- [15] J.M. Luttinger, J. Math. Phys. 4, 1154 (1963).
- [16] For a recent review, see J. Voit, Rep. Prog. Phys. 57, 977 (1994).

- [17] For an early extensive discussion on Fermi liquid versus non-Fermi liquid behavior in the cuprates, see K. Levin, J.H. Kim, J.P. Lu, and Q. Si, Physica C 175, 449 (1991).
- [18] A. Auerbach, Interacting Electrons and Quantum Magnetism (Springer-Verlag, Berlin, 1994).
- [19] M. Berciu, and S. John, preprint, http://xxx.lanl.gov/abs/cond-mat/9805229.
- [20] P.W. Anderson, Science **235**, 1196 (1987).
- [21] R. Eder, preprint, http://xxx.lanl.gov/abs/cond-mat/9810216 and 9801234.
- [22] M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
- [23] P. Fulde, *Electron Correlations in Molecules and Solids* (Springer-Verlag, Berlin, 1995).
- [24] T. Timusk, Physcia C **317-318**, 18 (1999).
- [25] For reviews on optical spectroscopy, see the contributions of T. Timusk and D.B. Tanner in Vol. I and III of *Physical Properties of High Temperature Superconductors*, edited by D.M. Ginsberg (World Scientific, Singapore, 1989 and 1992).
- [26] R.T. Collins, Z. Schlesinger, F. Holtzberg, P. Chaudhari, and C. Feild, Phys. Rev. B 39, 6571 (1989).
- [27] Z. Schlesinger, L.D. Rotter, R.T. Collins, F. Holtzberg, C. Feild, U. Welp, G.W. Crabtree, J.Z. Liu, Y. Fang, and K.G. Vandervoort in *Electronic Properties of High-T<sub>c</sub> Superconductors*, edited by H. Kuzmany, M. Mehring, and J. Fink, Springer Series in Solid-State Sciences **113** (Springer, Berlin, 1993), p. 225.
- [28] J. Orenstein, G.A. Thomas, A.J. Millis, S.L. Cooper, D.H. Rapkine, T. Timusk, L.F. Schneemeyer, and J.V. Waszazak, Phys. Rev. B 42, 6342 (1990).
- [29] S.L. Cooper, D. Reznik, A. Kotz, M.A. Karlow, R. Liu, M.V. Klein, W.C. Lee, J. Giapintzakis, D.M. Ginsberg, B.W. Veal, and A.P. Paulikas, Phys. Rev. B 47, 8233 (1993).
- [30] A.V. Puchkov, D.N. Basov, and T. Timusk, J. Phys. Condens. Matter 8, 10049 (1996).
- [31] D.N. Basov, R. Liang, B. Dabrowski, D.A. Bonn, W.N. Hardy, and T. Timusk, Phys. Rev. Lett. 77, 4090 (1996).
- [32] C.C. Homes, T. Timusk, R. Liang, D.A. Bonn, and W.N. Hardy, Phys. Rev. Lett. 71, 1645 (1993); C.C. Homes, T. Timusk, D.A. Bonn, R. Liang, and W.N. Hardy, Physica C 254, 265 (1995); Can. J. Phys. 73, 663 (1995).
- [33] D.J. Van Harlingen, Rev. Mod. Phys. 67, 515 (1995).
- [34] D.J. Scalapino, Phys. Rep. **250**, 329 (1995).
- [35] ARPES data have been reviewed in Z.-X. Shen, and D.S. Dessau, Phys. Rep. 253, 1 (1995); and M. Randeria, and J.-C. Campuzano, preprint, http://xxx.lanl.gov/abs/condmat/9709107.

- [36] H.S. Somal, B.J. Feenstra, J. Schützmann, J.H. Kim, Z.H. Barber, V.H.M. Duijn, N.T. Hien, A.A. Menovsky, M. Palumbo, and D. van der Marel, Phys. Rev. Lett. 76, 1525 (1996).
- [37] W.N. Hardy, D.A. Bonn, D.C. Morgan, R. Liang, and K. Zhang, Phys. Rev. Lett. 70, 3999 (1993); W.N. Hardy, S. Kamal, and D.A. Bonn, in NATO Advanced Studies Institue Series 371, 373 (1998).
- [38] A.J. Leggett, Braz. J. Phys. **22**, 129 (1992).
- [39] S.L. Cooper, and K.E. Gray in *Physical Properties of High Temperature Superconductors* IV, edited by D.M. Ginsberg (World Scientific, Singapore, 1994).
- [40] J.H. Kim, H.S. Somal, M.T. Czyzyk, D. van der Marel, A. Wittlin, A.M. Gerrits, V.H.M. Duijn, N.T. Hien, and A.A. Menovsky, Physica C 247, 297 (1995).
- [41] A.A. Tsvetkov, D. van der Marel, K.A. Moler, J.R. Kirtley, J.L. de Boer, A. Meetsma, Z.F. Ren, N. Koleshnikov, D. Dulic, A. Damascelli, M. Grüninger, J. Schützmann, J.W. van der Eb, H.S. Somal, and J.H. Wang, Nature **395**, 360 (1998).
- [42] J. Schützmann, H.S. Somal, A.A. Tsvetkov, D. van der Marel, G.E.J. Koops, N. Koleshnikov, Z.F. Ren, J.H. Wang, E. Brück, and A.A. Menovsky, Phys. Rev. B 55, 11118 (1997).
- [43] D. van der Marel, and A. Tsvetkov, Czech. J. Phys. 46, 3165 (1996).
- [44] G.A. Thomas in High-Temperature Superconductivity, Proceedings of the Thirty-Ninth Scottish Universities Summer School in Physics, edited by D.P. Tunstall and W. Barford (Adam Hilger, Bristol, 1991).
- [45] J.P. Falck, A. Levy, M.A. Kastner, and R.J. Birgeneau, Phys. Rev. B 48, 4043 (1993).
- [46] A.P. Litvinchuk, C. Thomsen, and M. Cardona in *Physical Properties of High Temperature Superconductors IV*, edited by D.M. Ginsberg (World Scientific, Singapore 1994), p. 375.
- [47] L. Gao, Y.Y. Xue, F. Chen, Q. Xiong, R.L. Meng, D. Ramirez, C.W. Chu, J.H. Eggert, and H.K. Mao, Phys. Rev. B 50, 4260 (1994); Physica C 235-240, 1493 (1994).
- [48] M. Nuñez-Regueiro, J.-L. Tholence, E.V. Antipov, J.-J. Capponi, and M. Marezio, Science 262, 97 (1993).
- [49] D.T. Jover, R.J. Wijngaarden, H. Wilhelm, R. Griessen, S.M. Loureiro, J.-J. Capponi, A. Schilling, and H.R. Ott, Phys. Rev. B 54, 4265 (1996).
- [50] J. Röhler, J. Supercond. 9, 457 (1996).
- [51] R.M. Hazen in *Physical Properties of High Temperature Superconductors II*, edited by D.M. Ginsberg (World Scientific, Singapore, 1990).
- [52] M.K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang, and C.W. Chu, Phys. Rev. Lett. 58, 908 (1987).

- [53] J. Rossat-Mignod, L.P. Regnault, M.J. Jurgens, C. Vettier, P. Burlet, J.Y. Henry, and G. Lapertot, Physica B 163, 4 (1990).
- [54] A. Erb, private communication.
- [55] P.W. Anderson, The Theory of Superconductivity in the High-T<sub>c</sub> Cuprates (Princeton University Press, Princeton, 1997).
- [56] S. Chakravarty, Eur. Phys. J. B 5, 337 (1998).
- [57] A.J. Leggett, Phys. Rev. Lett. 83, 392 (1999); Proc. of the National Academy of Sciences of the United States of America 96, 8365 (1999); J. Phys. Chem. Solids 59, 1729 (1998).
- [58] C. Bernhard, R. Henn, A. Wittlin, M. Kläser, Th. Wolf, G. Müller-Vogt, C.T. Lin, and M. Cardona, Phys. Rev. Lett. 80, 1762 (1998).
- [59] Contributions of G.A. Sawatzky, V.J. Emery and T.M. Rice in High-Temperature Superconductivity, Proceedings of the Thirty-Ninth Scottish Universities Summer School in Physics, edited by D.P. Tunstall and W. Barford (Adam Hilger, Bristol, 1991).
- [60] E. Dagotto, Rev. Mod. Phys. 66, 763 (1994).
- [61] W. Brenig, Phys. Rep. **251**, 153 (1995).
- [62] A.P. Kampf, Phys. Rep. **249**, 219 (1994).
- [63] H. Eskes, Ph.D. Thesis, University of Groningen, 1992.
- [64] For a review on band structure calculations, see W.E. Pickket, Rev. Mod. Phys. 61, 433 (1989).
- [65] S. Uchida, T. Ido, H. Takagi, T. Arima, Y. Tokura, and S. Tajima, Phys. Rev. B 43, 7942 (1991).
- [66] M.S. Hybertsen, M. Schlüter, and N.E. Christensen, Phys. Rev. B 39, 9028 (1989).
- [67] A.K. McMahan, J.F. Annett, and R.M. Martin, Phys. Rev. B 42, 6268 (1990).
- [68] J. Zaanen, G.A. Sawatzky, and J.W. Allen, Phys. Rev. Lett. 55, 418 (1985).
- [69] V.J. Emery, Phys. Rev. Lett. 58, 2794 (1987).
- [70] P.W. Anderson, Phys. Rev. **115**, 2 (1959).
- [71] H. Eskes, and J.H. Jefferson, Phys. Rev. B 48, 9788 (1993).
- [72] P. Horsch, and W. Stephan in *Electronic Properties of High-T<sub>c</sub> Superconductors*, edited by H. Kuzmany, M. Mehring, and J. Fink, Springer Series in Solid-State Sciences **113** (Springer, Berlin, 1993), p. 351.
- [73] F.C. Zhang, and T.M. Rice, Phys. Rev. B **37**, 3759 (1988).
- [74] H. Eskes, and G.A. Sawatzky, Phys. Rev. Lett. **61**, 1415 (1988).

- [75] H. Eskes, and G.A. Sawatzky, Phys. Rev. B 44, 9656 (1991).
- [76] D. Poilblanc, T. Ziman, H.J. Schulz, and E. Dagotto, Phys. Rev. B 47, 14267 (1993).
- [77] H. Nakano, and M. Imada, preprint, http://xxx.lanl.gov/abs/cond-mat/9902235.
- [78] J. Wagner, W. Hanke, and D.J. Scalapino, Phys. Rev. B 43, 10517 (1991).
- [79] A.L. Chernyshev, P.W. Leung, and R.J. Gooding, Phys. Rev. B 58, 13594 (1998).
- [80] E. Dagotto, and T.M. Rice, Science **271**, 618 (1996).
- [81] T.M. Rice, S. Haas, M. Sigrist, and F.-C. Zhang, Phys. Rev. B 56, 14655 (1997).
- [82] Z.-X. Shen, J.W. Allen, J.J. Yeh, J.-S. Kang, W. Ellis, W. Spicer, I. Lindau, M.B. Maple, Y.D. Dalichaouch, M.S. Torikachvili, and J.Z. Sun, Phys. Rev. B 36, 8414 (1987).
- [83] H. Eskes, M.B.J. Meinders, and G.A. Sawatzky, Phys. Rev. Lett. 67, 1035 (1991); M.B.J. Meinders, H. Eskes, and G.A. Sawatzky, Phys. Rev. B 48, 3916 (1993).
- [84] C.T. Chen, F. Sette, Y. Ma, M.S. Hybertsen, E.B. Stechel, W.M.C. Foulkes, M. Schluter, S.-W. Cheong, A.S. Cooper, L.W. Rupp, Jr., B. Batlogg, Y.L. Soo, Z.H. Ming, A. Krol, and Y.H. Kao, Phys. Rev. Lett. 66, 104 (1991).
- [85] H. Romberg, M. Alexander, N. Nücker, P. Adelmann, and J. Fink, Phys. Rev. B 42, 8768 (1990).
- [86] C.M. Varma, Phys. Rev. B 55, 14554 (1997).
- [87] C.M. Varma, S. Schmitt-Rink, and E. Abrahams, Solid State Comm. 62, 681 (1987); P.B. Littlewood, C.M. Varma, S. Schmitt-Rink, and E. Abrahams, Phys. Rev. B 39, 12371 (1989).
- [88] W. Weber, Z. Phys. B **70**, 323 (1988).
- [89] M.A. Kastner, R.J. Birgeneau, G. Shirane, and Y. Endoh, Rev. Mod. Phys. 70, 897 (1998).
- [90] L.F. Feiner, J.H. Jefferson, and R. Raimondi, Phys. Rev. Lett. 76, 4939 (1996); L.F. Feiner, M. Grilli, and C. Di Castro, Phys. Rev. B 45, 10647 (1992).
- [91] O.K. Andersen, A.I. Liechtenstein, O. Rodriguez, I.I. Mazin, O. Jepsen, V.P. Antropov, O. Gunnarsson, and S. Gopalan, Physica C 185-189, 147 (1991).
- [92] J.J. Yu, S. Massida, A.J. Freeman, and D.D. Koelling, Phys. Lett. A 122, 203 (1987).
- [93] I.I. Mazin, preprint, http://xxx.lanl.gov/abs/cond-mat/9903061, and references therein.
- [94] R. Fehrenbacher, and T.M. Rice, Phys. Rev. Lett. 70, 3471 (1993).
- [95] Z. Zou, J. Ye, K. Oka, and Y. Nishihara, Phys. Rev. Lett. 80, 1074 (1998).
- [96] A. Shukla, B. Barbiellini, A. Erb, A. Manuel, T. Buslaps, V. Honkimäki, and P. Suortti, preprint, http://xxx.lanl.gov/abs/cond-mat/9805225.

- [97] L. Er-Rakho, C. Michel, J. Provost, and B. Raveau, J. Solid State Chem. **37**, 151 (1981).
- [98] A. Erb, A.A. Manuel, M. Dhalle, F. Marti, J.-Y. Genoud, B. Revaz, A. Junod, D. Vasumathi, S. Ishibashi, A. Shukla, E. Walker, Ø. Fischer, and R. Flükiger, preprint, http://xxx.lanl.gov/abs/cond-mat/9805222.
- [99] H. Shaked, Y. Shimakawa, B.A. Hunter, R.L. Hitterman, J.D. Jorgensen, P.D. Han, and D.A. Payne, Phys. Rev. B 51, 11784 (1995).
- [100] B. Grande, and Hk. Müller-Buschbaum, Z. Anorg. Allg. Chem. 417, 68 (1975); Hk. Müller-Buschbaum, Angew. Chem. Int. Ed. Engl. 16, 674 (1977).
- [101] Z. Hiroi, N. Kobayashi, and M. Takano, Nature **371**, 139 (1994).
- [102] M. Al-Mamouri, P.P. Edwards, C. Greaves, and M. Slaski, Nature **369**, 382 (1994).
- [103] T. Tatsuki, S. Adachi, M. Itoh, T. Tamura, X.-J. Wu, C.-Q. Jin, N. Koshizuka, and K. Tanabe, Physica C 255, 61 (1995).
- [104] B.O. Wells, R.J. Birgeneau, F.C. Chou, Y. Endoh, D.C. Johnston, M.A. Kastner, Y.S. Lee, G. Shirane, J.M. Tranquada, and K. Yamada, Z. Phys. B 100, 535 (1996).
- [105] For a detailed recent review on the magnetic properties of single layer cuprates, see D.C. Johnston in Handbook of Magnetic Materials, Vol. 10, edited by K.H.J. Buschow (Elsevier Science, Amsterdam, 1997), pp. 1 – 237.
- [106] A.J. Millis, and H. Monien, Phys. Rev. Lett. 70, 2810 (1993); *ibid.* 71, 210E (1993); Phys. Rev. B 50, 16606 (1994).
- [107] G.-Q. Zheng, T. Ogaguchi, T. Mito, Y. Kitaoka, K. Asayama, and Y. Kodama, J. Phys. Soc. Jpn. 62, 2591 (1993).
- [108] H.A. Mook, M. Yethiraj, G. Aeppli, T.E. Mason, and T. Armstrong, Phys. Rev. Lett. 70, 3490 (1993).
- [109] A.J. Millis, and H. Monien, Phys. Rev. B 54, 16172 (1996).
- [110] H.A. Mook, F. Doğan, and B.C. Chakoumakos, preprint, http://xxx.lanl.gov/abs/condmat/9811100.
- [111] Q. Si, Y. Zha, K. Levin, and J.P. Lu, Phys. Rev. B 47, 9055 (1993); Q. Si, Int. J. Mod. Phys. B 8, 47 (1994).
- [112] T. Tanamoto, H. Kohno, and H. Fukuyama, J. Phys. Soc. Jpn. 62, 717 (1993).
- [113] H.A. Mook, P. Dai, S.M. Hayden, G. Aeppli, T.G. Perring, and F. Doğan, Nature **395**, 580 (1998); P. Dai, H.A. Mook, and F. Doğan, Phys. Rev. Lett. **80**, 1738 (1998).
- [114] M. Grüninger, J. Münzel, A. Gaymann, A. Zibold, H.P. Geserich, and T. Kopp, Europhys. Lett. 35, 55 (1996).

- [115] D. Reznik, P. Bourges, H.F. Fong, L.P. Regnault, J. Bossy, C. Vettier, D.L. Milius, I.A. Aksay, and B. Keimer, Phys. Rev. B 53, R14741 (1996).
- [116] S.M. Hayden, G. Aeppli, T.G. Perring, H.A. Mook, and F. Doğan, Phys. Rev. B 54, R6905 (1996).
- [117] A. Erb, E. Walker, and R. Flükiger, Physica C 245, 245 (1995); *ibid.* 258, 9 (1996).
- [118] A. Erb, E. Walker, J.-Y. Genoud, and R. Flükiger, Physica C 282-287, 89 and 459 (1997).
- [119] I. Maggio-Aprile, Ch. Renner, A. Erb, E. Walker, and Ø. Fischer, Phys. Rev. Lett. **75**, 2754 (1995); H.P. Lang, A. Erb, P. Jess, U. Hubler, and H.-J. Güntherodt, J. Low Temp. Phys. **105**, 1373 (1996).
- [120] M. Roulin, A. Junod, A. Erb, and E. Walker, J. Low Temp. Phys. 105, 1099 (1996).
- [121] H.A. Bethe, Z. Phys. **71**, 205 (1931).
- [122] P.C. Hohenberg, Phys. Rev. **158**, 383 (1967).
- [123] N.D. Mermin, and H. Wagner, Phys. Rev. Lett. 22, 1133 (1966).
- [124] E.J. Neves, and J.F. Peres, Phys. Lett. A **114**, 331 (1986).
- [125] I. Affleck, T. Kennedy, E.H. Lieb, and H. Tasaki, Commun. Math. Phys. 115, 477 (1988).
- [126] A review is given by E. Manousakis, Rev. Mod. Phys. 63, 1 (1991).
- [127] S. Chakravarty, B.I. Halperin, and D.R. Nelson, Phys. Rev. B 39, 2344 (1989).
- [128] A.V. Chubukov, S. Sachdev, and J. Ye, Phys. Rev. B 49, 11919 (1994).
- [129] P. Carretta, T. Ciabattoni, A. Cuccoli, E. Mognaschi, A. Rigamonti, V. Tognetti, and P. Verucchi, preprint, http://xxx.lanl.gov/abs/cond-mat/9903450.
- [130] D. Coffey, T.M. Rice, and F.C. Zhang, Phys. Rev. B 44, 10112 (1991).
- [131] N.E. Bonesteel, Phys. Rev. B 47, 11302 (1993).
- [132] T. Yildirim, A.B. Harris, O. Entin-Wohlman, and A. Aharony, Phys. Rev. Lett. 73, 2919 (1994); Phys. Rev. B 52, 10239 (1995).
- [133] D. Vaknin, E. Caignol, P.K. Davies, J.E. Fischer, D.C. Johnston, and D.P. Goshorn, Phys. Rev. B 39, 9122 (1989).
- [134] B.B. Beard, R.J. Birgeneau, M. Greven, and U.-J. Wiese, Phys. Rev. Lett. 80, 1742 (1998).
- [135] J. Igarashi, Phys. Rev. B 46, 10763 (1992); J. Phys. Soc. Jpn. 62, 4449 (1993).
- [136] R.R.P. Singh, Phys. Rev. B **39**, 9760 (1989).
- [137] R.R.P. Singh, and M.P. Gelfand, Phys. Rev. B 52, R15695 (1995).
- [138] P.W. Anderson, Phys. Rev. 86, 694 (1952); R. Kubo, Phys. Rev. 87, 568 (1952).

- [139] T. Oguchi, Phys. Rev. **117**, 117 (1960).
- [140] P.W. Anderson, Mater. Res. Bull. 8, 153 (1973); P. Fazekas, and P.W. Anderson, Philos. Mag. 30, 432 (1974).
- [141] E. Fradkin. Field Theories of Condensed Matter Systems (Addison-Wesley, 1991).
- [142] I. Affleck, and J.B. Marston, Phys. Rev. B **37**, 3774 (1988).
- [143] B.O. Wells, Z.-X. Shen, A. Matsuura, D.M. King, M.A. Kastner, M. Greven, and R.J. Birgeneau, Phys. Rev. Lett. 74, 964 (1995).
- [144] C. Kim, P.J. White, Z.-X. Shen, T. Tohyama, Y. Shibata, S. Maekawa, B.O. Wells, Y.J. Kim, and R.J. Birgeneau, Phys. Rev. Lett. 80, 4245 (1998).
- [145] X.-G. Wen, and P.A. Lee, Phys. Rev. Lett. 76, 503 (1996).
- [146] T.C. Hsu, Phys. Rev. B **41**, 11379 (1990).
- [147] Y.R. Wang, M.J. Rice, and H.-Y. Choi, Phys. Rev. B 44, 9743 (1991); Y.R. Wang, Phys. Rev. B 43, 3786 and 13774 (1991).
- [148] H. Fukuyama, and H. Kohno, Czech. J. Phys. 46, 3146 (1996).
- [149] E. Dagotto, Int. J. Mod. Phys. B 5, 907 (1991).
- [150] V.N. Kotov, J. Oitmaa, O.P. Sushkov, and Z. Weihong, preprint, http://xxx.lanl.gov/abs/cond-mat/9903154.
- [151] H.J. Schulz, and T.A.L. Ziman, Europhys. Lett. 18, 355 (1992).
- [152] E. Dagotto, and A. Moreo, Phys. Rev. Lett. 63, 2148 (1989).
- [153] D.K. Morr, Phys. Rev. B 58, R587 (1998).
- [154] A.H. MacDonald, S.M. Girvin, and D. Yoshioka, Phys. Rev. B 37, 9753 (1988); see also comment by A.M. Oleś, Phys. Rev. B 41, 2562 (1990); and the reply by A.H. MacDonald, S.M. Girvin, and D. Yoshioka, Phys. Rev. B 41, 2565 (1990).
- [155] S. Sachdev, and R.N. Bhatt, Phys. Rev. B 41, 9323 (1990).
- [156] C.K. Majumdar, and D.K. Gosh, J. Math. Phys. 10, 1388 (1969).
- [157] T. Barnes, and J. Riera, Phys. Rev. B 50, 6817 (1994); A.W. Garrett, S.E. Nagler, D.A. Tennant, B.C. Sales, and T. Barnes, Phys. Rev. Lett. 79, 745 (1997).
- [158] M. Hase, I. Terasaki, and K. Uchinokura, Phys. Rev. Lett. **70**, 3651 (1993).
- [159] K. Ueda, and S. Miyahara, preprint, http://xxx.lanl.gov/abs/cond-mat/9904014.
- [160] H. Kageyama, K. Yoshimura, R. Stern, N.V. Mushnikov, K. Onizuka, M. Kato, K. Kosuge, C.P. Slichter, T. Goto, and Y. Ueda, Phys. Rev. Lett. 82, 3168 (1999).

- [161] T. Barnes, E. Dagotto, J. Riera, and E.S. Swanson, Phys. Rev. B 47, 3196 (1993).
- [162] A.W. Sandvik, and D.J. Scalapino, Phys. Rev. Lett. 72, 2777 (1994).
- [163] T. Matsuda, and K. Hida, J. Phys. Soc. Jpn. 59, 2223 (1990); K. Hida, J. Phys. Soc. Jpn. 61 1013 (1992).
- [164] A.V. Chubukov, and D.K. Morr, Phys. Rev. B 52, 3521 (1995).
- [165] K. Hida, J. Phys. Soc. Jpn. 67, 1540 (1998).
- [166] C. Gros, W. Wenzel, and J. Richter, Europhys. Lett. **32**, 747 (1995).
- [167] Y.Sasago, K. Uchinokura, A. Zheludev, and G. Shirane, Phys. Rev. B 55, 8357 (1997).
- [168] L.P. Regnault, J.P. Renard, G. Dhalenne, and A. Revcolevschi, Europhys. Lett. 32, 579 (1995).
- [169] H. Fukuyama, T. Tanimoto, and M. Saito, J. Phys. Soc. Jpn. 65, 1182 (1996).
- [170] M.P.A. Fisher, preprint, http://xxx.lanl.gov/abs/cond-mat/9806164; L. Balents, M.P.A. Fisher, and C. Nayak, preprint, http://xxx.lanl.gov/abs/cond-mat/9803086.
- [171] N. Andrei, and J.H. Lowenstein, Phys. Rev. Lett. 43, 1698 (1979).
- [172] N. Andrei, and J.H. Lowenstein, Phys. Lett. B **91**, 401 (1980).
- [173] L.D. Faddeev, and L.A. Takhtajan, Phys. Lett. A 85, 375 (1981).
- [174] I. Affleck, preprint, http://xxx.lanl.gov/abs/cond-mat/9705127.
- [175] G.S. Uhrig. F.S. Schönfeld, M. Laukamp, and E. Dagotto, Euro. Phys. J. 7, 67 (1999).
- [176] T.M.R. Byrnes, M.T. Murphy, and O.P. Sushkov, preprint, http://xxx.lanl.gov/abs/condmat/9902249.
- [177] M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Môri, and K. Kinoshita, J. Phys. Soc. Jpn. 65, 2764 (1996).
- [178] J. Kosterlitz, and D. Thouless, J. Phys. C 6, 1181 (1973); J. Kosterlitz, J. Phys. C 7, 1046 (1974).
- [179] B. Keimer, N. Belk, R.J. Birgeneau, A. Cassanho, C.Y. Chen, M. Greven, M.A. Kastner, A. Aharony, Y. Endoh, R.W. Erwin, and G. Shirane, Phys. Rev. B 46, 14034 (1992).
- [180] M. Greven, R.J. Birgeneau, Y. Endoh, M.A. Kastner, M. Matsuda, and G. Shirane, Z. Phys. B 96, 465 (1995).
- [181] R.J. Birgeneau, A. Aharony, N.R. Belk, F.C. Chou, Y. Endoh, M. Greven, S. Hosoya, M.A. Kastner, C.H. Lee, Y.S. Lee, G. Shirane, S. Wakimoto, B.O. Wells, and K. Yamada, J. Phys. Chem. Solids 56, 1913 (1995).

- [182] R.J. Birgeneau, M. Greven, M.A. Kastner, Y.S. Lee, B.O. Wells, Y. Endoh, K. Yamada, and G. Shirane, preprint, http://xxx.lanl.gov/abs/cond-mat/9903124.
- [183] P. Hasenfratz, and F. Niedermayer, Phys. Lett. B 268, 231 (1991).
- [184] M.S. Makivic, and H.-Q. Ding, Phys. Rev. B 43, 3562 (1991).
- [185] K. Nakajima, K. Yamada, S. Hosoya, Y. Endoh, M. Greven, and R.J. Birgeneau, Z. Phys. B 96, 479 (1995).
- [186] N. Elstner, A. Sokol, R.R.P. Singh, M. Greven, and R.J. Birgeneau, Phys. Rev. Lett. 75, 938 (1995).
- [187] P. Kopietz, Phys. Rev. Lett. **64**, 2587 (1990).
- [188] R.L. Leheny, R.J. Christianson, R.J. Birgeneau, and R.W. Erwin, Phys. Rev. Lett. 82, 418 (1999).
- [189] S.M. Hayden, G. Aeppli, H.A. Mook, T.G. Perring, T.E. Mason, S.-W. Cheong, and Z. Fisk, Phys. Rev. Lett. **76**, 1344 (1996); S.M. Hayden, G. Aeppli, P. Dai, H.A. Mook, T.G. Perring, S.-W. Cheong, Z. Fisk, F. Doğan, and T.E. Mason, Physica B **241-243**, 765 (1992).
- [190] P. Bourges, H. Casalta, A.S. Ivanov, and D. Petitgrand, Phys. Rev. Lett. 79, 4906 (1997).
- [191] S. Itoh, K. Yamada, M. Arai, Y. Endoh, Y. Hidaka, and S. Hosoya, J. Phys. Soc. Jpn. 63, 4542 (1994).
- [192] J.M. Tranquada, G. Shirane, B. Keimer, S. Shamoto, and M. Sato, Phys. Rev. B 40, 4503 (1989).
- [193] J.M. Tranquada, A.H. Moudden, A.I. Goldman, P. Zolliker, D.E. Cox, G. Shirane, S.K. Sinha, D. Vaknin, D.C. Johnston, M.S. Alvarez, A.J. Jacobson, J.T. Lewandowski, and J.M. Newsam, Phys. Rev. B 38, 2477 (1988).
- [194] T.A. Kaplan, S.D. Mahanti, and H. Chang, Phys. Rev. B 45, 2565 (1992).
- [195] D.E. MacLaughlin, J.P. Vithayathil, H.B. Brom, J.C.J.M. de Rooy, P.C. Hammel, P.C. Canfield, A.P. Reyes, Z. Fisk, J.D. Thompson, and S.-W. Cheong, Phys. Rev. Lett. 72, 760 (1994).
- [196] B. Keimer, A. Aharony, A. Auerbach, R.J. Birgeneau, A. Cassanho, Y. Endoh, R.W. Erwin, M.A. Kastner, and G. Shirane, Phys. Rev. B 45, 7430 (1992).
- [197] S.M. Hayden, G. Aeppli, R. Osborn, A.D. Taylor, T.G. Perring, S.-W. Cheong, and Z. Fisk, Phys. Rev. Lett. 67, 3622 (1991).
- [198] G. Aeppli, S.M. Hayden, P. Dai, H.A. Mook, R.D. Hunt, T.G. Perring, and F. Doğan, Proceedings of the International Conference on Solid State Spectroscopy (ICSSS) (Wiley and sons, 1999), to be published; G. Aeppli, private communication.
- [199] D.A. Tennant, R.A. Cowley, S.E. Nagler, and A.M. Tsvelik, Phys. Rev. B 52, 13368 (1995).

- [200] Y. Endoh, G. Shirane, R.J. Birgeneau, P.M. Richards, and S.L. Holt, Phys. Rev. Lett. 32, 170 (1974).
- [201] J. des Cloizeaux, and J.J. Pearson, Phys. Rev. **128**, 2131 (1962).
- [202] G. Blumberg, P. Abbamonte, M.V. Klein, W.C. Lee, D.M. Ginsberg, L.L. Miller, and A. Zibold, Phys. Rev. B 53, R11930 (1996).
- [203] F. Schönfeld, A.P. Kampf, and E. Müller-Hartmann, Z. Phys. B 102, 25 (1997).
- [204] S. Sugai, M. Sato, T. Kobayashi, J. Akimitsu, T. Ito, H. Takagi, S. Uchida, S. Hosoya, T. Kajitani, and T. Fukuda, Phys. Rev. B 42, 1045 (1990).
- [205] P.A. Fleury. and H.J. Guggenheim, Phys. Rev. Lett. 24, 1346 (1970).
- [206] R.R.P. Singh, P.A. Fleury, K.B. Lyons, and P.E. Sulewski, Phys. Rev. Lett. 62, 2736 (1989);
   R.R.P. Singh, Physica C 162-164, 829 (1989); Comments Cond. Mat. Phys. 15, 241 (1991).
- [207] A.W. Sandvik, S. Capponi, D. Poilblanc, and E. Dagotto, Phys. Rev. B 57, 8478 (1998).
- [208] C.M. Canali, and S.M. Girvin, Phys. Rev. B 45, 7127 (1992).
- [209] W.H. Weber, and G.W. Ford, Phys. Rev. B 40, 6890 (1989).
- [210] P. Knoll, C. Thomsen, M. Cardona, and P. Murugaraj, Phys. Rev. B 42, 4842 (1990).
- [211] D.U. Sänger, Phys. Rev. B 52, 1025 (1995); Phys. Rev. B 49, 12176 (1994).
- [212] F. Nori, R. Merlin, S. Haas, A.W. Sandvik, and E. Dagotto, Phys. Rev. Lett. 75, 553 (1995).
- [213] M.J. Reilly, and A.G. Rojo, Phys. Rev. B 53, 6429 (1996).
- [214] J.D. Lee, and B.I. Min, Solid State Comm. 99, 627 (1996); J. Phys. Soc. Jpn. 66, 442 (1997).
- [215] S. Basu, preprint, http://xxx.lanl.gov/abs/cond-mat/9809251.
- [216] Y. Honda, Y. Kuramoto, and T. Watanabe, Phys. Rev. B 47, 11329 (1993).
- [217] H.J. Schmidt, and Y. Kuramoto, Physica C 167, 263 (1990).
- [218] M. Roger, and J.M. Delrieu, Phys. Rev. B **39**, 2299 (1989).
- [219] J. Eroles, C.D. Batista, S.B. Bacci, and E.R. Gagliano, Phys. Rev. B 59, 1468 (1999).
- [220] A.V. Chubukov, and D.M. Frenkel, Phys. Rev. Lett. 74, 3057 (1995); Phys. Rev. B 52, 9760 (1995).
- [221] D.K. Morr, and A.V. Chubukov, Phys. Rev. B 56, 9134 (1997).
- [222] D.K. Morr, A.V. Chubukov, A.P. Kampf, and G. Blumberg, Phys. Rev. B 54, 3468 (1996).
- [223] A.V. Chubukov, and D.K. Morr, Phys. Rev. B 57, 5298 (1998).

- [224] J. Lorenzana and G.A. Sawatzky, Phys. Rev. Lett. 74, 1867 (1995); Phys. Rev. B 52, 9576 (1995).
- [225] M. Grüninger, D. van der Marel, A. Damascelli, A. Erb, Th. Wolf, T. Nunner, and T. Kopp, preprint, http://xxx.lanl.gov/abs/cond-mat/9904394.
- [226] J.D. Perkins, J.M. Graybeal, M.A. Kastner, R.J. Birgeneau, J.P. Falck, and M. Greven, Phys. Rev. Lett. 71, 1621 (1993).
- [227] J.D. Perkins, R.J. Birgeneau, J.M. Graybeal, M.A. Kastner, and D.S. Kleinberg, Phys. Rev. B 58, 9390 (1998).
- [228] J.D. Perkins, D.S. Kleinberg, M.A. Kastner, R.J. Birgeneau, Y. Endoh, K. Yamada, and S. Hosoya, Phys. Rev. B 52, R9863 (1995).
- [229] B.I. Shraiman, and E.D. Siggia, Phys. Rev. Lett. 61, 467 (1988); Phys. Rev. B 42, 2485 (1990).
- [230] R.J. Gooding, Phys. Rev. Lett. 66, 2266 (1991).
- [231] M. Fleck, A.I. Liechtenstein, A.M. Oleś, L. Hedin, and V.I. Anisimov, Phys. Rev. Lett. 80, 2393 (1998).
- [232] R. Frésard, M. Dzierzawa, and P. Wölfle, Europhys. Lett. 15, 325 (1991); R. Frésard, and P. Wölfle, J. Phys. C 4, 3625 (1992).
- [233] G. Seibold, Phys. Rev. B 58, 15520 (1998).
- [234] R.J. Gooding, and A. Mailhot, Phys. Rev. B 48, 6132 (1993).
- [235] R.J. Gooding, N.M. Salem, R.J. Birgeneau, and F.C. Chou, Phys. Rev. B 55, 6360 (1997).
- [236] F.C. Chou. N.R. Belk, M.A. Kastner, R.J. Birgeneau, and A. Aharony, Phys. Rev. Lett. 75, 2204 (1995).
- [237] E. Lai, and R.J. Gooding, Phys. Rev. B 57, 1498 (1998).
- [238] S. Haas, F.-C. Zhang, F. Mila, and T.M. Rice, Phys. Rev. Lett. 77, 3021 (1996).
- [239] J. Jaklič, and P. Prelovšek, to be published in Adv. Phys. (http://xxx.lanl.gov/abs/condmat/9803331).
- [240] S. Trugman, Phys. Rev. B **37**, 1597 (1988).
- [241] A. Kampf, and J.R. Schrieffer, Phys. Rev. B **41**, 6399 (1990); *ibid.* **42**, 7967 (1990).
- [242] R. Eder, Y. Ohta, and S. Maekawa, Phys. Rev. Lett. 74, 5124 (1995); R. Eder, P. Wróbel, and Y. Ohta, Phys. Rev. B 54, R11034 (1996).
- [243] M. Vojta, and K.W. Becker, Europhys. Lett. **38**, 607 (1997).
- [244] W. Marshall, Proc. R. Soc. London Ser. A **232**, 48 (1955).
- [245] D.N. Sheng, Y.C. Chen, and Z.Y. Weng, Phys. Rev. Lett. 77, 5102 (1996).
- [246] K. Retzlaff, J. Richter, and N.B. Ivanov, Z. Phys. B 93, 21 (1993).
- [247] Z.Y. Weng, D.N. Sheng, Y.-C. Chen, and C.S. Ting, Phys. Rev. B 55, 3894 (1997).
- [248] Z.Y. Weng, D.N. Sheng, and C.S. Ting, Phys. Rev. Lett. 80, 5401 (1998); see also preprints, http://xxx.lanl.gov/abs/cond-mat/9809362 and 9809363.
- [249] F. Ronning, C. Kim, D.L. Feng, D.S. Marshall, A.G. Loeser, L.L. Miller, J.N. Eckstein, I. Bozovic, and Z.-X. Shen, Science 282, 2067 (1998).
- [250] A. Nazarenko, K.J.E. Vos, S. Haas, E. Dagotto, and R.J. Godding, Phys. Rev. B 51, 8676 (1995).
- [251] B. Kyung, and R.A. Ferrell, Phys. Rev. B 54, 10125 (1996).
- [252] T. Xiang, and J.M. Wheatley, Phys. Rev. B 54, R12653 (1996).
- [253] V.I. Belinicher, A.L. Chernyshev, and V.A. Shubin, Phys. Rev. B 54, 14914 (1996).
- [254] R. Eder, Y. Ohta, and G.A. Sawatzky, Phys. Rev. B 55, R3414 (1997).
- [255] T.K. Lee, and C.T. Shih, Phys. Rev. B 55, 5983 (1997).
- [256] Z.-X. Shen, and G.A. Sawatzky, preprint.
- [257] A. Kaminski, J. Mesot, H. Fretwell, J.C. Campuzano, M.R. Norman, M. Randeria, H. Ding, T. Sato, T. Takahashi, T. Mochiku, K. Kadowaki, and H. Hoechst, preprint, http://xxx.lanl.gov/abs/cond-mat/9904390.
- [258] R.B. Laughlin, Phys. Rev. Lett. **79**, 1726 (1997).
- [259] R.B. Laughlin, J. Low Temp. Phys. 99, 443 (1995).
- [260] G. Baskeran, Z. Zou, and P.W. Anderson, Solid State Comm. 63, 973 (1987); Z. Zou, Phys. Rev. B 40, 2262 (1989).
- [261] G. Kotliar, Phys. Rev. B **37**, 3664 (1988).
- [262] P. Béran, D. Poilblanc, and R.B. Laughlin, preprint, http://xxx.lanl.gov/abs/cond-mat/9505085.
- [263] G.B. Martins, R. Eder, and E. Dagotto, preprint, http://xxx.lanl.gov/abs/cond-mat/9904030.
- [264] J. Zaanen, and O. Gunnarsson, Phys. Rev. B 40, 7391 (1989).
- [265] S.A. Kivelson, and V.J. Emery, preprint http://xxx.lanl.gov/abs/cond-mat/9809082; V.J. Emery, and S.A. Kivelson, preprint http://xxx.lanl.gov/abs/cond-mat/9809083; and references therein.
- [266] G. Aeppli, private communication.

- [267] G. Aeppli, T.E. Mason, S.M. Hayden, H.A. Mook, and J. Kulda, Science **278**, 1432 (1997).
- [268] J.M. Tranquada, B.J. Sternlieb, J.D. Axe, Y. Nakamura, and S. Uchida, Nature 375, 561 (1995); J.M. Tranquada, J.D. Axe, N. Ichikawa, A.R. Moodenbaugh, Y. Nakamura, and S. Uchida, Phys. Rev. Lett. 78, 338 (1997).
- [269] S.-W. Cheong, G. Aeppli, T.E. Mason, H. Mook, S.M. Hayden, P.C. Canfield, Z. Fisk, K.N. Clausen, and J.L. Martinez, Phys. Rev. Lett. 67, 1791 (1991); T.E. Mason, G. Aeppli, and H.A. Mook, *ibid.* 68, 1414 (1992); T.R. Thurston, P.M. Gehring, G. Shirane, R.J. Birgeneau, M.A. Kastner, Y. Endoh, M. Matsuda, K. Yamada, H. Kojima, and I. Tanaka, Phys. Rev. B 46, 9128 (1992); M. Matsuda, K. Yamada, Y. Endoh, T.R. Thurston, G. Shirane, R.J. Birgeneau, M.A. Kastner, I. Tanaka, and H. Kojima, *ibid.* 49, 6958 (1994); K. Yamada, C.H. Lee, K. Kurahashi, J. Wada, S. Wakimoto, S. Ueki, H. Kimura, Y. Endoh, S. Hosoya, G. Shirane, R.J. Birgeneau, M. Greven, M.A. Kastner, and Y.J. Kim, Phys. Rev. B 57, 6165 (1998).
- [270] M. Continentino, Physics Reports 239, 179 (1994); S.L. Sondhi, S.M. Girvin, J.P. Carini, and D. Shahar, Rev. Mod. Phys. 69, 315 (1997); and references in Ref. [267].
- [271] S. Caprara, C. Castellani, C. Di Castro, M. Grilli, A. Perali, and M. Sulpizi, to be published in J. Supercond. (http://xxx.lanl.gov/abs/cond-mat/9812279).
- [272] A recent review on nearly antiferromagnetic Fermi liquids can be found in D. Pines, Z. Phys. 103, 129 (1997).
- [273] V. Barzykin, and D. Pines, Phys. Rev. B 52, 13585 (1995).
- [274] J. Zaanen, Physcia C **317-318**, 217 (1999).
- [275] C. Castellani, C. Di Castro, and M. Grilli, Z. Phys. B 103, 137 (1997).
- [276] N.D. Mathur, F.M. Grosche, S.R. Julian, I.R. Walker, D.M. Freye, R.K.W. Haselwimmer, and G.G. Lonzarich, Nature 394, 39 (1998).
- [277] A. Rosch, Phys. Rev. Lett. 82, 4280 (1999).
- [278] H. Fukuyama, Prog. Theor. Phys. Suppl. 108, 287 (1992).
- [279] A.S. Alexandrov, and N.F. Mott, High Temperature Superconductors and other Superfluids (Taylor and Francis, London, 1994).
- [280] T. Kopp, F.J. Seco, S. Schiller, and P. Wölfle, Phys. Rev. B 38, 11835 (1988).
- [281] A.G. Loeser, D.S. Dessau, and Z.-X. Shen, Physica C 263, 208 (1996); A.G. Loeser, Z.-X. Shen, D.S. Dessau, D.S. Marshall, C.H. Park, P. Fournier, and A. Kapitulnik, Science 273, 3252 (1996).
- [282] H. Ding, T. Yokaya, J.-C. Campuzano, T. Takahashi, M. Randeria, M.R. Norman, T. Mochiku, K. Kadowaki, and J. Giapinzakis, Nature 382, 51 (1996).
- [283] A detailed review of various experimental techniques concerning the pseudogap has very recently been published by T. Timusk, and B. Statt, Rep. Prog. Phys. **62**, 61 (1999).

- [284] D.S. Marshall, D.S. Dessau, A.G. Loeser, C.-H. Park, A.Y. Matsuura, J.N. Eckstein, I. Bozovic, P. Fournier, A. Kapitulnik, W.E. Spicer, and Z.-X. Shen, Phys. Rev. Lett. 76, 4841 (1996).
- [285] P.J. White, Z.-X. Shen, C. Kim, J.M. Harris, A.G. Loeser, P. Fournier, and A. Kapitulnik, Phys. Rev. B 54, R15669 (1996).
- [286] J.M. Harris, Z.-X. Shen, P.J. White, D.S. Marshall, M.C. Schabel, J.N. Eckstein, and I. Bozovic, Phys. Rev. B 54, R15665 (1996).
- [287] J.M. Harris, P.J. White, Z.-X. Shen, H. Ikeda, R. Yoshizaki, H. Eisaki, S. Uchida, W.D. Si, J.W. Xiong, Z.-X. Zhao, and D.S. Dessau, Phys. Rev. Lett. 79, 143 (1997).
- [288] Ch. Renner, B. Revaz, J.-Y. Genoud, K. Kadowaki, and Ø. Fischer, Phys. Rev. Lett. 80, 149 (1998).
- [289] N. Miyakawa, P. Guptasarma, J.F. Zasadzinski, D.G. Hinks, and K.E. Gray, Phys. Rev. Lett. 80, 157 (1998).
- [290] J.L. Tallon, C. Bernhard, G.V.M. Williams, and J.W. Loram, Phys. Rev. Lett. 79, 5294 (1997).
- [291] G.V.M. Williams, J.L. Tallon, and J.W. Loram, Phys. Rev. B 58, 15053 (1998).
- [292] J.W. Loram, K.A. Mirza, J.R. Cooper, and J.L. Tallon, Physica C 282-287, 1405 (1997).
- [293] J.W. Loram, K.A. Mirza, J.M. Wade, J.R. Cooper, N. Athanassopoulou, and W.Y. Liang, Advances in Superconductivity VII (Springer, Tokyo, 1995), p. 75.
- [294] R.E. Walstedt, W.W. Warren, Jr., R.F. Bell, R.J. Cava, G.P. Espinosa, L.F. Schneemeyer, and J.V. Waszczak, Phys. Rev. B 41, 9574 (1990).
- [295] J.L. Tallon, Phys. Rev. B 58, R5956 (1998).
- [296] G.V.M. Williams, J.L. Tallon, J.W. Quilty, H.J. Trodahl, and N.E. Flower, Phys. Rev. Lett. 80, 377 (1998).
- [297] G.S. Boebinger, Y. Ando, A. Passner, T. Kimura, M. Okuya, J. Shimoyama, K. Kishio, K. Tamasaku, N. Ichikawa, and S. Uchida, Phys. Rev. Lett. 77, 5417 (1996).
- [298] S. Martin, A.T. Fiory, R.M. Fleming, L.F. Schneemeyer, and J.V. Waszczak, Phys. Rev. B 41, 846 (1990).
- [299] H. Takagi, B. Batlogg, H.L. Kao, J. Kwo, R.J. Cava, J.J. Krajewski, and W.F. Peck, Jr., Phys. Rev. Lett. 69, 2975 (1992).
- [300] B. Batlogg, H.Y. Hwang, H. Takagi, R.J. Cava, H.L. Kao, and J. Kwo, Physica C 235-240, 130 (1994).
- [301] K. Takenaka, K. Mizuhashi, H. Takagi, and S. Uchida, Phys. Rev. B 50, 6534 (1994).

- [302] A.I. Liechtenstein, O. Gunnarsson, O.K. Andersen, and R.M. Martin, Phys. Rev. B 54, 12505 (1996).
- [303] A. Hosseini, S. Kamal, D.A. Bonn, R. Liang, and W.N. Hardy, Phys. Rev. Lett. 81, 1298 (1998).
- [304] C. Bernhard, D. Munzar, A. Wittlin, W. König, A. Golnik, C.T. Lin, M. Kläser, Th. Wolf, G. Müller-Vogt, and M. Cardona, Phys. Rev. B 59, R6631 (1999).
- [305] J. Schützmann, S. Tajima, S. Miyamoto, Y. Sato, and R. Hauff, Phys. Rev. B 52, 13665 (1995); S. Tajima, J. Schützmann, S. Miyamoto, I. Terasaki, Y. Sato, and R. Hauff, Phys. Rev. B 55, 6051 (1997).
- [306] D.N. Basov, T. Timusk, B. Dabrowski, and J.D. Jorgensen, Phys. Rev. B 50, R3511 (1994).
- [307] M. Reedyk, T. Timusk, J.S. Xue, and J.E. Greedan, Phys. Rev. B 49, 15984 (1994); M. Reedyk, T. Timusk, Y.-W. Hsueh, B.W. Statt, J.S. Xue, and J.E. Greedan, Phys. Rev. B 56, 9134 (1997).
- [308] S. Uchida, K. Tamasaku, K. Takenaka, and H. Takagi, J. Low Temp. Phys. **95**, 109 (1994).
- [309] S. Uchida, K. Tamasaku, and S. Tajima, Phys. Rev. B 53, 14558 (1996).
- [310] D.N. Basov, H.A. Mook, B. Dabrowski, and T. Timusk, Phys. Rev. B 52, R13141 (1995).
- [311] T. Startseva, T. Timusk, A.V. Puchkov, D.N. Basov, H.A. Mook, M. Okuya, T. Kimura, and K. Kishio, preprint, http://xxx.lanl.gov/abs/cond-mat/9812134.
- [312] R. Hauff, S. Tajima, W.-J. Jang, and A.I. Rykov, Phys. Rev. Lett. 77, 4620 (1996).
- [313] M. Grüninger, D. van der Marel, A.A. Tsvetkov, and A. Erb, preprint, http://xxx.lanl.gov/abs/cond-mat/9903352.
- [314] T.R. Thurston, R.J. Birgeneau, M.A. Kastner, N.W. Preyer, G. Shirane, Y. Fujii, K. Yamada, Y. Endoh, Y. Hidaka, and T. Murakami, Phys. Rev. B 40, 4585 (1989).
- [315] A. Freimuth, private communication.
- [316] D.N. Basov, S.I. Woods, A.S. Katz, E.J. Singley, R.C. Dynes, M. Xu, D.G. Hinks, C.C. Homes, and M. Strongin, Science 283, 49 (1999).
- [317] S. Chakravarty, H.-Y. Kee, and E. Abrahams, Phys. Rev. Lett. 82, 2366 (1999).
- [318] L.B. Ioffe, and A.J. Millis, Phys. Rev. B 58, 11631 (1998).
- [319] D. van der Marel, Phys. Rev. B 60, R765 (1999).
- [320] N. Nagaosa, and P.A. Lee, Phys. Rev. Lett. 64, 2450 (1990).
- [321] J.M. Tranquada, D.J. Buttrey, V. Sachan, and J.E. Lorenzo, Phys. Rev. Lett. 73, 1003 (1994).

- [322] M. v. Zimmermann, A. Vigliante, T. Niemöller, N. Ichikawa, T. Frello, J. Madsen, P. Wochner, S. Uchida, N.H. Andersen, J.M. Tranquada, D. Gibbs, and J.R. Schneider, Europhys. Lett. 41, 629 (1998).
- [323] T. Niemöller, H. Hünnefeld, J.R. Schneider, N. Ichikawa, S. Uchida, T. Frello, N.H. Andersen, and J.M. Tranquada, preprint, http://xxx.lanl.gov/abs/cond-mat/9904383.
- [324] A.R. Moodenbaugh, Y. Xu, M. Suenaga, T.J. Folkerts, and R.N. Shelton, Phys. Rev. B 38, 4596 (1988).
- [325] J.M. Tranquada, Proceedings of the University of Miami Conference on High-Temperature Superconductors, Miami, 1999, to be published (http://xxx.lanl.gov/abs/condmat/9903458).
- [326] J.M. Tranquada in Neutron Scattering in Layered Copper-Oxide Superconductors, edited by A. Furrer (Kluwer Academic, Dordrecht, 1998), p. 225; J.M. Tranquada, J. Phys. Chem. Solids 59, 2150 (1998).
- [327] S.C. Zhang, Science **275**, 1089 (1997).
- [328] S.C. Zhang, preprint, http://xxx.lanl.gov/abs/cond-mat/9704135.
- [329] C.M. Varma, P.B. Littlewood, S. Schmitt-Rink, E. Abrahams, and A.E. Ruckenstein, Phys. Rev. Lett. 63, 1996 (1989).
- [330] D. Pines, Physica B **163**, 78 (1990).
- [331] A. Virosztek, and J. Ruvalds, Phys. Rev. B 42, 4064 (1990).
- [332] G.D. Mahan, Many-Particle Physics (Plenum Press, New York, 1990).
- [333] R.F. Wallis, and M. Balkanski, *Many-Body Aspects of Solid State Spectroscopy* (North-Holland, Amsterdam, 1986).
- [334] W. Nolting, Grundkurs: Theoretische Physik Vol. 7, Viel-Teilchen-Theorie (Zimmermann-Neufang, Ulmen, 1995).
- [335] F. Wooten, Optical Properties of Solids (Academic Press, New York, 1972).
- [336] C.F. Klingshirn, Semiconductor Optics (Springer, Heidelberg, 1997).
- [337] H. Mori, Prog. Theor. Phys. 34, 399 (1965).
- [338] P.B. Allen, Phys. Rev. B **3**, 305 (1971).
- [339] W. Götze, and P. Wölfle, Phys. Rev. B 6, 1226 (1972).
- [340] J.W. Allen, and J.C. Mikkelsen, Phys. Rev. B 15, 2952 (1977).
- [341] S.V. Shulga, O.V. Dolgov, and E.G. Maksimov, Physica C 178, 266 (1991).
- [342] F. Marsiglio, preprint, http://xxx.lanl.gov/abs/cond-mat/9811424.

- [343] B.P. Stojković, and D. Pines, Phys. Rev. B 56, 11931 (1997).
- [344] A.S. Chaves, and S.P.S. Porto, Solid State Comm. 13, 865 (1973).
- [345] D.W. Berreman, and F.C. Unterwald, Phys. Rev. **174**, 791 (1968).
- [346] K.S. Singwi, and M.P. Tosi, Phys. Rev. 147, 658 (1966).
- [347] A.A. Kukharskii, Sov. Phys. Solid State 14, 1501 (1972).
- [348] F. Gervais in Infrared and Millimeter Waves, Vol. 8, edited by K.J. Button (Academic Press, New York, 1983), pp. 279-339.
- [349] J.F. Baumard, and F. Gervais, Phys. Rev. B 15, 2316 (1977).
- [350] R.P. Lowndes, Phys. Rev. B 1, 2754 (1970).
- [351] R.P.S.M. Lobo, F. Gervais, C. Champeaux, P. Marchet, and A. Catherinot, Mat. Science Eng. B 34, 74 (1995).
- [352] U. Fano, Phys. Rev. **124**, 1866 (1961).
- [353] A. Damascelli, Ph.D. Thesis, University of Groningen, 1999.
- [354] D.J. Bergman, Phys. Rev. B 14, 1531 (1976); D.J. Bergman in *Electrical Transport and Optical Properties of Inhomogeneous Media*, AIP Conference Proceedings No. 40, edited by J.C. Garland, and D.B. Tanner (American Institute of Physics, New York, 1978), pp. 46-61.
- [355] Z. Hashin, and S. Shtrikman, J. Appl. Phys. **33**, 3125 (1962).
- [356] W. Woodside, and J.H. Messmer, J. Appl. Phys. **32**, 1688 (1961).
- [357] A.J. Leggett, Prog. Theor. Phys. 36, 901 (1966).
- [358] E.H. Hwang, and S. Das Sarma, Int. J. Mod. Phys. B 12, 2769 (1998); see also S. Das Sarma, and E.H. Hwang, Phys. Rev. Lett. 81, 4216 (1998); and S. Das Sarma, and E.H. Hwang, Phys. Rev. Lett. 80, 4753 (1998).
- [359] H. Shi, and A. Griffin, Phys. Rev. B 44, 11977 (1991); A. Griffin, and A.J. Pindor, Phys. Rev. B 39, 11503 (1989); A. Griffin, Physica C 162-164, 1427 (1989).
- [360] X. Zhu, X. Xia, J.J. Quinn, and P. Hawrylak, Phys. Rev. B 38, 5617 (1988).
- [361] R.E. Camley, and D.L. Mills, Phys. Rev. B 29, 1695 (1984).
- [362] M. Babiker, J. Phys. C **20**, 3321 (1987).
- [363] W. Luis Mochán, M. del Castillo-Mussot, and R.G. Barrera, Phys. Rev. B 35, 1088 (1987);
   E. López Olazagasti, G.H. Cocoletzi, and W. Luis Mochán, Solid State Comm. 78, 9 (1991).
- [364] D. Munzar, C. Bernhard, A. Golnik, J. Humlíček, and M. Cardona, preprint, http://xxx.lanl.gov/abs/cond-mat/9903291.

- [365] K. Tamasaku, Y. Nakamura, and S. Uchida, Phys. Rev. Lett. 69, 1455 (1992).
- [366] A.M. Gerrits, M.E.J. Boonman, A. Wittlin, P.J.M. van Bentum, V.H.M. Duijn, and A.A. Menovsky, Phys. Rev. B 51, 12049 (1995).
- [367] R.J. Bell, Introductory Fourier Transform Spectroscopy (Academic Press, New York, 1972).
- [368] P.R. Griffiths, and J.A. de Haseth, Fourier Transform Infrared Spectrometry (John Wiley & Sons, New York, 1986).
- [369] L. Pintschovius, and W. Reichardt in Physical Properties of High Temperature Superconductors IV, edited by D.M. Ginsberg (World Scientific, Singapore 1994), p. 295.
- [370] C. Thomsen, and M. Cardona in *Physical Properties of High Temperature Superconductors* I, edited by D.M. Ginsberg (World Scientific, Singapore 1989), p. 409.
- [371] C. Thomsen in Light Scattering in Solids VI, edited by M. Cardona and G. Güntherodt (Springer, Heidelberg, 1991), p. 285.
- [372] A review of data of ceramic samples has been given by R. Feile, Physica C 159, 1 (1989).
- [373] S.L. Chaplot, W. Reichardt, L. Pintschovius, and N. Pyka, Phys. Rev. B 52, 7230 (1995).
- [374] G. Burns, F.H. Dacol, P.P. Freitas, W. König, and T.S. Plaskett, Phys. Rev. B 37, 5171 (1988).
- [375] C. Thomsen, R. Liu, M. Bauer, A. Wittlin, L. Genzel, M. Cardona, E. Schönherr, W. Bauhofer, and W. König, Solid State Comm. 65, 55 (1988).
- [376] C. Thomsen, M. Cardona, W. Kress, R. Liu, L. Genzel, M. Bauer, E. Schönherr, and U. Schröder, Solid State Comm. 65, 1139 (1988).
- [377] M.K. Crawford, W.E. Farneth, R.K. Bordia, and E.M. McCarron III, Phys. Rev. B 37, 3371 (1988).
- [378] M.K. Crawford, W.E. Farneth, E.M. McCarron III, and R.K. Bordia, Phys. Rev. B 38, 11382 (1988).
- [379] M. Cardona, L. Genzel, R. Liu, A. Wittlin, Hj. Mattausch, F. García-Alvarado, and E. García-González, Solid State Comm. 64, 727 (1987).
- [380] M. Cardona, R. Liu, C. Thomsen, W. Kress, E. Schönherr, M. Bauer, L. Genzel, and W. König, Solid State Comm. 67, 789 (1988).
- [381] H.J. Ye, R.P. McCall, W.E. Farneth, E.M. McCarron III, and A.J. Epstein, Phys. Rev. B 43, 10574 (1991).
- [382] A.V. Bazhenov, Sov. Phys. JETP **75**, 566 (1992).
- [383] M.K. Crawford, G. Burns, and F. Holtzberg, Solid State Comm. 70, 557 (1989).
- [384] S. Tajima, T. Ido, S. Ishibashi, T. Itoh, H. Eisaki, Y. Mizuo, T. Arima, H. Takagi, and S. Uchida, Phys. Rev. B 43, 10496 (1991).

- [385] A.V. Bazhenov, and V.B. Timofeev, J. Supercond. 3, S27 (1990).
- [386] A.V. Bazhenov, and V.B. Timofeev, Physica C 162-164, 1247 (1989).
- [387] M. Bauer, Ph.D. Thesis, University of Tübingen, Germany (1990).
- [388] M. Bauer, I.B. Ferreira, L. Genzel, M. Cardona, P. Murugaraj, and J. Maier, Solid State Comm. 72, 551 (1989).
- [389] T. Pham, H.D. Drew, S.H. Moseley, and J.Z. Liu, Phys. Rev. B 41, 11681 (1990).
- [390] K.F. Renk, B. Gorshunov, J. Schützmann, A. Prückl, B. Brunner, J. Betz, S. Orbach, N. Klein, G. Müller, and H. Piel, Europhys. Lett. 15, 661 (1991).
- [391] J. Humlíček, A.P. Litvinchuk, W. Kress, B. Lederle, C. Thomsen, M. Cardona, H.-U. Habermeier, I.E. Trofimov, and W. König, Physica C 206, 345 (1993).
- [392] K. Takenaka, Y. Imanaka, K. Tamasaku, T. Ito, and S. Uchida, Phys. Rev. B 46, 5833 (1992).
- [393] W. Weber, Phys. Rev. Lett. 58, 1371 (1987).
- [394] Y. Ohta, T. Tohyama, and S. Maekawa, Phys. Rev. Lett. 66, 1228 (1991).
- [395] H. Krakauer, W.E. Pickett, and R.E. Cohen, Phys. Rev. B 47, 1002 (1993).
- [396] T.B. Lindemer, J.F. Hunley, J.E. Gates, A.L. Sutton, Jr., J. Brynestad, C.R. Hubbard, and P.K. Gallagher, J. Am. Ceram. Soc. 72, 1775 (1989).
- [397] A. Erb, T. Traulsen and G. Müller-Vogt, J. Cryst. Growth 137, 487 (1994).
- [398] Th. Wolf, W. Goldacker, B. Obst, G. Roth, and R. Flükiger, J. Cryst. Growth 96, 1010 (1989).
- [399] T.J. Kistenmacher, Phys. Rev. B 38, 8862 (1988).
- [400] M. Grüninger, D. van der Marel, H.P. Geserich, Th. Wolf, A. Erb, and T. Kopp, Physica B 244, 60 (1998).
- [401] M. Grüninger, D. van der Marel, H.P. Geserich, A. Erb, Th. Wolf, T. Kopp, J. Low Temp. Phys. 105, 389 (1996).
- [402] W. Reichardt, L. Pintschovius, N. Pyka, P. Schweiß, A. Erb, P. Bourges, G. Collin, J. Rossat-Mignod, I.Y. Henry, A.S. Ivanov, N.L. Mitrofanov, and A.Yu. Rumiantsev, J. Supercond. 7, 399 (1994).
- [403] L. Pintschovius, N. Pyka, W. Reichardt, A.Yu. Rumiantsev, N.L. Mitrofanov, A.S. Ivanov, G. Collin, and P. Bourges, Physica C 185-189, 156 (1991).
- [404] D. Zech, H. Keller, K. Conder, E. Kaldis, E. Liarokapis, N. Poulakis, and K.A. Müller, Nature 371, 681 (1994).
- [405] F.E. Bates, Phys. Rev. B **39**, 322 (1989).

- [406] W. Reichardt, private communication.
- [407] T. Strach, T. Ruf, E. Schönherr, and M. Cardona, Phys. Rev. B 51, 16460 (1995).
- [408] R. Henn, T. Strach, E. Schönherr, and M. Cardona, Phys. Rev. B 55, 3285 (1997).
- [409] J.J. Capponi, C. Chaillout, A.W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J.L. Soubeyroux, J.L. Tholence, and R. Tournier, Europhys. Lett. 3, 1301 (1987).
- [410] L.L. Miller, X.L. Wang, S.X. Wang, C. Stassis, D.C. Johnston, J. Faber, Jr., and C.-K. Loong, Phys. Rev. B 41, 1921 (1990).
- [411] Y. Le Page, T. Siegrist, S.A. Sunshine, L.F. Schneemeyer, D.W. Murphy, S.M. Zahurak, J.V. Waszczak, W.R. McKinnon, J.M. Tarascon, G.W. Hull, and L.H. Greene, Phys. Rev. B 36, 3617 (1987).
- [412] T. Egami, and S.J.L. Billinge, Progr. Mater. Sci. 38, 359-424 (1994).
- [413] J. Mustre de Leon, S.D. Conradson, I. Batistić, and A.R. Bishop, Phys. Rev. Lett. 65, 1675 (1990).
- [414] C. Thomsen, and M. Cardona, Phys. Rev. B 47, 12320 (1993).
- [415] A. Bussmann-Holder, and A.R. Bishop, Phys. Rev. B 51, 3246 and 6640 (1995).
- [416] D. Mihailović, K.F. McCarty, and D.S. Ginley, Ferroelectrics 130, 107 (1992).
- [417] C. Ambrosch-Draxl, and P. Knoll, Physica B **194-196**, 2091 (1994).
- [418] W. Reichardt, N. Pyka, L. Pintschovius, B. Hennion, and G. Collin, Physica C 162-164, 464 (1989).
- [419] E.B. Wilson, Jr., J.C. Decius, and P.C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).
- [420] J.P. Franck in *Physical Properties of High Temperature Superconductors IV*, edited by D.M. Ginsberg (World Scientific, Singapore 1994), p. 189.
- [421] R. Zeyher, and G. Zwicknagl, Z. Phys. B 78, 175 (1990); Solid State Comm. 66, 617 (1988).
- [422] G. Hastreiter, U. Hofmann, J. Keller, and K.F. Renk, Solid State Comm. 76, 1015 (1990).
- [423] R.T. Collins, Z. Schlesinger, F. Holtzberg, C. Feild, U. Welp, G.W. Crabtree, J.Z. Liu, and Y. Fang, Phys. Rev. B 43, 8701 (1991).
- [424] G.A. Thomas, D.H. Rapkine, S.-W. Cheong, and L.F. Schneemeyer, Phys. Rev. B 47, 11369 (1993).
- [425] R. Claus, L. Merten, and J. Brandmüller, Light Scattering by Phonon-Polaritons, Springer Tracts in Modern Physics 75 (Springer, Berlin, 1975).
- [426] T. Nunner, T. Kopp, M. Grüninger, and D. van der Marel, to be published.

- [427] R. Newman, and R.M. Chrenko, Phys. Rev. **114**, 1507 (1959).
- [428] Y. Mizuno, and S. Koide, Phys. Kondens. Materie 2, 179 (1964).
- [429] M. Grüninger, D. van der Marel, A. Damascelli, A. Zibold, H.P. Geserich, A. Erb, M. Kläser, Th. Wolf, T. Nunner, and T. Kopp, Physica C 317-318, 286 (1999).
- [430] H. Suzuura, H. Yasuhara, A. Furusaki, N. Nagaosa, and Y. Tokura, Phys. Rev. Lett. 76, 2579 (1996).
- [431] J. Lorenzana, and R. Eder, Phys. Rev. B 55, R3358 (1997).
- [432] Y.Y. Wang, F.C. Zhang, V.P. Dravid, K.K. Ng, M.V. Klein, S.E. Schnatterly, and L.L. Miller, Phys. Rev. Lett. 77, 1809 (1996); and F.C. Zhang, and K.K. Ng, Phys. Rev. B 58, 13520 (1998).
- [433] K. Widder, A. Zibold and H.P. Geserich, private communication.
- [434] A. Zibold, H.L. Liu, S.W. Moore, J.M. Graybeal, and D.B. Tanner, Phys. Rev. B 53, 11734 (1996).
- [435] M. Yoshida, N. Koshizuka, and S. Tanaka, Phys. Rev. B 42, 8760 (1990).
- [436] S.L. Cooper, G.A. Thomas, A.J. Millis, P.E. Sulewski, J. Orenstein, D.H. Rapkine, S.-W. Cheong, and P.L. Trevor, Phys. Rev. B 42, 10785 (1990).
- [437] J.M. Graybeal, private communication.
- [438] A. Damascelli, D. van der Marel, M. Grüninger, C. Presura, T.T.M. Palstra, J. Jegoudez, and A. Revcolevschi, Phys. Rev. Lett. 81, 918 (1998).
- [439] A. Zibold, H.L. Liu, D.B. Tanner, J.Y. Wang, M. Grüninger, H.P. Geserich, T. Kopp, Th. Wolf, W. Widder, and H.F. Braun, Phys. Rev. B 55, 11096 (1997).
- [440] O.K. Andersen, A.I. Liechtenstein, O. Jepsen, and F. Paulsen, J. Phys. Chem. Solids 12, 1573 (1995).
- [441] W.A. Harrison, Electronic Structure and the Properties of Solids (Freeman, San Francisco, 1980).
- [442] M.C. Aronson, S.B. Dierker, B.S. Dennis, S.-W. Cheong, and Z. Fisk, Phys. Rev. B 44, 4657 (1991).
- [443] J. Lorenzana, R. Eder, M. Meinders, and G.A. Sawatzky, J. Supercond. 8, 567 (1995).
- [444] H. Eskes, L.H. Tjeng, and G.A. Sawatzky, Phys. Rev. B 41, 288 (1990).
- [445] R.L. Martin, and P.J. Hay, J. Chem. Phys. 98, 8680 (1993).
- [446] C. de Graaf, Ph.D. Thesis, University of Groningen (1998).
- [447] J.B. Grant, and A.K. McMahan, Phys. Rev. B 46, 8440 (1992).

- [448] R. Liu, D. Salamon, M.V. Klein, S.L. Cooper, W.C. Lee, S.-W. Cheong, and D.M. Ginsberg, Phys. Rev. Lett. 71, 3709 (1993).
- [449] D. Salamon, R. Liu, M.V. Klein, M.A. Karlow, S.L. Cooper, S.-W. Cheong, W.C. Lee, and D.M. Ginsberg, Phys. Rev. B 51, 6617 (1995).
- [450] J.P. Falck, J.D. Perkins, A. Levy, M.A. Kastner, J.M. Graybeal, and R.J. Birgeneau, Phys. Rev. B 49, 6246 (1994).
- [451] J.P. Falck, A. Levy, M.A. Kastner, and R.J. Birgeneau, Phys. Rev. Lett. 69, 1109 (1992).
- [452] P. Kuiper, J.-H. Guo, C. Såthe, L.-C. Duda, J. Nordgren, J.J.M. Pothuizen, F.M.F. de Groot, and G.A. Sawatzky, Phys. Rev. Lett. 80, 5204 (1998).
- [453] H.P. Geserich, G. Scheiber, J. Geerk, H.C. Li, G. Linker, W. Assmus, and W. Weber, Europhys. Lett. 6, 277 (1988).
- [454] G.A. Sawatzky, private communication.
- [455] C. Vermeulen, and W. Barford, J. Phys.: Condens. Matter 7, 3615 (1995).
- [456] M.E. Simón, A.A. Aligia, C.D. Batista, E.R. Gagliano, and F. Lema, Phys. Rev. B 54, R3780 (1996).
- [457] M. Grüninger, Diploma Thesis, University of Karlsruhe, Germany (April 1994).
- [458] S. Shamoto, M. Sato, J.M. Tranquada, B.J. Sternlieb, and G. Shirane, Phys. Rev. B 48, 13817 (1993).
- [459] C. Vettier, P. Burlet, J.Y. Henry, M.J. Jurgens, G. Lapertot, L.P. Regnault, and J. Rossat-Mignod, Phys. Scripta **T29**, 110 (1989).
- [460] J. Rossat-Mignod, L.P. Regnault, J.M. Jurguens, P. Burlet, J.Y. Henry, and G. Lapertot, in Dynamics of Magnetic Fluctuations in High-Temperature Superconductors, edited by G. Reiter, P. Horsch and G.C. Psaltakis (Plenum Press, New York, 1989).
- [461] B.L. Altshuler, and L.B. Ioffe, Solid State Commun. 82, 253 (1992).
- [462] M.U. Ubbens, and P.A. Lee, Phys. Rev. B 50, 438 (1994).
- [463] T. Moriya, J. Appl. Phys. **39**, 1042 (1968), and references therein.
- [464] R.J. Elliott, and M.F. Thorpe, J. Phys. C 2, 1630 (1969).
- [465] F. Barriquand, and G.A. Sawatzky, Phys. Rev. B 50, 16649 (1994).
- [466] F. Zuo, A.J. Epstein, E.M. McCarron III, and W.E. Farneth, Physica C 167, 567 (1990).
- [467] H.A. Kramers, Physica 1, 182 (1934).
- [468] P.W. Anderson, Phys. Rev. **79**, 350 (1950).
- [469] W. Geertsma, Physica B **164**, 241 (1990).

- [470] Y. Mizuno, T. Tohyama, and S. Maekawa, Phys. Rev. B 58, R14713 (1998).
- [471] H. Eskes, G.A. Sawatzky, and L.F. Feiner, Physica C 160, 424 (1989).
- [472] J. Zaanen, Ph.D. Thesis, University of Groningen (1986); J. Zaanen, and G.A. Sawatzky, Can. J. Phys. 65, 1262 (1987).
- [473] E.B. Stechel, and D.R. Jennison, Phys. Rev. B 38, 4632 (1988).
- [474] A. Zibold, D.B. Tanner and Th. Wolf, Bull. of the American Physical Society 42, 237 (1997).
- [475] Th. Wolf, private communication.
- [476] P. Bourges, Y. Sidis, B. Hennion, R. Villeneuve, G. Collin and J.F. Marucco, Physica C 235-240, 1683 (1994).
- [477] J.M. Tranquada, D.E. Cox, W. Kunnmann, H. Moudden, G. Shirane, M. Suenaga, P. Zolliker, D. Vaknin, S.K. Sinha, M.S. Alvarez, A.J. Jacobson and D.C. Johnston, Phys. Rev. Lett. 60, 156 (1988).
- [478] A. Zibold, and Th. Wolf, private communication.
- [479] G.-M. Zhao, K.K. Singh, and D.E. Morris, Phys. Rev. B 50, 4112 (1994).
- [480] K. Hanzawa, J. Phys. Soc. Jpn. 64, 4856 (1995).
- [481] R. Hlubina, and G.K. Sadiek, Phys. Rev. B 55, 2733 (1997).
- [482] H. Shaked, J.D. Jorgensen, B.A. Hunter, R.L. Hitterman, A.P. Paulikas, and B.W. Veal, Phys. Rev. B 51, 547 (1995).
- [483] A.A. Maksimov, D.A. Pronin, S.V. Zaitsev, I.I. Tartakovskii, G. Blumberg, M.V. Klein, M. Karlow, S.L. Cooper, A.P. Paulikas, and B.W. Veal, Phys. Rev. B 54, R6901 (1996).
- [484] N.H. Andersen, and G. Uimin, Phys. Rev. B 56, 10840 (1997); H. Haugerud, G. Uimin, and W. Selke, preprint, http://xxx.lanl.gov/abs/cond-mat/9612072; P. Gawiec, D.R. Grempel, A.-C. Riiser, H. Haugerud, and G. Uimin, Phys. Rev. B 53, 5872 (1996); P. Gawiec, D.R. Grempel, G. Uimin, and J. Zittartz, Phys. Rev. B 53, 5880 (1996); G. Uimin, Phys. Rev. B 50, 9531 (1994); G. Uimin, and J. Rossat-Mignod, Physica C 199, 251 (1992).
- [485] A.A. Aligia, S. Koval, and R. Migoni, Phys. Rev. B 57, 1241 (1998).
- [486] J.L. Morán-López, J.M. Sanchez, A. Latgé, and E.V. Anda, Mat. Science Forum 116, 57 (1993).
- [487] L.E. Orgel, J. Chem. Soc. 48, 4186 (1958).
- [488] G. Roth, P. Adelmann, G. Heger, R. Knitter, and Th. Wolf, J. Phys. I 1, 721 (1991).
- [489] M. Isobe, K. Kosuda, and E. Takayama-Muromachi, Physica C 227, 351 (1994).
- [490] E. Takayama-Muromachi, and M. Isobe, Jpn. J. Appl. Phys. 33, L 1399 (1994).

- [491] C. Thomsen, E. Schönherr, B. Friedl, and M. Cardona, Phys. Rev. B 42, 943 (1990).
- [492] M. Rübhausen, N. Dieckmann, A. Bock, and U. Merkt, Phys. Rev. B 54, 14967 (1996).
- [493] R. Liu, M.V. Klein, D. Salamon, S.L. Cooper, W.C. Lee, S.-W. Cheong, and D.M. Ginsberg, J. Phys. Chem. Solids 54, 1347 (1993).
- [494] S. Koval, and C.J. Gazza, J. Phys. Condens. Matter 9, 2443 (1997).
- [495] S. Koval, and A. Greco, Solid State Comm. 90, 17 (1994).
- [496] D.N. Aristov, and D.R. Grempel, Phys. Rev. B 55, 11358 (1997).
- [497] H. Eskes, and G.A. Sawatzky in *Electronic Properties of High-T<sub>c</sub> Superconductors and Related Compounds*, edited by H. Kuzmany, M. Mehring, and J. Fink, Springer Series in Solid-State Sciences **99** (Springer, Berlin, 1990), p. 127.
- [498] Ch. Krüger, K. Conder, H. Schwer, and E. Kaldis, J. Solid State Chem. **134**, 356 (1997).
- [499] Y. Yoshinari, P.C. Hammel, J.A. Martindale, E. Moshopoulou, J.D. Thompson, J.L. Sarrao, and Z. Fisk, Phys. Rev. Lett. 77, 2069 (1996).
- [500] V.I. Anisimov, S. Yu. Ezhov, and T.M. Rice, Phys. Rev. B 55, 12829 (1997).
- [501] J. Münzel, Ph.D. Thesis, University of Karlsruhe, Germany (1995).
- [502] K. Yonemitsu, A.R. Bishop, and J. Lorenzana, Phys. Rev. Lett. 69, 965 (1992); Phys. Rev. B 47, 12059 (1993).
- [503] W. Stephan, and P. Horsch, Phys. Rev. B 42, 8736 (1990).
- [504] G.A. Thomas, D.H. Rapkine, S.L. Cooper, S.-W. Cheong, A.S. Cooper, L.F. Schneemeyer, and J.V. Waszczak, Phys. Rev. B 45, 2474 (1992).
- [505] Y.H. Kim, S.-W. Cheong, and Z. Fisk, Phys. Rev. Lett. 67, 2227 (1991).
- [506] F. Li, Y.H. Kim, and S.-W. Cheong, Physica C 257, 167 (1996).
- [507] D. Mihailović, C.M. Foster, K. Voss, and A.J. Heeger, Phys. Rev. B 42, 7989 (1990).
- [508] Y.H. Kim, C.M. Foster, A.J. Heeger, S. Cox, and G. Stucky, Phys. Rev. B 38, 6478 (1988).
- [509] A.J. Millis, and B.I. Shraiman, Phys. Rev. B 46, 14834 (1992).
- [510] V.I. Anisimov, M.A. Korotin, J. Zaanen, and O.K. Andersen, Phys. Rev. Lett. 68, 345 (1992).
- [511] A. Ramšak, P. Horsch, and P. Fulde, Phys. Rev. B 46, R14305 (1992).
- [512] J. Zaanen, and P.B. Littlewood, Phys. Rev. B 50, 7222 (1994).
- [513] G.A. Thomas, D.H. Rapkine, S.L. Cooper, S.-W. Cheong, and A.S. Cooper, Phys. Rev. Lett. 67, 2906 (1991).

- [514] Y.F. Yan, P. Matl, J.M. Harris, and N.P. Ong, Phys. Rev. B 52, R751 (1995).
- [515] I. Terasaki, Y. Sato, S. Miyamoto, S. Tajima, and S. Tanaka, Phys. Rev. B 52, 16246 (1995).
- [516] C.C. Homes, S. Kamal, D.A. Bonn, R. Liang, W.N. Hardy, and B.P. Clayman, Physica C 296, 230 (1998).
- [517] H. Shibata, and T. Yamada, Phys. Rev. Lett. 81, 3519 (1998).
- [518] M. Tinkham, Introduction to Superconductivity, 2nd edition (McGraw-Hill, New York, 1983).
- [519] M.C. Schabel, C.-H. Park, A. Matsuura, Z.-X. Shen, D.A. Bonn, R. Liang, and W.N. Hardy, Phys. Rev. B 57, 6090 (1998).
- [520] Y. Nakamura, and S. Uchida, Phys. Rev. B 47, 8369 (1993).
- [521] I. Tanaka, and H. Kojima, Nature **337**, 21 (1989).
- [522] T. Ito, H. Takagi, S. Ishibashi, T. Ido, and S. Uchida, Nature **350**, 596 (1991).
- [523] S. Uchida, and K. Tamasaku, Physica C **293**, 1 (1997).
- [524] J.T. Birmingham, S.M. Grannan, P.L. Richards, J. Kircher, M. Cardona, and A. Wittlin, Phys. Rev. B 47, 8369 (1993).

## List of Publications

- Mid-infrared absorption in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>: failure of spin-wave theory in undoped cuprates?, M. Grüninger, D. van der Marel, A. Damascelli, A. Erb, Th. Wolf, T. Nunner, and T. Kopp, submitted (http://xxx.lanl.gov/abs/cond-mat/9904394).
- Magneto-elastic polarons in the infrared spectrum of low doped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+δ</sub>, M. Grüninger, D. van der Marel, A. Erb, M. Kläser, J. Münzel, A. Zibold, and H.P. Geserich, submitted.
- Observation of out-of-phase bilayer plasmons in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>, M. Grüninger, D. van der Marel, A.A. Tsvetkov, and A. Erb, submitted, (http://xxx.lanl.gov/abs/cond-mat/9903352).
- Charged magnons and magneto-elastic polarons in the mid-infrared spectrum of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>, M. Grüninger, D. van der Marel, A. Damascelli, A. Zibold, H.P. Geserich, A. Erb, M. Kläser, Th. Wolf, T. Nunner, and T. Kopp, Physica C 317-318, 286 (1999).
- Infrared spectroscopy on Y<sub>1-x</sub> RE<sub>x</sub>Ba<sub>2</sub>Cu<sub>3-y</sub>Zn<sub>y</sub>O<sub>6</sub> (RE=Pr, Gd, x=0 and 0.8; y=0 and ≈ 0.15), M. Grüninger, D. van der Marel, H.P. Geserich, Th. Wolf, A. Erb, and T. Kopp, Physica B 244, 60 (1998).
- Direct two-magnon optical absorption in α'-NaV<sub>2</sub>O<sub>5</sub>: "charged" magnons,
   A. Damascelli, D. van der Marel, M. Grüninger, C. Presura, T.T.M. Palstra,
   J. Jegoudez, and A. Revcolevschi, Physical Review Letters 81, 918 (1998).
- Global and local measures of the intrinsic Josephson coupling in Tl<sub>2</sub>Ba<sub>2</sub>CuO<sub>6</sub> as a test of the interlayer tunneling model,
  A.A. Tsvetkov, D. van der Marel, K.A. Moler, J.R. Kirtley, J.L. de Boer, A. Meetsma,
  Z.F. Ren, N. Koleshnikov, D. Dulic, A. Damascelli, M. Grüninger, J. Schützmann,
  J.W. van der Eb, H.S. Somal, and J.H. Wang, Nature **395**, 360 (1998).
- Optical study of antiferromagnetic single crystals Y<sub>1-x</sub>Pr<sub>x</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> in high magnetic fields,
   A. Zibold, H.L. Liu, D.B. Tanner, J.Y. Wang, M. Grüninger, H.P. Geserich, T. Kopp, Th. Wolf, W. Widder, and H.F. Braun, Physical Review B 55, 11096 (1997).

- Far- and mid-infrared spectrum of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.0</sub> in high magnetic fields, M. Grüninger, D. van der Marel, P.J.M. van Bentum, A. Erb, H.P. Geserich, and T. Kopp, Journal of Low Temperature Physics **105**, 389 (1996).
- Probing the mid-infrared spectrum of YBa<sub>2</sub> Cu<sub>3</sub> O<sub>6.0</sub> with high magnetic fields and Zinc doping,
  M. Grüninger, D. van der Marel, P.J.M. van Bentum, A. Erb, Th. Wolf, and T. Kopp, Czechoslovak Journal of Physics 46 (S2), 1127 (1996).
- Spin-waves in the mid-infrared spectrum of antiferromagnetic YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.0</sub>,
   M. Grüninger, J. Münzel, A. Gaymann, A. Zibold, H.P. Geserich, and T. Kopp, Europhysics Letters 35, 55 (1996).

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