Preparation and Raman Studies of Cuprates with Low and Intermediate Doping

Diploma thesis of
Nathalie Munnikes

Prof. Dr. Rudolf Gross
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Technische Universität München
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Chapter 1

Introduction

More than twenty years after their discovery [1], the copper-oxide high-$T_c$ superconductors (HTSCs) now belong to the most intensively studied class of compounds in condensed matter physics. Still, while superconductivity in conventional metals is well understood in the framework of the BCS-theory [2], the mechanism that is responsible for the pairing of the carriers in the cuprates is far from being clear.

As opposed to conventional systems, high-$T_c$ superconductors emerge from antiferromagnetic insulators by doping. The strong electron correlations lead also to a richness of phenomena at relatively high doping. At least as elusive as the appearance of a superconducting phase is that it vanishes equally rapidly when the doping is further increased. It thus stands to reason to regard the doping dependence and the evolution of the electron correlations as the key to find the mechanism of superconductivity.

Of particular interest is the evolution with doping of the superconducting energy gap $\Delta_k$. Though the $d$-wave symmetry of the gap is well agreed on, the energy scale corresponding to the gap maximum could – surprisingly - not uniquely be identified. A comparison between the energy scales measured by various experiments was first drawn by Deutscher in 1999 [3], who concluded that there are two distinct gaps. One rises and falls with doping as the transition temperature does, with a maximum of the order of reportedly 40 meV for cuprates with a maximum transition temperature $T_c^{max} \sim 95$ K. The other one increases linearly when the doping is reduced, extrapolating to values of over 120 meV at the point where superconductivity vanishes in the underdoped regime. In the overdoped regime the energy scales allegedly merge, as stated also in a very recent review [4].

The gap scaling with $T_c$ has primarily been detected by two-particle techniques such
as Andreev reflection, magnetic penetration depth measurements, Raman spectroscopy in $B_{2g}$ symmetry (probing the nodal region around $(\pi/2, \pi/2)$) and neutron scattering (see [4] and references therein). Naturally, the gap scaling with $T_c$ was very soon related to (a collective excitation of) the condensate. The second energy scale $\Delta^*$ has primarily been detected by single-particle probes such as angle-resolved photoemission spectroscopy (ARPES) and tunnelling at high energy. $\Delta^*$ has a linear dependence on doping rather than following $T_c$ and appears in the normal state of underdoped materials. Often it is related to the formation of incoherent singlet pairs, which condense into a coherent state at lower temperature, and is associated with the pseudogap [5]. The momentum dependence is similar to that of the superconducting gap. Its magnitude is largest in the antinodal region around $(\pi, 0)$ but exceeds that of the coherence gap by approximately a factor of two around and slightly below optimal doping. Above optimal doping an increasingly strong peak is found in ARPES, tunnelling and $B_{1g}$ Raman scattering (probing the antinodal region around $(\pi, 0)$) at an energy that scales with doping in a similar fashion as the pseudogap [6, 7]. Neither its relationship to $\Delta^*$ nor to superconductivity is clarified.

This work presents Raman investigations on new samples in the optimally and slightly overdoped regime, which are combined with a large basis of data at hand [8, 7]. The main purpose is to shed light on the important issue of the interrelation of energy scales dominating different regions in momentum space. For its unique selection rules Raman spectroscopy is actually a powerful tool for this type of investigation. Not only does it afford to independently access electrons on different portions of the Fermi surface but also since it couples to the many-body interactions of spin and charge excitations that are so important in HTSCs. Actually, the two energy scales have been revealed by projecting out the nodal and antinodal regions [9, 10]. Beyond that this thesis presents a detailed analysis of the intensities of the related spectral features and challenges the common belief that the larger energy scale is related to the pseudogap or the pairing energy.

The work presented here is still suffering from or even hampered by the sample-related problems on the underdoped side of the phase diagram. This pertains in particular to studies of the two energy scales and of ordering phenomena in the doping range $0.10 < p < 0.16$ and, around the onset point of superconductivity at $p_{\text{onset}} \simeq 0.05$, of the electronic properties in general. Therefore, this work describes also the development of a method to prepare highly ordered underdoped YBCO samples. In this specific compound oxygen doping is possible while maintaining a highly ordered crystal structure since there exist partially ordered phases [11, 12]. Additionally, the crystal purity is very high because of the use of non-reactive BaZrO$_3$ crucibles [13].
1. Introduction

After a brief introduction to the cuprates (chapter 2), attention is given to the preparation of YBCO and BSCCO samples (chapter 3). The postannealed BSCCO samples are characterised via their critical temperature $T_c$. In the same chapter the method for measuring $T_c$ is described. Subsequently, the basic principles of inelastic light scattering and the Raman measurement setup are discussed (chapter 4). The results are presented in chapter 5.
Chapter 2

The cuprates

In the following review of the properties of the cuprates, the focus will be set on the issues relevant for this work. After introducing the structure of the specific compounds that will be used to represent the family of cuprates, the generic electronic properties will be given attention. The key features can be captured in the doping phase diagram. Even though in the remainder of this work emphasis is laid on the superconducting state, one should be aware of the existence of other complex phases in the cuprates – any pursuit to understand high-temperature superconductivity must be a pursuit to comprehend the trends in the phase diagram. Therefore the pseudogap region is briefly discussed.

2.1 Structure

2.1.1 \((Y_{1-y}Ca_y)\text{Ba}_2\text{Cu}_3\text{O}_x\)

The first of the two materials investigated in this work is yttrium barium copper oxide, often abbreviated YBCO or Y-123, the numbers referring to the ratio of elements in the compound in order of sequence. After its early discovery as a high-temperature superconductor with a maximum transition temperature \(T_{c,max} \approx 92\) K lying above the boiling point of liquid nitrogen, it became one of the most widely studied cuprates. Thanks to the use of non-reactive BaZrO\(_3\)-crucibles for crystal growth [13], the purity of single crystals has become better than 99.995%.

The crystal structure of YBCO consists of stacked layers, as shown in Fig. 2.1. The two characteristic copper oxide planes per unit cell are separated by \(Y^{3+}\) ions on the one hand and by a stack of \(\text{BaO}, \text{Cu}^+\) ions and \(\text{BaO}\) on the other hand. At least, this is the
2.1. Structure

Figure 2.1: Crystal structure of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \)

case for the parent compound, which has an oxygen content \( x = 6 \). The parent compound, however, can be doped with additional oxygen, which will occupy the sites between the off-planar copper ions. Instead of a mesh structure like the one in the \( \text{CuO}_2 \)-planes, chains will be formed, until they are fully evolved at an oxygen content of \( x = 7 \).

If an oxygen atom occupies a vacancy between two \( \text{Cu}^+ \) chain ions, the latter ones will change their valency from 1+ to 2+ due to the strong electronegativity of oxygen. This process is possible as long as the surrounding oxygen sites are vacant; when this is not the case anymore, the electrons from the negatively charged \( \text{CuO}_2 \)-planes will be attracted. Thus the oxygen dopants introduce holes in the \( \text{CuO}_2 \)-planes.

Hole doping in the \( \text{CuO}_2 \)-planes can also be achieved by replacing part of the trivalent yttrium ions by divalent calcium. The calcium releases one electron less, hence there is one more hole at the disposal of the negatively charged \( \text{CuO}_2 \)-bilayers. Up to a calcium concentration of at least \( y = 0.15 \) the experimental hole concentration per layer is approximately equal to the expected \( y/2 \) [14, 15].
2. The cuprates

2.1.2 \( \text{Bi}_2\text{Sr}_2(\text{Ca}_{1-y}\text{Y}_y)\text{Cu}_2\text{O}_{8+\delta} \)

The second material investigated in this work is bismuth strontium calcium copper oxide, also abbreviated BSCCO or Bi-2212. Since this compound has a natural cleavage plane between the BiO-layers, it is widely used for surface sensitive measurements such as scanning tunnelling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES). Another advantage is the availability of large single crystals. Due to sample quality problems, most experiments in this work and others have been carried out near optimal doping.

Like YBCO, BSCCO has a layered structure with two CuO\(_2\)-planes in the unit cell, as shown in Fig. 2.2. And like in YBCO, holes may be generated in these planes by adding oxygen dopants to the charge reservoir – in this case to the BiO-layer. In this way all doping levels in the range \(0.15 \leq p \leq 0.23\) can be accessed \([16]\). Below the lower limit the structure is possibly meta- or unstable; above the upper limit oxygen diffuses out of the material even at room-temperature. In order to obtain a carrier concentration below \(0.15\), the calcium ions separating the copper oxide planes may be replaced by yttrium. Each yttrium fills one hole out of the CuO\(_2\) double layers. Co-doping with yttrium has an accessory advantage: it helps to increase the chemical homogeneity on the Sr-sites \([17]\). Apparently the disorder introduced on the Ca-sites by the random replacement is the lesser of two evils, for the maximum \(T_c\) reported for a substitution of \(y = 0.08\) calcium atoms is 96 \(K\), which is 2 Kelvin higher than the typical \(T_c^{max}\) reported for Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_{8+\delta}\).

2.2 Generic properties

2.2.1 Electronic states

Comparing the investigated compounds with each other, it becomes obvious that they have certain aspects in common. For example, their carriers are sharply localised in the planes perpendicular to the c-direction, making the material extremely anisotropic (that is, almost 2-dimensional with only a weak interlayer coupling) in both the normal and the superconducting state. This is the case for all high-temperature superconductors. The heart of the electronic activities are the square CuO\(_2\) planes, of which each cuprate possesses one, two or three per unit cell. The interleaving planes are purely ionic; their sole purpose is to act as dopant reservoirs. An exception is YBCO, where the CuO-chains also contribute to normal conductivity and in which superconductivity may be induced as
Figure 2.2: Crystal structure of Bi$_2$Sr$_2$(Ca$_{1-y}$Y$_y$)Cu$_2$O$_8$
2. The cuprates

Surprisingly, the copper oxide planes in the undoped parent compound prove to be insulating, even though one might expect the single hole in the 3d⁹-configuration of the copper to form a half-filled metallic band. Yet the electronic density is so low that the equivalent of a Wigner lattice for an electron gas appears in the crystal: the electrons get trapped by the Coulomb potential of their neighbours. Thus they reside in the highest lying orbitals as in Fig. 2.3. Note that the orbitals in the d-shell of the copper cations have lost their degeneracy, making the dₓ²−ᵧ²-orbital the energetically highest lying. This is due to the crystal field of the surrounding oxygen octahedron (Jahn-Teller-effect) – a characteristic of perovskite structures.

In the so-called Mott-Hubbard insulating state described here, an antiferromagnetic spin arrangement is preferred because of virtual intersite-hopping of the electrons. Now, if the parent compound is doped with holes, real intersite-hopping starts to take place. The dₓ²−ᵧ²-orbitals extend into a nearly filled lower Hubbard band and an empty upper Hubbard band, still separated by the insulating gap. Around a doping level of p ≃ 0.03, the insulating state breaks down. One may now sketch the typical Fermi surface (see Fig. 2.4) of the cuprates as one would expect it to be if it weren’t for the Mott-Hubbard insulating effect. Caution should be taken when applying this picture to reality: in the underdoped, low energy regime the Fermi surface might look rather different [18, 19], either with pockets around \( \mathbf{k} = (\pi/2, \pi/2) \) (a notion which has recently been inferred also from quantum oscillation experiments [20]) or consisting of “Fermi arcs”, an expression used for the cut-back Fermi surface observed by angle-resolved photoemission spectroscopy [19].

Figure 2.3: Relevant orbitals in the CuO₂-plane
2.2. Generic properties

The disappearance of the Fermi surface near $\mathbf{k} = (\pi, 0)$ and symmetry related points (the so-called antinodal regions, to be investigated in due course of this work) is usually ascribed to the short-range antiferromagnetic correlations reminiscent after the undoped Mott-Hubbard state. Beside these surface modifications, Fermi surface nesting has been proposed to have strong effects [21].

Upon overdoping, the system starts to resemble a Fermi-Liquid. The major part of the normal state above the superconducting dome is far from behaving as a normal metal though: it lacks of well-defined quasiparticles, which would be seen as coherence peaks in ARPES studies. Instead a broad and featureless electronic continuum shows up. Since coherence peaks do show up below the critical temperature, one possible view is that “ready-to-pair” quasiparticle excitations are composed concurrently with the appearance of the superconducting condensate [22] – a concept which differs much from conventional BCS-type-behaviour.

2.2.2 The doping phase diagram

As already stated above, the superconducting phase forms a dome in the temperature versus doping phase diagram, shown in Fig. 2.5 on the next page. The maximum transition temperature is found at the optimal doping point $p = 0.16$; when moving away from this point in either direction, $T_c$ decreases, building a symmetrical parabola between the
doping levels $0.05 \leq p \leq 0.27$. The maximum transition temperature varies for different compound classes, but all cuprates intriguingly seem to abide by the empirical formula

$$\frac{T_c}{T_{c,\text{max}}} = 1 - 82.6(p - 0.16)^2$$

(2.1)

found by Tallon et al. [23]. At least they do for most carrier concentrations; around $p \simeq 1/8$ some compounds show a dip in the transition temperature. YBCO for example shows a suppression of up to $17\,K$ between the oxygen contents $6.5 < x < 6.75$ (see Fig. 2.6); though widely believed to be a peculiarity of the YBCO structure (resulting either from the oxygen ordering mechanism or from the chains assisting in superconductivity [24]), it has now been suggested to be an intrinsic effect due to competition with stripe ordering [25]. Still, the empirical curve may be used for determination of the carrier concentration from the conveniently measurable transition temperature in most cases.

### 2.2.3 The superconducting state: 2 energy gaps

One of the most prominent differences when comparing high-temperature superconductivity with metallic superconductors is that the symmetry of the superconducting order parameter is $d$-wave like (see Fig. 2.7). In BCS theory the order parameter coincides with half of the total energy gap $2\Delta_k$ in the electronic density of states. Hence the quasiparticle dispersion exhibits gapless nodes at the Fermi surface along the diagonals of the Brillouin zone. As opposed to these nodal points, the maximum gap is found in the region around
2.2. Generic properties

Figure 2.6: Transition temperature vs. oxygen concentration in YBCO. The upper dashed line corresponds to the oxygen ordered phase, to be elucidated in the following chapter. From Liang et al. [25].

Figure 2.7: $d$-wave symmetry of the order parameter $\Delta_k$. From [7].

$(\pi, 0)$ and equivalent points in the Brillouin zone, often termed “antinodal”.

One should be aware that in the discrete point group symmetry of a square crystal, the order parameter has a pure $d_{x^2-y^2}$-wave form. However, due to the orthorhombic distortions in both YBCO and BSCCO, there are fewer truly distinct irreducible presentations of the possible spin singlet pairing orders $s$, $d_{x^2-y^2}$, $d_{xy}$ and $g$, and $d_{x^2-y^2}$ mixes with $s$. The order parameter, which is still marked by the sign change under $90^\circ$ rotation, is then called $d$-wave like. A possible mixing with higher harmonics has not been ruled out so far and thus it is sometimes used as an argument to account for the U-shaped gap, which has been observed in ARPES studies of underdoped cuprates instead of the expected V-shaped gap. However, the present Raman study supports the notion that the order parameter
symmetry in the cuprates does not contain higher harmonics and that the mixing with $s$ is insignificant [26], independently of doping. In fact the anomalous ARPES spectra could be the signature of the two gaps that will be studied in chapter 5 [27, 28], given that these are seen in different regions of the Brillouin zone.

Unlike the overall agreement on the symmetry, the magnitude of the gap has not been identified unambiguously. Solving this issue deserves high priority since the pairing mechanism is directly reflected in the order parameter magnitude. A comparison between the energy scales measured by various experiments was first drawn by Deutscher [3], who concluded that there are two distinct energy scales. Fig. 2.8 shows a recent compilation of the experimental data [4]. The energy scale denoted by $E_0 = 2\Delta_0 \approx 5k_B T_c$ in the figure has the same doping dependence as the transition temperature. This falls into line with the BCS-theory, where the transition temperature and gap energy are directly related by $2\Delta_0 = 4.28 k_B T_c$ for weakly coupled $d$-wave superconductors. In the strong coupling limit, the ratio of gap and transition temperature increases. The other energy scale, denoted by $E^* = 2\Delta^*$, falls linearly with increasing doping. In the overdoped regime, the two energy scales seem to have the same magnitude within the resolution of the experiments – in particular in the case of Raman spectroscopy, which measures both energy scales, but in different regions of the Brillouin zone. The present study contradicts this (see chapter 5), demonstrating that $E_0 = 2\Delta_0 = 9k_B T_c$, which means that the second energy scale is smaller than the first in the overdoped regime.

The different gaps have been observed in several compound classes and by a variety of experiments. Whether the experiment is sensitive to $\Delta^*$ or $\Delta_0$ seems to depend much on its own nature: single-particle, high energy methods like angle-resolved photoemission spectroscopy (ARPES), tunnelling and heat conductivity are primarily sensitive to the upper gap, while two-particle, low energy methods like inelastic neutron and light scattering detect the lower one. Though the figure shows that from SIS-tunnelling and ARPES the $\Delta_0$-scale is derived as well, these data belong to indirect features in the spectra.

The division into single-particle and two-particle probes can be explained if the gap that scales with the transition temperature is related to the condensate, and if it is assumed that the excitations from the condensate have a collective character (c.f. rotons) rather than that one Cooper pair is removed. Such collective excitations cannot be measured directly by single-particle probes [4]. However, in recent ARPES measurements [27] both scales are detected directly: the gap that is associated with the coherent condensate is measured in the nodal region and $\Delta^*$ is measured around $(\pi, 0)$ and equivalent points in
2.2. Generic properties

Figure 2.8: Energy scales detected for Bi-2212, Y-123 or Tl-2201 with $T_c^{\text{max}} = 90 - 95 \, \text{K}$. The experimental techniques include angle-resolved photoemission spectroscopy (ARPES), Raman spectroscopy (RS), scanning tunnelling microscopy (STM), tunnelling by superconductor-insulator-superconductor and superconductor-insulator-normal metal junctions (SIS and SIN, respectively), heat conductivity (HC), Andreev reflection (AR) and inelastic neutron scattering (INS). The energy unit meV corresponds to 8.0655 cm$^{-1}$. From [4].
2. The cuprates

the Brillouin zone\(^1\). This is consistent with the findings of Raman spectroscopy.

2.2.4 The pseudogap and its relation to superconductivity

Whereas \(\Delta_0\) is generally related to the condensate, the second energy scale \(\Delta^*\) is often associated with the most controversial part of the phase diagram: the pseudogap, which stretches across the underdoped range to just above optimal doping, as indicated in the phase diagram in Fig. 2.5 on page 15. The main phenomenon in this region is a reduction of the spectral weight of e.g. ARPES spectra at the Fermi level. The depletion of spectral weight has a \(d\)-wave form in momentum space at zero temperature, but the nodes develop into gapless arcs for finite temperatures. The pseudogap differs from a superconducting gap in that there is no pile-up of spectral weight above the gap energy \(E_{PG}\). The crossover temperature \(T^*\), above which the gap vanishes, does not constitute a real phase transition either, since the specific heat does not show any anomaly. Both the gap energy and \(T^*\) decrease with increasing hole concentration.

The origin of the pseudogap is unknown. The host of possible explanations can roughly be divided into two opponent classes: one based on superconducting phase fluctuations and thus interpreting the pseudogap region as a precursor of superconductivity, the other assuming some kind of order which competes with the superconducting state. The simplest model that falls into the first category is the Bose-Einstein condensation (BEC)/BCS crossover scenario [30], in which the pairs in underdoped cuprates form long before they condense into the superconducting state. This is supported by the linear scaling of \(T_c\) with the superfluid density, which is referred to as the Uemura relation [31]. In the overdoped cuprates this relation breaks down and the transition temperature is determined by the low pairing energy rather than the phase coherence. Looking at the two energy scales that have been detected in the superconducting state from this point of view, the one decreasing with doping, \(\Delta^*\), should naturally be identified with the pairing energy and the pseudogap, while the other one reflects the strength of the condensate. The smooth evolution of \(\Delta_{PG}\) from \(\Delta^*\) [32] fits perfectly in this picture. Because the pseudogap and the second energy scale in the superconducting state show the same doping dependence, some authors tacitly assume \(\Delta_{PG} \equiv \Delta^*\); this is not supported by the present work (see chapter 5.2).

\(^1\)This is incompatible with the findings of Wen \textit{et al.} [29], who extrapolated a gap magnitude \(\Delta^*\) from the nodal slope. Both Tanaka and Wen assume that in the underdoped samples the antinodal regions themselves are not representative for the gap magnitude due to the Fermi arcs, which freeze below the transition temperature.
2.2. Generic properties

The second category places competing order at the root of the phase diagram. In the underdoped regime, Fermi liquid type behaviour breaks down due to the tendency of the carriers towards spatial ordering, and various electronic phases start competing. Examples are charge density waves (CDW) \[33\] and spin density waves (SDW), of which the Wigner crystal and the Néel state are the simplest examples, respectively \[34\]. These density waves can lead to a spatial separation of hole-rich and hole-poor regions in the form of stripes- or checkerboard-patterns \[35\]. When static, these kind of orders do indeed suppress superconductivity. The dynamical variant is believed to compete with the coherent superconducting phase as well, but it may coexist with superconductivity and even further the pairing of holes \[36\].

If the entire pseudogap can indeed be attributed to competing order, there are two possible scenarios for the evolution of the pseudogap with increasing carrier concentration: either it does not coexist with the superconducting state, or it does coexist with the superconducting state with \(T_{PG} \leq T_c\) in the overdoped regime. \(\Delta^*\) may still be the pairing energy (for instance in the case that stripes further the pairing of holes), but \(\Delta^*\) might also arise from the competing order or another – yet unidentified - phenomenon, which is merely triggered by superconductivity.
Chapter 3

Preparation and characterisation of samples

Before investigating the electronic properties, the as-grown samples are given a heat treatment to adjust their oxygen concentration. The samples are then characterised by means of a measurement of the critical temperature of the superconducting state. The contactless inductive method used for this is described first in this chapter, followed by a discussion of the conventional annealing methods of both Bi-2212 and Y-123. Details of the Bi-2212 samples that were investigated during this work are enlisted in section 3.2.

3.1 $T_c$-measurement

The transition temperature of the samples can be determined by measuring the non-linear part of the susceptibility during a temperature sweep through the transition region. The susceptibility is a magnetic response to the application of an ac electromagnetic field. Whereas the linear part of the response discloses information about shielding and global dissipation, the non-linear part discloses information about the pinning mechanism of vortices, as will be explained below. It has the advantage that its highly sensitive peak-like structure allows for an easy determination of the onset of the transition. The main advantage of the inductive method is that no contacts to the sample need to be made.

In general, the magnetisation of a material which is exposed to an ac magnetic field with amplitude $H_{ac}$ and frequency $\omega = 2\pi f_1$ can be expressed in terms of a Fourier expansion

$$M(\omega t) = H_{ac} \sum_{n=1}^{\infty} \text{Re} \left[ \chi_n e^{im\omega t} \right]$$

(3.1)
3.1. $T_c$-measurement

Figure 3.1: Qualitative magnetisation behaviour of a hard superconductor as a function of applied field. The nonlinearity causes a hysteresis, which in turn gives rise to higher harmonic susceptibilities when an alternating field is applied.

with $\chi_n = \chi'_n - i\chi''_n$ ($n = 1, 2, \ldots$) the fundamental and higher-harmonic susceptibilities [37]. The higher harmonics can be observed whenever the magnetisation as a function of the external field is nonlinear. This is the case for hard (= strong pinning) superconductors such as the cuprates, as is illustrated in Fig. 3.1. Up to the critical field $H_{c1}$ the external field is perfectly shielded by surface layer currents. Then the external field penetrates the material up to a depth where the field becomes small enough to be shielded by the Meissner state again. Finally, the superconducting slab is fully penetrated by the vortices, which together provide a finite, field-independent magnetisation $M = const. \cdot H^*$, with $H^*$ the “full penetration” field. The upper critical field $H_{c2}$ of the sample is far beyond the applied ac field, whose magnitude is of the order of 1–100 G. A sinusoidal variation of the applied field yields a hysteresis loop in $M$.

So how is the temperature dependence of the modulus of the third harmonic susceptibility $|\chi_3|$? This question is answered by Bean’s critical state model [38], which was the first model to describe the observed flux pinning effects on a macroscopic level by postulating that the vortices stay pinned up to a critical current density $J_c$. Bean’s critical state model and its variants do not say anything about the microscopic pinning mechanism controlling $J_c$. The current density of the vortex state is assumed maximal for any external field; only the penetration region can be narrowed down. Consequently, the full penetration field $H^*$ is directly proportional to $J_c$ as well as to the width of the superconducting slab.
3. Preparation and characterisation of samples

Figure 3.2: Temperature dependence of $|\chi_3|$ for various values of the applied ac field, as calculated from the critical state model. From [7].

Now, all ac responses are determined by a single parameter $\delta$ [39], which in the simplest model is the ratio between the full penetration field and the amplitude of the applied ac field: $\delta = H_{ac}/H^* \propto H_{ac}/J_c$. The temperature is involved in this parameter via the critical current density, which goes to zero as $T_c$ is approached. This causes $|\chi_3(\delta)|$ to increase and peak as illustrated in Fig. 3.2 [7]. The high-temperature base of the peak marks the onset of superconductivity. The smaller $H_{ac}$ is set, the sharper the onset will be. Well below $T_c$ the material may be seen as an ideal hard superconductor ($J_c \rightarrow \infty$); the signal is vanishingly small.

The experimental signal may deviate from the one predicted by the model. Effects which are not taken into account are e.g. the creep of vortices with a thermally activated velocity. Also geometrical surface and edge barriers contribute particularly strongly whenever the bulk pinning strength is reduced, as Moreno et al. claim is the case for deoxygenated YBCO crystals [40]. They argue that the deoxygenation reduces the coupling between the copper oxide layers and hence the stiffness of the vortices, which results in a considerable flattening of $|\chi_3(T)|$. This is relevant information when examining the response of the YBCO crystals in chapter 5.1.

The presence of a background dc field parallel to the ac-field does not disturb the qualitative peak behaviour: on the contrary, the critical state model is best applicable for situations where $H_{dc} >> H_{ac}$ [41].
3.2. $T_c$-measurement

![Figure 3.3: Electronic setup for the measurement of the third harmonic ac-susceptibility in an electromagnetic field. From [7].](image)

The experimental setup is made of a dip stick for use in a Helium transport vessel. The dip stick consists of three concentric thin-wall tubes. The volumes in between can be evacuated and/or filled with Helium contact gas at one’s own option. This enables a slow, controlled temperature sweep even without heater regulation. Cooling and heating rates of more than 1 K/min induce a hysteresis exceeding 0.5 K.

The sample itself is pressed against a pancake coil which drives the field $H(\omega t) = H_{ac} \cos(\omega t)$. The same coil is used to pick up the third harmonic signal at frequency $3\omega$. The corresponding electronic setup is shown in Fig. 3.3 [7]. The drive signal with frequency 33.31 kHz and variable voltage amplitude 0 – 5 V is generated by the internal generator of a lock-in amplifier (Stanford SR810). Before being sent through the coil, the drive signal is filtered in order to suppress the higher harmonic components which are generated along with the ground wave. This step is essential to achieve a higher signal to noise ratio. The third harmonic signal has an amplitude of the order of $10^{-10}$ nV and must be amplified by the lock-in amplifier. However, since the response is superimposed on the much stronger fundamental frequency signal, the latter must be filtered out as thoroughly as possible before amplification in order to avoid saturation.

This setup is used to measure the transition temperatures of the Bi-2212 samples discussed in the following.
3. Preparation and characterisation of samples

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Figure 3.4: Dependence of the transition temperature of BSCCO pellets on the annealing temperature and oxygen partial pressure. The lines represent iso-$T_c$ lines at 50, 55, ..., 90 K and at 92.5 K. Full and open squares mark individual samples; the grey areas represent regions where the crystal structure is not stable. From [42]

3.2 Preparation and characterisation of Bi-2212 samples

As-grown BSCCO samples are generally close to the optimal doping, and heat treatments can be used to vary the oxygen content $\delta$ and therefore the carrier concentration. To reach the highest $T_c$, the samples must be annealed for a few days at high temperatures in air. A detailed analysis of the properties of BSCCO pellets as a function of annealing temperature and oxygen partial pressure was performed in [42] and is shown in Fig. 3.4.

Two BSCCO single crystals were studied during this work, one of which contained 8% yttrium. Both crystals were optimally doped to start with; the crystal containing yttrium was subduced to a heat treatment at 400°C in 1 atm O$_2$ to obtain an overdoped sample. The specifications of the samples are enlisted in Table 3.1 and the measurement of the transition temperature is shown in Fig. 3.5. As can be seen is the maximal transition temperature of the sample with 8% Yttrium (Bi-OPT96) 2 K higher than the maximal $T_c$ of the sample without co-dopants (Bi-OPT94). The doping levels in the table are deduced from the phenomenological $T_c(p)$-dependence by Tallon (Eq. 2.1). The $T_c$-measurement of
3.3. Introduction to the preparation of Y-123

<table>
<thead>
<tr>
<th>Sample-ID</th>
<th>Dopants</th>
<th>Grown by</th>
<th>$T_c$ (K)</th>
<th>$\Delta T_c$ (K)</th>
<th>$p$</th>
<th>Annealing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi-OPT94</td>
<td>-</td>
<td>Y. Ando</td>
<td>94</td>
<td>0.1</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>Bi-OPT96</td>
<td>8%Y</td>
<td>A. Damascelli</td>
<td>96</td>
<td>0.4</td>
<td>0.16</td>
<td>-</td>
</tr>
<tr>
<td>Bi-OD87</td>
<td></td>
<td></td>
<td>87</td>
<td>6</td>
<td>0.19</td>
<td>400°C 1 bar O$_2$</td>
</tr>
</tbody>
</table>

Table 3.1: ID’s and characteristics of the Bi-2212 samples investigated in this work. The width of the transition $\Delta T_c$ is derived from the width of the onset of the peak in the third harmonic response.

the overdoped sample shows a tail above the bulk transition temperature, which could be ascribed to the presence of other phases with higher transition temperatures.

3.3 Introduction to the preparation of Y-123

For the preparation studies of YBCO, described in chapter 5, a more detailed discussion of its structural and annealing properties is necessary.

3.3.1 Conventional annealing and quenching

The conventional treatment of YBCO single crystals consists of adjusting the oxygen concentration by (reversible) heat treatments. These treatments are done at the conditions determined by Lindemer et al. [43] (see Fig. 3.6). The observed relationship between the oxygen partial pressure $P_{O_2}$, temperature $T$ and oxygen content $x$ can be simply explained by the dissolution of oxygen into the material. The typical annealing time used for crystals is 1–10 days, depending on temperature. This leads back to the oxygen diffusion coefficient, which is of the order of $D_{ab} \sim 10^{-6} \sim 10^{-5}$ mm$^2$/s in the annealing temperature range. Only the diffusion in the planes is relevant, since the diffusion rate in the c-direction is negligible in comparison [44]. At room temperature the diffusion is much slower, so the crystals may be stored safely for some time.

If a sample were cooled down slowly after a heat treatment conform the conditions of the calibration, the oxygen content would rise along with the $x(P_{O_2}, T)$-curves in the plot towards the limit $x = 7$. In order to maintain the value of $x$ upon cooling, either the oxygen
3. Preparation and characterisation of samples

Figure 3.5: Third harmonic signal $V_{3\omega} \propto |\chi_3|$ of (a) Bi-OPT94, (b) Bi-OPT96 and (c) Bi-OD87.
3.3. Introduction to the preparation of Y-123

Figure 3.6: Dependence of the oxygen concentration in YBCO on annealing temperature for different pressures. After Lindemer [43].
3. Preparation and characterisation of samples

partial pressure must be lowered during the cooling process or the cooling process must be done adiabatically ("quenching"). Quenching may be realised by simply dropping the crystal on a material with a high heat capacity, e.g. a copper plate, causing a practically instantaneous drop of the oxygen diffusion rate. Alternatively, the crystal may be immersed in a liquid with low boiling point such as liquid nitrogen (LN\textsubscript{2}). However, most tube furnaces are not well-designed for the quenching process, making it unavoidable that the warm sample is in contact with ambient air for tens of seconds. Consequently, the oxygen concentration is expected to deviate at the surface. The calibration by Lindemer is free of such quenching effects: the oxygen content was measured in situ by thermogravimetric analysis of ceramic probes.

3.3.2 The copper oxide chains

YBCO stands out from other cuprates because it contains copper-oxide chains which can be (partially) ordered. The chains make the crystal slightly orthorhombic above \(x \approx 6.28\) \cite{[12]}. At the higher crystal growth temperatures the structure becomes tetragonal again, though. Due to internal stresses, the short lattice constant \(a\) and the long lattice constant \(b\) swap positions at (110)- and (\(\bar{1}\)10)-planes upon cooling. Hence the as-grown crystals show a herringbone pattern of microcrystallites. These so-called twins can be removed by application of uniaxial pressure while heating the sample. A set-up in order to do this has been built by A. Erb parallel to this work (see chapter 5.1).

It is evident that the formation of copper-oxygen connections happens in a thermostatistical way, making the correlation between the oxygen content and the number of holes per CuO\textsubscript{2}-plane ambiguous. However, the chain pieces tend to order over time, a process that can be accelerated by low-temperature annealing. For an oxygen content of \(6.32 < x < 6.60\) (\(6.35 \leq x < 6.62\)), the ortho-II phase is predominantly present \cite{[12]} ([45]), as visualised in the structural phase diagram in Fig. 3.7 on the next page. This phase has alternating full and empty chains, doubling the unit cell of each microcrystallite. Though one would expect a perfect stoichiometry only at \(x = 6.50\), the longest correlation lengths are actually found to be near \(x \approx 6.55\) due to oxygen atoms occupying sites on the empty chains at room temperature. Between 6.28 and 6.32 the full chains may be separated by two empty ones, building the ortho-III* phase \cite{[46]}. This phase often has to make way for other (coexisting) phases though, varying from ortho-I (full chains) to ortho-VIII, the chain-filling sequence of which is given by (11010110), where 1 represents a completely full chain and 0 an empty one.
3.3. Introduction to the preparation of Y-123

Figure 3.7: Structural phase diagram for YBCO as determined with high energy x-ray diffraction by Zimmermann et al. [45]. T stands for tetragonal, whereas the O-phases denote various orthorhombic superstructures as discussed in the text. The O-III superstructure yields double full chains, whereas the O-III* superstructure yields double empty chains. The O-III* phase was not discussed by Zimmermann; its doping range is taken from reports by Monca et al. [46].

The relation between oxygen content and carrier concentration is shown in Fig. 3.8, where the upper dashed line corresponds to the ortho-II phase. For fully oxygenated YBCO the carrier concentration is $p_{max} = 0.194$. The carrier concentration in the figure has been determined by calculation for the ordered phases at 6$\frac{1}{2}$, 6$\frac{1}{3}$ etc. and comparison of these values with bond valence sum (BVS) results. The latter are derived from the bonding lengths in the copper oxide planes. Since measuring the parameters needed for BVS calculations is a tedious work, Fig. 3.8 will be used in chapter 5.1 to extrapolate $p$ from the oxygen content. Since $p$ and $x$ are interconnected with the superconducting transition temperature $T_c$, $p(x)$ will be compared with the value derived from the measurement of $T_c$ wherever possible.
Figure 3.8: Carrier concentration in the CuO$_2$-planes versus number of oxygen atoms per unit cell. The lower dashed line corresponds to the situation right after annealing while the upper dashed line corresponds to the oxygen ordered state. From [25].
3.3. Introduction to the preparation of Y-123
Chapter 4

Raman scattering

In this chapter the Raman scattering technique is being introduced. In the first part the necessary theoretical framework is set to analyse the electronic Raman spectra. The considerations lead to a prediction of the spectra in the superconducting state based on the Maki-Tsuneto function (see paragraph 4.1.4). Subsequently, the experimental setup will be described.

4.1 Theory of inelastic light scattering

Raman spectroscopy is the study of the small fraction of light that is not elastically (Rayleigh) scattered but inelastically scattered off a sample. The energy shift can be generated by any type of excitation that couples to light and does not require a large momentum transfer. Very commonly investigated are for instance the creation and annihilation of optical phonons near the centre of the Brillouin zone. These phonons appear as sharp peaks in the Raman spectra. An excitation typical for the cuprates is two-magnon scattering, which produces an exchange of two neighbouring spins on the antiferromagnetically ordered copper sublattice. Since the antiferromagnetic order becomes short-range for overdoped cuprates, the two-magnon peak softens and shifts to lower energies.

In this research we ignore the phonon- and magnon-features of the Raman spectra and focus instead on electronic features. The excitations in question create a background over the entire measured range up to 8000 cm$^{-1}$. Since the momentum transferred to the electrons by the photons is small ($q \approx 2\omega_i/c << k_F$) there are no particle-hole excitations at larger energies in the collisionless limit. Yet charge density variations with higher energies can be excited in case the electron momenta can be altered by collisions such as electron-electron or electron-phonon interaction or elastic scattering of electrons on
4.1. Theory of inelastic light scattering

impurities.

Well below the critical temperature of superconducting cuprates, the Raman scattering from the quasiparticles is very small (→ clean limit). Here another type of excitation is dominant, namely the breaking of Cooper pairs, which is allowed thanks to their vanishing total momentum. Thus the Raman spectra in the superconducting state render information about the bonding strength of the Cooper pairs in the condensate.

4.1.1 Electronic Raman scattering

Generally in scattering experiments the measured quantity is the count rate of the scattered particles. The count rate is directly proportional to the differential cross section $\frac{\partial^2 \sigma}{\partial \Omega \partial \omega_S}$, which denotes the probability that an incident photon with given momentum, energy and polarisation $(\mathbf{q}_I, \omega_I, \hat{\mathbf{e}}_I)$ is scattered in a solid angle interval $\partial \Omega$ and a frequency interval $\partial \omega_S$.

For electronic Raman scattering the differential cross section is

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega_S} = \hbar r_0^2 \frac{\omega_S}{\omega_I} S_{\gamma \gamma}(\mathbf{q}, \Omega)$$  \hspace{1cm} (4.1)$$

where $r_0 = e^2/mc^2$ is the Thompson radius and $S_{\gamma \gamma}(\mathbf{q}, \Omega)$ the transition rate for a momentum transfer $\mathbf{q} = \mathbf{q}_I - \mathbf{q}_S$ and an energy transfer $\Omega = \omega_I - \omega_S$. As shown in the following, the transition rate is a correlation function of the charge density fluctuation $\tilde{\rho}(\mathbf{q})$ that is realised for the given momentum transfer and polarisations of incoming and outgoing photon.

First $S_{\gamma \gamma}$ is stripped of a trivial temperature behaviour, leaving a bare susceptibility:

$$S_{\gamma \gamma}(\mathbf{q}, \Omega) = -\frac{1}{\pi} [1 + n(\Omega, T)] \Im \chi_{\gamma \gamma}(\mathbf{q}, \Omega)$$  \hspace{1cm} (4.2)$$

where $n(\Omega, T)$ is the Bose-Einstein distribution. All spectra in this work have been divided by the temperature dependent factor and are thus directly proportional to the imaginary part of the susceptibility. The formula above basically states that the linear response of a given system to an external perturbation, observed in a dynamic measurement, can be expressed in terms of fluctuation properties of the system in thermal equilibrium. The basis for this fluctuation-dissipation theorem is the fact that the scattering process is instantaneous and therefore invariant with regard to time reversal.
4. Raman scattering

As a matter of fact, the time-reversal symmetry is also the reason that the intensities on the energy loss (Stokes, S) and energy gain (Antistokes, AS) sides of the Raman spectra are related by the principle of detailed balance:

\[
\frac{\dot{N}_{AS}}{\dot{N}_{ST}} = \left( \frac{\omega_I + \Omega}{\omega_I - \Omega} \right)^2 \cdot e^{-\frac{\hbar \Omega}{k_B T}}. \tag{4.3}
\]

The increase of this intensity ratio with temperature expresses the fact that elementary excitations must be present for Antistokes transitions to occur. The formula above is used in the experiment to determine the temperature of the part of the sample which is illuminated by the laser. This temperature is typically 5–10 K higher than the temperature of the sample holder. If fluorescence effects (which do not obey time-reversal symmetry for not being instantaneous) would contribute to the intensity, the principle of detailed balance would not be applicable.

After applying the fluctuation-dissipation theorem, the effective density-density susceptibility \( \chi_{\gamma\gamma} \) can be further analysed using perturbation theory. The susceptibility can thus be expanded in terms such that the screening behaviour of the electron system becomes obvious.

Perturbations \( \delta n_k \) from the equilibrium momentum distribution \( n^0_k \) are introduced by the Hamiltonian for interactions with an external electromagnetic field,

\[
H_{ext} = \frac{e^2}{2mc^2} \sum_j \hat{\mathbf{A}}(\mathbf{r}_j) \cdot \hat{\mathbf{A}}(\mathbf{r}_j) + \frac{e}{2mc} \sum_j \left[ \hat{\mathbf{p}}_j \cdot \hat{\mathbf{A}}(\mathbf{r}_j) + \hat{\mathbf{A}}(\mathbf{r}_j) \cdot \hat{\mathbf{p}}_j \right] \tag{4.4}
\]

where \( \hat{\mathbf{A}}(\mathbf{r}_j) \) is the vector potential and \( \hat{\mathbf{r}}_j, \hat{\mathbf{p}}_j \) are the position and momentum of the \( j^{th} \) electron. The first term, called Raman response, gives rise to pure two-photon scattering, which we have already come across in the discussion of the Raman vertices (see Fig. 4.1 on page 37). The single-photon scattering terms, called current response, enter the susceptibility in second-order perturbation theory and give rise to scattering via intermediate states.

The perturbation that arises from the Hamiltonian above can be determined using either Green’s functions [47] or the kinetic equation method [26], as described in detail in the references. In a nutshell, one can say that for every electron with momentum \( \mathbf{k} \), the electronic polarisation potentials (also called vertex corrections) couple the energy fluctuations that arise from \( H_{ext} \) to the Coulomb renormalisation. For the total electronic system, the
4.1. Theory of inelastic light scattering

correlation between the energy fluctuation and the phase space distribution fluctuation is established by the susceptibility:

\[
\delta n_\gamma(q, \Omega) := \sum_{k, \sigma} \gamma_k \delta n_k(q, \Omega) = \chi_{\gamma \gamma} \delta \xi_\gamma(q, \Omega)
\] (4.5)

where the distribution fluctuation induced by the Raman process is defined as the sum over the individual electronic fluctuations, weighted by \(\gamma_k\) (see for comparison Eq. 4.8). Finally, the coupling of the external perturbation response (denoted by the subscript \(\gamma\)) and the pure charge density response (denoted by the subscript 1) leads to an exact expression for the susceptibility

\[
\chi_{\gamma \gamma}(q, \Omega) = \chi^0_{\gamma, \gamma} - \frac{(\chi^0_{\gamma, 1})^2}{\chi^0_{1, 1}} + \frac{1}{\epsilon(q, \Omega)} \frac{(\chi^0_{\gamma, 1})^2}{\chi^0_{1, 1}}
\] (4.6)

with \(\epsilon(q, \Omega) = 1 - V_q \chi^0_{1, 1}\) the dielectric function, where \(V_q\) the Fourier transform of the long-range Coulomb interaction. The first term is the susceptibility for a neutral system, while the other terms are a direct consequence of local charge conservation and gauge invariance. They are therefore also called screening or backflow terms. The fragmentation the susceptibility will be employed later on in the calculation of the theoretical response of the superconducting state.

Using Fermi’s Golden Rule for electron-photon coupling, it can be shown (see e.g. [16]) that

\[
\chi_{\gamma \gamma}(q, \Omega) = \int_0^\beta d\tau e^{i\Omega \tau} \langle T_\tau [\hat{\rho}(q, \tau), \hat{\rho}(-q, 0)] \rangle
\] (4.7)

with \(\beta = 1/k_B T\), \(T_\tau\) the time-ordering operator and \(\langle \ldots \rangle\) a thermal average. The charge density fluctuation \(\hat{\rho}(q)\) is a sum over the annihilation of electronic states \(k\) and the creation of states \(k+q\), weighted by scattering amplitudes:

\[
\hat{\rho}(q) = \sum_{k, \sigma} \gamma(k, q) \hat{c}_{k+q, \sigma}^\dagger \hat{c}_{k, \sigma}.
\] (4.8)

The scattering amplitudes \(\gamma\) always enter in (momentum-loss momentum-gain) pairs in the susceptibility. Therefore they are illustrated as such in Feynman diagrams. The diagram in Fig. 4.1 for instance represents a direct (first-order) transition as found for intraband scattering. In general though, the vertex \(\gamma\) is a complicated summation over the direct transition as well as all admissible transitions with intermediate electronic states. Hence only selected cases can be truly represented by a single Feynman graph. The contribution
4. Raman scattering

**Figure 4.1:** Feynman diagram of intraband scattering. The double photon-in photon-out process highlights the fact that the coupling amplitude goes in pairs into the final photon count rate.

of each (direct or intermediate state) transition to the scattering amplitude depends primarily on the polarisations, but also on the frequencies of incident and scattered light: if the energy of an intermediate state is approximately the same as the photon energy, resonance effects occur. The obvious significance of the vertices to the resulting correlation functions is marked by the subscripts $\gamma \gamma$.

4.1.2 The effective mass approximation and the band structure

A widely used approximation for the vertices is the effective-mass approximation, which is usable if direct transitions ($\propto \mathbf{A} \cdot \mathbf{A}$) are prohibited. Two limits yield the approximation, the first being that the incident light energy must be distinctly smaller than the optical band gap (non-resonant scattering). Since the vertex generally does not depend sensitively on the small momentum transfer, the second limit $\mathbf{q} \to 0$ is used in all considerations from this point onward. With this the vertex can be related to the curvature of the conduction band \[48\] as

$$\lim_{\omega_I, \omega_S \to 0} \gamma(\mathbf{k}, \mathbf{q} \to 0) = \sum_{i,j} e^I_i e^S_j \frac{1}{\hbar^2} \frac{\partial^2 \xi_k}{\partial k_i \partial k_j}$$

(4.9)

where $i, j = x, y$ a frame of reference in the plane of incidence. The approximation is only valid for weakly interacting systems, for it is based on the assumption that each intermediate state is just a single-particle excitation. Further it is assumed that the initial and final state find themselves in the same electron band.

This means that the vertex can be calculated from the band structure, which in the cuprates can be modelled in a 2D-like tight-binding picture. Only the antibonding band of the square lattice of the CuO$_2$ planes is considered. The result is

$$\xi_k = -2t \cos k_x a + \cos k_y a + 4t' \cos k_x a \cos k_y a - \mu$$

(4.10)

where $t$ and $t'$ are the nearest and next-nearest neighbour hopping parameters as in Fig. 4.2 and $\mu$ is the chemical potential. The parameters can be either derived from local density
4.1. Theory of inelastic light scattering

Figure 4.2: Hopping parameters from copper to copper in the CuO$_2$ plane, used for the calculation of the band structure. From [7].

approximation (LDA) calculations or determined by fitting the Fermi surface measured by ARPES. For the theoretical prediction of the superconducting spectra (see chapter 5.2) the same parameters are used as in the work of F. Venturini [7]:

$$\frac{\mu}{t} = -1.373, \quad \frac{t'}{t} = 0.45, \quad t = 250 \text{ meV}, \quad \frac{\Gamma}{t} = 0.05,$$

where the last parameter is a phenomenological damping to mimic the effects of impurities. These parameters are valid for optimally doped samples.

With equation 4.7 and 4.8 we now have a framework for the calculation of $\chi_{\gamma\gamma}$ in the effective mass approximation. However, two main concepts need an elaboration. Firstly, we are interested in the behaviour for different sets of $\hat{e}_I$ and $\hat{e}_S$. How these polarisations can be used to access different regions of the Fermi surface is the topic of the next section. Secondly, the equations are not practical for calculating the susceptibility – for that, basic effects such as screening and (in the superconducting state) final-state interactions need to be included. This will be the topic of paragraph ??.

4.1.3 Symmetry properties of the vertex

It is useful to decompose the vertices in such a way that the response for specific sets of $\hat{e}_I$ and $\hat{e}_S$ is a selection out of the components. Meaningful sets of linear polarisation vectors are orthogonal or parallel to each other and follow the symmetry lines of the CuO$_2$ lattice. Thus they are $xx$, $xy$, $x'x'$ and $x'y'$ in Porto notation, where $x$ and $y$ are defined as the directions along $a$ and $b$ in Fig. 4.2 and $x'$ and $y'$ are the directions along the diagonals of the square copper lattice. Circular polarisations are not considered in this work; for a complete description the reader is referred to [16].

Accordingly the vertices are decomposed into excitations transforming as the irreducible point groups $A_{1g}$, $B_{1g}$ and $B_{2g}$, respectively, which belong to the $D_{4h}$ symmetry class of...
4. Raman scattering

tetragonal cuprates. Excitations transforming as $A_{2g}$ do not couple to the light in the effective mass approximation [49]. Although Y-123 and Bi-2212 display orthorhombic distortions, the tetragonal symmetry classification generally works well for these materials, too [50, 16]. Each vertex component, yielded for an irreducible point group $\mu$, can be expanded in terms of even crystal harmonics $\Phi_{\mu}^L(k)$, with $L = 0, 2, 4, \ldots$ the order of expansion. In other words,

$$\gamma^\mu(k, q \to 0) = \sum_L \gamma_L^\mu \Phi_{\mu}^L(k) \quad \text{with} \quad \mu := \{A_{1g}, B_{1g}, B_{2g}\}. \quad (4.12)$$

In principle, all even $L$ channels can contribute to the full Raman (i.e. two-photon) response for bands which are nonparabolic. In contrast, pure charge and spin density responses only probe a single $L$-channel ($\gamma_k = 1, L = 0$), similar as the current density (i.e. single photon) response ($\gamma_k = k, L = 1$) [51]. The nonparabolicity is needed for the creation of charge fluctuations other than those screened by the long-range Coulomb interaction (plasma oscillations). Since the expansion converges rapidly for increasing $L$, it is sufficient to consider only the leading order $L = 2$ ($\Phi_0$ is constant for $A_{1g}$, otherwise it vanishes):

$$\begin{align*}
\Phi_2^{A_{1g}}(k) &= \frac{1}{2} (\cos k_x a + \cos k_y a) \\
\Phi_2^{B_{1g}}(k) &= \frac{1}{2} (\cos k_x a - \cos k_y a) \\
\Phi_2^{B_{2g}}(k) &= \sin k_x a \sin k_y a
\end{align*} \quad (4.13)$$

The basic functions for the $B_{1g}$ and $B_{2g}$ symmetries are mapped in Fig. 4.3. The figure shows that the basis function for $B_{1g}$ has maximal weight around the Brillouin Zone axes and is zero along the diagonals. For $B_{2g}$ the opposite is true. The $A_{1g}$ symmetry (not shown) does not project specific parts of the Fermi surface.

The choice of polarisations determines which $\gamma^\mu$s are selected. The symmetry properties can be expressed in terms of Pauli spin matrices as described elsewhere [49] and for the relevant linear polarisation sets one obtains

$$\begin{align*}
\gamma^{xx}(k) &= \gamma_2^{A_{1g}} \Phi_2^{A_{1g}}(k) + \gamma_2^{B_{1g}} \Phi_2^{B_{1g}}(k) \\
\gamma^{x'y'}(k) &= \gamma_2^{A_{1g}} \Phi_2^{A_{1g}}(k) + \gamma_2^{B_{2g}} \Phi_2^{B_{2g}}(k) \\
\gamma^{xy}(k) &= \gamma_2^{B_{2g}} \Phi_2^{B_{2g}}(k) \left( + \gamma_2^{A_{2g}} \Phi_2^{A_{2g}}(k) \right) \\
\gamma^{x'y}(k) &= \gamma_2^{B_{1g}} \Phi_2^{B_{1g}}(k) \left( + \gamma_2^{A_{2g}} \Phi_2^{A_{2g}}(k) \right)
\end{align*} \quad (4.14)$$

The contribution of $A_{2g}$, though vanishing for conduction electrons (and phonons), does become significant in the spectra of Bi-2212 for frequencies above 1000 cm$^{-1}$ [7]. However,
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![Figure 4.3: Mapping of the weight of the $B_{1g}$ (red) and $B_{2g}$ (green) basis functions in the Brillouin Zone. The respective weightings can be obtained for the indicated polarisation directions of incoming and outgoing light with respect to the CuO$_2$ plane. From [16].](image)

since the focus of this research is placed on the low-frequency pair-breaking excitations, we will ignore $A_{2g}$ henceforth. This means that the two crossed polarisations allow for a separate access to complementary regions of the Fermi surface, as shown in Fig. 4.3.

4.1.4 Raman response in the superconducting state

Now we proceed with the considerations that yield the theoretical Raman response for a cuprate superconductor.

To this end the unperturbed electron system must be specified, namely by the quasiparticle excitation energies $E_k = \sqrt{\xi_k^2 + |\Delta_k|^2}$, with $\xi_k$ the energy band dispersion (see Eq. 4.10) and $\Delta_k$ the energy gap. The equilibrium momentum distribution $n^0_k$ of the system is governed by the Fermi distribution $f(E_k)$. In a superconductor, apart from the normal phase space distribution there exists an anomalous one $g_k^0$ through which coherence is probed. Using these distributions, the susceptibility terms in Eq. 4.6, which are a consequence of gauge invariance, can be further specified. In the superconducting state, the gauge invariance is maintained by a collective mode of long-range order parameter phase fluctuations, the so-called Anderson-Bogoliubov mode. This mode comes into existence as a broken symmetry generator and is therefore an example of a Goldstone mode. In the discussion of the Raman spectra we will come upon another Goldstone mode with yet undiscovered origin. Apart from the Anderson-Bogoliubov mode, there may be several excitonic (massive) modes in the superconducting cuprates, which are not taken into consideration here because they do not affect the spectra strongly [26].

The screened Raman susceptibility can now be joined with the decomposition of the vertex in a (momentum dependent) crystal point group contribution and a (momentum-
independent) band structure contribution (Eq. 4.12). The third term on the right hand side of Eq. 4.6 is of the order of $q^2/\epsilon$ and small in a metal [49]. However, for parallel polarisations which project out the $A_{1g}$ symmetry, the transverse terms cancel out for the isotropic $L = 0$ channel and the response is governed by the longitudinal term, which represents the contribution from the plasma excitation. Anisotropic contributions ($L = 4, 8 \ldots$) to the $A_{1g}$ symmetry are partially screened [?]. Since only $B_{1g}$ and $B_{2g}$ symmetries are employed in this research, the longitudinal backflow term can be ignored.

The remaining response is brought about by intracell charge fluctuations that are screened by the Coulomb interaction for $B_{1g}$ and $B_{2g}$ symmetry in a $D_{4h}$ space group. There is no conservation law for light scattering from the excitations created by crossed polarisations, but there are sum rules which relate the Raman intensity to potential energies ??.

In chapter 5.2 a seemingly diverging intensity will be discussed.

The susceptibility now reads

$$\text{Im } \chi_{\gamma\gamma}^\nu(q \to 0, \Omega) = \text{Im } \chi_{\gamma\gamma}^\nu(q \to 0, \Omega + i0^+) = \text{Im } - (\gamma_2^\nu)^2 \left[ \langle K(k) \cdot (\Phi_2^E(k))^2 \rangle_{FS} - \frac{\langle K(k)\Phi_2^E(k) \rangle_{FS}^2}{\langle K(k) \rangle_{FS}} \right]$$

(4.15)

where $K(k)$ is a response kernel which contains all the information that is not yet contained in $\gamma$ - i.e. all details about the possible dissipative processes - and $\langle \ldots \rangle_{FS}$ is an average over the Fermi surface. For crossed polarisations the second term on the right hand side is zero if $k$ and $\Phi_L$ have no symmetry overlap. Since the scattering cross section is proportional to the imaginary part of the susceptibility (see Eq. 4.2), the complex frequencies that are employed for the calculation of the response kernels must be analytically continued on the real axis.

In the normal state the response kernel is designated by $\nu_k$ and contains information about the relaxation of quasiparticle excitations by collisions for $\Omega \approx \Gamma_k$. In the superconducting state Cooper pairs are broken for $\Omega \geq 2\Delta_k$ in addition to the quasiparticle relaxation. If the light is pair-breaking but collisions are not, the contributions can be separated in a two-fluid model [49], so that the contribution of the quasiparticles disappears in the limit $T \to 0$. Then the condensate response kernel, named Maki-Tsuneto function $\lambda_k$, reads

$$\lambda_k(\Omega + i0^+) = \frac{|\Delta_k|^2}{E(k)^2} \tanh \left( \frac{E(k)}{2k_B T} \right) \left[ \frac{1}{2E(k) + \hbar(\Omega + i0^+)} + \frac{1}{2E(k) - \hbar(\Omega + i0^+)} \right]$$

(4.16)
4.2. Theory of inelastic light scattering

The theoretical Raman spectra which follow from the Maki-Tsuneto function for a $d_{x^2-y^2}$-wave superconductor are shown in Fig. 4.4 for different relaxation rates $\Gamma_0$, which account for the impurity scattering investigated by Devereaux [52]. The quasiparticle scattering $\nu_\mathbf{k}$ which emerges at finite temperatures is not included, since it is expected to be very small (clean limit).

The symmetry of a $d_{x^2-y^2}$-wave order parameter can be written with the irreducible representation of a point group,

$$\Delta_\mathbf{k} = \Delta_0 \Psi_2^{B_{1g}}(\mathbf{k}) = \Delta_0 \left[ \cos k_x - \cos k_y \right] \frac{2}{2}.$$  \hspace{1cm} (4.17)

Thus the $B_{1g}$ symmetry, having the highest weight where the gap is maximal approximately projects out the amplitude of the order parameter; the pair-breaking peak frequency is related to the gap amplitude as

$$\Omega_{\text{peak}}^{B_{1g}} \approx 2\Delta_0.$$  \hspace{1cm} (4.18)

In $B_{2g}$ symmetry the maximum signal is located at lower frequencies of roughly $1.3 - 1.7\Delta_0$, depending on the impurity scattering.

The $B_{1g}$ symmetry of the order parameter manifests itself also in the relatively small increase of the $B_{1g}$ intensity for low frequencies. In the collisionless limit, the low-frequency behaviour can be written as

$$\text{Im} \chi^{B_{1g}}(\Omega \to 0) = 3N_F \left( \gamma_2^{B_{1g}} \right)^2 \left[ \frac{x^3}{4} + O(x^5) \right]$$

$$\text{Im} \chi^{B_{2g}}(\Omega \to 0) = N_F \left( \gamma_2^{B_{2g}} \right)^2 \left[ \frac{x}{2} + O(x^3) \right]$$  \hspace{1cm} (4.19)

with $x = \hbar\Omega/2\Delta_0$ and $N_F$ the density of states at the Fermi surface. The channel dependence is unique for the $d_{x^2-y^2}$ pair state. For finite impurity scattering the $B_{1g}$ spectrum initially rises linearly; only above the crossover frequency

$$\hbar\Omega^* = \sqrt{\Gamma_0 \cdot \Delta_0}$$  \hspace{1cm} (4.20)

it shows the typical cubic behaviour [52].

The theoretical Raman spectra are being discussed in chapter 5.2.
Figure 4.4: Pair breaking peaks in $B_{1g}$ and $B_{2g}$ symmetry for different relaxation rates $\Gamma_0$ due to scattering from impurities. From [52].
4.2 Experimental setup

The optical setup for the Raman experiment is shown in Fig. 4.5. A cw Ar$^+$ ion laser (Coherent Innova 304) serves as light source. Next to the selected stimulated transition of 457.9 nm ($21.837 \text{ cm}^{-1}$), the laser emits light from other, spontaneous transitions of the Ar$^+$-ion. A spatial filter S1 is used to eliminate plasma radiation with a divergence higher than that of the laser light. At the same time the beam diameter is enlarged.

The removal of divergent rays alone does not sufficiently suppress the plasma lines, therefore a prism-monochromator (PMC) and a slit (S2) sandwiched between two lenses are used as a spectrometer. The slit rejects lines which differ from the laser line by more than ca. 30 cm$^{-1}$.

The polarisation is adjusted by a Glan-Thompson polariser (P1). Since the light emitted from the laser is linearly polarised in vertical direction, the power of the beam can be regulated by rotating the polarisation in front of P1. This is done by means of a $\lambda/2$-retardation plate. The power is measured in front of the final mirror before the sample (M3) and can
be varied in the mW-range.

A Soleil-Babinet compensator (SB) and a $\lambda/4$ retardation plate can be used for the creation and detection of circularly polarised light, respectively. They will be disregarded here.

A spatial filter (S3) is used to obtain a homogeneous Gaussian intensity distribution. This filter should be placed as close as possible to the sample to avoid deterioration of the beam optical components. The filter is made of a microscope objective lens (Spindler and Hoyer, x10), a pin-hole with a diameter of 20 $\mu$m and an achromatic lens with focal length $f = 30$ mm.

The achromatic lens L6 focusses the laser beam via the mirror M3 on the surface of the vertically orientated sample. The angle $\alpha \approx 63^\circ$ is chosen so that the transmission of the light parallel to the plane of incidence is maximal (pseudo-Brewster angle). The transmission coefficients, which determine the absorbed laser power, are calculated using the Fresnel formulas for metals. The complex refraction index $\tilde{N} = n + ik$ required for this can be measured as described in detail elsewhere [7]. For the Bi-2212 samples studied in this work, the optical constants have not been remeasured. In agreement with older measurements on Bi-2212, the relative absorption of horizontally ($x$), diagonally ($x'$) and vertically ($y$) polarised light is given by $I_x/I_y = 0.6$ and $I_{x'}/I_y = 0.8$, respectively.

To achieve proper alignment of the Cu-O bonds with respect to the laboratory frame, a Laue image is taken after fixing the crystal on a manipulator. The latter is done by gluing the crystal on a copper piece with the adhesive GE Varnish 7031, which is a good heat conductor even at low temperatures. The copper is clamped in the manipulator, which allows for a rotation of the sample in the cold finger of the helium flow cryostat with a cryopumped high vacuum chamber with $p_{min} \approx 5 \cdot 10^{-7}$ mbar. The temperature of the sample holder can be varied in the range of 1.8 to 350 K and is measured with a Si diode.

A close-up schematic drawing of the backscattering geometry at the sample is shown in Fig. 4.6. While the specularly reflected light is absorbed by a beam stopper, the elastically and inelastically scattered light is collected by a camera objective O2 (Minolta, $f = 58$ mm, 1 : 1.4) within a solid angle $\Omega = 2\pi(1 - \cos \theta)$ with $\theta \simeq 15^\circ$. The penetration depth $\delta = \lambda/(4\pi k)$ has typical values of about 60 nm for Bi-2212. Thus bulk properties are studied by Raman spectroscopy. However, the adsorption of remaining molecules in the vacuum during the measurement cycle of a sample (typically several weeks) can induce
4.2. Experimental setup

![Diagram of scattering geometry](image.png)

Figure 4.6: Schematic detail of the scattering geometry of the sample in side view. I, R and T denote incident, reflected and transmitted light vectors, S is the scattered light that is collected in the solid angle $\Omega = 2\pi(1 - \cos \theta)$. The optical penetration depth is marked by $\delta$. From [7].

A frequency independent variation of the Raman intensity. Therefore extra attention was paid to the reproducibility of the measurements, especially after cooling to 4.2 K. The typical size of the laser spot is approx. 50x150 $\mu$m. The spot can be elongated by rotating lens L6 about a horizontal axis. This reduces the power density and thus the heating of the illuminated part of the sample.

The selection of the polarisation of the scattered light is achieved by a second polariser P2. The $\lambda/4$-retardation plate is only necessary in case of circular polarisations. A $\lambda/2$-retardation plate in front of the entrance of the spectrometer rotates the light into the direction of maximal transmission of the spectrometer.

The spectrometer is a double monochromator (Jarrell-Ash 25 100), the two dispersion stages of which are subtractively coupled as shown in Fig. 4.7. A single dispersion stage would not suffice to separate the weak Raman scattered light from the intense elastic scattering. The diverging light from the entrance slit is first reflected as a parallel beam by the spherical mirror SM1 and then dispersed by a holographic refraction grating. The dispersed light is focussed by a second spherical mirror and a planar mirror P1 on the intermediate slit, which only a specific wavelength range can pass. The identical second stage reverses the dispersion. Thus the intermediate slit has the function of an optical bandpass filter.

Because of losses at the mirrors and gratings, only 35% of the photons entering the spectrometer arrive at the detector [16]. The light that comes out of the spectrometer
Figure 4.7: Configuration of the spherical mirrors SM1-4, planar mirrors M1 and M2 and gratings G in the spectrometer. From [7].

is focussed on a CCD chip (Tetronix TK-512), which is cooled by liquid nitrogen. The read-out of the CCD camera and the control of the frequency measured by the spectrometer are both handled using a PC with the software MAPS (Photometrics) [8]. After a spectrum is measured, the photons counts are divided by the absorbed laser power and the exposure time per point. In addition, the spectra are corrected for the sensitivity of the instrument. A typical measurement cycle takes up to 13 hours.
4.2. Experimental setup
Chapter 5

Results and Discussion

The first part of this chapter is a report of the experimental study made on how to transform as-grown YBCO crystals into well-ordered samples with a doping level just beyond the onset point of superconductivity $p_{sc1} = 0.05$. Annealing and quenching of ceramic pellets appears to be a particularly important issue. The subsequent characterisation by $T_c$-measurements and thermogravimetric analysis is described in paragraph 3.1 and 5.1.5, respectively.

5.1 Preparation and characterisation of underdoped Y-123

The objective is to gather ortho-III* ordered single crystals which are still superconducting. This is a challenging task, seeing that the small doping range in which the phase with double empty chains may be found might not overlap at all with the superconducting range. While the ortho-III* phase is claimed to be present between $x = 6.28$ and $6.32$ only, the same group reported the onset of superconductivity to occur at $x_{sc1} = 6.345$ [12] and another group found $x_{sc1} = 6.33$ [53]. Since the priority criterium is the presence of superconductivity, the oxygen concentration strived for in the first treated crystals is $x = 6.33$. If successful, future projects could comprise co-doping of such crystals with calcium. This would open up the entire doping range in between $p = 0.05$ and 0.12.

Fig. 5.1 shows a schematic diagram of the preparation steps followed by Liang et al., which will be a guideline for the sample preparation investigations here. The individual steps are
5.1. Preparation and characterisation of underdoped Y-123

commented on in the following.

5.1.1 Detwinning

As discussed in the last chapter, as-grown YBCO crystals with an oxygen concentration above \( x \approx 6.28 \) are naturally twinned. The problem with twinned crystals is that the presence of microcrystallites hampers a homogeneous the carrier concentration, especially for low concentrations. This manifests itself in the appearance of multiple superconducting transitions. Since in the underdoped regime the \( T_c(p) \)-curve is much steeper than at optimal doping, the overall transition becomes very broad and undefined. Hence a detwinning step is necessary for the making of far underdoped YBCO.

To this end, A. Erb built the detwinning apparatus shown in Fig. 5.2. A quartz window on top allows observation by a polarising microscope, through which twin domains are seen as areas with contrasting brightness. Beneath the top window are two plates, between which a rectangular or square sample is placed. Crystals with an irregular shape are not usable, since the application of non-uniform stress would create cracks. The pressure on the crystal can be increased in a controlled way by a spring loaded microscrew. A heater is located below the crystal to control the temperature. Temperatures up to 700°C can be reached; the atmosphere can be adjusted appropriately.

The application of a constant stress of about \( 2.5 \cdot 10^7 \text{ Nm}^{-2} \) at a couple of hundred °C effectively moves the domain walls until one single orthorhombic domain is left. On a microscopic scale this means that a spatial redistribution by diffusive jumps of \(< 3 \text{ Å}\) is forced upon the O atoms and a shift of \( \sim 0.04 \text{ Å}\) is forced upon the Cu atoms. The relaxation process is anelastic [54].

Two as-grown YBCO crystals have been detwinned using the new device. The high-purity crystals were grown by A. Erb in non-reactive BaZrO_3 crucibles. Since the crystals have dimensions of 1x1 and 0.9x1.1 mm, respectively, we shall denote them in the following as square and rectangular to make a distinction. The crystals did not retwin after a subsequent high temperature annealing, even though then the crystals become underdoped and the orthorhombic to tetragonal (order-disorder) phase transformation temperature (mapped in the Fig. 3.7) is crossed. Clearly the orthorhombic structure shows a memory effect. This implies that detwinning can be the first step in the preparation procedure. Detwinning after annealing is in fact more difficult, since it would have to be done at lower
Figure 5.1: Block diagram of the guidelines to gather well-ordered YBCO-crystals. After [11].
5.1. Preparation and characterisation of underdoped Y-123

Figure 5.2: Detwinning device (built by A. Erb).

temperatures to avoid the oxygen concentration from changing.

5.1.2 Conventional annealing and quenching

The two detwinned crystals discussed above have been annealed for 5 days in a gas mixture with 1% O$_2$ in Argon flowing slowly through the tube furnace. The temperature was fixed at 670°C, corresponding to an equilibrium oxygen concentration of $x = 6.33$. For reasons explained later on, the crystals were annealed together with a ceramic crucible. Since the crucible had an oxygen concentration of $x \approx 6.9$ to start with, the total amount of oxygen which was set free is estimated to be about 8 times the amount present in the volume of the furnace when filled with 1% O$_2$. Since this would have seriously altered the oxygen concentration of the gas mixture, the tube furnace was flushed in between. The crystals and the crucible were quenched on a copper plate.

The oxygen concentration in single crystals can in principle be measured directly with a precision of 0.01 by neutron diffraction, but since this is quite an exclusive method, it is employed only occasionally. Other methods such as iodometric titration or weight change measurements cannot detect these small differences in the chemical formula of YBa$_2$Cu$_3$O$_x$, for the typical crystal mass of ten to hundred mg is not large enough compared to the resolution of these methods. Hence, the characterisation of YBCO samples is usually very poor, consisting only of the nominal value of $x(P_{O_2}, T)$. Alternatively, the hole
concentration is used to characterise a sample. We have seen in the last chapter that this value can be determined indirectly by using Tallon’s relation between the transition temperature and the doping (Equation 2.1).

5.1.3 \( T_c \) measurement of the single crystals

The \( T_c \)-measurements of the two untwinned crystals with nominal oxygen concentration \( x = 6.33 \) is shown in Fig. 5.3. Though the transition (if present at all) is in fact expected to fall below the temperature range of the setup, both crystals show an onset of superconductivity at \( T = 34 \) K. According to the universal \( T_c(p) \)-dependence (equation 2.1) with \( T_c^{\text{max}} = 94 \) K, this corresponds to a doping level \( p = 0.072 \). By using the \( p(x) \) dependence for unordered oxygen distributions as determined by Liang et al. (see Fig. 3.8), the corresponding oxygen concentration is estimated at \( x \approx 6.43 \). The increase of the slope of the rectangular sample points at an accumulation of transition peaks due to an inhomogeneous carrier distribution.

The transition at \( 34 \) K cannot be attributed to the bulk carrier concentration. A deviation of \( x \) that large is ruled out since the fixed annealing conditions (temperature and oxygen partial pressure) are considered trustworthy and the annealing time of 5 days should suffice to reach equilibrium. Also the quenching process was too fast for the bulk oxygen concentration to have changed. The high transition temperature must therefore be due to a deviating carrier concentration near the surface, caused by oxygen in-diffusion during the quench in ambient air. This could explain the soft onset of the peak as well: in the small surface layer, edge and surface barriers play a dominant role over bulk vortex pinning, hence the onset of superconductivity is marked by the start of a long tail in the third harmonic response.

5.1.4 The use of ceramic pellets

All in all the conventional annealing and quenching method has some deficits:

1. Deviations at the surface arise due to quenching in ambient air.

2. The oxygen concentration is determined indirectly with an imprecision of only a few percent. This is particularly problematic since the properties vary strongly with \( x \) and the only appropriate manner of investigation would be a systematic preparation of samples with slightly varying oxygen concentrations.
Figure 5.3: Third harmonic signal $V_{3\omega} \propto |\chi_3|$ of (a) the square and (b) the rectangular detwinned YBCO crystal with a nominal $x$ value of 6.33, measured one day after annealing. The hysteresis is negligible except for the fast cycle down. The arrows indicate the onset of the transition.
5. Results and Discussion

The use of sinter pellets of YBCO in the annealing procedure could solve both problems.

In this approach, the sample and a 100–1000 times larger YBCO sinter are first annealed and quenched so that they contain approximately the right amount of oxygen. It should be noted that the quenching is not straightforward for the sinter, since the large surface with micrometre-sized grains enables rapid oxygen exchange. It suffices if the oxygen contents of ceramic and crystal are approximately right though, for they subsequently undergo a heat treatment in which the concentrations are balanced out between the two. To this end, they are put in a quartz capsule which is vacuum-sealed. During the second heat treatment the YBCO sinter serves as a buffer, facilitating a complete equilibration of the deviating oxygen concentration at the crystal surface.

The quartz capsule for the homogeneity heat treatment is schematically drawn in Fig. 5.4. Since the diameter of the quartz tube must exceed that of the YBCO sinter, the sealing of the tube, which is done at a local temperature of about 1500 °C, will generate a lot of heat. Thus the distance to the sample must be large enough. Alternatively, a piece of quartz with a reflecting site can be put in between in order to absorb the heat. Evacuation is done at the opposite site of the tube, where a small capillary leads to a vacuum pump. This capillary is sealed last while the pump is still running.

Before this approach is carried out, one must assure oneself that the oxygen concentration

\[ \text{Figure 5.4: Schematic drawing of the quartz tube used for annealing.} \]
5.1. Preparation and characterisation of underdoped Y-123

stays homogeneous upon the second quench. For this reason we take a look at the oxygen diffusion into the spare volume of the quartz ampule. The initial oxygen content of the evacuated volume is negligible, but the oxygen partial pressure within the material increases with temperature. When in balance, the ambient partial pressure is the same. For a sinter with $x = 6.33$, the partial pressure that is established at an exemplary annealing temperature of $T = 570\, ^\circ\text{C}$ is $10^{-3}$ bar, as can be read from the calibration of Lindemer. If we take the evacuated volume to be roughly $1\, \text{cm}^3$, then the amount of oxygen that escapes from the material is of the order of $10^{-8}$ mol. Since the sinter weighs about $10\, \text{g}$, this would cause a negligible change in oxygen concentration of the order of $\Delta x \sim 10^{-6}$.

The capsule is quenched in an ice water bath. This is why the capsule is best made out of quartz, which is known for its high thermal shock resistance. Yet quartz has a low thermal conductivity, hence the quenching process will be slower than the original copper plate quench. The advantage over the first quench is that now the homogeneity of the sample is ensured in two ways: not only is the crystal shielded by the surrounding sinter, the ambient oxygen gas also has the same partial pressure to start with. For the lack of a thermal contact between ceramic and quartz, it is expected that the temperature adjustment of the oxygen gas is slightly faster than that of the ceramic. The partial pressure of the oxygen gas thus decreases while the sample is still warm, causing oxygen to diffuse out of the ceramic preferentially. The smaller the spare volume is, the smaller this effect will be.

Thus the ceramic offers a solution to issue number 1. It also allows for the determination of $x$, for whereas weight change measurements are not accurate enough for single crystals, they are for ceramic pellets. We have already tacitly assumed that the equilibrium oxygen concentrations for ceramic and single crystal are approximately the same (meaning that grain boundaries do not trap a significant amount of oxygen) in that we have used Lindemer’s $x(P_{O_2}, T)$ for both. Even if there would be a small systematic difference between the two, the relative precision is guaranteed as long as the same batch of ceramics is used. The oxygen out-diffusion during the second quench is presumed to be so low that it hardly changes the overall oxygen content. Hence the determined $x$ is a good representative for the crystal.

It should be emphasised that the reheating temperature should be as high as possible to ensure good oxygen diffusion. The maximal reheating temperature is limited in the first place by the reaction temperature with the quartz above ca. $600\, ^\circ\text{C}$. Secondly a potential retwinning above the tetragonal to orthorhombic transition temperature has to be kept in mind.
Now that the role of the ceramic pellets is outlined, we introduce the thermogravimetric analysis (TG) as a means to measure their absolute oxygen content. Subsequently the TG results of the pellet, which has been annealed together with the detwinned crystals and quenched on a copper plate, are discussed.

5.1.5 Thermogravimetric analysis

The absolute oxygen content of YBCO can be determined in two ways: either by oxygenating it to the maximum $x = 7$ or by reducing it. Since oxygenation either takes very long or requires high oxygen pressure environments, in which weight changes cannot be monitored, a destruction of the top pellet by complete reduction is preferable. The reduction reaction

\[ \text{YBa}_2\text{Cu}_3\text{O}_x + (x-3.5) \text{H}_2 \rightarrow \frac{1}{2} \text{Y}_2\text{O}_3 + 2 \text{BaO} + 3 \text{Cu} + (x-3.5) \text{H}_2\text{O} \]

takes place in forming gas, a mixture of 5% hydrogen in nitrogen. The dynamics of the reaction are monitored with a thermal analyser, which simultaneously features both thermogravimetry and differential scanning calorimetry (DSC). Thermogravimetry is a technique that monitors the weight of a sample during its interaction with the surrounding atmosphere. Differential scanning calorimetry (DSC) on the other hand sheds light on the reaction dynamics by measuring the enthalpy changes via the heat flux difference between the crucible with the sample and an empty reference pan, while the pans are subjected to a regulated temperature-time program.

The apparatus used for the TG/DSC-measurements is the Netzsch Simultaneous Thermal Analyzer 409C/CD shown in Fig. 5.5. The sample holder is situated on an arm of an electromagnetically compensated microbalance with sensitivity $5 \mu g$. The calorimetric technique applied in this device is heat flux DSC, which is characterised by the symmetric alignment of the sample and reference pan on a single sample holder. The electrical analogue of heat flux DSC is shown in Fig. 5.6. In this model the furnace is seen as a heat generator $\theta$, while $\phi$ is the power of the exo- or endothermic physical transformation in the sample. $C_1$ and $C_2$ are the heat capacities of the sample and (if at hand) the reference material, respectively, inclusive of the heat capacities of common sample holder and respective crucible. The thermal resistances between the furnace and the sample holder and inside the sample holder are denoted by $R_1 \equiv R_2 = R$ and $r$. From this model
5.1. Preparation and characterisation of underdoped Y-123

it follows [55] that the heat flux difference between sample and reference $\phi_1 - \phi_2$ generates a small temperature difference

$$\phi_1 - \phi_2 = \left( \frac{1}{R} + \frac{2}{r} \right) (T_1 - T_2) \quad (5.1)$$

which is measured with two inversely arranged thermocouples (disc-type heat flux DSC). An integration over this signal gives the enthalpy of the transformation.

A test TG/DSC-analysis of YBCO$_7$

For our investigation purposes, a batch of YBCO pellets with two different diameters (~5 and 10 mm, respectively) has been prepared. This was done by pressing a calcinate of the proper ratio of Y$_2$O$_3$, BaCO$_3$ and CuO into pellets and sintering these for 20 h in oxygen atmosphere at $T = 930 \, ^\circ\text{C}$. For the determination of the absolute oxygen content only thermogravimetric analysis is needed, but DSC curves are helpful for testing whether the pellet is completely reduced and for identifying any unexpected side-effects. Simultaneous TG/DSC-measurements can only be done on the small pellets since the large pellets do not fit in the double sample holder. Thus the first step was to bring the small pellets to $x = 7$ for a test measurement. They were enclosed in a high pressure cell filled with liquid oxygen. The typical pressure of the evaporated oxygen at the applied annealing temperature $T = 300 \, ^\circ\text{C}$ is roughly 1300 bar. Such high partial pressures result in a fully saturated oxygenation. Moreover, an annealing time of 3 days is sufficient, whereas under atmospheric pressure typical annealing times are of the order of 2 weeks.

After oxygenation, a pellet with $m_1 = 206.9690 \, \text{mg}$ (measured with a Mettler AT261 microbalance) was reduced in one of the aluminium oxide pans which are typically used for the thermal analysis of ceramics. The stability of the pan was checked by weighing it before and after the measurement. The furnace volume was first evacuated using a turbo molecular drag pump and then backfilled with forming gas. Subsequently, a constant flow of 30 mL/min of forming gas was applied. The system was programmed to heat the crucible at a rate of 10 K/min from room temperature to 800 °C, then to keep the temperature constant for 2 h and to cool down. To account for the influence of temperature and gas flow on the buoyant force on the sample holder, a baseline correction measurement was conducted beforehand and automatically subtracted from the TG curve of the actual experiment. The result is displayed in Fig. 5.7.

The TG curve shows a continuous decrease of mass, the maximum mass loss being $\Delta m_1 =$
Figure 5.5: Scheme of the Simultaneous Thermal Analyzer (Netzsch STA 409C/CD)
5.1. Preparation and characterisation of underdoped Y-123

**Figure 5.6:** Electrical analogue of a heat flow differential scanning calorimeter. \( \theta \) is the heat generator (furnace), \( \phi \) the exo- or endothermic power in the sample, \( C_1 \) and \( C_2 \) the heat capacities of the sample and the reference material, respectively. The thermal resistances between the components are denoted by \( R_{1,2} \) and \( r \). From [55].

**Figure 5.7:** TG response in mg (green) and DSC response in \( \mu V/mg \) (blue) as a function of time during a short temperature program (red dotted curve) for a completely oxygenated sample.
5. Results and Discussion

$-16.70 \pm 0.2 \text{mg}$. Using the molecular mass $M(YBCO_7) = 666.213 \text{g/mol}$ a corresponding loss of $3.360 \pm 0.040$ O-atoms per YBCO$_7$ unit is calculated, which is less than the 3.5 expected from the reduction reaction. From the slowly continuing loss of mass during the entire constant temperature interval it follows that the pellet was not completely reduced. Examining the DSC curve we see several bumps in the exothermic reduction peak, which are related to the development of intermediate compounds (Ba$_2$CuO$_3$, Ba$_3$CuO$_4$, Ba$_2$Y$_2$O$_5$ and Ba$_4$Y$_2$O$_7$) [56]. Apart from geometrical restrictions, the slow dissociation of these interphases may be the cause for the sudden slow-down of the reaction. The positive humps in the beginning of each ramp are ascribed to the delay of the temperature adjustment of the sample with respect to the empty reference pan, due to its additional heat capacity.

In a second attempt, a pellet with $m_2 = 307.1220 \text{mg}$ has been reduced over an interval of 8h constant temperature, as shown in Fig. 5.8. After 6h the weight stayed constant. From $\Delta m_2 = -26.01 \pm 0.2 \text{mg}$ follows a loss of $3.527 \pm 0.027$ O-atoms per YBCO$_7$, which is just compatible with the expected value.

All in all the six hour longer wait yielded an additional mass loss of only 0.13%, equals 0.054 O-atoms per YBCO$_7$. Thus the difference between the two results must be explained otherwise. For better comparison, the normalised TG-response and the DSC-response of the two pellets are shown as a function of temperature in Fig. 5.9. The relative mass changes are as good as identical but for the sudden mass loss between 130°C and 180°C in the long program, which seems to go hand in hand with a prolonged endothermic peak and thereupon a distinctly smaller exothermic peak. This gives reason to believe that the second pellet was in fact unclean. It can be concluded that the maximal reduction of fully oxygenated pellets during an eight hour constant temperature interval lies at $3.414 \pm 0.027$ O-atoms.

**Weight analysis of YBCO$_{6.33}$ quenched on copper**

Nonetheless, the thermogravimetric analysis is adopted for the investigation of the ceramic pellet with nominal oxygen concentration 6.33. The pellet has been annealed together with the detwinned crystals and a YBCO sinter crucible; all parts were quenched in air on a copper plate.

The true oxygen concentrations of crucible and top pellet were first estimated by the mass difference before ($x = 6.92 \pm 0.02$, extrapolated from annealing conditions) and after
5.1. Preparation and characterisation of underdoped Y-123

Figure 5.8: TG response in mg (green) and DSC response in $\mu$V/mg (blue) as a function of time during a long temperature program (red dotted curve) for a completely oxygenated sample.
Figure 5.9: Comparison of the TG and DSC curves as a function of temperature for reduction of fully oxygenated YBCO during a long and short temperature program, respectively.
5.1. Preparation and characterisation of underdoped Y-123

annealing, which yielded $x(\text{crucible}) = 6.53 \pm 0.02$ and $x(\text{pellet}) = 6.49 \pm 0.02$. These values are credible since the crystalline grains of the ceramic are micrometre-sized and the diffusion coefficient at the annealing temperature is roughly of the order of $D \sim 1 \mu m^2/s$ [44]. Thus a significant change in the total oxygen content must be expected.

The reduction of the top pellet (Fig. 5.10) carried out two days after the quench on the other hand gave a much higher value: $x = 6.83 \pm 0.05$ (where the maximal reduction is assumed to be $3.414 \pm 0.027$ O-atoms as explained in the last paragraph). A probable source for the discrepancy might be the incorrect identification of the baseline due to the strong buoyancy oscillations in the beginning. When a baseline is drawn in for a mass loss corresponding to $x(\text{pellet}) = 6.49$, it indeed coincides with the average mass during the oscillation.

It follows that ceramics cannot be brought to $x \approx 6.33$ by quenching in air since the oxygen in-diffusion is too rapid.

5.1.6 Quenching in liquid nitrogen

As a solution to the problem of quenching in air, a small furnace with a possibility to quench directly in liquid nitrogen was put together. This way the sample cools slowly (within approximately one minute) under the protection of a boiling film, which in the ideal case does not contain oxygen. The effect of quenching in various liquid gases after annealing under 1 atm of O$_2$ has been investigated by Knizhnik et al. [57] for a 1:2:3-type cuprate other than YBCO, namely $(\text{Ca}_x\text{La}_{1-x})\cdot(\text{Ba}_{c-x}\text{La}_{2-c+x})\cdot\text{Cu}_3\text{O}_y$. It was concluded that a quench in liquid argon or oxygen free liquid nitrogen produces samples with the equilibrium oxygen content. This indicates that even at the highest annealing temperatures oxygen is not desorbed. In contrast, quenching in gases that do contain liquid oxygen (such as technical LN$_2$, which contains about 2% of oxygen) from temperatures above ca. 700°C does lead to oxygen absorption. The first aim is to establish whether or not these effects occur under our conditions.

The short cylindrical furnace used for this purpose is closed with alumina fibre stopper on one end; on the other end it is open so that a quartz tube can be pulled in and out. The temperature is measured by a thermocouple in the exact middle of the furnace, beneath which the sample lies on a tile of BaZrO$_3$. In order to perform the quench, the sample and the tile fall together within one second from the quartz tube into a liquid nitrogen
Figure 5.10: Thermogravimetric response during reduction of a pellet, annealed together with the detwinned crystals, with mass $m = 1.6816 \, g$. The striped line marks the mass difference that would correspond to the expected value of $x = 6.49$. 
reservoir. The mass of the tile helps to keep the temperature constant until contact with the liquid. At the end of the fall, the sample and the tile are cooled separately. Finally, the sample is brought to room temperature in a protective nitrogen gas environment.

The construction has been tested by quenching a pellet from various annealing temperatures and conducting weight change measurements each time. The sample was annealed along with a grain of another pellet of the same batch in order to determine the transition temperature. The results are listed in table 5.1. After the 8th annealing step \( T_{ann} = 800 \, ^\circ C \) the pellet showed a white spot, indicative of secondary products such as hydroxides, oxides and carbonates (e.g. Ba(OH)\(_2\), BaCO\(_3\), Y(OH)\(_3\) and Y\(_2\)(CO)\(_3\)) formed during water degradation \([58]\). Thus the last few measurements were made together with a second pellet and grain, as shown in the table.

Since the secondary products are not always visible as white amorphous phases, they may well have been present before. To test this, the second pellet was annealed twice at 350°C: the first time without and the second time with quenching. From the very small mass loss two conclusions are made: 1) no significant oxygen desorption occurred and 2) no mass-changing water degradation had taken place. A subsequent thermogravimetric reduction of the second pellet however yielded a mass loss corresponding to \( x > 7 \) and an inhomogeneous residue, which could be ascribed to the reactions of the secondary phases with hydrogen. The presence of secondary phases in the residue was indeed detected subsequently by X-ray diffraction. From these arguments it follows that the pellets were not degraded during the warming up in the nitrogen gas environment, but already during storage or even at the preparation, due to the use of contaminated sinter powder.

Nevertheless, the \( x_i(T_{ann}) \)-values plotted in Fig. 5.11 show a reproducibility and resemblance to the calibration by Lindemer. Since the absolute oxygen content of the YBCO phase could not be determined by thermogravimetry, the oxygen concentrations are iterated starting with \( x_2 \), which is assumed to be equal to the equilibrium value at 650°C in air. This in order to stress the similarity to the calibration. The highest sequence of oxygen concentrations can be received by starting the iteration with \( x_{\max} := 7 \). The lowest sequence starts with step 0 and a10: according to the characteristic \( T_c(x) \) dependence \([25]\), their \( T_c \) of 89K can only be established for \( x \geq 6.842 \). These upper and lower boundaries outline the grey area in the figure. The saturation of \( x \) around 6.9 instead of 7 is ascribed mostly to the total molar amount of YBCO being smaller than its mass would suggest, since the sample is partly degraded. A small part is due to the saturation of oxygen chains in air being lower than the calibration predicts \([13]\), as we shall see from the transition
Table 5.1: Results of quenching YBCO in liquid nitrogen. Annealing step 9*/a9* was followed by a slow cooling instead of a quench. The oxygen concentration values are calculated from the weight changed starting with $x_2$; the initial oxygen concentration of the second pellet is assumed to be equal to the first one since they both originate from the same batch. The $x$-values are corrected for mass loss in between annealing steps. In the deviation of $x$ both statistic and systematic errors are included.
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Figure 5.11: Oxygen concentrations after annealing in air and quenching in liquid nitrogen, compared to the calibration of Fig. 3.6 on page 28. The numbers indicate the sequence of annealing steps, while the error bars indicate the deviations relative to each other. Depending on the start value of the iteration, the absolute oxygen concentrations may be moved vertically within the grey area.

The examination of the transition temperatures yields information about the effect of the secondary phases on the carrier concentrations. The $T_c$’s are plotted in Fig. 5.12 as a function of the nominal oxygen concentrations of the respective heat treatments $x_{\text{nominal}} = x(P_{O_2} = 0.2\,\text{bar}, T_{\text{ann}})$. The majority of the data points falls on the normal $T_c(x)$-curve if the latter is moved by 0.11 to the right. Thus the impurities have the effect of reducing the hole concentration without reducing $T_{c\text{max}}$. Provided that there is indeed such a constant shift, the deviating transition temperatures after annealing must have other than their nominal oxygen concentrations. After step 3 (low temperature annealing in order to fully saturate the oxygen chains) the actual oxygen concentration is lower than the nominal one, which can be explained by an incomplete saturation after a finite annealing time at low oxygen partial pressures which lies at $x^{\text{max}} = 6.965$, due to the decaying equalisation. After step 7 the actual concentration $x = 6.495$ is 0.040 higher than the nominal one. This is consistent with the oxygen in-diffusion predicted for high annealing temperatures.
Figure 5.12: Transition temperatures as a function of the equilibrium oxygen concentration during annealing, compared to the $T_c(x)$-dependence determined by Liang [25]. The numbers correspond to the sequence of annealing steps. The dashed curve has the same shape as the curve determined by Liang, but is shifted by 0.11 to the right to mimic the effects of a reduced hole concentration.

However, since step 7 is the last one before the white spot appeared, it’s reliability is arguable.

5.1.7 The use of ceramic pellets: concluding remarks and outline

In conclusion, quenching in nitrogen shows a little more potential than quenching on a copper plate. It may be carefully postulated that the oxygen in-diffusion for non-degraded samples at $x_{\text{nominal}} = 6.455$ is about 0.040. Quenching on copper in air raised the oxygen concentration from 6.33 to approximately 6.49. Since the absorption in LN$_2$ is lesser and probably more reproducible, annealing at a temperature of 860°C or higher might return the desired results. The best option at this point however is quenching in oxygen free liquid gases like argon. The single crystals could in principle be annealed and quenched together with the ceramic, but annealing in a colder atmosphere with 1% O$_2$ is preferred to prevent structural decomposition and retwinning.

Once both crystals and ceramic have the right content of oxygen, the rest of the proposed treatment can be carried out. The thermogravimetric analysis that follows the heat treatment has so far not delivered oxygen concentrations with the precision ex-
5.1. Preparation and characterisation of underdoped Y-123

The major uncertainty of TG comes from the mass change uncertainty \( \delta x \approx \delta \Delta m/m \cdot M(\text{YBCO}_x)/M(\text{O}) \). The pulverisation of the pellet before the TG measurement would be an improvement, since it would enable dividing the measurement in two (increasing the chance on a measurement without buoyancy oscillations) and it would shorten the measurement time. In fact, the pellet may be pulverised even before the homogeneity heat treatment in order to increase its contact with the crystal.

5.1.8 Oxygen ordering

The last step in preparing ortho-III\(^*\) ordered YBCO is the oxygen ordering itself, which occurs naturally at room temperature. This slow process can be accelerated by storing the crystals just below the ordering transition temperature. For the ortho-II superstructure this is \( T_{\text{OII}} = 95^\circ \text{C} \), for ortho-III it is \( T_{\text{OIII}} = 48 \pm 5^\circ \text{C} \) [45]. The ortho-III\(^*\) superstructure can be obtained by storing the capsule for 3 weeks in a water bath of 23\(^\circ\)C [12]. To prevent oxygen in-diffusion, the crystal must be stored in low vacuum (10\(^{-2}\) bar).

The detwinned and annealed crystals with an oxygenated surface layer have been enclosed in separate, small quartz capsules. They were annealed for 2 weeks at 80\(^\circ\)C. After this treatment the crystals did not show a superconducting “tail” in the third harmonic susceptibility anymore. This supports the notion that the surface oxidation layer had been of micrometre scale or less, given that the diffusion rate is still very low at 80\(^\circ\)C. No superconductivity could be observed in the temperature reach of the setup, hence the samples have been put in storage. The slow ortho-III\(^*\) ordering might raise the transition temperature to an accessible level.

5.1.9 Preparation of YBa\(_2\)Cu\(_3\)O\(_{6.33}\): outline

The preparation procedure illustrated in the block diagram in the beginning of this chapter (Fig. 5.1 on page 51) is hereby completely worked out. The individual preparation steps that were carried out have proved themselves potentially practical for use on any Y-123-based cuprate. As far as the specific aim of this project is concerned, YBCO single crystals with a nominal oxygen concentration \( x = 6.33 \) showed an absence of bulk superconductivity with a transition higher than 6 K. This means that a next attempt must be made at annealing conditions \( T_{\text{ann}} = 655^\circ \text{C} \) and \( P_{\text{O}_2} = 0.01 \text{ bar} \), so that \( x = 6.35 \). Concurrently, YBCO pellets (and grains to measure the transition temperature) are to
be annealed in air and quenched in liquified oxygen free gases to reach $x = 6.35$. The homogeneity heat treatment of the pellets and the crystal is then to be conducted as described earlier. Last, the crystal must be stored at room-temperature for the ortho-III$^*$ ordering process. However, it should be borne in mind that as the oxygen concentration increases, obtaining an ortho-III$^*$ ordered phase will become an even greater challenge.
5.2 Raman studies on superconducting Bi-2212

In this chapter the electronic Raman spectra of three new superconducting Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)-Cu$_2$O$_{8+\delta}$ samples are investigated. One sample contains 8% yttrium and is labelled (according to the transition temperature) Bi-OPT96 in the optimally doped state and Bi-OD87 after overdoping, the other sample has only been measured in the optimally doped state and carries the label Bi-OPT94. Further details of these samples are described in chapter 3. For comparison and for the investigation of general trends, the collected data of a large set of Bi-2212 and Y-123 samples measured previously [7, 8] are incorporated.

As addressed in the general introduction to the cuprates, the properties of the superconducting state are not yet understood (cf. the energy scales in Fig. 2.8 on page 18). In the Raman response this is manifest in the appearance of superconductivity-induced structures in the $B_{1g}$ and $B_{2g}$ channel, respectively, that cannot arise from one and the same excitation. A close investigation of the evolution with carrier concentration of these separated features, important for the understanding why superconductivity in the cuprates emerges and vanishes with doping, has been commenced earlier [7, 8]. However, so far the appearance of two energy scales could not be explained.

This chapter starts with a consistency check of the spectra measured here with the data from the mentioned references. Subsequently the doping dependence of the peak energies and trends of the spectra are reinvestigated, which leads to a substantiation of the scaling behaviour of the gap magnitude and its momentum dependence deduced from $B_{2g}$ data.

Yet the study of the behaviour in $B_{1g}$ symmetry profits most notably from the addition of data and a renewed investigation, since the general trends with doping have so far been concealed due to large variations between individual samples. In contrast to the earlier research, where the focus was placed on the peak energy and low-frequency behaviour, here the evolution of the intensity of the $B_{1g}$ feature will be emphasised. This provides a deeper insight as to its possible origin. Depending on whether or not the peak observed in $B_{1g}$ symmetry is indeed linked to the second energy scale obtained from other experiments, this result could be of crucial importance to the understanding of the two energy scales in general.
5. Results and Discussion

5.2.1 Doping dependence of the Raman spectra

In Fig. 5.13 the long frequency range Raman spectra of the new samples at both $T \approx 10 - 20\,\text{K}$ and just above $T_c$ are plotted for the $B_{1g}$ and the $B_{2g}$ channel, which probe the antinodal and nodal region near the Fermi surface, respectively. The temperatures are those of the illuminated spot. Since at low temperatures the Antistokes intensity is too small to deduce $T$ from the principle of detailed balance (Eq. 4.3), the laser heating is taken to be constant at all temperatures. The Raman response $R\chi''(\Omega)$, measured in counts per second and milliwatt absorbed laser power, is divided by the Bose-factor (see Eq. 4.2) and thus directly proportional to the imaginary part of the Raman susceptibility $\chi_{\gamma\gamma}$. Since the possibility of resonance effects has been ruled out for the Bi-2212 material [7], the laser line at 458 nm was used for excitation in all measurements.

The spectra measured in the superconducting state show a suppression of spectral weight at low frequencies, followed by a pile-up. At higher frequencies $\Omega >> 2\Delta_0$, the energy gap obviously does not influence the quasiparticle excitations anymore. The theoretical predictions plotted in Fig. 4.4 fail to describe the spectra at these frequencies, since they neglect the strong interactions. These originate from the large self energy of the electrons which gives rise to the high energy spectrum. In the normal state, variations of the quasiparticle excitations with temperature occur predominantly in the low frequency range, too. The changes there can be partly associated with the evolution of the effective scattering rate of the quasiparticles $\Gamma''(\Omega, T)$, which is proportional to the inverse of the Raman slope for $\Omega \rightarrow 0$ if other effects are neglected. In the range between 800 and 1000 cm$^{-1}$ the quasiparticle response is practically temperature independent, so that the spectra at 10–20 K indeed merge with the spectra at $\approx 100$ K.

We compare the Raman spectra up to 1000 cm$^{-1}$ with those of the sample collection at hand in Fig. 5.14 and Fig. 5.15, which show the $B_{2g}$ and $B_{1g}$ channel, respectively. The samples are ordered by their carrier concentrations, which have been deduced from the transition temperature using the phenomenological $T_c(p)$-dependence given in Eq. 2.1. The samples that were measured during this work are marked with an asterisk.

The total intensity at high frequencies in $B_{2g}$ symmetry seems to depend in the first place on the sample quality: for samples with similar doping levels the intensities differ by 40 – 60%. In the second place, a decrease with increasing carrier concentration can be observed. In $B_{1g}$ symmetry the total scattering does not show a general trend with doping except for the strong suppression of the far underdoped sample Bi-UD57, which is ascribed
Figure 5.13: Raman response $R\chi''(\Omega, T)$ (raw data) of the new samples in normal and superconducting state in $B_{1g}$ (left hand side) and $B_{2g}$ (right hand side) symmetries. The insets show the selected polarisations of incoming and outgoing light with respect to the CuO$_2$ plane and the corresponding sensitivity in the Brillouin zone. A magnification of the low-energy part of the spectrum is given in Figs. 5.14 and 5.15.
5. Results and Discussion

Figure 5.14: Raman response $R\chi''(\Omega, T)$ (raw data) for Bi$_2$Sr$_2$(Ca$_{1-x}$Y$_x$)Cu$_2$O$_{8+\delta}$ in $B_{2g}$ symmetry in the normal and superconducting states. The samples are sorted from overdoped (OD, upper panel on the left) to underdoped (UD, bottom panel on the right) and are primarily characterised by their transition temperature. The manufacturer and the doping level $p$ are also indicated. New data are marked by an asterisk, the other data are from [7] and [8]. The arrows show the amplitude $A_{sc}$ and the position $\Omega_{peak}$ of the superconductivity-induced peak.
5.2. Raman studies on superconducting Bi-2212

Figure 5.15: Raman response $R_\chi''(\Omega, T)$ (raw data) for $Bi_2Sr_2(Cu_{1-x}Y_x)Cu_2O_{8+\delta}$ in $B_{1g}$ symmetry in the normal and superconducting states. New data are marked by an asterisk, the other data are from [7] and [8]. The arrows show the amplitude $A_{sc}$ of the superconductivity-induced peak while the dashed lines mark the merging energies $\Omega_{\text{merge}}$. 
to the loss of coherence near the antinodal points in the pseudogap region, observed in many experiments. The intensity variations for the remaining doping levels depend on the sample preparation specifics, in the same qualitative manner as in $B_{2g}$ symmetry. The scattering strength of the two samples made by A. Damascelli is for instance about $37\%$ lower than the total scattering of the samples prepared by B. Revaz. Since the overall scattering cross-section does not depend uniquely on doping but rather on the individual sample, the spectra will in the detailed analysis in the following sections be normalised to 1 at energies between 800 and 1000 cm$^{-1}$.

The energies at which the superconducting and normal state merge are in both figures marked by a dashed line. They have been determined very accurately by plotting the difference on a logscale. It appears that the merging energy, within some deviation, scales with $T_c$ in both symmetries. This notable result will become more apparent in the next section.

In $B_{2g}$ symmetry the frequencies of the superconductivity-induced peaks, which are marked by the position of the arrows in the spectra, decrease steadily with both over- and underdoping. The amplitudes, marked by the length of the arrows, vary mostly with the total scattering cross section – the overall lineshape of the superconducting spectra remains constant.

As in $B_{2g}$ symmetry, the peak positions measured in the $B_{1g}$ channel decrease when moving from optimal to overdoping, but this time the decrease is not as steady: the peak energy of Bi-OPT96 is for instance approximately 25% higher than that of Bi-OPT94, while the transition temperature hardly changes. As a general trend, the energy does not scale with $T_c$ but rather decreases more strongly with increasing carrier concentration. This becomes obvious when comparing the peak energies at optimal and overdoping in the two symmetries. Though for optimal doping they are about 40% higher in $B_{1g}$ symmetry, the difference has practically vanished for $p \approx 0.23$.

For the underdoped sample Bi-UD57 the super- and normalconducting state-spectra coincide. This is a generic feature of cuprates with carrier concentrations lower than $p \sim 0.13$, which occurs in the same doping range as the suppression of the normal state spectra [59]. A striking trend in the evolution of the $B_{1g}$ spectra is the increase of the amplitude with overdoping. Like the energies, the amplitude is subdued to sample dependent variations.

The figures so far showed the raw data with phonons superimposed on the electronic
5.2. Raman studies on superconducting Bi-2212 background. For the detailed comparison of the superconductivity-induced features it is necessary to separate the electronic contribution from the phononic part. Since the bandwidths of the phonons are usually much smaller than that of the electron-hole continuum, the contribution of the vibrational excitations can be isolated by subtracting a smooth “background” from the response averaged over all temperatures (see, e.g. [60]). In the superconducting state the subtraction of the isolated contribution sometimes leads to peculiarities which are due to a renormalisation of the phonons.

\[ B_{2g} \text{ symmetry} \]

Since the peak energies in \( B_{2g} \) symmetry appear to scale with the transition temperature, the energy axis of each sample is normalised to the respective \( T_c \) before the spectra are plotted in one figure. As a result, the normalised spectra \( \chi''_0\left(\hbar\Omega/(k_B T_c)\right) \) in the superconducting state collapse on a universal curve (Fig. 5.16, panel (b)). The same holds true for the YBCO samples studied in the underdoped range [7, 61], shown in panel (a) of the figure. The hatched area around \( \hbar\Omega/(k_B T_c) \approx 12 \) indicates the range in which the normal and superconducting spectra merge.

The spectra can be described by the theory based on the Maki-Tsuneto function for a \( d_{x^2-y^2} \) wave superconductor (see chapter 4). Using the parameters for the bandstructure from Eq. 4.11 and a gap magnitude

\[ 2\Delta_0 = 9.0 \pm 0.5 \ k_B T_c, \quad (5.2) \]

the dashed curve in the figure is created. The gap magnitude lies well above the weak coupling value \( 4.2 \ k_B T_c \) for \( d \)-wave pairing and indicates strong coupling. Since the average gap in the projected nodal region is smaller than the gap amplitude, the peak maximum lies at approximately \( 1.3 \Delta_0 \). The sample-dependent impurity effects clearly do not influence the spectra much, even though according to Fig. 4.4 the peak position does shift upwards in frequency for higher impurity levels.

The universal linear increase of the spectra at low energies is a characteristic feature of a \( d_{x^2-y^2} \)-wave superconductor. Since the shape of the spectra depends uniquely on the order parameter symmetry [51], the general consensus that the momentum dependence of the gap is invariant in the entire superconducting region, and that there is no mixing with a more anisotropic symmetry, is affirmed.
Figure 5.16: Normalised electronic Raman response $\chi''_0$ of Y-123 (a) and Bi-2212 (b) in $B_{2g}$ symmetry. The energy axes are normalised to the individual transition temperatures. All superconducting spectra merge with the normal-state response in the shaded range.
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Figure 5.17: (a) Electronic Raman response $R\chi''(\Omega)$ of Bi-2212 in $B_{1g}$ symmetry. In (b) the average intensities between 800 and 1000 cm$^{-1}$ are set to unity and the energy axes are normalised to the individual transition temperatures. All superconducting spectra merge with the normal-state response in the shaded range. The dashed curve represents the theoretical prediction on the basis of Eq. 4.16.

$B_{1g}$ symmetry

The superconducting spectra in $B_{1g}$ symmetry are compiled in Fig. 5.17. Whereas in panel (a) merely the phononic contribution is removed, in panel (b) additionally the height of the spectra is adjusted and the energy shifts are normalised to the respective transition temperatures, along the lines of the $B_{2g}$ procedure. The sample Bi-UD57 is not included in the normalised plot since the phononic contribution, which could not be removed properly, conceals the electronic behaviour.

Both the raw and adjusted spectra demonstrate a dramatic increase of the peak intensities. However, the strong individual variations remain also after normalisation. For instance, Bi-OD87 violates the general trend by having a smaller amplitude and energy than Bi-OD78. Bi-OD94 on the other hand shows a much higher intensity than the other optimally doped samples.

The theoretical prediction for the $B_{1g}$ response, made with the same gap magnitude and parameters as in $B_{2g}$ symmetry, is also shown along with the normalised spectra. The agreement is reasonable for two of the optimally doped samples and for the slightly underdoped sample. The overdoped spectra however carry extra weight. Obviously, the doping dependence of the $d$-wave gap cannot be changed without affecting the $B_{2g}$ spectra. Thus the effect must be strongly peaked around $(\pi, 0)$. An explanation in terms of a resonance can be dismissed forthwith, since this possibility has been excluded in the past [7].
At this point it is worth referring to an earlier investigation of the detailed temperature dependence of the $B_{1g}$ peak [7] for Bi-OD78 and Bi-OD56. It was found that the weight of the peak is reduced very steadily with increasing temperature until it merges with the normal state spectrum at $T_c$, yet surprisingly the peak position decreases only weakly, as opposed to the expectations for a BCS-like $d$-wave superconducting gap.

5.2.2 Energy scales

The observations made with regard to the energy scales are summarised in Fig. 5.18, panel (a), which shows a plot of the peak positions and the positions at which the superconducting spectra merge with the normal state spectra versus the doping level. The peak positions in $B_{1g}$ symmetry clearly do not scale with $T_c$. In contrast to popular belief these peak positions actually lie under the energy scale for the gap amplitude $2\Delta_0$ that follows from $B_{2g}$. Thus the comparison of the energy scales measured by various experimental techniques, that was introduced in Fig. 2.8 on page 18, actually gives a false picture of the energy scale measured in the $B_{2g}$ channel in Raman spectroscopy. Noteworthy in Fig. 5.18 is that the $B_{1g}$ peak energy for one of the far overdoped samples lies not only below $2\Delta_0$ but even below the $B_{2g}$ peak position. On the underdoped side the question rises whether or not the peak energy exceeds $2\Delta_0$ between $p = 0.16$ and the carrier concentration at which the superconducting feature disappears, $p \sim 0.13$. Here, the data are still inconclusive.

In spite of the large scatter of the individual peak frequencies, a linear fit to the $B_{1g}$ data has been employed so far [7] and based on the new data still seems adequate. The fit corresponds to the function

$$\Omega_{\text{peak}}^{B_{1g}}(p) = 1294 \text{ cm}^{-1} \cdot (0.275 - p).$$

(5.3)

Though with overdoping the intensity of the peak deviates more and more from the expected value, the peak energy extrapolates to zero close to $p_{\text{sc}}$ where superconductivity is expected to disappear [23].

In panel (b) of Fig. 5.18 the peak energies normalised to the individual $T_c$s are shown. The average $B_{2g}$ peak energy

$$\hbar \Omega_{\text{peak}}^{B_{2g}} = 5.73 \pm 0.15 \ k_B T_c$$

(5.4)
5.2. Raman studies on superconducting Bi-2212

Figure 5.18: (a) Peak energies $\Omega_{\text{peak}}(p)$ of the superconductivity-induced features and energies $\Omega_{\text{merge}}(p)$ at which the normal and superconducting spectra merge for the materials Y-123 (full symbols) and Bi-2212 (open symbols) in $B_{1g}$ (diamonds) and $B_{2g}$ (squares) symmetry. The dashed parabola represents the peak energy from the theoretical fit of the $B_{2g}$ spectra; the solid parabola reflects the corresponding theoretical prediction for the $B_{1g}$ peak energy, which would be equivalent to the gap amplitude $2\Delta_0$. A linear fit of the real $B_{1g}$ peak energies is included. (b) Peak energies normalised to the respective transition temperatures. The dotted line represents a constant fit of $h\Omega_{\text{peak}}^{B_{2g}}/k_B T_c$. 

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shows the largest deviations for carrier concentrations far away from the optimum. Since
the energies are assumed to be directly related to the transition temperature, an inaccuracy
of the phenomenological \( T_c(p) \) dependence cannot be responsible for this. Rather, increased
impurity levels and unevenly distributed carrier concentrations play a role. A minor role
may be reserved for the temperature dependence of the gap magnitude, given the increased
\( T/T_c \) ratio.

No specific correlation can be found between the normalised \( B_{1g} \) peak energies and
the carrier concentration. A transmission of the linear fit to the normalised energy axis
however demonstrates that the energies extrapolate to values below the average \( B_{2g} \) energy.

5.2.3 The amplitude

Obviously, the anomalous intensity evolution of the \( B_{1g} \) peak should give a further in-
dication as to its origin. In Fig. 5.19 on the following page the amplitude \( A_{sc}(p) \) of the
difference between the superconductivity-induced peak and the normal state, as indicated
by the arrows in Fig. 5.15, is plotted as a function of doping. The figure is completed by
the addition of the amplitudes in \( B_{2g} \) symmetry.

Since the normalised spectra in \( B_{2g} \) symmetry all collapse on top of each other, the
deviations of the average amplitude in this symmetry, \( A_{B_{2g}}^{sc}(p) = 1.18 \pm 0.11 \), arise foremost
from the variations of the total scattering cross section.

In \( B_{1g} \) symmetry the difference with respect to the normal state vanishes completely
for those samples which have \( p \leq 0.10 \). For the samples with \( p \geq 0.15 \) the observed
ascent of the amplitude might be partly explained by the coherence gain when leaving
the pseudogap regime. An extrapolation from higher doping levels can be employed to
give the doping at which the amplitude vanishes, \( p \sim 0.12 - 0.14 \). However, the seemingly
diverging amplitude for \( p > 0.18 \) cannot be ascribed to the regaining of the coherence. A
plot of the inverse of the amplitudes in the lower panel of Fig. 5.19 confirms the tendency
of the amplitude to diverge when nearing the onset point of superconductivity in the
overdoped regime, as can be seen from the linear fit

\[
[A_{sc}(p)]^{-1} = (-2.77 \pm 0.81) \cdot [(0.264 \pm 0.023) - p].
\]

This is a remarkable result, since it concerns true amplitudes, which are uncorrected for
the individual scattering cross sections and represent the induced change with respect to
5.2. Raman studies on superconducting Bi-2212

Figure 5.19: Panel (a): doping dependence of the amplitudes $A_{sc}(p)$ of the superconductivity-induced features in $B_{1g}$ and $B_{2g}$ symmetry for both Y-123 and Bi-2212. Panel (b): inverse of the $B_{1g}$ amplitudes of Bi-2212. The straight line is a linear fit to the data.
5. Results and Discussion

Figure 5.20: Spectral weight of the superconductivity-induced feature with respect to the normal state in $B_{1g}$ symmetry. The triangles pointing downward symbolise the lost spectral weight up to the point where the normal and sc spectra cross, whereas the triangles pointing upward symbolise the pile-up between the crossing and merging point. Different shades enable a direct comparison of the suppression and pile-up for individual samples, if samples have similar doping levels. The line is a guide to the eye.

the normal state. Yet there is no conservation law for light scattering, such as the $f$-sum rules for the conductivity, so a divergence is in theory well possible.

For the sake of completeness, the total spectral weight of the superconductivity-induced feature is plotted in Fig. 5.20. The missing spectral weight up to the point where the superconducting spectra cross with the normal state spectra and the pile-up of spectral weight from the crossing point to the merging point are plotted individually as well. As can be seen, the divergence of the amplitude is not reflected in the spectral weight. The suppression due to the energy gap at low frequencies seems to be constant except for low doping levels, where it extrapolates to zero (clarified by the guide to the eye), affirming the notion that the increase of $A_{sc}$ at the other doping levels cannot be explained in terms of coherence changes.

5.2.4 $B_{1g}$ as a superposition of the pair-breaking peak and a collective mode

Given the variation of $\Omega_{\text{peak}}^{B_{1g}}(p)/kBT_c$ by a factor of two as well as the tendency of $A_{sc}^{B_{1g}}$ to diverge – and that without affecting the $B_{2g}$ spectrum - it can be concluded that
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Figure 5.21: Raman response $\chi''_{B1g}$ as a function of normalised energy after subtraction of the doping-independent pair-breaking peak.

The feature is not compatible with a mere pair-breaking response. However, it is linked to the opening of the gap in several ways. First, Fig. 5.18 shows that the normal and superconducting spectra merge in the same range for both symmetries. In addition, when we look at Fig. 5.17 again, the doping-independent pair-breaking prediction forms the lower envelope to the spectra in the low frequency range. Past their maximum amplitude, the spectra meet again on an upper envelope which merges with the spectrum that is calculated in the collisionless limit, just before this description loses its applicability. These envelopes hence also corroborate the invariant shape of the gap $\Delta_k$: even if the $B_{1g}$ peaks move substantially with strong individual variations, the spectral range modified by superconducting correlations is determined only by $T_c$.

The appearance of envelopes in Fig. 5.17 and the fact that the spectra for samples with $p > 0.15$ are all higher than the predicted pair-breaking peak are reasons to suspect a doping-dependent collective mode from being superimposed on the pair-breaking peak. Though an interrelation with the pair-breaking excitations may generally not be excluded, the remarkable gaussian shape after subtraction of the doping-independent pair-breaking peak, as shown in Fig. 5.21, does invite for a separate analysis. The upper envelope becomes even more obvious in this figure. For overdoped samples, the maximum of the gaussian distribution is tilted slightly towards lower energies, while for underdoped samples it tends towards higher energies.
5. Results and Discussion

Figure 5.22: Spectral weight of \( \chi''^{B_{1g}}_0 \) after subtraction of the doping-independent pair-breaking peak, in panel (a) as a function of the position of the maximum after subtraction and in panel (b) as a function of doping. The red line in panel a) is a linear fit to the data; the vertical line marks the position of 2\( \Delta_0 \).

The separate examination of the superimposed mode can be expanded by plotting the areas under the nearly gaussian distributions versus the peak positions and versus the doping level, respectively, as shown in Fig. 5.22. Concordantly with the observations described in the former sections, the spectral weights show considerable sample-dependent variations when plotted against the doping level. However, when plotted against the energy, there are only minor deviations from a linear dependence. Thus the intensity of the mode is directly correlated with its energy. In this picture, remembering that \( \Omega_{B_{1g}}^{\text{peak}} \) extrapolates to approximately 4\( k_B T_c \) (see Fig. 5.18, panel (b)), the amplitude does not diverge.

Since the mode, when considered separately, disappears for \( p \leq 0.15 \), it is hard to predict the behaviour in the underdoped regime.

5.2.5 Discussion

How can the simultaneous increase of amplitude and split-off below 2\( \Delta_0 \) at the approach of \( p_{sc2} \) be explained? Here some possible explanations are discussed.

Recently, Chubukov et al. [62] argued that Raman scattering in \( B_{1g} \) symmetry allows one to distinguish between phonon-mediated and spin-mediated \( d \)-wave superconductivity, because in the latter case a resonance develops at a frequency \( \Omega_{\text{res}} < 2\Delta_0 \). This resonance has energy and intensity variations similar to those observed here, with a simultaneous increase of both amplitude and split-off below 2\( \Delta_0 \). However, since the origin of a spin-
fluctuation induced mode is antiferromagnetic, this split-off would occur for decreasing doping instead of increasing doping.

Alternatively, a band with a smaller gap could start cutting into the Fermi surface above optimal doping. This idea springs from the observation of hole- and electron-like bands with different gaps in self-doped Ba$_2$Ca$_3$Cu$_4$O$_8$F$_2$ [63]. However, a second Fermi surface sheet was never observed in, e.g., overdoped Tl$_2$Ba$_2$CuO$_6$+$\delta$ (Tl-2201) [64], though the $B_{1g}$ peak position of this compound has the same doping dependence as the compounds investigated in this work [16]. The Fermi surface of Tl-2201 consists of one large hole pocket encircling $(\pi,\pi)$ very similar to the one in Bi-2212 if the double layer splitting is disregarded. Additionally, the quite complicated multi-sheeted Fermi surface of Y-123 [20] seems to have only little influence on the spectra in the superconducting state, as far as the covered doping range reaches. Hence, there is no evidence either that the effects described here originate from the Fermi surface or the band structure.

Since these more traditional possibilities fail to provide a qualitatively correct description, a new scenario is explored, which rests on the observation that the unconventional evolution with doping of the $B_{1g}$ intensity is compatible with the behaviour of a Goldstone mode appearing (without necessarily being Raman active) when a symmetry is broken. The emergence of new collective modes is a key experimental manifestation of a higher symmetry. The SO(5) model for the cuprates [65], which unifies the antiferromagnetic and superconducting state, provides such a higher symmetry and thus naturally predicts a new class of symmetry generators, called the $\pi$ resonance. This resonance becomes a pronounced feature in the spin dispersion above the transition to superconductivity in the far underdoped regime $p > p_{sc1}$. Along with the diverging intensity, the energy of the mode is predicted to vanish in the case of a second order transition. The phenomenology of the $\pi$ resonance can also be applied to other doping levels and thus it can be used to explain the observations [59].

In this scenario the $B_{1g}$ spectrum is a superposition of the weak coupling pair-breaking feature and an additional mode, originating from a broken symmetry. The latter one depends both on doping and on details of the sample while the first scales with $T_c$. There are two possibilities why the new mode is only seen in the superconducting state. First, the excitation is overdamped in the normal state due to strong electron-electron interactions. Below $T_c$ the spectrum is gaped and the damping is reduced. Secondly, the mode is not only peaked in energy but also in k-space at a momentum $Q$. Then, due to the $q = 0$ selection rule in Raman scattering it becomes activated only below $T_c$ by the appearance
of Cooper pairs which carry away two momenta $\mathbf{Q}$ and $-\mathbf{Q}$. For the very same reason pair-breaking features can be observed by Raman scattering in the clean limit, where the normal state response vanishes.

The microscopic origin of the symmetry breaking remains open. However, because of the selection rules in Raman scattering, some of the possibilities can be excluded [59]. For example, a spin-density modulation with $\mathbf{Q} = (\pi, \pi)$ would not appear in $B_{1g}$ symmetry [66]. Others, such as charge instabilities with the modulation along the principle axes and $\mathbf{Q} = (0, 0.2\pi/a)$ are compatible [67, 68].
5.2. Raman studies on superconducting Bi-2212
Chapter 6

Summary

This work is devoted to the study of hole-doped copper-oxide superconductors at low and intermediate doping levels by inelastic scattering of light. In order to get well-defined samples close to the onset point of superconductivity at $p_{sc1} \approx 0.05$ holes/CuO$_2$, a preparation project was started as a part of this thesis.

YBa$_2$Cu$_3$O$_x$ (YBCO) prepared in BaZrO$_3$ crucibles is the bed material for homogeneous samples. For optimal results a single crystal is co-annealed and equilibrated with a large piece of ceramic material. The oxygen content can then be determined very precisely either by measuring the weight change or by thermogravimetric analysis of the large pellet (typically 1 g) rather than of the small crystal (10 mg). So far, the adjustment of the oxygen content by quenching on copper in ambient atmosphere and quenching under the protection of technical liquid nitrogen both proved unsuccessful due to oxygen in-diffusion.

As part of the preparation project, two detwinned YBCO single crystals were annealed in a conventional way to set the oxygen concentration to $x = 6.33$, corresponding to a doping level of approximately $p_{sc1}$. They did not show bulk superconductivity above 6 K.

The second part of this work describes an inelastic light scattering study of pair-breaking excitations in superconducting cuprates. New optimally and slightly overdoped Bi$_2$Sr$_2$(Ca$_{1-y}$Y$_y$)Cu$_2$O$_{8+\delta}$ (Bi-2212) samples have been investigated as a function of polarisation and temperature. Crossed polarisation directions of incoming and outgoing light were employed to separately access the nodal ($\pi/2$, $\pi/2$) and antinodal ($\pi$, 0) region of the Brillouin zone. The results are analysed along with previously measured data of Bi-2212 and Y-123 samples in the doping range $0.07 \leq p \leq 0.23$. 

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In $B_{2g}$ symmetry, which corresponds to the nodal direction, the spectra altogether scale with the transition temperature. Their shape is consistent with the pair-breaking Raman response predicted for a $d_{x^2−y^2}$-wave superconductor.

In $B_{1g}$ symmetry, which projects out the antinodal direction, only the Raman response of the slightly underdoped sample with $p = 0.15$ coincides with the expected spectrum. For the samples with doping levels below $p = 0.10$ any superconductivity-induced feature is absent. The suppression of the feature occurs in the same doping range as the loss of coherence close to the antinodal points observed in other experiments.

For all overdoped samples the peak energies of the $B_{1g}$ maxima are smaller than $2\Delta_0$. Approaching $p = 0.26 \pm 0.03$ the amplitude of the peak blows up. Given the invariance of the momentum dependence of $\Delta(k)$ and of the gap ratio of $\Delta_0/(k_B T_c)$ on the one hand and, on the other hand, the variation of the peak energy ratio $\Omega_{\text{peak}}^{B_{1g}}/(k_B T_c)$ by a factor of two and the tendency of the amplitude to diverge, the traditional interpretation of the spectra in terms of pair breaking alone must be abandoned.

Interpretations based on a spin-fluctuation induced mode or a change of the Fermi surface topology are excluded. Instead, it is proposed that the $B_{1g}$ spectrum is a superposition of the pair-breaking feature and an additional mode which originates from a broken symmetry and appears at the onset point of superconductivity on the overdoped side. Since there is no influence on the $B_{2g}$ spectra, the mode must be strongly peaked around the antinodal point.

The spectral shape of the additional mode is close to a gaussian distribution superimposed on the $d$-wave pair-breaking feature. The excitation is either activated by the opening of a gap or by the appearance of Cooper pairs which carry away opposite momenta, so that the $\mathbf{q} = 0$ selection rule in Raman scattering can be eluded. The microscopic origin of the symmetry breaking mode remains open.
Zusammenfassung

Diese Arbeit beschreibt die inelastische Lichtstreuung an Kuperoxid-Supraleitern mit niedriger und mittlerer Lochdotierung. Um wohldefinierte Proben mit einer Dotierung nahe am Einsatzpunkt der Supraleitung bei \( p_{\text{sc1}} \approx 0.05 \) Löcher/CuO\(_2\) zu erhalten, wurde zudem ein Projekt zur Vorbehandlung der Proben angefangen.

\( \text{YBa}_2\text{Cu}_3\text{O}_x \) (YBCO), hergestellt in BaZrO\(_3\)-Tiegeln, dient als Arbeitsgrundlage für die Herstellung homogener Proben. Um optimale Resultate zu erreichen wird ein Einkristall zusammen mit einem großen Stück keramischen Materials abgeschreckt und ausbalanciert. Der Sauerstoffgehalt kann dann sehr präzise über die Messung der Massendifferenz oder mittels einer thermogravimetrischen Analyse des großen Pellets (typischerweise etwa 1 g) anstelle des kleinen Kristalls (etwa 10 mg) bestimmt werden. Bisher stellte sich die Justierung des Sauerstoffgehalts sowohl bei der Abschreckung auf Kupfer unter Raumbedingungen als auch unter Schutzatmosphäre in flüssigem Stickstoff als nicht erfolgreich heraus, da Sauerstoff in die Proben hereindiffundierte.

Als Teil der Probenvorbereitung wurden zwei entzwillingte YBCO-Einkristalle in der herkömmlichen Art und Weise wärmebehandelt um die Sauerstoffkonzentration \( x = 6.33 \) zu erreichen, was einer Dotierung von etwa \( p_{\text{sc1}} \) entspricht. Die Proben zeigten keine Supraleitung im Hauptvolumen oberhalb von 6 K.

Der zweite Teil dieser Arbeit beschreibt die Studie von paarbrechenden Anregungen mit Hilfe von inelastischer Lichtstreuung in supraleitenden Kupraten. Neue optimal und leicht überdotierte Bi\(_2\)Sr\(_2\)(Ca\(_{1-y}\)Y\(_y\))Cu\(_2\)O\(_{8+\delta}\) (Bi-2212) Proben wurden in Abhängigkeit der Polarisation und der Temperatur untersucht. Gekreuzte Polarisationsrichtungen des einfallenden und ausgehenden Lichts wurden genutzt um die Bereiche der Brillouinzone nahe den Knoten (Noden) der Energielücke (\( \pi/2 \), \( \pi/2 \)) und die Bereiche nahe den 'Antinoden' (\( \pi \), 0) zu untersuchen. Die Resultate werden zusammen mit früher gemessenen Daten von Bi-2212- und Y-123-Proben mit Dotierungen im Bereich 0.07 \( \leq p \leq 0.23 \) analysiert.
6.0.

In der $B_{2g}$-Symmetrie, die der Richtung der Knoten entspricht, skalieren die Spektren gänzlich mit der Übergangstemperatur. Ihre Form ist konsistent mit der paarbrechenden Raman-Response, die für einen $d_{x^2-y^2}$-Wellen Supraleiter vorausgesagt wird.

In der antinodischen Richtung der $B_{1g}$-Symmetrie entspricht nur die Response der leicht unterdotierten Proben mit $p = 0.15$ dem erwarteten Spektrum. Proben mit Dotierungen unterhalb von $p = 0.10$ zeigen keinerlei durch die Supraleitung induzierten Erscheinungen. Die Unterdrückung dieser Features fällt in den gleichen Dotierungsbereich wie der Verlust der Kohärenz in der Nähe des antinodischen Punktes, wie er in anderen Experimenten beobachtet wurde.

Bei allen überdotierten Proben sind die Peakenergien der $B_{1g}$-Maxima kleiner als $2\Delta_0$. Mit zunehmender Nähe zu $p = 0.26 \pm 0.03$ vergrößert sich die Amplitude der Peaks stark. Betrachtet man die Invarianz der Impulsabhängigkeit von $\Delta(k)$ und des Lückenverhältnisses von $\Delta_0/(k_B T_c)$ auf der einen Seite und die Variation des Peakenergiequotienten $\Omega_{\text{peak}}^{B_{1g}}/(k_B T_c)$ um einen Faktor zwei sowie die Neigung der Amplitude zur Divergenz auf der anderen Seite, so muss die traditionelle Interpretation der Spektren, die alleinig auf der Paarbrechung basiert, aufgegeben werden.

Interpretationen die auf durch Spinfluktuationen induzierten Moden oder der Änderung der Topologie der Fermifläche beruhen, werden ausgeschlossen. Anstelligdessen wird eine Interpretation vorgeschlagen, die das $B_{1g}$-Spektrum als Superposition von paarbrechenden Merkmalen und einer zusätzlichen Mode, die aus einer gebrochenen Symmetrie am Sprungpunkt der Supraleitung entsteht, ansieht. Da kein Einfluss auf die $B_{2g}$-Spektren zu beobachten ist, muss die Mode stark um den antinodischen Peak zentriert sein.

Die spektrale Form der zusätzlichen Mode ist eine Gaußverteilung ähnlich, die einem $d$-Wellen Paarbrechungspeak überlagert ist. Die Anregung wird entweder durch das Öffnen der Lücke oder durch das Erscheinen von Cooperpaaren, die das Umgehen der $q = 0$-Auswahlregel der Ramanstreuung mittels der entgegengesetzten Impulse der Quasiteilchen ermöglichen, aktiviert. Der mikroskopische Ursprung der Symmetriebrechung bleibt ungeklärt.
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