# Electronic and Phononic Raman Scattering in Twin-Free $YBa_2Cu_3O_{6+x}$

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# Deutsche Zusammenfassung

Bald jährt sich die Entdeckung der Hochtemperatur-Supraleitung Supraleitung zum 25. Mal. Seither wurden viele Experimente durchgeführt und viele Versuche unternommen, den supraleitenden Paarungsmechanismus zu erklären. Allerdings sind viele Hindernisse wegen der ungewöhnlichen Normalzustandseigenschaften der Kuprate aufgetaucht. Eine der größten Herausforderungen ist das Pseudogap, welches im unterdotierten Bereich unterhalb einer dotierungsabhängigen Temperatur T<sup>\*</sup>, welche die supraleitende Sprungtemperatur T<sub>c</sub> übersteigt, beobachtet wird. Bis jetzt sind der Paarungsmechanismus der Hochtemperatur-Supraleitung und der Ursprung des Pseudogaps kontrovers; um diese Phänomene zu erklären sind daher mehr Experimente an diesen Materialien nötig.

Kuprat-Supraleiter sind Schichtsysteme. Die einzigen gemeinsame Lagen in allen Kupraten sind Ebenen der chemischen Zusammensetzung CuO<sub>2</sub>, bestehend aus quadratischen Kupfer-Sauerstoff Plaketten. Diese Schichten können daher als das strukturelle Element identifiziert werden, welches die supraleitenden Cooper-Paare beinhaltet. Es ist im Moment allgemein akzeptiert, dass die Cooper-Paar Wellenfunktion der Hochtemperatur Supraleiter hauptsächlich  $d_{x^2-y^2}$ -Wellen Symmetrie besitzt. In Verbindungen, in welchen die CuO<sub>2</sub>-Ebenen orthorhombisch verzerrt sind, inklusive dem weitestgehend untersuchten  $YBa_2Cu_3O_{6+x}$ , erwartet man eine s-Wellen Beimischung zur führenden d-Wellen Paarung. Diese führt zu einer Anisotropie der supraleitenden Energielücke  $2\Delta$  zwischen der *a*- und *b*-Achse. In den letzten Jahrzehnten wurden die meisten Experimente an verzwillingten  $YBa_2Cu_3O_{6+x}$ Proben durchgeführt, die aus kristallographischen "Twins" zusammengesetzt sind, bei denen die a- und b-Hauptachsen in den Ebenen jeweils vertauscht sind. Daher ist dieser *ab*-Unterschied in der supraleitenden Energielücke im verzwillingten  $YBa_2Cu_3O_{6+x}$  schwer zu beobachten. Auf der anderen Seite kann im unverzwillingten  $YBa_2Cu_3O_{6+x}$ -Kristall, die *ab*-Anisotropie inklusive die der supraleitenden Energielücke, erforscht werden.

Wegen Problemen mit der Oberfläche ist allerdings eine genaue Bestimmung der  $2\Delta$ -Lücke von YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> mit Hilfe winkelaufgelöster Photoemissions-Spektroskopie

(ARPES) schwierig. Raman-Streuung ist ein leistungsstarkes, viel weniger oberflächensensibles Instrument, um die *ab*-Anisotropie in der  $2\Delta$ -Lücke und damit den *s*-Wellenbeitrag zur d-Wellenpaarung zu messen. Im ersten Teil der Arbeit haben wir unverzwillingte, leicht überdotierte YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub> ( $T_c=92$  K) und moderat überdotierte  $Y_{0.85}Ca_{0.15}Ba_2Cu_3O_{6.95}$  (T<sub>c</sub>=75 K) Einkristalle mit Hilfe der Raman-Lichtreuungstechnik untersucht. In Raman-Streuexperimenten mit polarisiertem Licht sind die Anregungen  $A_g + B_{1g}$ ,  $A_g + B_{2g}$ ,  $B_{1g}$ , und  $B_{2g}$  zugänglich indem man jeweils xx (bzw. yy), x'x' (bzw. y'y'), x'y' (bzw. y'x') und xy (bzw. yx) polarisierte einfallende und gestreute Lichtfelder benutzt. Hierbei bedeuten x und y die Richtung des elektrischen Feldes vom Licht entlang der a- und b-Achsen, wohingegen x'und y' die diagonalen Richtungen bezeichnen. Weil das Ziel der Arbeit darin besteht, die s-Wellenkomponente zum fhrenden d-Wellen Ordnungsparameters zu bestimmen, fokussieren wir unsere Raman-Studie auf die xx, yy, und x'y' Polarisationsgeometrien. In beiden Proben wurden Modifikationen in den elektronischen Paarbrechungs-Peaks beobachtet, wenn die a- und b-Achse miteinander vertauscht wurde. Zusätzlich besitzen die Linienformen von einigen Moden, einschlielich Eben- und Sauerstoff-Schwingungen, starke Ansiotropien bezüglich der Konfigurationen von einfallenden und gestreuten Lichtfeldern. Diese Moden zeigen eine ausgeprägte asymmetrische Linienform (d.h. ein Fano-Profil), die eine starke Wechselwirkung mit dem elektronischen Kontinuum nahelegt. In dieser Arbeit werden die Raman-Spektren auf zwei verschiedene Weisen analysiert. Zunächst haben wir den konventionellen Fano-Zugang benutzt, mit ihm erhält man Abschätzungen der intrinsischen Phononen-Parameter (d.h. Phononenfrequenzen, Linienbreiten und Asymmetrie-Parameter). Zweitens haben wir ein theoretisches Modell, basierend auf dem Fano-Effekt, entwickelt, um sowohl elektronische als auch phononische Beiträge zum Raman-Spektrum gleichberechtigt zu behandeln. Unsere Theorie erlaubt uns, das elektronische Raman-Signal vom phononischen Teil zu entflechten und zugehörige Interferenz-Terme zu identifizieren. Uberdies sind wir nocheinmal auf die supraleitungsinduzierten Anderungen in den Phononen-Linienformen zurückgekommen. Wir führen die ab-Anisotropie des elektronischen Raman-Signals und die supraleitungsinduzierten Anderungen in den Phonon-Linienform auf eine kleine s-Wellen Beimischung zur  $d_{x^2-y^2}$ -Paarwellen-Funktion zur ück. Wir argumentieren, dass die Raman-Spektren im Einklang mit einer s-Wellen Beimischung von bis zu 20% (oder gleichbedeutend mit einem 20%-tigen Unterschied in der Amplitude der supraleitdenden Energielücke in der Ebene) sind.

Der zweite Teil dieser Arbeit wirft Licht auf unterdotiertes, unverzwillingtes  $YBa_2Cu_3O_{6+x}$  mit x = 0.45 ( $T_c=35$  K) und x = 0.6 ( $T_c=62$  K). Weil die Öffnung des Pseudogaps das elektronische Signal in dieser Doping-Region unterdrückt, liegt das Hauptaugenmerk auf dem vibronischen Raman-Response. Zusätzlich zu den quadratischen, planaren CuO<sub>2</sub>-Schichten enthält die Kristallstruktur von YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub>

CuO-Ketten entlang der *b*-Achse, die bei x < 1 teilweise entleert werden. Insbesondere ist bei YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.5</sub> jede zweite Kette komplett leer und es bildet sich die sog. ortho-II-Struktur mit einer verdoppelten Einheitszelle aus. Es wurden verschiedene Überstrukturen, inklusive die der ortho-V-Struktur mit einer fünfmal größeren Einheitszelle beobachtet.

In dieser Arbeit präsentieren wir eine detaillierte Klassifikation der Schwingungs-Moden von YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.45</sub> und YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub>. Diese Moden können in zwei Kategorien unterteilt werden: die konventionellen Moden von YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> und die zusätzlichen Moden, welche durch die neue Periodizität der Kupfer-Sauerstoff-Ketten erzeugt werden. Diese induzierten Moden sind entweder z-Achsen polarisiert, beobachtbar in den Raman-Symmetrien xx und yy, oder x-Achsen polarisiert und daher nur in xx-Polarisation zu beobachten. Demzufolge sind die x-Achsen polarisierte Moden ein ausgezeichnetes Werkzeug, um die xy-Anisotropie des elektronischen Systems von unterdotiertem YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> zu untersuchen.

Wir haben detaillierte Untersuchungen der Temperatur-Abhängigkeit von Raman-Spektren in xx- und yy-Polarisation an YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.45</sub> (ortho-II) und YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> (ortho-V) durchgefhrt. Unsere Messungen zeigen eine fast komplette Unterdrückung der x-Achsen polarisierten Moden, und zwar die der Yttrium- und die der planaren Sauerstoff-Schwingungen aus den Ebenen heraus oberhalb T<sup>\*</sup> ~ 200K. Die z-Achsen polarisierten Moden bestehen fort bis hin zur Raumtemperatur. Weiterhin haben wir die Rolle möglicher Resonanzeffekte in den phononischen Spektren überprüft, haben aber gefunden, dass die anomale Temperaturabhängigkeit unabhängig von der Photonenenergie ist. Außerdem haben wir Kontrollexperimente durchgeführt, in denen die Temperaturabhängigkeit der Sauerstoff-Überstruktur direkt untersucht wurde, und fanden dass diese temperaturunabhängig ist. Die beobachtbare Anomalie tritt also eng verknüpft mit einer elektronischen Instabilität auf. Der wahrscheinlichste Kandidat ist eine "elektronische, nematische" Phase, welche kürzlich durch inelastische Neutronen-Streuung identifiziert wurde.

Diese Arbeit ist wie folgt gegliedert. In Kapitel 1 wird ein Uberblick über die Hochtemperatur-Supraleitung, ihr generisches Phasendiagramm und die strukturellen Phasen von  $YBa_2Cu_3O_{6+x}$  gegeben. Kapitel 2 präsentiert die Theorie für phononische und elektronische Raman-Streuung, gruppentheoretische Berechnungen und Raman-Auswahlregeln sowie deren Anwendung auf Hochtemperatur-Supraleiter. Eine Einführung in unser theoretisches Modell und zu der Analyse der Daten wird in Kapitel 3 gegeben. Eine Beschreibung der experimentellen Daten wird in Kapitel 4 präsentiert. Die experimentellen Resultate werden in Kapitel 5 gezeigt und diskutiert.

# Abstract

The silver jubilee of the discovery of high temperature superconductivity in cuprates is coming soon. Since its discovery, numerous experiments have been performed, and many attempts have been made to explain the superconducting pairing mechanism in cuprates. But several obstacles have arisen because of the anomalous normal state properties of cuprates. One of the most challenging issues is the pseudogap, which has been observed in the underdoped regime below a doping-dependent temperature  $T^*$  that exceeds the superconducting transition temperature  $T_c$ . Today, the pairing mechanism of high-temperature superconductivity and the origin of the pseudogap state are still controversial, hence more experiments on these materials are required to explain these phenomena.

Cuprate superconductors are layered materials. The only common layers in all cuprates are planes of chemical composition CuO<sub>2</sub> comprised of quadratic copperoxygen plaquettes. These layers can therefore be identified as the structural element that hosts the superconducting Cooper pairs. It is now generally accepted that the Cooper pair wave function of high temperature superconductors (HTSCs) has a predominant  $d_{x^2-y^2}$  symmetry. For compounds in which the CuO<sub>2</sub> layers are orthorhombically distorted, including the extensively studied compound YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub>, one also expects an s-wave admixture to the predominant d-wave pairing. This results in an anisotropy of the superconducting energy gap 2 $\Delta$  between the a- and b-axes. Over the past decades, most of the experiments have been performed on twinned YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> specimens, which are composed of crystallographic "twins" in which the two principal in-plane axes a and b are interchanged. Hence, the ab-difference in the superconducting energy gap in twinned YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> is difficult to observe. In detwinned YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> crystals, on the other hand, the ab-anisotropy of various physical observables, including the superconducting energy gap, can be explored.

A precise determination of the  $2\Delta$ -gap of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> using angle-resolved photoemission spectroscopy (ARPES) is, however, also difficult due to sample surface problems. Raman light scattering is another powerful, much less surface-sensitive tool to measure the *ab*-anisotropy in the  $2\Delta$ -gap and therefore the *s*-wave admixture to d-wave pairing symmetry. In the first part of this thesis, we have investigated detwinned, slightly overdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub> (superconducting  $T_c=92$  K) and moderately overdoped Y<sub>0.85</sub>Ca<sub>0.15</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub> ( $T_c=75$  K) single crystals using the Raman light scattering technique. In polarized Raman scattering experiments, excitations of  $A_g+B_{1g}$ ,  $A_g+B_{2g}$ ,  $B_{1g}$ , and  $B_{2g}$  symmetries are accessible by using xx (or yy), x'x' (or y'y'), x'y' (or y'x'), and xy (or yx) polarizations of the incident and scattered light fields, respectively. Here, x and y correspond to the direction of the electric field of light along the a- and b-axes, whereas x' and y' correspond to the diagonal directions. Since the purpose of this thesis is to determine the s-wave component of the predominant d-wave order parameter, we focused our study on the Raman signals in the xx, yy, and x'y' polarization geometries.

In both samples, modifications of the electronic pair-breaking peaks when interchanging the a and b axis were observed. In addition, the lineshapes of several phonon modes involving plane and apical oxygen vibrations exhibit pronounced anisotropies with respect to the incident and scattered light-field configurations. These modes display a pronounced asymmetric lineshape (*i.e.*, Fano-profile) suggesting a strong interaction with the electronic continuum. In this thesis, the Raman spectra were analyzed in two ways. Firstly, we have used the conventional Fano approach, from which we have obtained estimates of the intrinsic phonon parameters (*i.e.*, phonon frequencies, linewidths, and asymmetry parameters). Secondly, we have developed a theoretical model based on the Fano effect to treat both electronic and phononic contributions to the Raman spectra on equal footing. Our theory allows us to disentangle the electronic Raman signal from the phononic part and to identify corresponding interference terms. Besides that, we have revisited the superconductivity-induced changes in the phonon lineshapes. We attribute the ab-anisotropy of the electronic Raman signals and of the superconductivity-induced changes in the phonon lineshapes to a small s-wave admixture to the  $d_{x^2-y^2}$  pair wave function. We argue that the Raman spectra are consistent with an s-wave admixture with an upper limit of 20% (or equivalently, a 20% in-plane difference in the magnitude of the superconducting gap).

The second part of this thesis sheds light on underdoped, detwinned YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> with x = 0.45 (T<sub>c</sub>=35 K) and x = 0.6 (T<sub>c</sub>=62 K). Since the opening of the pseudogap suppresses the electronic signal in this doping range, we have focused our attention on the vibronic Raman response. In addition to the square-planar CuO<sub>2</sub> layer, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> crystal structure contains layers of CuO chains running along the *b*-axis, which are partially depleted when x < 1. In YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.5</sub>, in particular, every second chain in completely depleted, and the so-called ortho-II superstructure with a doubled unit cell along *a* is formed. Various other superstructures including the ortho-V structure with a five times larger unit cell have also been observed.

In this work, we present a detailed classification of the vibrational modes of  $YBa_2Cu_3O_{6.45}$  and  $YBa_2Cu_3O_{6.6}$ . The modes can be categorized in two groups: the conventional modes of  $YBa_2Cu_3O_7$ , and extra modes induced due to the new periodicity of the copper-oxygen chains. The periodicity-induced modes are either z-polarized, which are observable in *both* xx and yy Raman symmetries, or x-polarized, which are visible *only* in the xx polarization geometry. Hence, the x-polarized modes are excellent tools to probe the xy-anisotropy of the electronic system of underdoped  $YBCO_{6+x}$ .

We performed a detailed temperature dependence study on YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.45</sub> (ortho-II) and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> (ortho-V) Raman spectra in both the xx and yy polarizations. Our measurements revealed almost a complete suppression of the x-polarized modes, namely the out-of-phase vibrations of yttrium and planar oxygen ions above T<sup>\*</sup> ~ 200 K. The z-polarized modes in either xx or yy polarization geometries persist up to room temperature. We also examined the possible role resonance effects on the phononic spectra by performing temperature dependent Raman experiments using a different exciting laser line, but found that the anomalous temperature dependence of the phonon intensities is independent of photon energy. We also performed control experiments in which the temperature dependence of the oxygen superstructure was studied directly, and found that it is temperature independent. The anomaly we observed thus appears to be tied to an electronic instability. The most likely candidate is an "electronic nematic" phase recently identified by inelastic neutron scattering.

This thesis is organized as follows. In Chapter 1, an overview of the hightemperature superconductivity, their generic phase diagram, and the structural phases of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> are given. Chapter 2 presents the theory of phononic and electronic Raman scattering, group theoretical calculations, and Raman selection rules and their applications to high-temperature superconductors. An introduction to our theoretical model and to the data analysis is given in Chapter 3. A description of the experimental details is presented in Chapter 4. The experimental results are shown and discussed in Chapter 5.

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# Chapter 1

# Introduction

## **1.1** Conventional Superconductivity

After liquifying helium on 1908, H.K. Onnes [Nobel Prize, 1913] discovered superconductivity (a conduction of an electrical current without resistance below  $T_c$ ) in mercury. Later on, superconductivity was found in several other elements, e.g. lead and tin. these are the so-called conventional type-I superconductors. One of the most important observations in this class of superconductors is the complete exclusion of an applied small magnetic field  $H < H_{c1}$  ( $H_{c1}$  is the critical magnetic field above which superconductivity is destroyed) when they are cooled below  $T_c$ (i.e., perfect diamagnetism). This is the so-called Meissner-Ochsenfeld effect. Other conventional superconductors, e.g. niobium, have two critical magnetic fields  $H_{c1}$ and  $H_{c2}$  with  $H_{c1} < H_{c2}$ . Below the lower critical field  $H_{c1}$ , they show a perfect diamagnetism, whereas at  $H_{c1} < H < H_{c2}$  they undergo a mixed state of superconducting and normal state regions (i.e., Shubnikov phase), and they completely leave the superconducting state above the upper critical field  $H_{c2}$  [46]. These are the so-called conventional type-II superconductors.

Numerous attempts have been made to explain the conventional superconductivity. The phenomenological theory proposed by Ginzburg and Landau [47] in 1950 was able to describe some of the observed phenomena in superconductors, whereas an exhaustive microscopic understanding that unlocked the mysteries of conventional superconductivity was first achieved by Bardeen, Cooper and Schrieffer, the so-called BCS theory, in 1957 [48].

In metals, *individual* electrons carry the electrical current. These electrons (described by Bloch wavefunctions  $|k, \sigma \rangle$ , with k and  $\sigma$  are the electron wavevector and spin, respectively) propagate in a perfect crystal without scattering. How-



Figure 1.1: (a) Polarization of the lattice of atomic ions due to the movement of electrons. (b) Schematic representation of the effective electron-electron interaction via the exchange of a phonon q.

ever, atomic vibrations (phonons) lead to deviation of the atoms from the perfect lattice positions, and therefore the electrons get scattered by phonons. This results in an energy dissipation (electrical resistance). In superconductors, the supercurrent is carried by *pairs* of electrons without energy dissipation. BCS theory shows that electron pairs are formed because of the instability of the Fermi liquid to any non-zero attractive interaction [Details about the BCS theory are presented in Refs.[48, 49, 50]]. In conventional superconductors, the attractive force arises from the exchange of phonons. This hypothesis was strongly supported by experiments showing that the superconducting transition temperature  $T_c$  of mercury changes for different isotopes [51, 52]. The  $T_c$  dependence on the atomic mass M was found to vary as  $T_c \propto M^{-1/2}$ .

Let us consider a lattice of atomic ions, in which free electrons propagate. At a finite temperature, the ions are deflected from their equilibrium positions. A moving electron will deform the lattice by attracting the neighboring positive ions. Hence, a dense region of positive charges around the moving electron will be generated. This results in an attraction of a second electron to the positively charged area, and therefore to the first electron (Fig. 1.1(a)).

Quantum mechanically, a phonon will be either generated or annihilated if a moving electron is scattered by the ions. The resulting phonon, e.g. created, can be annihilated in another scattering process with a second electron. Thus, a phonon is virtually exchanged between the two electrons. This exchange process leads to an attractive interaction that binds momentarily every two electrons with opposite momenta and opposite spins to form the so-called Cooper pairs:  $\{k \uparrow, -k \downarrow\}$ , that possess zero total momentum and zero total spin (Fig. 1.1(b)).

#### 1.1. Conventional Superconductivity

Within the framework of BCS theory, only electrons near the Fermi level, i.e. ~ 0.1% of all electrons, take part in superconductivity. One of the most remarkable features emerging from the formation of Cooper pairs is the energy gain (or, equivalently, the condensation energy). When a metal becomes superconducting, it lowers its energy by  $-N(E_F)\Delta^2/2$ , with  $N(E_F)$  being the density of states at the Fermi energy (note that the condensation energy depends on the electron-phonon coupling V through  $\Delta^2$ ). Consequently, the energy of a quasiparticle (an unpaired electron influenced by the system) can be given as

$$E_k = \sqrt{(\varepsilon - E_F)^2 + \Delta^2},\tag{1.1}$$

where  $\Delta$  is an energy gap between the BCS ground state and the first excited state (i.e., the superconducting gap). Hence, if  $\Delta$  in Eq.(1.1) is assumed to be zero, the energy of non-interacting electrons is recovered, whereas  $\Delta \neq 0$  implies that an energy of at least two times the superconducting gap energy is required to break the Cooper pairs and create two quasiparticles.

BCS theory assumes the pairing interaction to be weak and independent of momentum  $(V(k) = V_0)$  for all pairs within an energy interval of  $\hbar\omega_D$  ( $\omega_D$  refers to the Debye frequency) around the Fermi surface, and zero elsewhere. Using these approximations, BCS theory predicts the dependence of the transition temperature  $T_c$  and the superconducting gap  $\Delta$  on the BCS coupling parameter  $VN(E_F)$  and the Debye cutoff energy  $\hbar\omega_D$  as

$$T_c = 1.14 \frac{\hbar\omega_D}{k_B} exp(-\frac{1}{N(E_F)V})$$
(1.2)

and

$$\Delta = 2\hbar\omega_D exp(-\frac{1}{N(E_F)V}),\tag{1.3}$$

respectively. Besides that, the approximations noted above can explain the isotropic s-wave order parameter of conventional superconductors.

However, the BCS theory is limited since it is unable to provide a reasonable estimate for the  $T_c$ 's in the strong-coupling limit. This problem was overcome by Midgal–Eliashberg theory, in which all information about phonons and electron-phonon (*ele-ph*) couplings are included in the so-called Eliashberg function  $\alpha^2 F(\omega)$ . The total *ele-ph* coupling constant

$$\lambda = \lambda_{tot} = 2 \int_0^{\omega_0} \frac{\alpha^2 F(\omega)}{\omega} d\omega$$
(1.4)

is obtained by summing over all phonons. Within the framework of the Midgal– Eliashberg theory, the superconducting gap and the transition temperature are given as

$$\Delta = 2\hbar\omega_c exp(-\frac{1+\lambda}{\lambda-\mu*}),\tag{1.5}$$

and

$$T_c = 1.14 \frac{\hbar\omega_c}{k_B} exp(-\frac{1+\lambda}{\lambda-\mu*}), \qquad (1.6)$$

respectively, with  $\omega_c$  a cutoff frequency dependent on the phonon density of states and  $\mu *$  the electron-electron (*ele-ele*) Coulomb repulsion parameter. However, the maximum superconducting T<sub>c</sub> predicted by Midgal–Eliashberg calculations (and later by the McMillan equation) is about 30 K. Thirty years later, these predictions were violated by the discovery of high temperature superconductivity (HTSC) in cuprates which can be easily attained by cooling in liquid nitrogen (77 K).

## **1.2** High Temperature Superconductivity

The discovery of superconductivity with a  $T_c$  of about 35 K in lanthanum and barium copper oxides [53] by J. Bednorz and K. Müller [Nobel prize, 1987] has encouraged scientists throughout the world to search for superconductors with higher temperatures. Superconductivity with a  $T_c$  of about 90 K, i.e. higher than the boiling temperature of nitrogen, was discovered in the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> system [54]. Later, a  $T_c$  higher than 100 K was found in Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+x</sub> [55] and Tl<sub>2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>8+x</sub> [56]. Nowadays, the highest temperature superconductor in this family is the mercurybased copper oxide (i.e. HgBa<sub>2</sub>CaCu<sub>2</sub>O<sub>6+x</sub>), with  $T_c$  of about 138 K at ambient pressure [57], which increases to 164 K under hydrostatic pressure of 30 GPa [58].

Cuprate superconductors have a perovskite-like structure which is based on an ABO<sub>3</sub> unit where B refers always to copper  $Cu^{2+}$  ions and A-ions are different for each cuprate system. This structure is clearly visible in the high temperature tetragonal phase of the La<sub>2</sub>CuO<sub>4</sub> compound, in which the Cu<sup>2+</sup> ion is surrounded by six oxygen ions forming the CuO<sub>6</sub> octahedron (Fig. 1.2a). In cuprates, the CuO<sub>2</sub> planes in which superconductivity is believed to occur are the main building



Figure 1.2: Crystal structure of (a)  $La_2CuO_4$  (in the high temperature tetragonal phase) and (b)  $YBa_2Cu_3O_7$  compounds. The shaded area denote the  $CuO_2$  planes.

blocks (Fig. 1.2). The number of the CuO<sub>2</sub> plaquettes n vary from one copper oxide to another. For instance, La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> has one CuO<sub>2</sub> layer per unit cell, while REBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> unit cell (RE=Y, Eu, Dy, Er, or Tm) contains two per unit cell. A<sub>2</sub>B<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+4+x</sub> compounds with A=Bi(Tl) and B=Sr(Ba) can have one, two, or three CuO<sub>2</sub> planes, whereas Hg<sub>2</sub>Ba<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+2+x</sub> can have up to 6 layers in the unit cell [59, 60]. The number of the CuO<sub>2</sub> planes per unit cell affects the value of T<sub>c</sub>. In case that the cuprate compound can have more than one CuO<sub>2</sub> layer per unit cell, the T<sub>c</sub> increases, for example, with increasing n reaching a maximum value for n = 3 [60]. A precise determination of T<sub>c</sub> is achieved by tuning the oxygen (or the cation) concentration x, which controls the electronic balance and thus the net charge per unit cell. Table 1.1 gives and overview of the several families of cuprates, the possible number of planes, and the maximum T<sub>c</sub> for each of them.

### **1.3** Doping Mechanisms of HTSCs

Insertion of oxygen ions or partial replacement of the cations lead to an increase of the hole concentration p in the CuO<sub>2</sub> planes of the cuprates. Tuning x and y presented in table 1.1 can vary the hole doping from 0 (undoped) to 0.3 holes per Cu ion (extremely overdoped). For p = 0, the system is antiferromagnetic insulator below a Néel temperature  $T_N$  of about 400 K (Fig. 1.3). Within the

Compound	Abbreviation	No. of planes	Maximum $T_c$
$La_{2-x}Sr_xCuO_4$	0201	1	40 K
$La_{2-x}Ba_xCuO_4$	0201	1	40 K
$Tl_2Ba_2CuO_{6+x}$	2201	1	95 K
$Tl_2Ba_2CaCu_2O_{8+x}$	2212	2	110 K
$Tl_2Ba_2Ca_2Cu_3O_{10+x}$	2223	3	130 K
$\operatorname{Bi}_2\operatorname{Sr}_2\operatorname{CuO}_{6+x}$	2201	1	25 K
$\operatorname{Bi}_2\operatorname{Sr}_{1+x}\operatorname{La}_{1-x}\operatorname{CuO}_{6+y}$	2201	1	$25 \mathrm{K}$
$\mathrm{Bi}_{2}\mathrm{Sr}_{2}\mathrm{Ca}\mathrm{Cu}_{2}\mathrm{O}_{8+x}$	2212	2	80 K
$Bi_2Sr_2Ca_2Cu_3O_{10+x}$	2223	3	110 K
$\operatorname{Bi}_2\operatorname{Sr}_2\operatorname{Ca}_{1-x}\operatorname{Y}_x\operatorname{Cu}_2\operatorname{O}_{8+y}$	2212	2	$35~{ m K}$
HgBa <sub>2</sub> CuO <sub>4+<math>x</math></sub>	1201	1	95 K
$HgBa_2CaCu_2O_{6+x}$	2212	2	$125 \mathrm{~K}$
$HgBa_2Ca_2Cu_3O_{8+x}$	2223	3	$135 \mathrm{~K}$
$YBa_2Cu_3O_{6+x}$	123	2	93 K
$Y_{1-y}Ca_yBa_2Cu_3O_{6+x}$	123	2	93 K
$YBa_2Cu_4O_8$	124	2	80 K

Table 1.1: Different families of cuprates together with the number of possible planes and the maximum transition temperature. After Ref. [62].

hole dopings  $0 , cuprates remain nonconducting whereas <math>T_N$  decreases monotonically. Beyond a hole doping  $p_{sc1}$  and at low temperatures, the system becomes a superconductor. All HTSCs possess a maximum  $T_c$  at a particular doping level, i.e.,  $p_m = 0.16$ . Between  $p_{sc1}$  and  $p_m$ , i.e. in the underdoped regime, the  $T_c$ increases (from left to right) following Tallon's empirical relation [61]

$$\frac{T_c}{T_{c,max}} = 1 - 82.6(p - 0.16)^2, \tag{1.7}$$

with an exception for  $p \approx 0.10 - 0.125$ , at which a T<sub>c</sub> plateau (depression) is observed in YBCO (LSCO) (Fig. 1.4). In the overdoped regime 0.16 < p, the T<sub>c</sub> decreases following Tallon's relation, although the hole density increases. The maximum hole concentration at which the superconductivity diminishes  $p_{sc2} \approx 0.27$ . For hole concentrations higher than 0.27, cuprates behave as metals at all temperatures.

In YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> (YBCO), Y<sup>3+</sup>, Ba<sup>2+</sup>, and Cu<sup>2+</sup> cations have a total electronic charge of +13, whereas the oxygen anions contribute with a total charge of -12-2x. Thus, the net charge balance of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> system is 1 - 2x per unit cell. The -2x term is the most important for controlling the doping level of the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub>



Figure 1.3: Generic phase diagram of HTSCs.  $P_{sc1}$  and  $P_{sc2}$  correspond to the hole dopings between which superconductivity sets in.  $T_N$ ,  $T^*$  and  $T_c$  correspond to the Néel, pseudogap, and superconducting transition temperatures, respectively. The arrow indicates the doping around which a  $T_c$  suppression or plateau occur. After Hossain *et.* al [64].

system. The minus sign indicates that electrons are missing, i.e., that the material is a hole conductor, at least for x > 0.5. The -2x charge amount is determined experimentally through annealing of YBCO crystals at temperatures T~ 500°C using appropriate gas flows (see chap. 4). In this process, holes can be introduced into the planes by inserting oxygen ions into the Cu-O chains (Fig.1.2). Each incorporated oxygen atom attracts two electrons to form an O<sup>2-</sup> ion. These electrons are partly drawn from the CuO<sub>2</sub> planes. This process results in the reduction of the number of electrons in the CuO<sub>2</sub> plaquettes, i.e., more holes are generated. The oxygen content x can vary from 0 (empty chains) to 1 (full chains). In YBCO<sub>6+x</sub>, the optimal doping is achieved at  $x_m \approx 0.93$  (Tc=93 K), whereas when the chains are totally full the system is slightly overdoped with a T<sub>c</sub> of about 86 K. Further enhancement of the hole density requires a partial replacement of the Y<sup>3+</sup> by Ca<sup>2+</sup> ions [63]. The maximum hole concentration for YBCO<sub>6+x</sub> at which the superconductivity vanishes is achieved when the chains are fully occupied and almost 30% of the yttrium are replaced by calcium ions [61].

Now, we shortly discuss the limitations of Tallon's formula. This formula is not



Figure 1.4: The superconducting critical temperature  $T_c$  as a function of p for YBCO<sub>6+x</sub>. The dotted line displays the parabolic relationship between  $T_c$  and p (Tallon's formula). The inset shows  $\Delta T_c$ , the difference between the measured  $T_c$ 's and the parabolic relationship. The figure is taken from [67].

accurate enough to describe the superconducting dome at hole doping levels close to p = 0.1. Around this doping level, the superconducting transition temperature is suppressed and exhibits a canyon shape (inset in Fig. 1.4). In YBCO<sub>6+x</sub>, however, an additional complication arises from the presence of oxygen superstructures (see Sec. 1.5). The T<sub>c</sub> suppression may originate from the formation of exotic static spin and charge stripes (see Sec.1.4.4). Therefore, the T<sub>c</sub>-plateau of YBCO<sub>6+x</sub> remains an unsettled issue.

## 1.4 Generic Phase Diagram of HTSCs

The phase diagram (Fig. 1.3) of HTSC can be divided into five regimes: antiferromagnetic(AF), pseudo-gap (PGS), strange metal, normal metal, and superconducting (SC) regime. In the next subsections, the physics as well as an experimental overview of these regimes will be shortly presented.

### 1.4.1 Antiferromagnetic (AF) Regime

In the undoped state, each  $\operatorname{Cu}^{+2}$  ion has a single electron that resides in the  $d_{x^2-y^2}$  orbital, which overlaps with either  $p_x$  or  $p_y$  orbitals of the neighboring oxygen ions. Hence, the CuO<sub>2</sub> planes have a half-filled energy band, and are expected to be metallic. However, the undoped YBCO<sub>6</sub> system was found to be an insulator. This indicates the existence of strong electron-electron correlations. An explanation for this problem was presented based on the Hubbard model [68], which treats the kinetic energy of the electrons and their mutual Coulomb repulsion on equal footing. Since the Coulomb repulsion dominates this competition, the electrons prefer to localize at the Cu ions giving rise to the well-known *Mott insulator* [69], rather than forming a Fermi liquid (defined below). The main difference between a Mott insulator and a band insulator is that the latter contains two electrons in the highest occupied band, thus conductivity is blocked by the requirements of the Pauli exclusion principle, whereas the conductivity of a Mott insulator is prevented due to electron-electron repulsion.

Neutron scattering (NS) is a straightforward probe for the spin system in solids. For undoped HTSC compounds, NS experiments [70, 71, 72] have revealed antiferromagnetic Bragg peaks at wavevectors  $Q=(\pm \pi/a, \pm \pi/a)$  (for convenience, we set a = 1 throughout this thesis) below  $T_N$ , thus showing that the magnetic moments of the copper electrons are antiferromagnetically ordered. A possible way for the electrons to lower their kinetic energy in the Néel-ordered state is to virtually hop forth and back between the neighboring copper ions, thus generating a "super-exchange" interaction. In this case, the electrons must keep the antiferromagnetic (AF) configuration in order to satisfy the Pauli principle. Decreasing the average electron occupancy from 1 results in lowering the Néel temperature, which reachs zero at around p = 0.05.

### 1.4.2 Normal Metal

At the other side of the phase diagram (i.e. the heavily overdoped state with 0.2 < p), the kinetic energy of the electrons exceeds their mutual Coulomb repulsion, hence electrons become delocalized and form a Fermi liquid state [69]. Experimentally, the normal state properties of overdoped cuprates were found to be described reasonably well by the Fermi liquid picture. For instance, the in-plane resistivity varies as  $\rho = \rho_0 + aT^2$  at temperatures above  $T_c$  [73, 74]. The  $T^2$ -behavior of the in-plane resistivity originates from predominant fermion-fermion scattering. In addition, for temperatures above  $T_c$ , the specific heat was found to vary linearly with temperature  $C_e = \gamma T$  [75], which again implies the emergence of Fermi liquid behavior.

### 1.4.3 Strange Metal Phase

The extension of the Fermi liquid regime in the underdoped part of the phase diagram of HTSC remains a controversial issue (Fig. 1.3). However, the normal-state physical properties of cuprate systems with hole density close to optimal doping p = 0.16 can not be well described by the Fermi liquid picture. One long standing puzzle is the linear temperature dependence of the in-plane resistivity  $\rho = \rho_0 + aT$ , for  $T > T_c$  [76, 77], which is neither described by the Fermi liquid model nor by standard electron-phonon models.

The anomalous behavior of the normal state in-plane resistivity may be related to critical fluctuations at the vicinity of a quantum critical point (QCP), which takes place around optimal doping. This hypothesis was recently reviewed by Tallon and Loram [23]. These authors have reviewed the doping and temperature dependences of different physical quantities (e.g. specific heat, NMR Knight shift, and in-plane resistivity) and found a clear distinction between the underdoped and the moderately overdoped regimes. The authors [23] argued that the QCP occurs around the hole density p = 0.19, at which the energy of the pseudogap (discussed in sec. 1.4.5) determined from the mentioned physical quantities, falls to zero. In addition to the spectroscopic techniques just mentioned, it has been demonstrated that the frequency and intensity of the superconducting Raman pair breaking peaks in the  $A_{1g}$ and  $B_{1q}$  symmetries [78] as well as the two magnon peak intensity [79] strongly change at around the presumed QCP (p = 0.19). Moreover, the spin resonance mode (presented in next section), which originates from coherent spin fluctuations, becomes stronger when the hole doping departs from the optimal towards the underdoping regime [more details are presented in ref. [80]].

### 1.4.4 The Superconducting State

So far, we have shown that cuprates become superconductors at hole densities p between 0.05 and 0.27 and at doping dependent transition temperatures that possess a dome-like shape (Eq. 1.7). Inside the superconducting dome, a long-range ordered state is achieved. This state can be phenomenologically described by the GinzburgLandau "order parameter"  $\Psi(r)$  which can be identified as the wave function of the phase coherent Cooper pair condensate. It is a complex function, i.e.  $\Psi(r) = \psi(r) \exp(i\varphi(r))$ , with the modulus  $\psi(r)$  and phase  $\varphi(r)$ , that can be normalized so that the density of the superconducting charge carriers is given by  $\psi(r)^2$ .

The superconducting transition is associated with a breakdown of the full symmetry group which includes gauge, crystal lattice, spin rotations, and time reversal symmetries. For conventional superconductors with an isotropic *s*-wave gap, the gauge invariance is the only symmetry that is broken below  $T_c$ . If more than one symmetry breaks down below  $T_c$ , the resulting superconductor is classified as unconventional with an order parameter (gap function) that may have zeros at some points of the momentum space [81]. This is the case for a *d*-wave state, which has a symmetry lower than that of the crystal lattice.



Figure 1.5: (a) The YBCO-Pb corner SQUID geometry used by Wollman *et al.* (b) Calculated magnetic flux dependence of the SQUID critical current for the s- and d-wave pairing symmetries. The figure is obtained from [1].

In momentum space, the pair wave function becomes wavevector dependent and scales with the superconducting gap function  $\Delta(k)$  as  $\Psi(k) = \Delta(k)/2E_k$ , with  $E_k$  being the quasiparticle energy. In order to determine the order parameter (or equivalently, the gap symmetry) of HTSCs, it is necessary to figure out whether Cooper pairs form a singlet- or triplet-state. Among different experimental techniques, Josephson tunneling is the best to do that, since the Josephson current vanishes if two weakly coupled superconductors have different spin pairing states. Thanks to this advantage, tunneling measurements provided experimental evidences that HTSCs and low-T<sub>c</sub> conventional superconductors possess similar spin pairing state, i.e. spin-singlet pair state (S = 0). This implies that the superconducting gap function has an even parity ( i.e.,  $\Delta(k) = \Delta(-k)$  ) [82].

Although there is no consensus about the microscopic mechanism of HTSC, the symmetry and magnitude of the superconducting gap function  $\Delta(k)$  can be determined experimentally. A powerful technique to probe the phase of the superconducting order parameter is the phase-sensitive Josephson tunneling (PSJT). Wollman *et al.* [1] have performed the first PSJT measurements on a weakly linked *Pb* thin film between two orthogonally oriented *ac*- (or *bc*-) plane faces of twinned YBCO single crystals in the so-called corner SQUID geometry (Fig.1.5). The idea of this experiment is elegant and simple. If the YBCO compound had an s-wave pairing symmetry, the phase of the order parameter would be the same for the *a* and *b* faces of the YBCO crystal, thus the phase difference between the two faces,  $\delta_{a-b}$ , would be zero. In this case the critical current would be maximum at zero applied magnetic flux [similar to that observed for s-wave superconductor (Fig.1.5(a))]. On the other hand, if YBCO had a *d*-wave order parameter



Figure 1.6: (a) Schematic of the experimental ring geometry studied in [8]. (b) Polar arrangement of all the rings.  $\theta$  denotes the angle between the junction normals and the YBCO crystalline axes. The rings were cooled and imaged by a SQUID microscope in zero field (outer rings) and in 0.2  $\mu$ T (inner rings). The crossed lines denote the angle at which the spontaneous magnetic flux changes (i.e, the nodal direction of the d+s pair state). (c) Integrated flux (solid points) through the rings as a function of  $\theta$ . The solid line is the best theoretical fit to the experimental data using  $\Delta_k = \Delta_d(\cos 2\theta) + \Delta_s$  with  $\Delta_s = 0.9\%$ 

. The green, vertical dotted lines denote the angles of the nodal directions in twin-free YBCO film, which are shifted from those expected for pure  $d_{x^2-y^2}$  superconductor. This figure is taken from [8].

$$\Delta_k = \Delta_{max} (\cos k_x - \cos k_y), \tag{1.8}$$

this would give rise to a phase difference  $\delta_{a-b}$  of  $\pi$  and to a minimum current at zero applied field (Fig.1.5(b)). The latter case was revealed by the experiment of Wollman *et al.*, thus showing that HTSC have a *d*-wave symmetry.

In cuprates of the YBCO<sub>7</sub> type with orthorhombic crystal symmetry, an *s*-wave admixture to the predominant  $d_{x^2-y^2}$ -wave order parameter has been recently established. Angle-resolved phase-sensitive measurements have been performed [8]

on optimally doped, twin-free YBCO thin films in the so-called  $\pi$ -ring Josephson junction (Fig. 1.6(a)). In this configuration, if the normal components of the gap at the two junctions of the  $\pi$ -ring have an intrinsic phase shift of  $\pi$ , a spontaneous supercurrent flows in the ring below  $T_c$  (at zero applied magnetic field), and therefore a spontaneous magnetic flux  $\Phi$  will be generated. Otherwise, the spontaneous supercurrent as well as  $\Phi$  will be zero. Figure 1.6(b) shows a sketch for the sample studied by Kirtley et al. [8], which contains 72 rings with the angles between the junction normals and the YBCO principal axes vary by  $5^{\circ}$ . The resulting flux  $\Phi$  (normalized to the superconducting flux quantum  $\Phi_0 = h/2e$ ) in the rings are shown in fig. 1.6(c) (after [8]). The authors have found that the nodal direction in twin-free YBCO film (vertical dotted lines in fig. 1.6(c)) is shifted by a few degrees from the (2m+1) expected for pure  $d_{x^2-y^2}$ -wave order parameter indicating the different gap size between the a and b directions. Besides that, the best fit (solid line) to the experimental data was obtained using the the admixed  $d_{x^2-y^2}+s$  pair state (i.e.,  $\Delta_k = \Delta_d(\cos 2\theta) + \Delta_s$ ) with  $\Delta_s/\Delta_d \sim 9\%$  (solid line in fig. 1.6(c)). Hence, the authors [8] argue that the gap along the *b*-axis is at least 20% larger than that along the a-axis. Since PSJT measurements yield only lower bounds to the s-wave contribution, we will extract an upper limit to the s-wave admixture from our Raman results (see chapter. 5).

In addition to the PSJT measurements just presented, angle-resolved photoemission spectroscopy (ARPES) is advantageous for probing the wave vector dependence of the superconducting gap  $\Delta(k)$ . Technically, ARPES is sensitive to the quality of the crystals surface, thus a necessary condition for performing ARPES experiment is the sample cleavage. Unfortunately, the cleavage interface of YBCO prefers to be located between the Cu1-O1 and BaO layers. The polarity of this interface generates an electronic reconstruction, which in turn enhances the surface doping level well into the overdoped regime [9]. Therefore, we limit our discussion to considering BSCCO samples in which the ARPES response corresponds to the nominal doping level. Figure 1.7 demonstrates the momentum dependence of the superconducting energy gap of a Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+x</sub> ( $T_c = 87K$ ) sample measured at a temperature well below  $T_c$  [24]. As seen, the largest energy gap is observed along the a- (or b-) axis and the smallest one (zero) along the diagonal line between them. In addition, the experimental data were fitted using a simple d-wave model (solid line) and the result agrees well with the measured data. The ARPES results indeed confirm that the gap function has a *d*-wave order parameter with nodes on the Fermi surface. It is worth mentioning that ARPES measurements on twin-free  $YBCO_{6.993}$  [7] have indicated a 50% anisotropy in the size of the  $2\Delta$ -gap between the *a*- and *b*-axes. These observations point to a large s-wave admixture to the predominant d-wave order parameter, significantly exceeding the one determined by the SQUID experiments described. However, these results are still controversial, because the surface



Figure 1.7: (a) Superconducting gap versus angle on the normal-state Fermi surface (FS) of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+x</sub> ( $T_c = 87K$ ) measured by ARPES at 13K. The solid curves correspond to fits to the experimental data using a d-wave gap  $\Delta(k) = \Delta_0(\cos k_x - \cos k_y)$ . The numbers 1 and 15 denote the gap values measured at two different locations on the FS as shown in panel (b). The figure is taken from [24]. (b) Sketch of the Fermi surface (green solid line) and anisotropic d-wave superconducting gap (red and blue area) of Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+x</sub> as determined by ARPES. In the  $\Gamma$ -M (or, equivalently (0,0)-( $\pi$ ,0) or (0,0)-(0, $\pi$ )) direction, a maximum gap in the density of states opens, whereas in the  $\Gamma$ -Y direction (or, equivalently (0,0)-( $\pi$ , $\pi$ )), the gap is zero. The red and blue colors in (b) indicate the change in sign of the order parameter under rotation.

properties of  $YBCO_{6+x}$  differ from those in the bulk [9].

Electronic Raman scattering is complementary to ARPES since it is capable of probing independently different portions of the FS by adjusting the polarizations of the incident and scattered light (details are presented in sec. 2.5.3). In HTSCs,  $B_{1g}$  and  $B_{2g}$  Raman symmetries sample electronic states at the vicinity of the antinodes (AN) and nodes (N) of the gap function, respectively. Recently, Le Tacon *et al* [83] have studied the doping dependence of the energy of the superconducting Raman pair breaking peaks at the nodal and antinodal regions in differently doped HgBa<sub>2</sub>CuO<sub>4+x</sub> samples. The results are shown in Fig. 1.8. The B<sub>1g</sub> and B<sub>2g</sub> peaks were found to be close in energy, i.e.  $\omega_{AN} = \omega_N$ , for the optimally doped sample. As the hole density is lowered below the optimal level, the energy of the B<sub>1g</sub> peak  $\omega_{AN}$  increases, whereas the energy of the B<sub>2g</sub> peak follows the superconducting dome (Fig. 1.8(a)). The doping dependences of the characteristic ratios  $\omega_{AN}/T_{c,max}$ and  $\omega_N/T_{c,max}$  extracted from Raman measurements [83] and other spectroscopic



Figure 1.8: (a) Raman responses in the nodal (left) and antinodal (right) regions of differently doped HgBa<sub>2</sub>CuO<sub>4+x</sub> samples. The doping decreases from up to down. Ov., Opt., and Und. refer to overdoped, optimally doped, and underdoped, respectively. The maxima of the superconducting  $2\Delta$ -peaks are denoted with arrows. The dashed lines on B<sub>2g</sub> (B<sub>1g</sub>) spectra represent linear (cubic) energy dependence of the nodal (antinodal) Raman responses. Two energy scales that depend on doping in opposite ways are seen. The intensity of B<sub>1g</sub> peak decreases with progressive underdoping while the B<sub>2g</sub> peak intensity prevails down to the lowest doping investigated. (b) Universal doping dependence of the ratios  $\omega_{AN}/T_{c,max}$  and  $\omega_N/T_{c,max}$  of the antinodal and nodal superconducting  $2\Delta$ -peaks in different families of cuprate superconductors extracted from Raman scattering and other techniques represented in [83]. The figure is obtained from [83].

methods (references are in [83]) for various cuprate superconductors are displayed in fig. 1.8(b). The two ratios possess a universal doping dependence and behave oppositely in the underdoped regime (Fig. 1.8). The authors [83] argue that the existence of two energy scales associated with the nodal and antinodal gaps of un-



Figure 1.9: (a) energy scan performed on slightly overdoped YBCO<sub>6.97</sub> ( $T_c = 92.7K$ ) at the planar AF wave vector  $Q_{AF} = (0.5, 0.5)$  at 5 K in the superconducting state. (b) Constant energy scan at 40 meV measured as shown in the inset, i.e., along the (110) direction around  $Q_{AF}$ . A magnetic excitation, fitted with a Gaussian line-shape, observed at 5K (open circles) completely disappears above the superconducting transition, where only a featureless nuclear background is seen (solid circles). (c) Temperature dependence of the magnetic intensity at 40 meV, which seems to follow the superconducting order parameter and change significantly at  $T_c$ . Open and closed circles correspond to intensities measured below and above the SC-transition, respectively. The figure is obtained from [86].

derdoped HTSCs reflects the different dynamical properties of the quasiparticles in the two regions. Moreover, from these observations one may speculate that this has to do with the superconducting and pseudogap states probably being different.

#### Magnetic resonance mode in the superconducting state

Besides the observation of the HTSC pairing symmetry by PSJT and ARPES measurements, one important discovery, which might be relevant to the superconducting mechanism, is an unusual magnetic excitation in the superconducting state, i.e., the so-called "magnetic resonance mode" firstly observed in neutron scattering spectra by J. Rossat-Mignot *et al.* [84]. This magnetic peak possesses the following features:

• It is observed in a neutron scattering spectrum around the wave vector  $Q_{AF} = (\pi,\pi)$  which is characteristic of the AF-ordered state in the undoped cuprates (Fig. 1.9 (b)) [85].

• Close to optimal doping, the peak intensity seems to follow the superconducting order parameter and vanishes above  $T_c$  (Fig.1.9(c)), whereas its energy (~ 40 meV) remains almost unchanged [85, 86].



Figure 1.10: Doping dependence of the resonance mode energy at  $(\pi, \pi)$  in YBCO (red circles) and BSCCO (blue squares) plotted with twice the maximum SC-gap (green squares) as measured in BSCCO by ARPES. The figure is taken from [88].

• The energy of this mode follows the superconducting dome (Fig. 1.10) [87, 88].

The salient features of this mode can be understood in the framework of a model that considers it as an exciton-like collective excitation in the superconducting gap of HTSCs. The wave vector dependence of the magnetic mode energy (Fig. 1.11(a)) is governed by the threshold of the e - h spin flip continuum  $\omega_c(q)$ , which depends on the SC-order parameter. Since the SC-order parameter has its maximum value in the antinodal region near  $(\pi, 0)$  or  $(0, \pi)$ ,  $\omega_c(q)$  reaches a maximum value at the wave vector that connects the antinodal points of the Fermi surface (or equivalently, the hot spots) i.e. at  $Q_{AF}$  (red arrow in Fig. 1.11(b)). Departing towards the nodes of the *d*-wave order parameter,  $\omega_c(q)$  decreases rapidly reaching zero around the wave vector  $q_n$  that connects the the nodal points of the gap function. Beyond  $q_n$  (region 2), the spin excitations reappear again at higher energies but with lower intensity than that observed in region 1. The excitations in region 1 can be understood in terms of direct e - h spin excitations. Combining the downward and upward magnetic mode dispersion results in an X-like or hourglass-like dispersion [86].

The spin excitations measured by constant-energy cuts at energies below the magnetic resonance were found to be incommensurate. That is, the magnetic peak observed for the parent cuprates splits in the superconducting state into four, each of which is shifted from  $Q_{AF}$  by a small incommensurability constant  $\delta$ . Besides the spin exciton scenario presented above, scattering at  $Q_{AF} \pm \delta$  can also arise from rigid arrays of antiferromagnetically ordered spins, i.e. stripe phase (discussed below).



Figure 1.11: (a) Dispersion of the spin excitation. The shaded area denotes the e - h spin flip continuum. In region 1, the magnetic mode disperses in a dome-like shape until it disappears at around  $q_n$ . In region 2 it reappears again and disperses upwards. (b) Schematic of the d-wave order parameter with the red circles at the antinodes correspond to the hot spots whereas the blue ones at the nodal direction refer to the cold spots. The wave vectors connecting the hot spots and independently the cold spots are  $q_{AF}$  and  $q_n$ , respectively. (c) calculated magnetic susceptibility  $\text{Im}\chi$  in the superconducting state within the spin exciton scenario. The figure is obtained from [86].

Although electron-phonon interaction may also be relevant for the pairing mechanism of high  $T_c$  superconductivity (see Sec. 1.6), the observance of the resonant magnetic mode in the SC state points to an important role of magnetic interactions for superconductivity in the cuprates.

#### The stripe phase

Uni-axial spin and charge density wave (SDW and CDW, respectively) orders were first introduced by J. Tranquada [32] to explain the incommensurate magnetic Bragg reflections of the La<sub>1.6-x</sub>Nd<sub>0.4</sub>Sr<sub>x</sub>CuO<sub>4</sub> system. The authors [32] proposed the ordering structure shown in Fig. 1.12. Based on this model, the distance between charge stripes, i.e. charge periodicity, is a/2x, where a is the Cu-Cu separation. The antiferromagnetic order of the spin system results in doubling the periodicity, that is, a/x [69]. The reason behind static stripe formation is that the holes tend to escape from regions of localized, antiferromagnetically ordered spins. A complete charge-spin separation is, however, unlikely since the long range Coulomb interaction frustrates this separation. Finally, the competing interactions result in the formation of striped and/or checkerboard phases as a compromise.



Figure 1.12: Schematic of a stripe-ordered phase. The arrows show the spin order. Red and gray circles represent copper atoms with and without a hole, respectively. Charge rivers exist between undoped antiferromagnetically-ordered spin domains.

Besides the static spin order observed in  $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$ , static charge stripes in this system were observed by x-ray experiments on  $La_{2-x}Ba_xCuO_4$  with  $x \sim 1/8$  [37]. Recently, Raman scattering measurements also provided evidence for dynamical charge stripes within the pseudogap state (discussed below) in the  $La_{2-x}Sr_xCuO_4$  system [33]. Magnetic excitations observed in twinned and partially detwinned  $YBCO_{6+x}$  by Mook *et al.* [12] appeared to show quasi one-dimensional static magnetic stripes formed in the superconducting state. However, Mook's results remain under debate since fully detwinned  $YBCO_{6+x}$  samples have been investigated by V. Hinkov et al. and a two-dimensional geometry for the spin excitations was observed. Additionally, temperature dependent x-ray measurements on underdoped YBCO<sub>6+x</sub> [40] associated the opening of pseudogap state (see next subsection) to static charge stripes order in the  $CuO_2$  planes. However, this claim is also under debate [41]. Up to the time of this writing, the nature of the stripe dynamics, i.e. static or fluctuating, remains an unsettled issue. Although it is still largely unclear whether stripes are advantageous or detrimental to the superconducting or the pseudogap states, the observations just mentioned indicate the presence of stripes at least in some families of cuprates.

### 1.4.5 The Pseudogap State

One of the most challenging features of cuprates is the so-called *pseudogap state* (PG), which is most pronounced at low doping levels in the underdoped regime. This normal state gap was found to set in below a doping-dependent temperature T<sup>\*</sup> far above the superconducting dome, and manifests itself in several experimental methods as a suppression of the spectral response on cooling below T<sup>\*</sup>. One of the first observations was in nuclear magnetic resonance (NMR) measurements in underdoped YBCO<sub>6+x</sub> by Warren et al. [89]. NMR is an excellent probe for the spin system at different nuclear sites and at different k-regions of the FS. In cuprates, the NMR Knight shift measures the k = 0 spin susceptibility to an applied magnetic field, whereas the spin-lattice relaxation rate  $1/^{63}T_1$  is dominated by AF-spin



Figure 1.13: (a)  $^{63}$ Cu spin spin-lattice relaxation rate  $1/^{63}T_1T$ , and (b) Knight shift  $\Delta K = K_{measured}-K(4.2 \text{ K})$  as a function of temperature in underdoped, optimally doped, and overdoped Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+x</sub> (Bi2212) with T<sub>c</sub>'s of 79 K, 86 K, and 77.3 K, respectively. T<sub>c</sub>, T<sup>\*</sup>, and T<sub>0</sub> for each sample are denoted by arrows. Open circles in panel (b) refer to <sup>17</sup>O Knight shift of optimally doped Bi2212 [the reference is cited in [90]]. The figure is obtained from [90].

fluctuations around  $Q_{AF} = (\pi, \pi)$ . The opening of the normal state PG was seen in both the NMR Knight shift and the  $1/^{63}T_1$  spin-lattice relaxation rate of the copper nuclei in the CuO<sub>2</sub> planes.

Figure 1.13(a) shows the temperature dependence of the planar <sup>63</sup>Cu spin-lattice relaxation rate  $1/^{63}T_1$  and Knight shift  $^{63}\Delta K$  in underdoped ( $T_c = 79$  K), optimally doped ( $T_c = 86$  K), and overdoped ( $T_c = 77.3$  K) Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+x</sub> samples. In the overdoped sample, approaching the  $T_c$  from above,  $1/^{63}T_1$  increases continuously since the AF spin coherence increases. In contrast, for the optimal and underdoped samples, the  $1/^{63}T_1$  tends to decrease well above  $T_c$  due to the opening of the pseudogap state below T<sup>\*</sup>. Simultaneously, the NMR Knight shift of planar <sup>63</sup>Cu of underdoped HTSC decreases gradually below temperatures high above  $T_c$ , i.e. below  $T_0$  which is higher than  $T^*$  (Fig. 1.13(b)). This suppression in the Knight shift has been referred to as the opening of the PGS.

Besides NMR measurements shown above, the occurrence of the pseudogap at  $T < T_0$  has been demonstrated in resistivity measurements. The temperature dependence of the normal state in-plane resistivity of underdoped HTSC revealed a characteristic deviation of  $\rho$  from the linear behavior seen above T<sub>0</sub> (Fig.1.14). This anomalous behavior of  $\rho$  below T<sub>0</sub> is understood as a consequence of the opening of the pseudogap.



Figure 1.14: (a) Resistivity  $\rho$  versus temperature T in differently doped YBCO thin films. (b)  $d\rho/dT$  vs temperature as a function of the oxygen content. The arrows refer to the maxima from which T<sub>0</sub> is obtained. The figure is taken from [91].

Various experimental techniques found different values for the pseudogap temperature. For instance, the NMR Knight-shift revealed two temperature scales for the pseudogap (i.e.  $T_0$  and  $T^*$  with  $T^* < T_0$ ). T<sup>\*</sup> determined by NMR measurements of the spin-lattice relaxation rate and Knight shift of <sup>63</sup>Cu (Fig. 1.13) is lower than T<sub>0</sub> extracted from resistivity (Fig. 1.14) and NMR Knight-shift (Fig. 1.13(b)) measurements although both temperature scales are much higher than T<sub>c</sub>. However, there still exists no consensus regarding the definition of PG temperature, and the nature of the PG state.

The origin of the PG is still one of the most intriguing questions concerning the physics of cuprates. However, the HTSC community agreed on two possible scenarios (or, equivalently, phase diagrams (Fig. 1.15)), regarding the physics of the PG. The PG can be either intrinsic or extrinsic with respect to superconductivity. The intrinsic scenario implies that incoherent Cooper pairing with *d*-wave symmetry takes place at much higher temperature than  $T_c$ , i.e., precursor to superconductivity, while long range phase coherence is established when entering the SC-state. In contrast, extrinsic models associate the PG state with a hidden order parameter (e.g., exotic spin or charge orders) competing with superconductivity. In the earlier model, the T<sup>\*</sup> line decreases from a high value at weak doping and merges with the superconducting dome on the overdoped side (Fig. 1.15a), whereas in the latter approach it falls to zero around p = 0.19 (Fig. 1.15b) [23].



Figure 1.15: Two scenarios of the phase diagram of HTSC cuprates. AF, PGS, SC, SM, FL, NM refer to the antiferromagnetically ordered Mott insulator, pseudogap, superconducting, strange metal, Fermi liquid, and normal metal phases, respectively.  $T_N$ ,  $T^*$ and  $T_c$  correspond to the Néel, pseudogap, and superconducting transition temperatures, respectively. This figure is taken from Tallon *et. al* [23].

Various experimental probes provide controversial results for the PGS. For instance, ARPES measurements performed by Ding et al. [24] and recently by Kanigel et al. [92] (see also Refs. [25] and [35]) on various HTSCs have revealed that the magnitude and the wavevector dependence of the PG are consistent with that of a d-wave superconductor with a node in the  $\Gamma$ -Y direction and a maximum gap along the  $\Gamma$ -M direction (see fig.1.7). Based on these observations, the PG was considered to be associated with superconductivity. On the other hand, ARPES measurements on underdoped  $Bi_2Sr_2CaCu_2O_{8+x}$  samples performed by Lee *et al.* [27] revealed a sharp contrast between the superconducting and pseudogap states in the HTSC. That is, near the nodal direction, a gap was found to open below  $T_c$  and follow the conventional BCS-like behavior as the temperature is increased. Close to the antinodes of the d-wave gap function, a gap that deviates from d-wave symmetry persists above  $T_c$ , i.e., the pseudogap (Fig.1.16). Based on these two rather different temperature evolutions of the two gaps, the authors [27] expect distinct origins for them. These observations were later confirmed by other ARPES measurements performed by Kondo et al. [28] on slightly overdoped, optimally doped, and underdoped  $(Bi,Pb)_2(Sr,La)_2CuO_{6+x}$  samples with  $T_c$ 's of 29 K, 35K, and 23K, respectively (Fig.1.17(a-c)). In addition, the authors [28] have studied the wavevector dependence of the coherent spectral weight of the superconducting gap (Fig.1.17(df)). The spectral weight measured at temperatures deep inside the SC-dome  $W_{CP}$ was found to increase when departing from the nodal direction, but then starts to decrease at the vicinity of the antinodes. At that particular angle on the FS, the spectral weight recorded at a temperature  $T_c < T < T^*$ , i.e.  $W_{PG}$  increases



Figure 1.16: (a) Symmetrized energy distribution cuts near the nodes of the *d*-wave gap function in underdoped Bi2212 ( $T_c=92$  K) taken at various temperatures. The measurements were performed along cuts parallel to the M ( $\pi$ ,0)Y ( $\pi$ , $\pi$ ) direction (inset in b). Open circles and solid lines denote the experimental data and fit results using a phenomenological model described in [27], respectively. The vertical dashed line indicates the Fermi energy. (b) Temperature dependence of the SC-gap energy that opens at points A and B close to the nodes. The dashed lines show the temperature evolution of the SC-gap based on weak-coupling BCS theory. The superconducting  $T_c$  is denoted with the vertical line. (c) Plot of the gap values near the nodes (blue and green squares) and antinodes (red squares) against the simple *d*-wave gap function,  $|\cos k_x - \cos k_y|/2$ , at temperatures below and above  $T_c$ . Note that 102 K < T<sup>\*</sup>. The lines are guides to the eye. The figure is obtained from [27].

monotonically as the antinodal region is approached. The non-monotonicity of the SC-spectral weight seems to be small for the overdoped samples whereas it gets stronger with progressive underdoping (Fig.1.17(d-f)). The authors [28] argue that their observations arise from a competition between the superconductivity and an exotic order parameter formed in the pseudogap state.

Probes for the electronic spin dynamics in underdoped HTSCs revealed pronounced discrepancies between the superconducting and pseudogap states. Recently, INS experiments [30] performed on detwinned underdoped YBCO<sub>6.6</sub> have demonstrated that the topology of the dispersion surface of the magnetic excitations is different in the SC- and PG-states (Fig. 1.18). That is, the incommensurability constant  $\delta$  is strongly energy-dependent in the SC-state, hence the famous hourglass dispersion is reproduced (Fig. 1.9), whereas  $\delta$  in the PG-state is only weakly energy-dependent that results in an ill-defined hour-glass dispersion. Furthermore,



Figure 1.17: Momentum dependence of (a-c) the SC- (blue squares) and PG- (red circles) energies, and (d-f) their corresponding spectral weight in overdoped ( $T_c=29$  K), optimally ( $T_c=35$  K) doped and underdoped ( $T_c=23$  K) Bi2201 samples. The measurements were performed at temperatures below and above  $T_c$ , respectively. Dotted lines denote fits using the *d*-wave model  $\Delta \cos(2\varphi)$  to data in the nodal region (apart from the proximity to the pseudogap region). The arrows in (d-f) refer to  $\varphi$  range in which the weight of the coherent peak dominates over the pseudogap weight. The figure is taken from [27].

a-b anisotropies in the spin excitation spectrum have been found to be qualitatively different in the two states (Fig.1 in ref. [30]). The authors [30] suggest that these observations point to a competition between high T<sub>c</sub> superconductivity and the PG state in which an ordering phenomenon such as "Pomeranchuk" state may develop.

The plethora of experimental as well as theoretical attempts to discover the physics of the PG state raised more questions than they have answered and left the mechanism of the PG far from being understood. Therefore, additional work


Figure 1.18: Colour representation of the magnetic intensity of detwinned YBCO<sub>6.6</sub> observed in triple-axis neutron scattering measurements at temperatures below (a,b) and above (c,d) T<sub>c</sub>. (a,c) and (b,d) Results obtained from scans along the *a*-axis and *b*-axis, respectively. The crossings of black lines are measured data points. The white lines connect the magnetic peak positions obtained from constant-energy scans. The hour glass dispersion is obtained in the SC-state whereas in the PG state it is no longer discernible. The dotted lines in (d) represent upper limits on the incommensurability  $\delta$ . The figure is obtained from [30].

is still required to shed more light on the PG state, which may open the door for understanding the SC-pairing mechanism of HTSCs.

## **1.5** Structural Phases of the YBCO<sub>6+x</sub> Compound

The crystallographic structure of  $\text{YBCO}_{6+x}$  is more complicated than the simple perovskite structure demonstrated in Fig. 1.2 since the earlier contains additional layers in the unit cell (Fig. 1.19). Starting from the copper oxide planes, the Cu<sup>2+</sup> ion together with the surrounding four oxygen ions form the unit CuO<sub>2</sub>. The CuO<sub>2</sub> planes are arranged in bilayers with Y<sup>3+</sup> ions in the center. Each CuO<sub>2</sub> bilayer is surrounded by a layer comprised of barium and oxygen (the so-called apical oxygen)



Figure 1.19: The unit cell of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> compound.

ions. Connecting the Cu<sup>2+</sup> ion with the nearest neighboring oxygen ions produces the CuO<sub>5</sub> tetrahedron. The two tetrahedra of YBCO are separated by a yttrium  $Y^{3+}$  ion. Finally, each Ba-O layer is followed by a Cu1-O1 layer. For YBCO<sub>6+x</sub> with x > 0.3, the copper Cu1 and oxygen O1 ions in this layer are arranged in a chain-like sequence, i.e. Cu1-O1-Cu1-O1... running along the crystallographic *b*-axis whereas along the *a*-axis the O1 ions sitting between the Cu1 ions are missing. The existence of these chains produces a small difference between the *a*- and *b*-axes, hence the YBCO unit cell becomes orthorhombically distorted. Besides the structural deformation just mentioned, the chains play a major role in the doping mechanism of the YBCO system (discussed in Sec. 1.3).

YBCO structural phases are determined by the amount of oxygen ions incorporated in the Cu1-O1 chains. For instance, the YBCO<sub>6</sub> system, in which the O1 ions are completely depleted, has a tetragonal structure, i.e., a = b (Fig. 1.20). For 0 < x < 0.3, the oxygen ions were found to be randomly distributed in the Cu1-O1 layer, hence the structure of the YBCO unit cell remains tetragonal (Fig. 1.21). As x = 0.35 is approached from below, the Cu1-O1 chains tend to form, thus the YBCO<sub>6+x</sub> unit cell starts to be orthorhombically distorted, i.e., a < b. This orthorhombic distortion increases with a successive increase of the oxygen density in the chains (Fig. 1.20) reaching a maximum value for YBCO<sub>7</sub>, where the Cu1-O1 chains are completely full with O1 ions.

X-ray measurements [93] have revealed, for YBCO, six main structural phases.



Figure 1.20: Doping dependence of the lattice parameters a and b in the orthorhombic phase and  $a_T$  in the tetragonal phase, determined by neutron diffraction measurements. The figure is taken from [94].

In addition to the tetragonal phase discussed above, five orthorhombic superstructures (at  $0.35 < x \le 1$ ) were found (Fig. 1.21). These superstructures start to form below the high temperature tetragonal to orthorhombic phase transition, i.e., below  $T_{T-O} \sim 900$  K. Below room temperature, the order parameter is largely saturated. This results in forming the superstructures shown in Fig. 1.21 with full Cu-O and empty Cu-vacancy chain segments along the *b*-direction with periodic modulation *na* along the *a*-axis.

The superstructures just mentioned, are categorized according to the periodic arrangement they possess along the *a*-axis (Fig. 1.21). For instance, when all O1 sites are completely full with oxygen ions, the fundamental ortho-I structure is produced. This structure is equivalent to the conventional unit cell of YBCO<sub>7</sub> (Fig. 1.19). Between the fundamental tetragonal and ortho-I structures, ortho-II, ortho-III, ortho-V, and ortho-VIII superstructures have been obtained for YBCO<sub>6+x</sub>. In the ortho-II (ortho-III) phase, oxygen ions are completely depleted in every second (third) chain. The chain ordering sequence in ortho-V and ortho-VIII phases are, however, more complicated. In the former, every third and fifth chains are complectly missing whereas oxygen ions in the third, fifth and eighth chains of the latter phase are absent. In x-ray measurements, these superstructures are indicated by diffuse peaks which appear at modulation vectors  $Q=(nh_m,0,0)$  with *n* being an integer and h = 1/m. Here, m= 2, 3, 5 and 8 for ortho-II, ortho-III, ortho-V, and ortho-VIII superstructures, respectively (results of ortho-II and ortho-V are presented in chapter. 5). Among the orthorhombic phases, ortho-I (x = 1) and ortho-II



Figure 1.21: YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> structural phases as determined by x-ray measurements. T denotes the tetragonal phase, whereas OI–OVIII correspond to the orthorhombic ortho-I– ortho–VIII phases. The oxygen densities expected for the structural phases are given in parenthesis. The figure is obtained from [93].

(x = 0.5) structures possess a stable long range order, i.e., the correlation length  $(\xi = 1/\Gamma_m)$ , where  $\Gamma_m$  is the width of the observed diffuse peak, reaches several hundred Angstroms. The structure of the samples studied in this work (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub>) and Y<sub>0.85</sub>Ca<sub>0.15</sub> Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub>) and (YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> and YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.45</sub>) are very close to ortho-I and ortho-II, respectively. Vibronic Raman scattering data of each sample set look basically the same, hence the assignment of the Raman phonons presented in chapter 5 will be based on these two structures.

Furthermore, the formation of YBCO<sub>6+x</sub> single crystals below  $T_{T-O}$  is usually accompanied with spontaneous arrangement of polydomain twin structure. That is, the as-grown crystals possess equiprobable domains of twins in which the Cu1-O1 chains are perpendicular to each other. The existence of the twin domains leaves the crystallographic *a* and *b* axes indistinguishable, thus investigating the in-plane anisotropy of YBCO physical properties is prevented. Since the main goal of this work is to probe the *xy*-discrepancy in the Raman signals of detwinned YBCO, a description of the twin formation and the thermomechanical detwinning procedure will be presented in chapter 4.



Figure 1.22: (a-c) Electronic dispersion relation extracted from momentum distribution curves measured along  $(0, 0)-(\pi, \pi)$  direction of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO), Pb-doped  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  (Bi2212), and Pb-doped  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$  (Bi2201) copper oxides with different hole densities. Arrows denote the energy at which a sudden change "kink" in the dispersion occurs. (d,e) Electronic dispersion of LSCO (p = 0.15) and Bi2212 (p = 0.16) recorded at various temperatures below and above  $T_c$ . The figure is obtained from [103].

### **1.6** Electron-Phonon Interaction in HTSCs

After the discovery of HTSCs, experimental [95, 96] as well as theoretical [97] efforts have been devoted to examine the role of the electron-phonon (ele-ph) interaction in the Cooper pairing mechanism. Since Raman scattering is a powerful tool to study the *ele-ph* interaction, it has been intensively used to study the *ele-ph* interaction in HTSCs. For instance, ele-ph coupling constants of the CuO<sub>2</sub> plane phonons of  $RBa_2Cu_3O_{6+x}$  superconductors (R is a rare earth element) have been deduced from their superconductivity-induced anomalous broadenings below  $T_c$  [95] (see also Refs. [98], [99]). Based in part on these experiments as well as the absence of an isotope effect on  $T_c$  in optimally doped HTSCs [100], the *ele-ph* coupling was found to be too weak to solely explain the high  $T_c$  superconductivity. Besides that, it is difficult to explain the *d*-wave symmetry of the order parameter solely based on a phonon-mediated pairing mechanism [101]. In addition, the discovery of the magnetic resonance mode discussed above, has promoted more interest towards alternative models with a spin-based pairing interaction [102]. Recently, there has been several experimental evidences indicating that the *ele-ph* coupling plays a considerable role in the physics of cuprates and must be involved in any microscopic theory of HTSCs.

Renewed interest has been focused on the *ele-ph* coupling after the discovery of an abrupt anomaly (kink) in the electronic quasiparticle dispersion along the  $\Gamma$ -Y (nodal) direction in various copper oxide superconductors [103]. This kink appears as a generic feature of all HTSC investigated in [103] and is present around 60-



Figure 1.23: (a) Displacement pattern of oxygen ions for the q=(0.25, 0, 0) half breathing mode propagating perpendicular to the stripe orders. The corresponding atomic displacements are indicated by arrows. Large and small circles refer to copper and oxygen ions, respectively. Open (filled) large circles represent hole-depleted (hole-rich) regions. (b) Spectra of the half breathing mode of  $La_{2-x}Sr_xCuO_4$  with dopings p=0, 0.07, 0.15, 0.3, obtained from INS energy scans at 10 K. (c) Dispersion of the main peak of the half breathing mode of LSCO observed in (a) together with the bond-stretching branch along the chain direction in YBCO<sub>6.6</sub> and YBCO<sub>6.95</sub>. The figure is obtained from [43].

70 meV for temperatures below and above the SC-transition. The authors [103] argued that neither the opening of the superconducting gap, nor the magnetic resonance mode can explain this kink, because of the following: firstly, the SC-gap energy is material dependent, whereas the energy at which the kink occurs is the same in different cuprates. Secondly, the SC-gap as well as the magnetic mode of optimal and overdoped HTSCs vanishes above  $T_c$  whereas the kink persists in the normal state. Third, the electronic renormalization is seen in LSCO in which the magnetic mode is apparently weak. A key alternative candidate proposed for this coupling is the in-plane oxygen-stretching phonon mode seen by neutron scattering (Fig. 1.23), since it appears at energy close to the kink energy. Besides the kink, Lanzara et al have studied the so-called peak-dip-hump structure (Fig.2 in ref. [103]) in which the position of the *peak* and *dip* denote, respectively, the SC-gap energy  $\Delta$  and  $\Delta + \Omega$  where  $\Omega$  is the energy of a bosonic mode. Along the nodal direction, the authors [103] have found that the position of the dip agrees with the energy of the phonon mode just noted. The explanation proposed in [103] has been recently contested by a theoretical work, in which the authors [102] argue that charge- and spin-excitation spectra recorded by ARPES and INS, respectively, can be described simultaneously by spin-fermion based theory. Although there still exists controversy regarding the explanation of the "ARPES-kink", the relevance of *ele-ph* coupling to high  $T_c$  superconductivity should not be ignored.

Signatures of strong ele-ph coupling have also been found by nuclear INS experiments. For instance, the stretching phonon mode of the  $CuO_2$  plane oxygens around  $\sim 560 \text{ cm}^{-1}$  of different cuprate families has received a large amount of attention [43, 104]. Reznik et al. [43] have investigated the wavevector dependence of the stretching mode of the stripe-ordered La<sub>1.875</sub>Ba<sub>0.125</sub>CuO<sub>4</sub> and La<sub>1.48</sub>Nd<sub>0.4</sub>Sr<sub>0.12</sub>CuO<sub>4</sub> systems and compared the results with data obtained from differently doped LSCO and YBCO. The results reproduced from [43] are shown in Fig. 1.23. The stretching mode was found to have one single sharp peak at q-values close to the center of the BZ, whereas close to half-way to the zone boundary, i.e. q=(0.25,0,0), the main peak loses a substantial fraction of its intensity and the missing intensity goes into a low energy tail (Fig. 1.23a). Simultaneously, the main peak acquires a broadening and disperses strongly at the same wavevector. The authors [43] attribute this strong phonon anomaly to coupling between the phonon and charge inhomogeneities and charge stripes in the superconducting copper oxides. The absence of such an anomaly in the non-superconducting compounds suggests that *ele-ph* coupling is related to the physics of HTSCs [43].

# Chapter 2

# Theory of Raman Light Scattering in Solids

As light travels through a medium, changes may occur either to its propagation direction or to *both* its direction and energy. Deviations in the light direction without changes in frequency, i.e. *elastic scattering*, is mainly caused by static scatterers in a medium, *e.g.* defects or dislocations in a crystal. Fluctuations in the medium such as atomic vibrations or charge fluctuations can modify the energy and direction of light, i.e. scattering the light *inelastically*. Inelastic light scattering by molecular vibrations was first reported by the Indian physicist C.V. Raman [105]. In this chapter, I will present a classical as well as a quantum-mechanical theory of Raman scattering [more theoretical details of Raman scattering are available in refs. [16, 106, 107, 108, 109]]. This will be followed by group theory, selection rules, and vibrational mode analysis of YBCO<sub>6+x</sub>. The rest of the chapter is devoted to fundamentals of electronic light scattering in superconductors.

In an inelastic Raman scattering process, the incident photon is annihilated while a new scattered photon is generated. This process is accompanied with either creation (Stokes line) or annihilation (anti-Stokes line) of an elementary excitation, e.g. phonon. As for all scattering processes, the energy and momentum conservation conditions must be satisfied, that is,

$$\hbar\omega_i - \hbar\omega_s \pm \hbar\Omega = 0, \tag{2.1}$$

$$\hbar \overrightarrow{k}_{i} - \hbar \overrightarrow{k}_{s} - \hbar \overrightarrow{q} - \hbar \overrightarrow{G} = 0, \qquad (2.2)$$

where  $\omega_i$ ,  $k_i$ ,  $\omega_s$ ,  $k_s$ ,  $\Omega$ , and q denote the frequencies and momenta of the incident photon, scattered photon and the elementary excitation, respectively. G is a vector belonging to the reciprocal lattice. A minus (plus) sign in Eq. (2.1) refers to a creation (annihilation) of an elementary excitation. The advantage of Eq. (2.2) is to limit the scattering process to the portion of reciprocal space enclosed by the first Brillouin zone. In a Raman scattering process, an incident monochromatic light obtained usually from a laser is used. The wavelength of the visible light is of about 500 nm whereas a typical lattice constant a of a solid is around 0.5 nm. Hence, the wave vectors of the incident and scattered laser photons ( $k = 2\pi/\lambda$ ) are very small compared with the dimensions of the Brillouin zone. Therefore, G=0 and q $\approx$ 0 in Eq. (2.2). That is, the light photons can couple only with excitations close to the center of the Brillouin zone [109].

## 2.1 Classical Theory of Raman Scattering by Phonons

Consider an infinite medium with an electronic susceptibility  $\chi$  illuminated with a monochromatic light beam of frequency  $\omega_i$  and wavevector  $k_i$ . For simplicity,  $\chi$ , which is a second rank tensor, is assumed to be isotropic and therefore treated as a scalar. The traveling light has a sinusoidal electromagnetic field  $E(t) = E_0 cos(\omega_i t)$  that polarizes the electronic susceptibility of the medium  $\chi$  and induces a sinusoidal polarization  $P(t) = \chi E$ .

At a finite temperature, the atoms in a solid are usually displaced from their equilibrium position. The atomic displacement, which is small compared to the lattice constant, can be written as  $u(r,t) = u(q,\omega_0)cos(q.r - \omega_0 t)$  with q and  $\omega_0$ are the phonon wavevector and frequency, respectively. Since Raman scattering is associated with zone-center phonons  $(q \approx 0)$ , we can ignore the spatial dependence of the atomic displacement, which becomes  $u(t) = u(\omega_0)cos(\omega_0 t)$ . In the framework of the adiabatic (quasi-static) approximation, the electrons follow instantaneously the slow motion of the heavy ions. Therefore,  $\chi$  can be momentarily modulated by the atomic vibrations, hence expanded as

$$\chi(k_i, \omega_i, u) = \chi_0(k_i, \omega_i) + \frac{\partial \chi}{\partial u} u(t) + \dots, \qquad (2.3)$$

where  $\chi_0$  is the bare electronic susceptibility (without the effect of ionic motion) and the second term of  $\chi(k_i, \omega_i, u)$  is the susceptibility induced by atomic vibrations. Ignoring the higher terms of  $\chi(k_i, \omega_i, u)$ , the electric polarization becomes

$$P(t,u) = \chi_0 E_0 cos(\omega_i t) + \frac{\partial \chi}{\partial u} u(t) E_0 cos(\omega_i t)$$
  
$$= \chi_0 E_0 cos(\omega_i t) + \frac{1}{2} \frac{\partial \chi}{\partial u} u(\omega_0) E_0$$
  
$$\{ cos[(\omega_i - \omega_0)t] + cos[(\omega_i + \omega_0)t] \}.$$
(2.4)

The first term on the right hand side of Eq.(2.4) denotes the elastic Rayleigh scattering, whereas the second term describes an inelastic light scattering process which produces a Stokes (anti-Stokes) line with and a frequency  $\omega_S = \omega_i - \omega_0 (\omega_{AS} = \omega_i + \omega_0)$ .

So far, we have discussed the second term of  $\chi(k_i, \omega_i, u)$  (Eq. 2.3) which describes the *one-phonon* Raman scattering. Higher orders of  $\chi(k_i, \omega_i, u)$  give rise to higher-order Raman scattering processes. For instance, the third term of  $\chi(k_i, \omega_i, u)$ governs the *two-phonon* Raman scattering process in which the phonon frequencies are shifted from the laser frequency  $\omega_i$  by  $\pm \omega_1 \pm \omega_2$  ( $\omega_1$  and  $\omega_2$  are the frequencies of the two involved phonons) [108]. Assuming  $\omega_1$  to be larger than  $\omega_2$ , one may observe either combinations ( $\omega_1 + \omega_2$ ) or difference modes ( $\omega_1 - \omega_2$ ) in Raman spectra. Again, the momentum conservation principle must be satisfied, i.e.  $q_1 \pm q_2 \approx 0$ , where  $q_1$  and  $q_2$  are the wavevectors of the two phonons.

What do we measure in a Raman experiment? The scattering efficiency  $I(\omega, T)$  which is defined as "the ratio of the energy of electromagnetic waves scattered per unit time divided by the energy of incident electromagnetic modes crossing the scattering area per unit time" [108].  $I(\omega, T)$  of an elementary excitation, e.g. Stokes lines, can be given as

$$I_S(\omega, T) = \frac{\omega_S^4 V}{c^4} \mid \hat{e}_i \cdot (\frac{\partial \chi}{\partial u})_0 u(\omega_0) \cdot \hat{e}_s \mid^2 (n(\omega, T) + 1),$$
(2.5)

where  $\hat{e}_i$  ( $\hat{e}_s$ ) corresponds to the electric field vector of the incident (scattered) light,  $n(\omega, T) = [exp(\hbar\omega/K_BT) - 1]^{-1}$  is the Bose-Einstein statistical factor (or equivalently, the phonon occupation number), and V = AL, with A and L are the area of the incident beam and the scattering length, respectively. If the sample is transparent, L becomes equal to the thickness of the sample along the propagation direction of light propagation, otherwise  $L=(\alpha_i + \alpha_s)^{-1}$  where  $\alpha$  is the absorption coefficient [108].

Since the Stokes and anti-Stokes lines differ only in their frequencies, one can simply obtain the scattering efficiency of anti-Stokes lines from Eq.(2.5) through replacing  $(n(\omega, T) + 1)$  by  $n(\omega, T)$  and  $\omega_S$  by  $\omega_{AS}$ . An important consequence following from the intensities of the Stokes and anti-Stokes lines in Raman spectra is that the ratio  $I_S/I_{AS}$  allows the determination of the sample temperature. Since the anti-Stokes process can occur only if the medium is initially in an excited state and the anti-Stokes line intensities are proportional to  $n(\omega, T)$  that vanishes at low temperatures, we have focused our study on the Stokes scattering.

By introducing a unit vector parallel to the atomic displacement  $\hat{u}$ , one can obtain a second-rank tensor **R** known as the "Raman tensor"

$$\mathbf{R} = \left(\frac{\partial \chi}{\partial u}\right)_0 \hat{u}(\omega_0). \tag{2.6}$$

Substituting Eq. 2.6 into Eq. 2.5 reveals that the scattering intensity is proportional to  $|\hat{e}_i \cdot R \cdot \hat{e}_s|^2$ . This suggests that it is possible to deduce the symmetry of the Raman tensor and the symmetry of the corresponding Raman-active phonons from the analysis of the polarization-dependence of the Raman intensities [108].

## 2.2 Quantum-mechanical Theory of Raman Scattering by Phonons

A microscopic description of inelastic light scattering by phonons results from thirdorder time-dependent perturbation calculations of the three quantum steps shown by the diagrams of Fig. 2.1. In this approach, events involving photons take place through the coupling of electrons with the incident or scattered photons. The electron-photon hamiltonian  $H_{e-r}$  can be given as

$$H_{e-r} = \frac{e}{mc} \mathbf{A} \cdot \vec{p} + \frac{e^2 \mathbf{A}^2}{2mc^2}$$
(2.7)

where **A** is the vector potential of the light field,  $\vec{p}$  denotes the electron momentum, *c* indicates the velocity of light, and *e* and *m* are the charge and mass of the electron, respectively. The first term in Eq.(2.7) is linear in the vector potential **A** and dominates the electron-light coupling process, whereas the second term is quadratic in **A** and thus can be neglected. For a typical Raman experiment, the most important contribution to the electronic susceptibility comes from the coupling of light to the electronic excitations [106]. Since the direct coupling of light to the ionic excitation is small, events involving phonons rely mainly on the *ele-ph* interaction Hamiltonian  $H_{e-ph}$  given as

$$H_{e-ph} = \sum_{k,q,\mu,\sigma} g^{\mu}_{k,q} c^{\dagger}_{k+q,\sigma} c_{k,\sigma} (b_{q,\mu} + b^{\dagger}_{-q,\mu}).$$
(2.8)



Figure 2.1: Schematic energy band diagrams and the corresponding Feynman diagrams of (a) two band (b) three band Stokes scattering processes. In panel (a), the *ele-ph* interaction gives rise to an intraband transition, whereas in (b) the hole undergoes an interband transition. The numbers denote the order of the quantum events described in the text. e and h denote the electron and hole, respectively.  $H_{e-r}$  and  $H_{e-ph}$  refer to the electron-photon and electron-photon Hamiltonians, respectively [107].

where  $g_{k,q}^{\mu}$  is the *ele-ph* interaction vertex,  $c_{k+q,\sigma}^{\dagger}$   $(b_{q,\mu}^{\dagger})$  and  $c_{k,\sigma}(b_{q,\mu})$  are the creation and annihilation operators of electrons (phonons).  $\mu$  denotes the phonon branch and  $\sigma = \uparrow, \downarrow$  refers to the spin state. Note that for optical (zone-center) phonons, q in Eq.(2.8) must be set to zero.

A first-order Raman scattering process takes place in three distinct quantum events [106, 107, 108, 110, 111]:

(1) An electron-hole pair intermediate state  $|\alpha\rangle$  is generated by absorbing the incident photon  $\hbar\omega_i$ .

(2) The electron-hole pair is scattered into another state  $|\beta\rangle$  by means of

creating a phonon via the electron-phonon Hamiltonian  $H_{e-ph}$ .

(3) By emitting a photon, the electron-hole pair in state  $|\beta\rangle$  recombines and falls back to the ground state.

Since the electrons that mediate the Raman scattering process go back to the ground state, the electronic system after the Raman process is assumed to be unchanged. In each of the three steps just mentioned the wavevector must be conserved, whereas the energy conservation condition must be satisfied in the total process. The time order of the three quantum events is arbitrary and thus 3!=6 possible diagrams have to be considered. Using Fermi's Golden rule with the help of Feynman diagrams [more details can be found in ref. [108]], the scattering probability is given by

$$P_{ph}(\omega_s) = \left(\frac{2\pi}{\hbar}\right) \left|\sum_{\alpha,\beta} \frac{\langle i|H_{e-r}(\omega_s)|\beta \rangle \langle \beta|H_{e-ph}(\omega_s)|\alpha \rangle \langle \alpha|H_{e-r}(\omega_i)|i\rangle}{[\hbar\omega_i - (E_\alpha - E_i)][\hbar\omega_i - \hbar\omega_{ph} - (E_\beta - E_i)]} + 5\text{perm}\right|^2 \times \delta[\hbar\omega_i - \hbar\omega_{ph} - \hbar\omega_s], \qquad (2.9)$$

where  $|i\rangle$  is the initial state of the electronic system which appears twice since the final state in this case is identical to the initial state.

Due to the many intermediate states (real and virtual) involved in the Raman process, extracting information about electron-phonon, electron-photon and electron band structure together is barely feasible. This becomes possible if a small number of intermediate states dominates the Raman process. To achieve that, one should tune the energy of the incident laser light to resonate with the interband distance and thus an enhanced real electronic transitions will take place. This is the so-called *ingoing resonant* Raman scattering. Similarly, if the energy of the scattered light matches the recombination energy of an electron in the upper band with a hole in the lower band, an *outgoing resonant* Raman process can be achieved.

## 2.3 Raman Selection Rules and their Applications to Tetragonal and Orthorhombic HTSCs

Raman scattering in solids is a powerful probe for electronic and lattice vibrational excitations in different symmetries. The application of a particular polarization configuration of the electric field of the incident and scattered light allows us to probe *selectively* the elementary excitations on specific parts of the Fermi surface. Therefore, performing a polarized light Raman measurements requires a good knowl-

#### 2.3. Raman Selection Rules and their Applications to Tetragonal and **Orthorhombic HTSCs**

edge of the selection rules and their applications on precisely oriented single crystals.

In order to understand the Raman symmetries of HTSC, we recall the approximate expression of Eq. (2.5)

$$I_S(\omega, T) = |\hat{e}_i \cdot R \cdot \hat{e}_s|^2 .$$
(2.10)

If the Raman intensity of a particular excitation mode is non-vanishing when certain choices of the incident and scattered ( $e_i$  and  $e_s$ , respectively) polarizations are applied, this mode is considered as Raman-active (Raman-allowed) [107]. Besides that, measuring the dependence of the Raman intensity on the geometry of the incident and scattered polarizations allows us to obtain the symmetry of the Raman tensor (Eq. 2.6) and hence the symmetry of the Raman-active modes [108]. These are the so-called Raman selection rules which hold for all elementary excitations of ions (phonons) and of electrons (e.q. transitions across the superconducting gap). Therefore, polarized light Raman measurements are capable to determine both, the energy and the symmetry of the zone-center active modes [108].

HTSCs have either  $D_{2h}$  (orthorhombic) or  $D_{4h}$  (tetragonal) point groups. Tables 2.1 and 2.2 show the irreducible representations of their Raman tensors, respectively. To obtain the Raman symmetries of HTSC, one has to evaluate Eq. (2.5) for the possible Raman tensors in tables 2.1 and 2.2, with all possible polarization configurations of the electric fields of the incident and scattered light [112, 113, 114, 115].

${\bf Orthorhombic}{\bf D}_{2h}$			
$A_g$	$B_{1g}$	$B_{2g}$	$B_{3g}$
$ \begin{array}{ccc} \begin{pmatrix} xx & 0 & 0 \\ 0 & yy & 0 \\ 0 & 0 & zz \end{pmatrix}  \left( \begin{array}{c} \\ \end{array} \right) $	$\begin{pmatrix} 0 & xy & 0 \\ yx & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$ \left(\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$ \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & yz \\ 0 & zy & 0 \end{pmatrix} $

Table 2.1: Irreducible representations of the Raman tensor in orthorhombic HTSC with  $D_{2h}$  point group [112, 113].

In polarized Raman experiments, the polarization configurations are usually written in Porto notation, i.e. i(kl)j, where i and j denote the propagation direction of the incident and scattered photons, and k and l are the polarization of their electric fields, respectively. In this work, we are concerned with probing the *ab*-plane elementary excitations in various polarization geometries, therefore the propagation direction of the incident and scattered photons was always nearly parallel to the crystallographic *c*-axis. For convenience, we skip the propagation direction of light

Tetragonal $D_{4h}$		
$A_{1g}$	$A_{2g}$	$B_{1g}$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{pmatrix} 0 & xy & 0 \end{pmatrix}$	$\begin{pmatrix} xx & 0 & 0 \end{pmatrix}$
0  xx  0	-xy  0  0	0  -xx  0
$\begin{pmatrix} 0 & 0 & zz \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 \end{pmatrix}$
$B_{2g}$	$E_g$	$E_g$
$\begin{pmatrix} 0 & xy & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & xz \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 \end{pmatrix}$
xy  0  0	0 0 0	0  0  xz
	$\left[ \begin{array}{ccc} zx & 0 & 0 \end{array} \right]$	$\begin{pmatrix} 0 & zx & 0 \end{pmatrix}$

Table 2.2: Same as table 2.1 but in tetragonal HTSC with  $D_{4h}$  point group [112, 113].

and give only the polarization directions of the incident and scattered photons (letters inside the parentheses).

For orthorhombic HTSCs, excitations of  $A_g$ ,  $B_{1g}$ ,  $A_g+B_{1g}$ , and  $A_g$  symmetries are accessible by using xx (or yy), xy (or yx), x'x' (or y'y'), and x'y' (or y'x') polarizations of the incident and scattered light fields, respectively [17, 117]. In this notation x and y correspond to the direction of the electric field of light along the a- and b-axes, whereas x' and y' denote axes rotated by 45° from a- or b- axes, i.e.  $x' \sim x + y$  and  $y' \sim x - y$ , respectively. Here, the beam direction is nearly along the c-axis. For HTSC with tetragonal point group  $D_{4h}$  (e.g.  $La_{2-x}Sr_xCuO_4$  at low temperatures [118, 119], HgBa<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8+x</sub> [120], and Tl<sub>2</sub>Ba<sub>2</sub>CuO<sub>6+x</sub> [121, 122]), excitations of  $A_{1g}+B_{1g}$  symmetry are accessible for either xx or yy polarization,  $B_{2g}$  for either xy or yx polarization,  $A_{1g}+B_{2g}$  for either x'x' or y'y' polarization, and  $B_{1g}$  for either x'y' or y'x' polarization of the electric field vectors. In table 2.3, we summarize the possible in-plane polarization geometries and the corresponding Raman symmetries in orthorhombic and tetragonal notations.

As noted in sec. 1.5, there exists two types of YBCO, twinned and detwinned. As-grown samples display twinning in the a - b plane along [110] and [110] directions, and thus x- and y-axes are barely distinguishable. Hence, twinned samples are approximated as tetragonal. Thermomechanically detwinned samples have orthorhombic structure with  $a \neq b$ . Due to the small difference between a- and b-axis lengths in detwinned YBCO, the structure can be described in terms of the closely related tetragonal structure. As most previous work on YBCO has been performed on twinned specimens [16], we follow previous publications and use the tetragonal notation of the polarization symmetries throughout this thesis.

2.4. Group Theory Analysis of q = 0 Modes of Twinned and Twin-Free  $YBa_2Cu_3O_{6+x}$ 

Polarization geometry	Raman symmetry	Raman symmetry	
	for tetragonal HTSC	for orthorhombic HTSC	
xx/yy	$A_{1g} + B_{1g}$	$A_g$	
xy/yx	$B_{2g}$	$B_{1g}$	
x'x'/y'y'	$A_{1g} + B_{2g}$	$A_g + B_{1g}$	
x'y'/y'x'	$B_{1g}$	$A_g$	
xz/zx	$E_g$	$B_{2g}$	
yz/zy	$E_{q}$	$B_{3a}$	

Table 2.3: possible polarization geometries and their corresponding symmetries in Raman experiments on orthorhombic and tetragonal HTSC.

#### Group Theory Analysis of q = 0 Modes of 2.4Twinned and Twin-Free $YBa_2Cu_3O_{6+x}$

HTSCs have complicated structures with N atoms per unit cell. Group theory is particularly helpful to identify the symmetries of the 3N - 3 optical phonons. Ortho-I  $YBa_2Cu_3O_7$  and tetragonal  $YBa_2Cu_3O_6$  contain 13 and 12 atoms per unit cell, respectively. Hence, group theory predicts for these two compounds 36 and 33 optical phonon modes, respectively. Here, I will present the group theoretical classification of these optical modes.

The Raman-active modes are those that transform according to one of the symmetries of the possible Raman tensors and scattering process achieved by the proper scattering geometry (selection rules) [107]. This means that Raman tensors must have even symmetry, *i.e.*  $R_{ij} = R_{ji}$  [125], and thus odd symmetry excitations are Raman forbidden but infrared (henceforth IR) active. This holds for centrosymmetric compounds, i.e. compounds that possess a center of inversion like HTSCs, in which optical phonon modes at q = 0 cannot be both Raman and IR active.

For centrosymmetric structures, there must be at least one site of the unit cell which sustains the full symmetry of the point group. In  $YBa_2Cu_3O_7$  (Fig. 1.19), yttrium, chain copper (Cu1), and chain oxygen (O1) ions are at the inversion center and thus have  $D_{2h}$  site symmetry. Each of these atoms has three degrees of freedom and can vibrate along z, y, and x axes giving rise to  $B_{1u}$ ,  $B_{2u}$ , and  $B_{3u}$  IR-active modes, respectively. The remaining pairs of atoms, *i.e.* planar oxygen (O2 and O3), planar copper (Cu2), barium, and apical oxygen, have  $C_{2v}$  symmetry. Each of these pairs vibrate in three dimensions and contribute with three odd and three even modes:  $B_{1u}$ ,  $B_{2u}$ , and  $B_{3u}$  IR-allowed modes and  $A_g$ ,  $B_{2g}$ ,  $B_{3g}$  Raman-allowed modes (fig. 2.2). The atomic vibrations in the  $A_g$ ,  $B_{2g}$ , and  $B_{3g}$  symmetries are parallel to the c-, a-, and b-axis, respectively. The subscripts u and g are abbreviations for the german "ungerade" (odd symmetry) and "gerade" (even symmetry), respectively. Summing up these modes and subtracting the three acoustic ones gives rise to 36 optical modes for the orthorhombic YBCO unit cell [116].

$YBa_2Cu_3O_7, Orthorhombic, D_{2h}$		
Atom	Site symmetry	Allowed modes
Y	$D_{2h}$	$B_{1u} + B_{2u} + B_{3u}$
O1	$D_{2h}$	$\mathbf{B}_{1u} + \mathbf{B}_{2u} + \mathbf{B}_{3u}$
Cu1	$D_{2h}$	$B_{1u} + B_{2u} + B_{3u}$
Ba	$C_{2v}$	$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$
Cu2	$C_{2v}$	$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$
O2	$C_{2v}$	$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$
O3	$C_{2v}$	$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$
O4	$C_{2v}$	$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$
$\textbf{YBa}_{2}\textbf{Cu}_{3}\textbf{O}_{6}, \textbf{Tetragonal}, \textbf{D}_{4h}$		
Atom	Site symmetry	Allowed modes
Y	$D_{4h}$	$A_{2u}+E_u$
Cu1	$D_{4h}$	$A_{2u}+E_u$
Ba	$C_{4v}$	$A_{1g} + E_g + A_{2u} + E_u$
Cu2	$C_{4v}$	$A_{1g} + E_g + A_{2u} + E_u$
O2 (or O3)	$C_{2v}$	$A_{1g}+2E_g+B_{1g}+A_{2u}+2E_u+B_{2u}$
O4	$C_{4v}$	$A_{1q}+E_q+A_{2u}+E_u$

Table 2.4: Atomic site symmetries and their corresponding optical modes of orthorhombic  $(D_{2h})$  and tetragonal  $(D_{4h})$  YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> systems. Note that the E<sub>u</sub> and E<sub>g</sub> modes are doubly degenerate [116].

For tetragonal YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub>, the O1 ions are completely missing, thus yttrium and Cu1 ions have the full symmetry of the D<sub>4h</sub> point group. Each of these ions contribute with three IR-allowed modes, i.e.  $A_{2u}+E_u$ . The Ba, Cu2, and O4 ions have C<sub>4v</sub> site symmetry, hence each atom gives  $A_{1g}+E_g+A_{2u}+E_u$  optical modes. Here, the oxygen ions (O2 and O3) in the CuO<sub>2</sub> planes become indistinguishable and possess C<sub>2v</sub> site symmetry. Therefore, they produce  $A_{1g}+2E_g+B_{1g}+A_{2u}+2E_u+B_{2u}$ phonon modes. Note that in the  $A_{1g}/A_{2u}$  symmetries, the ions move parallel to the *c*-axis, whereas in the  $E_g/E_u$  symmetries they either move along the *a*- or *b*- axes, respectively. The Raman B<sub>1g</sub> and the IR-B<sub>2u</sub> symmetries represent the out-of-phase vibrations of planar oxygen atoms along the *c*-axis. As a result, one obtains 33 optical modes after excluding the three acoustic modes. In table 2.4, we summarize the site symmetry and the corresponding optical modes for each atom of the orthorhombic and tetragonal YBCO unit cells [116].

Here, It is worth mentioning the peculiarity of the Raman symmetry of the out-of-phase vibrations of planar oxygens [the so-called  $B_{1g}$ -like mode or buckling mode]. It belongs to the  $A_q$  symmetry in orthorhombic notations, whereas it has  $B_{1q}$ symmetry in tetragonal structure. Since the orthorhombic distortion in detwinned YBCO is small, the buckling mode still holds the character of  $B_{1q}$  symmetry.

After classifying the optical mode symmetries of YBCO, it is necessary to assign the energy of the phonon modes in order to understand the observed spectrum. The phonon frequencies can be estimated by lattice dynamical calculations following spring and masses [126] or shell-model calculations [127, 128]. In fig. 2.2, we show the Raman and IR- eigenmodes of YBCO<sub>7</sub> and their expected frequencies (in  $\rm cm^{-1}$ ) obtained within the shell-model calculations. For the purpose of this thesis, I will pay attention only to the Raman-active modes.

Using tetragonal notation, the  $4A_{1g}+1B_{1g}$  (c-polarized) modes are the following [60, 116, 127, 128, 129]: the lowest-frequency phonon, which is expected to appear at 115 cm<sup>-1</sup> ( $A_{1q}$ ), originates predominantly from vibrations of the barium atoms. The next lowest frequency phonon, predicted at 157 cm<sup>-1</sup> ( $A_{1q}$ ), corresponds mainly to vibrations of copper (Cu2) ions. The vibrations of the apical oxygen ions (O4) is anticipated at 509 cm<sup>-1</sup> (A<sub>1q</sub>). The two modes estimated to appear at 353  $cm^{-1}$  (B<sub>1g</sub>) and 477 cm<sup>-1</sup> (A<sub>1g</sub>) are predicted to originate from out-of-phase and in-phase vibrations of the planar oxygen ions (O2 and O3), respectively. Note that the Local Density Approximation (LDA) predicts a small admixture of the Ba and Cu vibrational amplitudes [130]. Since the frequencies of the remaining phonons are well separated, the admixture, if it exists, is expected to be negligible [131].

The  $B_{2q}$  ( $B_{3q}$ ) phonon modes originating from vibrations of Ba, Cu2, O4, O3, and O2 are expected to appear at 70 (91), 142 (137), 346 (490), 428 (411) and 584 (545), respectively. In the Raman spectrum of HTSC, the  $A_{1g}$  phonon modes are 10 to 100 times more intense than those of  $B_{2q/3q}$  symmetry [113, 60]. For this reason, we will focus from now on only on the  $4A_{1q}+1B_{1q}$  modes. Table 2.5 shows the  $4A_{1g}+1B_{1g}$  phonon frequencies calculated by spring and masses, shell-model and ab *initio* approaches together with those observed in previous Raman measurements as well as the phonon frequencies observed in our spectra (Fig. 2.3).

In detwinned YBCO<sub>6+x</sub>, the previously discussed  $4A_{1q}+1B_{1q}$  modes are observable for polarizations along a- and b-axis (Fig. 2.3). In addition, two defect-induced modes appear in the yy symmetry at 232 cm<sup>-1</sup> and at 579 cm<sup>-1</sup>. They originate from vibrations of the copper (Cu1) and the oxygen (O1) ions, respectively, in



Figure 2.2: Eigenmodes of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> at q = 0 and their expected frequencies (in cm<sup>-1</sup>) obtained within the shell-model calculations [127, 128]. The first two rows represent the Raman-active  $4A_{1g}+1B_{1g}$  and  $B_{2g}/B_{3g}$  modes whereas the lower two rows display the IR-active  $B_{1u}$ ,  $B_{2u}/B_{3u}$  modes, respectively. The green arrows in the lower two rows indicate the atoms which dominate the vibrational IR-active mode whereas red arrows indicate almost equal contribution of the atoms. This figure is obtained from [127].

2.4. Group Theory Analysis of q = 0 Modes of Twinned and Twin-Free YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub>



Figure 2.3: Raman spectra of a detwinned, almost optimally doped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub> single crystal in xx, yy and zz polarizations taken with an Ar<sup>+</sup> laser line ( $\lambda$ =514.5 nm). The mode assignment corresponds to Refs. [109, 116, 127, 128, 60, 135]. The intensity scales in the three panels are the same whereas the zz spectrum was divided by 6.

the Cu–O chains, which are aligned along the crystallographic *b*–axis [135]. In YBCO crystals with fully oxygenated chains, these two modes are Raman forbidden but infrared–allowed with  $B_{1u}$  symmetry (Fig. 2.2 third row, third and last modes from left) [136, 137, 138]. They become Raman-active due to breaking of the translational symmetry by defects, i.e. unoccupied oxygen positions in the Cu1-O1

Phonon	spring mass	shell-	ab <i>initio</i>	Previous Raman	our results
	approach	model		Experiment	
Ba $(A_{1g})$	125	115	119	112	113
Cu2 (A <sub>1g</sub> )	193	157	151.5	154	148
O2-O3 $(B_{1g})$	346	353	339	340	340
$O+O3(A_{1g})$	352	377	406	440	446
$O4(A_{1g})$	496	509	472	500	501

Table 2.5: calculated phonon frequencies of the  $4A_{1g}+1B_{1g}$  Raman modes using spring-masses [126], shell model [128] and ab *initio* [129] approaches together with previous Raman results [128] and our phonon frequencies (Fig. 2.3). The  $B_{2g}/B_{3g}$ modes are less important for the goal of this thesis and if one is concerned, more information are available in Refs. [132, 133, 134]

chains. [116, 135, 140]. A characteristic feature of these defect-induced modes is their strong resonance for the yellow line of the Kr<sup>+</sup>-laser [135]. These modes are very helpful to estimate the detwinning ratio of the YBCO crystal. For instance, the absence of these modes in the xx-spectra indicates a high detwinning quality of the YBCO samples [135, 136, 137, 138].

### 2.4.1 Polarization-Dependence of the $4A_{1g}+1B_{1g}$ Phonon Intensities in Detwinned YBCO<sub>6+x</sub>

Since the laser spot is much larger than the size of the twin microdomain, the ab-plane Raman tensor elements of the  $4A_{1g}+1B_{1g}$  phonons in twinned YBCO are indistinguishable (table 2.2). The observed Raman spectra in the xx and yy symmetries are therefore the same, but they differ from that observed in the zz polarization geometry. In detwinned YBCO<sub>6+x</sub> crystals, the in-plane Raman tensor elements become polarization-dependent ( $xx \neq yy \neq zz$  (see table 2.1)). This gives rise to different phononic as well as electronic scattering efficiencies for light polarizations along the a-, b- and c-axis of detwinned YBCO samples. The main difference in the Raman spectra taken for twinned and detwinned crystals is seen when light polarizations are parallel to the a- and b-axes whereas the c-axis polarized spectrum should be the same in both cases.

Figure 2.3 shows Raman spectra of nearly optimally doped YBCO<sub>6.95</sub> taken at room temperature in xx, yy and zz polarization symmetries. The polarizationdependence of the phonon intensities reflects the differences in the phonon polarizabilities ( $\alpha_{ij}$  with *i* and *j* denote the Raman tensor element) when light polarizations

2.4. Group Theory Analysis of q = 0 Modes of Twinned and Twin-Free  $YBa_2Cu_3O_{6+x}$ 

Phonon	Raman Polarizability $(\alpha_{ij})$
Ba(z)	$\alpha_{xx} \approx 0.5 \alpha_{yy},  \alpha_{zz} \approx \alpha_{yy}$
Cu2(z)	$\alpha_{xx} \approx \alpha_{yy},  \alpha_{zz} \approx 1.2 \alpha_{yy}$
O2(z)-O3(z)	$\alpha_{xx} \approx 1.4 \alpha_{yy},  \alpha_{zz} \approx 0$
O(z)+O3(z)	$\alpha_{xx} \approx \alpha_{yy},  \alpha_{xx}, \alpha_{yy} \ll \alpha_{zz}$
O4(z)	$\alpha_{xx} < \alpha_{yy},  \alpha_{xx}, \alpha_{yy} \ll \alpha_{zz}$

Table 2.6: Raman  $A_q$  phonons, and their relative polarizabilities  $\alpha_{ij}$  for YBCO<sub>7</sub> [125, 140].

are projected along the a-, b- or c-axis.

In tetragonal YBCO, the O2 and O3 atoms are equivalent and thus their displacements are equal. For orthorhombic  $YBCO_{6+x}$ , the existence of the chain O1 atoms induces a repulsive interaction with the planar O3 ions (parallel to the b-axis) and thus the Raman polarizability of O3 is reduced. Therefore, the intensity of the out-of-phase vibrations of the planar oxygens (the  $B_{1q}$ -mode) is smaller in the yythan in the xx symmetry [125, 140]. Since the zz component of the  $B_{1g}$  Raman tensor in the tetragonal symmetry is zero, the  $B_{1g}$  phonon is absent in the Raman spectrum for polarizations along the c-axis (Fig. 2.3). This again indicates that this phonon keeps the  $B_{1g}$  character even though it has  $A_g$  symmetry in orthorhombic YBCO<sub>6+x</sub>. The Cu1–O1 chains play a major role in the polarizability of the neighboring atoms, i.e. Ba and O4 atoms. Hence, their intensity is greater when light polarizations are projected parallel to the b-axis. The polarizability of the Ba vibrations along the c-axis is comparable to that along the b-axis, whereas for O4 atoms  $\alpha_{zz}$  has been found to be almost 10 times larger than  $\alpha_{yy}$  [125, 140].

The in-phase vibrations of planar oxygens are usually weak compared to other phonon peaks and thus it is difficult to observe the xy-anisotropy of this phonon intensity. However, it is expected that this mode has higher scattering intensity in the yy symmetry [140]. The plane Cu2 vibrations show almost the same intensity in the xx and yy symmetries indicating the low sensitivity of the Cu2 to the increase of O1 atoms in the chain. Again the Raman polarizability of these two modes in zz symmetry is larger (and their intensity is stronger) than in both, xx and yy scattering geometries. Table 2.6 summarizes the Raman tensor elements (or, equivalently, Raman polarizabilities) of the five Raman-active phonons in detwinned  $YBCO_{6+x}$ in xx, yy, and zz Raman symmetries.

So far, I have presented a group theoretical identification of the Raman phonon modes of tetragonal and orthorhombic (ortho-I) YBCO<sub>6+x</sub>, their energies and their

x, y, and z relative intensities. Now, I will discuss the case in which the doping of  $YBCO_{6+x}$  crystal is close to 0.5.

### 2.4.2 Phonon Analysis of Ortho-II YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.5</sub>: Effect of Periodicity

In YBCO<sub>6.5</sub>, the Cu1-O1 chains are ordered in the so-called ortho-II phase (D<sub>2h</sub> space group) in which  $2a \times b \times c$  supercells are formed (Fig. 1.21). Therefore, the number of Raman- and IR-allowed phonons becomes higher [138, 139, 141, 142, 143]. The doubled YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.5</sub> unit cell (or, equivalently, Y<sub>2</sub>Ba<sub>4</sub>Cu<sub>6</sub>O<sub>13</sub>) has 25 atoms per supercell unit, thus 75 vibrational modes at the center of the ortho-II Brillouin zone are expected. That is,  $11A_g + 4B_{1g} + 11B_{2g} + 8B_{3g} + 2A_u + 14B_{1u} + 12B_{2u} + 13B_{3u}$ . In addition to the known modes in ortho-I YBCO<sub>7</sub>, six A<sub>g</sub>, four B<sub>1g</sub>, six B<sub>2g</sub> and three B<sub>3g</sub> extra modes exist for ortho-II YBCO. Since the B<sub>g</sub> modes are 10 times weaker than the A<sub>g</sub> ones, and the extra B<sub>g</sub> modes have no analogs to those of YBCO<sub>7</sub>, the extra B<sub>1g</sub>, B<sub>2g</sub>, and B<sub>3g</sub> modes are hardly distinguishable. However, one can recognize the strong A<sub>g</sub> modes, therefore I will focus only on them. Again, in the tetragonal notations the 11A<sub>g</sub> modes are 10 A<sub>1g</sub> plus the well-known B<sub>1g</sub> mode at 340 cm<sup>-1</sup>.

Figure 2.4 shows the eigenvectors of the  $10A_{1g}+1B_{1g}$  Raman-active modes in YBCO<sub>6.5</sub> predicted by LDA calculations [138]. Similar to ortho-I YBCO<sub>7</sub>, the z-polarized displacements of the Ba, Cu2, plane oxygen [(O2-O3) and (O2+O3)], and O4 atoms are predicted to appear at 118, 151, 331, 444, and 478 cm<sup>-1</sup>, respectively [138]. Additional  $A_{1g}$  modes expected at 78, 146, 346, and 414 cm<sup>-1</sup> are attributed to z-axis vibrations of (Cu2(z)-Cu2'(-z)—out of phase), mixed Ba/Cu, (O4(z)-O4'(-z)—out of phase), O4'(z), respectively (Fig. 2.4). The  $A_{1g}$  modes anticipated to appear at 171 and 593 cm<sup>-1</sup> originate from x-polarized displacements of yttrium Y(x) and plane oxygen O2(x) atoms.

Since xx and yy symmetries are indistinguishable for twinned YBCO<sub>6.5</sub>, the 11 A<sub>g</sub> modes appear in *both*, xx and yy Raman spectra. The case is different for detwinned YBCO<sub>6.5</sub>. For instance, the z-polarized atomic vibrations are expected to be present in either xx or yy polarization geometries, whereas the x-polarized vibrations of yttrium and planar oxygen O2 ions are expected to appear *only* when light polarizations are parallel to the *a*-axis. Therefore, Y(x) and O2(x) are excellent tools to probe the xy-anisotropy of the electronic system of underdoped YBCO<sub>6+x</sub> with x close to 0.5.

2.4. Group Theory Analysis of q = 0 Modes of Twinned and Twin-Free  $YBa_2Cu_3O_{6+x}$ 



Figure 2.4: Main atomic displacements of the  $A_g$  modes of  $YBa_2Cu_3O_{6.5}$  (ortho-II) as obtained by LDA calculations. The LDC predicted frequencies (in parentheses) are compared to the experimentally obtained values. The circles surround the five  $A_g$  modes  $(4A_q+1B_{1q}$  in tetragonal notations) of ortho-I structure whereas the rectangles enclose the x-polarized periodicity-induced phonon modes. The figure is taken from Ref. [138].

In the literature, Raman peaks observed for  $YBCO_{6.5}$  at 171 cm<sup>-1</sup> [138], 187  $cm^{-1}$  [142], and 215  $cm^{-1}$  [143] have been assigned to the Y(x) mode whereas those observed at 579 cm<sup>-1</sup> [138], 593 cm<sup>-1</sup> [141], and 615 cm<sup>-1</sup> [142] have been attributed to the plane stretching mode  $O_2(x)$ . Thus, the exact nature of these modes is still controversial. Aiming to solve this controversy, we will present a comprehensive temperature and doping dependent study of these modes in sec. 5.3.

### 2.5 Fundamentals of Electronic Light Scattering

In a crystal, light can be scattered by electronic excitations in two ways; interband and intraband processes. The earlier contribution is resonant and usually dominates the Raman scattering in insulators and semiconductors whereas the latter is non-resonant and common for doped semiconductors or metals. Here, we will be concerned with low-energy intraband transitions in metallic and superconducting YBCO.

#### 2.5.1 Electronic Raman Scattering in Metals

In a pure metal, the low energy elementary excitations are inaccessible by optical techniques [109, 81]. Raman allowed excitations with a frequency  $\omega$  must have a small wavevector K compared to the dimensions of the BZ, i.e.  $0 < K \ll BZ$ . The minimum wavevector transfer must be

$$K = 2\omega(\frac{K_F}{\omega_F}),\tag{2.11}$$

where  $K_F$  and  $\omega_F$  denote the Fermi wavevector and Fermi energy, respectively. In pure metals, the initial and final states are nearly the same. That is, for any initial state below the Fermi energy (Fig. 2.5a), there is no final state for which the momentum transfer condition (Eq. 2.11) is satisfied. Hence, no optical transitions are allowed for pure metals.



Figure 2.5: (a) Band diagram for a metal in the normal state.  $E_F$  represents the Fermi energy. The arrow labeled  $\hbar\omega$  symbolizes intraband excitations which are optically forbidden (no real final state). (b) Corresponding diagram for the superconducting state with  $\Delta$  denotes the superconducting gap [109].

A pure metal can hardly be obtained. Impurities, atomic displacement, disorders or any crystal defects results in breaking of the translational symmetry of the crystal. Hence, a finite electron mean free path l will be generated. This leads to a smearing of the wavevector of the Raman excitation at the center of the BZ by an amount of 1/l. As a result, Eq. (2.11) can be fulfilled and intraband electronic excitations become Raman-active [109, 81].

A second reason for the low intensity of Raman scattering signals in pure metals is that the incoming light is usually screened by the electrons of the metal. Therefore, the optical penetration depth  $\lambda$  is small which results in a weak scattering cross section.

### 2.5.2 Electronic Raman Scattering in Conventional Superconductors

Below the SC-transition, the low energy electronic continuum of a conventional superconductor undergoes a frequency redistribution accompanied with an electronic gap  $\Delta$  opening around the Fermi surface (Fig. 2.5). In contrast to metals, in which Raman excitations requires a minimal momentum difference between the initial and final states (Eq. 2.11), vertical transitions can destroy the Cooper pairs and promote quasiparticles across the SC-gap. BCS theory predicts that an energy of  $2\Delta$ is needed to break the Copper pairs. This energy can be obtained from the exciting laser used in a Raman experiment. Hence, the opening of the SC-gap allows the intraband electronic excitations to be Raman-active although the momentum transfer is zero [81].

Raman spectra of BCS superconductors, e.g. Nb<sub>3</sub>Sn, reveal a complete suppression of the electronic scattering at low frequencies, i.e.  $\omega < 2\Delta$ , accompanied with a well-defined maximum at  $2\Delta$ . Klein and Dierker [144, 145] were able to describe the imaginary part of Raman response of a conventional superconductor. Based on their calculations, the imaginary part of the Raman susceptibility, at T = 0, can be written as

$$\chi'' = \frac{2\pi N_F}{\omega} \operatorname{Re} \left\langle \frac{|\gamma_{\boldsymbol{k}}|^2 |\Delta_{\boldsymbol{k}}|^2}{\sqrt{\omega^2 - 4|\Delta_{\boldsymbol{k}}|^2}} \right\rangle_{\boldsymbol{FS}} = \langle \gamma_{\boldsymbol{k}}^2 \theta_{\boldsymbol{k}}(\omega) \rangle_{\boldsymbol{FS}}, \tag{2.12}$$

where  $N_F$  is the density of states at the Fermi surface,  $\gamma_k$  is a Raman vertex element selected by the polarization geometries of the incident and scattered light (to be defined below),  $\Delta_k$  is the wavevector-dependent SC-gap.  $\langle ... \rangle_{FS}$  stands for an average over the Fermi surface, and can be written as [146]

$$\langle (\cdots) \theta_{\mathbf{k}}(\omega) \rangle = \frac{1}{V} \sum_{\mathbf{k}} (\cdots) \Delta_{\mathbf{k}}^{2} \tanh\left(\frac{E_{\mathbf{k}}}{2T}\right) \\ \times \left(\frac{1/E_{\mathbf{k}}^{2}}{\omega + i\eta + 2E_{\mathbf{k}}} - \frac{1/E_{\mathbf{k}}^{2}}{\omega + i\eta - 2E_{\mathbf{k}}}\right), \qquad (2.13)$$

with  $\theta_{\mathbf{k}}(\omega)$  is the Tsuneto function given by

$$\theta_{\mathbf{k}}(\omega) = N_F \frac{4|\Delta_{\mathbf{k}}|^2}{\omega\sqrt{\omega^2 - 4|\Delta_{\mathbf{k}}|^2}}.$$
(2.14)

The approximation behind Eq.(2.12) is valid when  $\Delta_{\mathbf{k}}$  (and also  $\gamma_{\mathbf{k}}$ ) does not change significantly for small deviations of  $\mathbf{k}$  perpendicular to the Fermi surface, e.g., a constant *s*-wave gap. Figure 2.6 displays a SC-electronic Raman peak of a BCS superconductor modeled using Eqs. (2.12)-(2.14). The Tsuneto function (Eq. 2.14) describes the singularity in the electronic signal at  $\omega = 2\Delta$ . For a simple isotropic *s*-wave gap  $\Delta = \Delta_0 = \text{constant}$ , the Raman intensity is zero for energies less than the  $2\Delta$ -gap. The curve above  $\omega = 2\Delta$  describes the density of electronic states of a BCS superconductor.

An important consequence arising from Eq.(2.12) is that the Raman response is proportional to the square of the amplitude of the SC-gap. This suggest that Raman scattering is phase insensitive, *i.e.* insensitive to the sign of the order parameter. Therefore, Raman scattering provides information only about the magnitude of the superconducting gap and not about the phase. In addition, the Raman efficiency is proportional to the square of the Raman vertex  $\gamma_{\mathbf{k}}$ , which can be defined as a contraction of the curvature of the electronic band  $\varepsilon_{\mathbf{k}}$  and the incident and scattered plane waves with polarization vectors  $e_i^{\alpha}$  and  $e_s^{\beta}$ , respectively. In the non-resonant limit,  $\gamma_{\mathbf{k}}$  can be approximated as

$$\gamma_{\mathbf{k}} = \frac{m}{\hbar^2} \sum_{\alpha,\beta} e_s^{\alpha} \frac{1}{m^*} e_i^{\beta}$$
$$= \frac{m}{\hbar^2} \sum_{\alpha,\beta} e_s^{\alpha} \frac{\partial^2 \varepsilon_{\mathbf{k}}}{\partial k_{\alpha} \partial k_{\beta}} e_i^{\beta}$$
(2.15)

with  $m^*$  being the effective mass tensor.

Equation 2.15 suggests that one can probe selectively different portions of the Fermi surface. Strictly speaking, choosing a particular scattering configuration is



Figure 2.6: (a) Calculated spectra for an isotropic s-wave gap of a conventional superconductor using Eq. (2.12). (b) Raman spectrum of MgB<sub>2</sub> taken at various temperatures in the  $E_{2g}$  symmetry. Panel (b) is taken from Ref. [147]

equivalent to selecting a particular component of the effective mass tensor. The different components of the effective mass tensor may have different wavevector dependences, and thus one can probe the superconducting gap on different portions of the FS. Note that Raman scattering differs from angle resolved photoemission spectroscopy (ARPES). Raman measurements probe an average of the electronic states around a particular k-point of the FS whereas ARPES measurements can precisely determine the topology of the FS for materials with quasi-two-dimensional electronic structure. Since BCS superconductors have an isotropic s-wave pairing symmetry, the  $2\Delta$  gap is insensitive to the scattering polarization geometry.

#### 2.5.3 Electronic Raman Scattering in Tetragonal HTSCs

Raman scattering in HTSCs is different than in BCS superconductors because of the different pairing symmetry. The application of different polarization geometries allows probing different portions of the FS [148, 149, 150]. For instance, the x'y' light polarizations (B<sub>1g</sub> symmetry) allows the coupling of light to the electronic states in the vicinity of the antinodal region whereas the xy polarization configuration probes



Figure 2.7: Relationship between the  $A_{1g}$ ,  $B_{1g}$  and  $B_{2g}$  scattering geometries (second raw) and the corresponding weighted portions of the Fermi surface (third raw). In the second raw, the squares indicates the CuO<sub>2</sub> planes and the orange (blue) circles correspond to copper (oxygen) ions. The incident and scattered photon polarizations with respect to the Cu–O bond (x– or y–axes) are indicated with arrows. In the third raw, the solid lines represent the Fermi surface of HTSCs in the Brillouin zone whereas the circles refer to weighted parts of the Fermi surface.

the  $B_{2g}$  excitations around the nodes of the FS (Fig. 2.7). The fully symmetric  $A_{1g}$  electronic continuum can not be probed independently, but it can be obtained by subtracting the crossed polarization spectra from the parallel polarization ones, i.e either xx - x'y' or x'x' - xy [16, 148, 151].

The Raman spectra of HTSCs show no  $2\Delta$  peak for any polarization geometry, instead they show in the superconducting state a broad hump even at very low temperatures [152, 153]. Electronic Raman scattering shows that the maximum value of the gap  $(\Delta_{max})$  is located near the  $(\pm k_x, 0)$  and  $(0, \pm k_y)$  axes of the Brillouin zone. Since the B<sub>2g</sub> spectrum reflects the density of the electronic states around the nodes  $(\pm k_x, \pm k_y)$ , the frequency of the B<sub>2g</sub> peak appears at  $\Delta(B_{2g}) \approx 0.6\Delta(B_{1g})$  [154]. The fully symmetrical A<sub>1g</sub> geometry probes simultaneously a combination of both, the B<sub>1g</sub> and B<sub>2g</sub> electronic states. In general, it has been observed for HTSCs that  $\Delta(A_{1g}) \leq \Delta(B_{2g}) < \Delta(B_{1g})$  (see fig. 2.8). Although different energies observed for the superconducting gap in different scattering geometries are consistent with *d*-wave pairing symmetry, they cannot be taken as a direct evidence for it.



Figure 2.8: Electronic Raman spectra of Bi2212 ( $T_c=91$  K) taken at 100 K (normal state) and 10 K (superconducting state) in various symmetries as indicated. The  $2\Delta$  peak position is marked with arrows. This figure is taken from [81].

Since complete suppression of scattering at low frequencies has never been ob-



Figure 2.9: Cubic and linear behaviors of the low energy parts of the 20 K Raman spectra of Bi2212 ( $T_c=90$  K) in the  $B_{1g}$  and  $B_{2g}$  symmetries, respectively. This figure is taken from [148](see also Refs. [154, 155, 156]).

served in HTSC, the frequency-dependence of the low energy part in  $B_{1g}$  and  $B_{2g}$ Raman spectra (the power laws) must be considered. Several experimental Raman studies for different HTSCs show that the  $\chi''(B_{1g})$  is proportional to  $\omega^3$  for  $\omega \ll 2\Delta$ whereas  $\chi''(B_{2g})$  decreases linearly for  $\omega \to 0$  (Fig. 2.9). This behavior is consistent with a *d*-wave gap with maximum value at  $(\pm k_x, 0)$  or  $(0, \pm k_y)$  points of the BZ [153, 118, 154].

The polarization dependence of the electronic signal intensities also provides insight into the symmetry of the superconducting gap since the Raman intensity is a measure of the density of electronic states excited across the gap. In contrast to conventional superconductors, the Raman intensities of a *d*-wave gap look different when changing the scattering geometry. Figure 2.10 shows the intensity ratios of the continua observed in the  $A_{1g}$ ,  $B_{1g}$  and  $B_{2g}$  geometries of  $La_{1.83}Sr_{0.17}CuO_4$  (After [154]). Comparison of the continuum intensities at energies far from the  $2\Delta$ broad peak shows that the ratios  $\chi''(A_{1g}):\chi''(B_{1g}):\chi''(B_{2g})$  are almost 8:4:1 for optimally doped HTSCs consistent with *d*-wave pairing [154, 157, 158].

Due to the differences in the pairing symmetry and the Raman signals between conventional and tetragonal HTSCs noted above, Eqs.(2.12) and (2.15) must be modified to account for the polarization dependence of the HTSC spectra. Now, we present a theoretical approach for Raman scattering in optimally doped tetragonal HTSCs. High  $T_c$  superconductivity is believed to take place in the copper-oxygen planes. The simplest way to describe the two-dimensional "normal-state" band structure of a single CuO<sub>2</sub> plane is [154, 167]



Figure 2.10: Electronic Raman spectra of  $La_{1.83}Sr_{0.17}CuO_4$  taken below the SC-transition in various symmetries as indicated. The 2 $\Delta$  peak position is marked with arrows. Note that the relative intensities  $\chi''(A_{1g}):\chi''(B_{1g}):\chi''(B_{2g})$  around 400 cm<sup>-1</sup> are almost 8:4:1. This figure is taken from [154].

$$\varepsilon_{\mathbf{k}} = -2t \left[ \cos k_x + \cos k_y \right] - 4t' \cos k_x \cos k_y - \mu, \qquad (2.16)$$

where t and t' are the hopping parameters to the nearest and next nearest neighbors, respectively, and  $\mu$  is the chemical potential. Accordingly, the vertices of the A<sub>1g</sub>, B<sub>1g</sub>, and B<sub>2g</sub> Raman scattering channels can be identified, respectively, as

$$\gamma_{A_{1g}} = t(\cos k_x + \cos k_y) + 4t' \cos k_x \cos k_y, \qquad (2.17a)$$

$$\gamma_{\boldsymbol{B_{1q}}} = t(\cos k_x - \cos k_y), \qquad (2.17b)$$

$$\gamma_{\boldsymbol{B_{2g}}} = 4t' \sin k_x \sin k_y. \tag{2.17c}$$

Devereaux *et al.* [148, 150] have calculated the Raman responses of HTSCs. In this model, long range Coulomb interaction  $V_r = \frac{4\pi e^2}{r^2}$  was taken into account. Using the gap function  $\Delta(\mathbf{k})$  as given in Eq.(1.8), the  $A_{1g}$ ,  $B_{1g}$ , and  $B_{2g}$  Raman responses of tetragonal HTSC are expressed as

$$\chi(\omega)_{A_{1g}} = \langle \gamma^2_{A_{1g}} \theta_k(\omega) \rangle - \frac{\langle \gamma_{A_{1g}} \theta_k(\omega) \rangle}{\langle \theta_k(\omega) \rangle}, \qquad (2.18a)$$

$$\chi(\omega)_{\boldsymbol{B_{1g}}} = \langle \gamma^2_{\boldsymbol{B_{1g}}} \theta_{\boldsymbol{k}}(\omega) \rangle, \qquad (2.18b)$$

$$\chi(\omega)_{\boldsymbol{B_{2g}}} = \langle \gamma_{\boldsymbol{B_{2g}}}^2 \theta_{\boldsymbol{k}}(\omega) \rangle.$$
(2.18c)

The second term on the right hand side of Eq.(2.18a) represents the so-called "screening effect" which arises from the long range Coulomb interaction. This term vanishes in the  $B_{1g}$  and  $B_{2g}$  symmetries. Devereaux and Einzel [150] showed that the screening gives rise to the following effects: firstly, it smears the  $A_{1g}$  peak intensity. Secondly, it results in a significant shift of the  $A_{1q}$  peak to lower frequencies. The influence of the screening effect on the Raman spectra has been experimentally observed in the polarization dependence of the  $2\Delta$ -gap energy, i.e.  $\Delta(B_{2g}) \leq \Delta(A_{1g}) < \Delta(B_{1g})$ . On the other hand, the intensity of the  $A_{1g}$  peak is larger than both, the  $B_{1q}$  and  $B_{2q}$  signals (Figs. 2.8 and 2.10). Krantz and Cardona [159] have reexamined this problem and concluded that the screening effect takes place only in HTSCs with a single CuO<sub>2</sub>-layer, whereas multilayer HTSCs possess interband scattering and thus an intense unscreened  $A_{1g}$  signal can be expected. Experimentally, the case is different. For instance, the  $A_{1q}$  scattering intensity of monolayer HTSCs, e.g.  $La_{2-x}Sr_xCuO_4$  (fig. 2.10),  $Tl_2Ba_2CuO_{6+x}$  [121, 160] and HgBa<sub>2</sub>CuO<sub>4+x</sub> [161, 162], was found to be more intense than that of  $B_{1g}$  and  $B_{2g}$ symmetries, leaving this puzzle unsolved.

Since the orthorhombic distortion influences the pairing order parameter as well as the Raman vertices of HTSCs, orthorhombicity effects must be included in Eqs.(1.8-2.18c). This will be discussed later in subsec.(3.3).

# Chapter 3

# Analysis of Raman Signals of Optimally and Overdoped HTSCs

The low energy Raman response (i.e.  $\omega < 1000 \text{ cm}^{-1}$ ) in HTSCs is dominated by electronic (intraband) and vibronic excitations. Most previous work focused either on the superconducting gap or on the phonon self-energy effects below  $T_c$ . Here, we treat the electronic and vibronic Raman responses as well as their interdependence on equal footing. In this section, we present the analysis procedure for the Raman spectra of optimally and overdoped HTSCs. We start with a description for the conventional Fano theory which we use to fit the phonons individually. Afterwards, a generalized form of the Fano formula used to fit the overall Raman spectrum, i.e. global fit, will be presented. We will show that both fit procedures are capable of extracting the phonon self-energy effects below  $T_c$ , whereas a realistic shape of the electronic signal is achieved only by using the global fit.

### **3.1** Conventional Fano Theory

The Fano effect, named after the Italo-American physicist Ugo Fano [163], is related to phonon lineshape asymmetries observed by optical spectroscopies *e.g.* Raman or infrared (IR). This effect is seen in the spectra as a characteristic distortion of the Lorenzian phonon lineshape [see fig. 3.2].

A system with two coupled excited levels is shown in fig. 3.1. The system has a ground ground state  $|G\rangle$ , excited electronic continuum  $|e_i\rangle$  with i=1,2,3,...,and a one-phonon excited state  $|p\rangle$ . Higher-phonon states are neglected for simplicity. Transitions from the ground state to the excited states  $|e_i\rangle$  and  $|p\rangle$  are Raman active and are represented by the Raman matrix elements  $\gamma$  and T, respectively. The matrix element g represents the *ele-ph* coupling between  $|e_i\rangle$  and  $|p\rangle$ . Here,



Figure 3.1: System with discrete phononic and continuous electronic continuum coupled by a matrix element g.

 $\gamma \propto \langle G|H_{e-r}|e \rangle$  and  $g \propto \langle e|H_{e-ph}|p \rangle$  whereas T involves both  $\gamma$  and g as  $T \propto \langle G|H_{e-r}|e \rangle \langle e|H_{e-ph}|p \rangle \langle e|H_{e-r}|G \rangle$  (the numerator of Eq.( 2.9)). If the wavefunctions of  $|p \rangle$  and  $|e_i\rangle$  interact *incoherently*, they will simply produce a Lorenzian peak superimposed on top of a broad electronic continuum. On the contrary, the presence of a *coherent* interaction g between  $|p\rangle$  and  $|e_i\rangle$  will generate a constructive and destructive interference observed as a maximum and minimum, respectively (Figs. 3.1 and 3.2). This is the so-called "Fano-type lineshape". In other words, the Fano profile does not consist anymore of one Lorenzian peak centered at the intrinsic frequency  $\omega_0$ , but it rather becomes asymmetric with a maximum  $(\omega_{max})$  and minimum  $(\omega_{min})$  shifted from  $\omega_0$  [106, 116, 17].

The Raman scattering cross section of the "Fano-type lineshape" is given by [17, 106, 116]

$$I_F(\omega) = \frac{\pi \rho(\omega) \gamma^2 (\hbar \omega_0 - \hbar \omega - g\frac{T}{\gamma})^2}{[\hbar \omega_0 - \hbar \omega + g^2 R(\omega)]^2 + \pi^2 g^4 \rho(\omega)^2}.$$
(3.1)

The Kramers-Kronig related functions  $R(\omega)$  and  $\rho(\omega)$  denote real and imaginary parts of the electronic response function  $\chi(\omega) = R(\omega) + i\rho(\omega)$ , respectively, and  $\omega_0$ is the renormalized (intrinsic) phonon frequency. Equation 3.1 can be reformulated as

$$I_F(\omega) = C_F \frac{(q+\epsilon)^2}{1+\epsilon^2} + \text{background}, \qquad (3.2)$$


Figure 3.2: Calculated Fano profile for different values of the asymmetry parameter q. The curves have been normalized to the amplitude at the maximum [17]. The vertical green line indicates the position of the intrinsic phonon frequency  $\omega_0$ .  $\omega_{max}$  and  $\omega_{min}$  denotes the position of the maximum (constructive interference) and minimum (destructive interference) intensities of a Fano-type lineshape, respectively.

with

$$q = \frac{\left[gT/\gamma + g^2 R(\omega)\right]}{\pi g^2 \rho(\omega)} \quad \text{and} \quad \epsilon = \frac{\left[\omega - \omega_0 - g^2 R(\omega)\right]}{\pi g^2 \rho(\omega)}, \tag{3.3}$$

where q is the so-called "Fano asymmetry parameter" and  $C_F$  is a proportionality factor. One notices the main difference between a Lorentzian and a Fano formula in the numerator of Eq.( 3.2). The numerator is replaced by one for a Lorenzian peak.

Equations (3.1)-(3.3) contain the following information [17]:

(i) The lineshape of a Fano-type phonon peak is highly dependent on the sign of q. If q is negative, the low energy part of the phonon peak is lifted up while the high energy side is pushed down (Fig. 3.2). A good example for that is the buckling mode at 340 cm<sup>-1</sup> of YBCO [details will be presented in chap. 5]. The reverse happens for a positive sign of q like, for example, the apical oxygen phonon mode

in LSCO [164]. The value of q plays the major role in determining the strength of distortion of the Fano lineshape. For example, when  $q \to \infty$  ( $g\rho\gamma \to 0$ ) a Lorenzian lineshape is recovered whereas the Fano lineshape becomes apparent with decreasing q. In the special case |q| = 1, the lineshape is maximally asymmetric (Fig. 3.2).

(ii) As mentioned earlier, the extrema at  $\omega_{max}$  and  $\omega_{min}$  of a Fano-line are shifted from the intrinsic phonon frequency  $\omega_0$ . To extract  $\omega_0$ , one has to find the roots of  $(\partial I_F(\omega)/\partial \epsilon)$  and substitute them in Eq.(3.2). The results are

$$(1)\epsilon = -q \Rightarrow \omega_0 = \omega_{min} + q\Gamma \qquad (2)\epsilon = 1/q \Rightarrow \omega_0 = \omega_{max} - \Gamma/q. \qquad (3.4)$$

Simultaneously, the apparent linewidth  $(\Gamma_{HWHM})$  is related to the intrinsic linewidth  $(\Gamma)$  by

$$\Gamma_{HWHM} = 2\Gamma |\frac{(1+q^2)}{(1-q^2)}|.$$
(3.5)

Usually, the standard Fano formula (Eq. 3.2) is appropriate to fit qualitatively the Fano lineshapes seen in xx (or yy) Raman spectra of YBCO. For a particular Raman phonon of detwinned YBCO, the intrinsic position and linewidth observed in the xx and yy symmetries must be identical. That is, at the center of Brillouin zone

$$\omega_0^{xx} = \omega_0^{yy} \qquad \Gamma_0^{xx} = \Gamma_0^{yy}. \tag{3.6}$$

Note that the derivation of Eq. (3.4) assumes that the Raman intensity  $I(\omega)$  is described by Eq.(3.2) with an  $\omega$ -independent background. Moreover, if  $I(\omega) = \frac{(q+\epsilon)^2}{1+\epsilon^2} + \alpha \,\omega + \beta$  (with  $\alpha \neq 0$ ) is assumed, one obtains higher correction terms for q > 1:  $\omega_{max} - \omega_0 = \Gamma/q + \frac{1}{2}\frac{1+q^2}{q^4}\Gamma^2 \alpha + \dots$  Since, however, the slope  $\alpha$  is relatively small, those higher corrections are of the order of 2% for the  $B_{1g}$ -phonon, for example. Therefore, it is reasonable to work with Eq.(3.4).

(iii)  $\rho(\omega)$  and  $R(\omega)$  are energy-dependent. For a flat continuous electronic background,  $\rho(\omega)$  can be assumed as constant and therefore R = 0. Hence,  $\epsilon$  and qbecome  $(\omega - \omega_0)/\Gamma$  and  $T/\pi\rho g\gamma$ , respectively. This can be applied to the Raman spectra of high  $T_c$  superconductors in the normal state (at  $T > T_c$ ). Since a broad pair-breaking peak develops in the electronic continuum below  $T_c$ ,  $g^2 R(\omega)$  which is highly dependent on the assumed background, has to be taken into account (see next subsections). (iv) The denominator of Eq.(3.1) implies that due to the *ele-ph* coupling, the phonon acquires an intrinsic linewidth of  $2\Gamma = 2\pi g^2 \rho(\omega)$  where  $\Gamma$  is the half-width at half-maximum (HWHM).

(v) Regardless of the nature of the matrix elements  $\gamma$ , T, g, the asymmetry parameter  $q \approx T/\pi\rho g\gamma$  implies that any anomaly occurring in the phonon linewidth is always accompanied by changes in q.

(vi)  $|\gamma|^2$  and  $|T|^2$  measure, respectively, the strength of light coupling to the electronic and phononic excitations.  $|\gamma|^2$  ( $|T|^2$ ) is proportional to the electronic (phononic) Raman efficiency, hence they are highly dependent on the incident photon energy.

(vii) In principle, the asymmetry parameter is a complex quantity, that is,  $\hat{q} = q_r + iq_i$ . Throughout this thesis, we assume the Raman matrix elements  $T, \gamma$ , and g to be real and therefore q is real.

(viii) When the phonon lineshape is fitted with Eq.(3.2), the quantity  $I_p = \pi C_F q^2 \Gamma$  is a measure for the phonon integrated intensity ( $\sim |T|^2$ ), equivalent to the area enclosed by a Lorenzian lineshape.

In a Raman experiment on HTSCs, a nonzero intensity usually remains (even after subtracting the dark current of the detector) at the frequency where a destructive interference between the phononic state and the electronic background should cancel the signal, i.e.  $I_F(\omega_{min}) \neq 0$ . Such effects may arise from an intrinsic noninteracting background, i.e. an inactive part of the electronic system, or from other excitations such as two-phonon or two-magnon processes. Besides that, anharmonic decay may also contribute to the phonon linewidth. In addition, incoherent contributions to the Fano line may arise from the existence of isotopes or the variation of atomic concentration within the scattering volume [116, 17].

### 3.2 Phenomenological Model of the Electronic Raman Response of Optimally and Overdoped HTSCs: Generalized Fano Theory

The measured Raman intensity  $I_{\sigma}(\omega)$  is related to the imaginary part of the electronic response function  $\operatorname{Im} \chi_{\sigma}(\omega)$  via

$$I_{\sigma}(\omega) = A \left[ 1 + n(\omega) \right] \operatorname{Im} \chi_{\sigma}(\omega), \qquad (3.7)$$

where  $\sigma$  represents the symmetry projected out by the incoming and outgoing polarization vectors,  $n(\omega)$  denotes the Bose distribution and A is a coupling constant. The Raman response of optimally and overdoped HTSC at  $\omega < 1000 \text{ cm}^{-1}$  is dominated by electronic (intraband) and phononic excitations. In order to disentangle the electronic and phononic Raman excitations of highly doped cuprates, it is necessary to employ a proper fitting procedure. A phonon interacting with intraband excitations acquires a renormalized self-energy and exhibits an asymmetric, Fanotype line shape (see sec. 3.1). To describe such an electron-phonon coupled Raman spectrum, the following formula can be employed [165, 166, 167, 168, 169, 170, 171]

$$\operatorname{Im} \chi_{\sigma}(\omega) = \rho_{\sigma}(\omega) + \frac{g_{\sigma}^{2}}{\gamma(\omega) \left[1 + \epsilon^{2}(\omega)\right]} \times \left\{ S^{2}(\omega) + 2\epsilon(\omega)S(\omega)\rho_{\sigma}(\omega) - \rho_{\sigma}^{2}(\omega) \right\},$$
(3.8)

where  $\epsilon(\omega) = (\omega^2 - \Omega^2)/2\omega_0\gamma(\omega)$  and  $S(\omega) = S_0 + R_{\sigma}(\omega)$ . The renormalized phonon frequency and the renormalized phonon line width are given by  $\Omega^2 = \omega_0^2 - 2\omega_0 g_{\sigma}^2 R_{\sigma}(\omega)$ , and  $\gamma(\omega) = \Gamma_0 + g_{\sigma}^2 \rho_{\sigma}(\omega)$ , respectively, with the intrinsic phonon frequency  $\omega_0$  and the intrinsic phonon line width  $\Gamma_0$ . The parameter  $S_0$ , which represents the phonon asymmetry, can be expressed in terms of the electron-phonon coupling  $g_{\sigma}$ , the Raman phonon matrix element  $T_{\sigma}$ , and the Raman electronic matrix element  $\gamma_{\sigma}$ , that is,  $S_0 = T_{\sigma}/(\gamma_{\sigma}.g_{\sigma})$ . Since  $g_{\sigma}$ ,  $T_{\sigma}$ , and  $\gamma_{\sigma}$  are assumed in our model to be real,  $S_0$  will be real. While the first term in Eq.(3.8),  $\rho_{\sigma}(\omega)$ , describes the "bare" electronic Raman response, the second term represents the phononic contribution and its coupling to the electronic background. Note that by setting S to zero, Eq.(3.8) will simply produce a Lorenzian peak superimposed on a broad electronic continuum.

The frequency-dependent electronic response function  $\chi_{\sigma}(\omega)$  can either be computed from a microscopic model [167] or be determined from a fit to the Raman data using a phenomenological model function [168, 169, 170, 18]. These two approaches will be described in the following two subsections.

It is instructive to note that formula 3.8 can be brought into the form of the widely used "standard" Fano profile, Eq.(3.2) with the asymmetry parameter rewritten as

$$q = -S(\omega)/[\rho(\omega)]. \tag{3.9}$$

To extract renormalized phonon parameters the Raman spectra are often fitted using the simplified Fano profile, Eq. 3.2, with the Fano parameter q, the renormalized phonon frequency  $\omega_0$ , and the renormalized phonon line width  $\Gamma$  (half-width at halfmaximum, HWHM) kept frequency independent. In this fitting procedure (Eq. 3.2), only a small frequency region of the electronic continuum near to the phonon is analyzed [see section 5.2]. While such an approach can give valuable insights into the temperature dependence of the phonon line shapes, the *intrinsic* electron-phonon coupling constants and the shape of the electronic continuum  $\chi(\omega)$  in the SC state cannot be determined. We will compare the simplified Fano formula (3.2) with our generalized theory [Eq.(3.8)] in sec. 5.2.

To complete the phenomenological model function [Eq. 3.8], we need to either assume an expression that describes the real and imaginary parts of the electronic response function  $\chi(\omega)$ , or compute the electronic Raman response from a microscopic model. Let us first describe a phenomenological model function for  $\chi(\omega)$ . Following along the lines of Refs. [168, 169, 170, 172] we express the imaginary part of the electronic Raman efficiency with three terms

$$\rho(\omega) = C_n \frac{\omega}{\sqrt{\omega^2 + \omega_T^2}} + \left[\frac{C_1}{1 + \epsilon_1^2(\omega)} - (\omega \to -\omega)\right] - \left[\frac{C_2}{1 + \epsilon_2^2(\omega)} - (\omega \to -\omega)\right], \qquad (3.10)$$

where  $\epsilon_1(\omega) = (\omega - \omega_1)/\Gamma_1$  and  $\epsilon_2(\omega) = (\omega - \omega_2)/\Gamma_2$ . The first term in Eq.(3.10) models an incoherent electronic background, which dominates the response in the normal state of cuprate superconductors. It is linear in  $\omega$  at small frequencies and becomes constant for large Raman shifts [171]. Another frequently used expression is  $I_{\infty} \tanh(\omega/\omega_T)$  where  $I_{\infty}$  (or, equivalently,  $C_n$ ) and  $\omega_T$  are fit parameters [168, 169, 173, 174, 175]. The second and third terms are Lorentzians describing the pair-breaking peak located below  $2\Delta$ , and the suppression of spectral weight at low frequencies, respectively. The latter is due to the opening of the SC gap. The last two terms in Eq.(3.10) decrease in intensity and peak at lower frequency as the superconducting transition temperature  $T_c$  is approached from below. The ( $\omega \rightarrow$  $-\omega$ ) terms, similar to the  $C_1$  and  $C_2$  terms but with  $\omega$  replaced by  $-\omega$ , are essential to achieve the symmetry requirements for the Raman response. In the normal state, the electronic response function is entirely described by the incoherent contribution [first term in Eq.(3.10)]. The real part of the electronic response function,  $R(\omega)$ , is obtained from the Kramers-Kronig transform of  $\rho(\omega)$  as [172]

$$R(\omega) = \frac{C_n}{\pi} \left[ \ln \frac{\sqrt{\omega_T^2 + \omega_{cut}^2 + \omega_{cut}} + \omega_{cut}}{\sqrt{\omega_T^2 + \omega_{cut}^2 - \omega_{cut}}} + \frac{\omega}{\sqrt{\omega^2 + \omega_T^2}} \ln \left( \frac{\omega_{cut} - \omega}{\omega_{cut} + \omega} + \frac{\omega_T^2 - \omega_{cut} + \sqrt{(\omega_T^2 + \omega_{cut}^2)(\omega^2 + \omega_T^2)}}{\omega_T^2 + \omega_{cut} + \sqrt{(\omega_T^2 + \omega_{cut}^2)(\omega^2 + \omega_T^2)}} \right) \right].$$
(3.11)

Since  $R(\omega)$  renormalizes the phonon frequency  $\omega_0$  and the parameter  $S_0$ , formula (3.8) together with Eq.(3.10) and its Kramers-Kronig transform yield a fully selfconsistent analysis of the Raman spectra. To compute the Kramers-Kronig transform of the incoherent part in Eq.(3.10), a cut-off frequency  $\omega_{cut}$  has to be introduced, which results in a constant offset in the real part of the electronic response  $R(\omega)$ . Provided  $\omega_c$  is chosen large enough ( $\omega_c \sim 8000 \text{ cm}^{-1}$ ), however, this error only leads to negligibly small corrections.

An electron-phonon coupled Raman spectrum modeled with Eqs.(3.8) and (3.10) is illustrated in fig. 3.3. In panel (a), the Raman efficiency is well reproduced by the overall fit and therefore the intrinsic phonon parameters ( $\omega_0$  and  $\Gamma_p$ ) (Fig. 3.3(a)) and the bare electronic response (Fig. 3.3(b)) can be extracted. Figure 3.3a shows that  $\omega_0$  extracted from this fit procedure is equivalent to the intrinsic frequency of a Lorenzian phonon peak measured, for instance, in inelastic neutron scattering experiments. In fig. 3.3(b), the imaginary part of the electronic response function  $\rho(\omega)$  (henceforth, the electronic response) is depicted where  $\omega_1$  and  $\Gamma_1$  display the center frequency and the width (HWHM) of the 2 $\Delta$  peak, respectively. The electronic response for  $\omega \to 0$  (the solid curve below the horizontal dotted line) arises from a combination of the the first and third terms of Eq.( 3.10) and describes the suppression of spectral weight due to the opening of the 2 $\Delta$ -gap below T<sub>c</sub>.

We will use expression (3.8) together with (3.10) to describe the coupling of the electronic background to the phonons whose lineshapes exhibit the clearest manifestations of the electron-phonon interaction (e.g., the in-plane  $B_{1g}$  phonon at around 340 cm<sup>-1</sup>) (subsec. 5.1.1). If several phonons are fitted using Eqs. (3.8) and (3.10), each acquires an interference term. In order to reduce the number of free fit parameters, the remaining phonons at 115, 150, 232, 440, 501, and 578 cm<sup>-1</sup> can be described using Lorentzian profiles  $I(\omega)$ 

$$I(\omega) = \frac{A}{\left[\Gamma^2 + (\omega - \Omega_0)^2\right]}$$
(3.12)

with A,  $\Omega_0$  and  $\Gamma$  being the phonon amplitude, frequency and linewidth (HWHM), respectively. In the next subsection this procedure will be improved for the SC state



Figure 3.3: (a) An electron-phonon coupled Raman spectrum (open circles) in the superconducting state (T < T<sub>c</sub>) with the overall fit of Eqs. 3.8 and 3.10 (red solid line) are displayed. At the bottom, the bare phonon contribution (blue solid line) with the intrinsic phonon parameters ( $\omega_0$  and  $\Gamma_p$ ) are demonstrated. The inset in (a) presents the difference between the maximum of the Fano-type peak  $\Omega$  and the intrinsic phonon frequency  $\omega_0$ . (b) The phonon subtracted Raman spectrum (open circles) with the electronic response [Eq. 3.10] (red solid line) are shown. The suppression of spectral weight due to the opening of the 2 $\Delta$ -gap observed for  $\omega \to 0$  [combination of the first and last terms of Eq. 3.10] is denoted by the the area below the horizontal dotted line. The inset in (b) describes the first term of Eq. 3.10 and shows the crossover frequency  $\omega_T$  above which the maximum of the frequency-independent Raman intensity is observed. For clarity, the spectra and the fits are vertically shifted. The short horizontal ticks denote the offsets.

by employing a microscopic description of the pair-breaking excitations.

### 3.3 Microscopic Description of the Superconducting State in Orthorhombic Optimally and Overdoped HTSCs

To describe the polarization-dependent electronic response function  $\chi_{\sigma}(\omega)$  in the superconducting state, we employ a microscopic model using a realistic tight-binding band structure with anisotropic hopping parameters and a superconducting gap with a mixture of  $d_{x^2-y^2}$  and s-wave symmetries. Such a microscopic approach in conjunction with the analysis of the Raman spectra based on Eq.(3.8) allows us to obtain precise information about the wavevector dependence of the superconducting order parameter. In particular, we are interested in estimating the magnitude of a possible s-wave admixture to the  $d_{x^2-y^2}$  pair wave function.

The starting point of our calculation is the microscopic model introduced in Ref. [21]. Since the unit cell of metallic and superconducting YBCO is orthorhombically distorted, the normal state band structure, the gap symmetry, and the Raman vertices are expected to be slightly different from those describing the tetragonal structure [Eqs.(1.8), (2.16)-(2.18)]. Here, the normal state band dispersion of a single copper-oxygen plane becomes

$$\varepsilon_{\mathbf{k}} = -2t \left[ (1+\delta_0) \cos k_x + (1-\delta_0) \cos k_y \right] -4t' \cos k_x \cos k_y - \mu, \qquad (3.13)$$

and the gap function

$$\Delta_{\boldsymbol{k}} = \frac{\Delta_0}{2} \left( \cos k_x - \cos k_y \right) + \Delta_s, \qquad (3.14)$$

where  $\delta_0$  and  $\Delta_s$  represent symmetry-breaking terms that lower the symmetry from tetragonal to orthorhombic in an effective one-band description of a single copper-oxygen plane [21].

Since the  $\Delta_s$  admixture to the *d*-wave pairing is assumed to be isotropic, the gap function is expected to change only along the *x* and *y* axes of the Brillouin zone while the nodes remain the same. Therefore, only the  $A_{1g}$  and  $B_{1g}$  Raman vertices will be affected (for convenience, we use tetragonal representations), that is,

$$\gamma_{A_{1g},\boldsymbol{k}} \propto t \left[ (1+\delta_0) \cos k_x + (1-\delta_0) \cos k_y \right] + 4t' \cos k_x \cos k_y, \quad (3.15a)$$
  
$$\gamma_{B_{1g},\boldsymbol{k}} \propto t \left[ (1+\delta_0) \cos k_x - (1-\delta_0) \cos k_y \right] \quad , \quad (3.15b)$$

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respectively. Eq.(2.17c) is still valid for describing the  $B_{2g}$  Raman vertex. Finally, the electronic Raman response function in the SC state (for  $\sigma = A_{1g}$  and  $B_{1g}$  channels) will be given by [21]

$$\chi_{\sigma}(\omega) = \left\langle \gamma_{\sigma}^{2} \theta_{k}(\omega) \right\rangle - \frac{\left\langle \gamma_{\sigma} \theta_{k}(\omega) \right\rangle^{2}}{\left\langle \theta_{k}(\omega) \right\rangle}.$$
(3.16)

Note that for orthorhombic HTSCs, both  $A_{1g}$  and  $B_{1g}$  Raman spectra are influenced by the screening term, whereas in tetragonal HTSCs the screening acts only on the Raman  $A_{1g}$  spectrum.

### Chapter 4

# **Experimental Aspects**

# 4.1 Preparation of Twin-Free $YBa_2Cu_3O_{6+x}$ Samples

The high quality single crystals of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> and Y<sub>1-y</sub>Ca<sub>y</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> used in this thesis were grown by the top-seeded solution (flux) growth method. The growth procedure is described in refs.[177, 178]. Since the starting mixture is molten at temperatures of about 1000°C, the as-grown crystal structure at this particular temperature is tetragonal. When cooling the crystals slowly through the tetragonal to orthorhombic transition temperature (T<sub>T-O</sub> which is between 750 and 500 °C) in the presence of an oxygen atmosphere, they become orthorhombically distorted due to formation of the Cu-O chains along the *b*-axis. The T-O transition is usually accompanied with elastic shear stresses that relax through formation of a polydomain twin structure, i.e. two equiprobable families of twins [179, 180]. Annealing the YBCO<sub>6+x</sub> crystals (annealing conditions of our samples are listed in table 4.1) allows obtaining the desired oxygen concentration in the samples, whereas its influence on the polydomain twin structure is small.

By examining the as-grown crystals under polarized light microscope, the polydomain twin arrangement appears as successively ordered bright and dark fringes aligned parallel to [110] and [110] directions. Vlasko-Vlasov *et al.* [181] have found that thin YBCO crystals are opaque (transparent) for light polarized along the b-axis (a-axis) and thus, the light phase shift coming from both axes is different. Therefore, the image contrast of the twin domains changes as the analyzer is rotated by 90° around the microscope axis indicating the reciprocal exchange of the a- and b-axes (Fig. 4.1(a)).

Due to the presence of twin polydomains in the as-grown YBCO samples, the



Figure 4.1: Microphotographs of the same single crystal (a)before and (b) after detwinning. The pictures are taken under a polarized light microscope. This figure is taken from ref. [179]

*ab*-anisotropy of their physical properties cannot be determined. In order to obtain twin-free YBCO samples, the as-grown single crystals should be thermomechanically treated using the so-called "detwinning procedure" in which the twin domain walls move due to the application of high temperature and pressure [179, 182, 30].



Figure 4.2: Schematic diagram of detwinning device used in this thesis. This figure is taken from ref. [179]

A schematic diagram of the detwinning device is shown in fig.(4.2). The detwinning procedure requires crystals with sharp edges, i.e. squares or rectangles. Therefore, our samples were cut into rectangular shapes of typical size of  $3 \times 3 \times 1$ mm<sup>3</sup> to be detwinned individually. Each sample was then placed between two quartz

Sample	Ann.	Ann.	Det.	Det.	$T_c$ (K)	$\Delta T_c$
	Gas	Temp.(°C)	Gas	Temp.		(K)
YBCO <sub>6.95</sub> :Ca	$O_2$	400	$O_2$	520	75	6
YBCO <sub>6.95</sub>	$O_2$	520	$O_2$	520	92	3
YBCO <sub>6.6</sub> :Ca	Synthetic Air	585	$O_2$	500	82	8
YBCO <sub>6.6</sub>	Synthetic Air	585	Ar	400	62	2
YBCO <sub>6.45</sub>	$99.5\% \text{ Ar} + 0.5\% \text{O}_2$	585	Ar	400	35	3

Table 4.1: Annealing and detwinning conditions of the YBCO samples investigated in this thesis. The crystals were annealed for almost one week and then quenched in liquid nitrogen in order to avoid further oxygen diffusion whereas detwinning was performed in about 3-4 hours and the samples were cooled quickly without using liquid nitrogen.

stress-plates (horizontal arrows in fig. 4.2). Afterwards, a constant mechanical stress of about  $1 \times 10^7$  N/m<sup>2</sup> was applied along the [100] direction. In order to keep the required oxygen concentration of our sample unchanged and to avoid any further oxygen exchange between the sample and the surrounding atmosphere, the sample chamber was sealed and a suitable gas flow was adjusted during the detwinning process. Afterwards, the temperature of the crystal was rapidly elevated (within less than 5 minutes) to an appropriate detwinning temperature and kept fixed during the detwinning process. The subsequent development of the twin domains was monitored by a polarized light microscope. When a single domain sample was observed (usually after almost 3 hours), the heater was switched off and the sample was cooled down quickly (within less than 5 minutes) to about 150°C. Finally, the sample was left inside the detwinning chamber until it cooled down to room temperature. Table 4.1 summarizes the annealing and detwinning conditions of the samples used in this thesis.

### 4.2 Sample Characterization

After the detwinning process, we have measured the superconducting transition temperatures of our samples using a superconducting quantum interference device (SQUID). The magnetization curves of the Y<sub>0.85</sub>Ca<sub>0.15</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub> (henceforth YBCO<sub>6.95</sub>:Ca), YBCO<sub>6.95</sub>, Y<sub>0.87</sub>Ca<sub>0.13</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> (henceforth YBCO<sub>6.6</sub>:Ca), YBCO<sub>6.6</sub> and YBCO<sub>6.45</sub> crystal show an onset of T<sub>c</sub>= 75 K, 92 K, 82 K, 62 K and 35 K, with a transition width  $\Delta$ T<sub>c</sub> of less than 6 K, 3 K, 8 K, 3 K and 3 K, respectively (Fig. 4.3). This indicates good homogeneity of the samples. Employing Tallon's phenomenological expression (Eq. 1.7) with T<sub>c,max</sub> = 93K, the hole doping p levels of our samples



Figure 4.3: Temperature dependence of the dc-magnetization of the samples studied in this work.

are estimated as 0.21 (moderately overdoped), 0.17 (slightly overdoped), 0.125 (underdoped), 0.1 (underdoped), and 0.07 (underdoped) per planar Cu ion, respectively.

Using light microscopy, the sample surfaces, which are of high importance in Raman scattering experiments, appeared to be in good condition (clean and shiny). In order to obtain higher surface quality, we followed along the lines of Ref. [183] and etched our samples in a 1% Br/Ethanol solution for 2-3 minutes and then cleaned them with pure ethanol.

Determining the orientations of the crystallographic axes for each single crystal is necessary for the application of Raman selection rules. Polarized light microscopy and Laue x-ray diffraction show that the a-, b- and c-axes are always parallel to the edges of our rectangular-shaped samples. Raman scattering is indeed a powerful tool to determine the crystallographic axes as well as the detwinning ratio of the crystals, because the number of the phonon modes as well as the electronic background in xx, yy and zz symmetries are different (see subsec. 5.1.1). Raman spectra measured at different spots of the *ab*-surface of each sample look nearly identical, confirming the homogeneity of our single crystals.

### 4.3 Raman Setup

A schematic diagram of one of the Raman spectrometers at the Max-Planck-Institute-Stuttgart is shown in fig. 4.4. Like any other spectroscopic technique, Raman scattering requires at least a source of excitations, an efficient system to collect the weak scattered intensity, a spectrometer for analyzing the scattered intensity, and a sensitive detector.

For excitation, a discrete monochromatic line emitted from an  $Ar^+/Kr^+$  mixed gas laser is used. This laser source is tunable, i.e. capable to give ten discrete laser lines (from red to violet light). The emmitted laser light is usually accompanied with plasma lines, which have higher strength than phonons. To exclude these lines from the measured signal, a plasma filter is installed in the optical track. In order to avoid sample overheating which may cause severe damage to the sample surface, the incident laser intensity must be adjusted depending on the sample sensitivity. As light travels along the optical path, it spreads out with a small angle, therefore pin holes are needed to collimate the divergent light beam. For opaque samples, the Raman experiment is usually performed in backscattering geometry. For this reason, a prism is used to rotate the direction of the laser light by 90 degrees. The prism (which acts here as a mirror) is of small size and hence it cuts a negligible fraction of the scattered intensity towards the entrance of the spectrometer.

Since Raman scattering is a probe for polarization-dependent excitations, a polarizer and an analyzer were placed into the light path before and after the sample (pieces number 4 and 11 in fig. 4.4). Selection rule analysis can be achieved by either rotating the polarizer and the analyzer or by rotating the sample while the polarizer and analyzer are kept fixed to a particular geometry.

The intensity of the inelastically scattered light is 4-6 orders of magnitude weaker than the incident laser intensity. Besides that, imperfections of the optics and/or light scattering by dust particles can produce a strong background of stray light. Therefore, a good spectrometer is required to detect such weak excitations and to exclude the undesired stray light. To achieve this goal, a single-monochromator with 1800 grooves per millimeter equipped with a Notch-filter is sufficient. Our spec-



Figure 4.4: Schematic of Raman setup. 1: Laser light source, 2: Plasma filter, 3: Mirrors, 4: Polarizer, 5: Power meter, 6: Pinhole, 7: Prism, 8: Lens, 9: Cryostat, 10: Sample position, 11: Analyzer, 12: Spectrometer, 13: CCD camera, 14: Spectrum.

trometers consist of three monochromators with 1800 grooves/mm (Dilor XY-triple grating spectrometer) designed in a subtractive mode. The first two monochromators are used to cut the stray light whereas the third disperses the Raman spectra. For instance, the scattered radiation (polychromatic light) enters the first monochromator through the entrance slit S1 and gets dispersed by the grating G1 (Fig. 4.5).



Figure 4.5: Schematic of the Raman spectrometer. S1, S1/2, and S2/3 denote the entrance and the intermediate slits, respectively. G1, G2, and G3 refer to the triple monochromator gratings. After [62].

The slit between the first and the second monochromators S1/2 selects a spectral range between  $\lambda_1$  and  $\lambda_2$  and cuts the undesired radiation. Afterwards, the dispersed radiation recombine after the second grating G2. The resulting radiation is polychromatic but limited to only the spectral range between  $\lambda_1$  and  $\lambda_2$ . Then, the spectrum is transmitted through the third slit S2/3 and analyzed by the third grating G3. Finally, the analyzed radiation is recorded by a charge-coupled device (CCD) camera.

### 4.4 Measurements

The Raman scattering experiments were performed in backscattering geometry. For excitation, the 514.5 nm line of an  $Ar^+/Kr^+$  mixed gas laser was used. In order to avoid laser-induced heating of the sample, the power of the incident laser was kept below 10 mW at the sample surface with a laser spot of 100  $\mu m$  in diameter. Some of the spectra presented in this work were also measured using a Labram (Jobin Yvon) single-grating Raman spectrometer equipped with a Notch-filter. For excitation, a solid-state exciting laser ( $\lambda$ =532 nm) and a He<sup>+</sup>/Ne<sup>+</sup> mixed gas laser  $(\lambda = 632.8 \text{ nm})$  were used. In this case, the power density at the sample surface was kept to less than 4 mW with a laser spot of 15  $\mu m$  in diameter. The resolution of our spectrometers was of about  $3 \text{ cm}^{-1}$ . The direction of the incident laser light was always nearly parallel to the crystallographic *c*-axis. For accurate study of the temperature dependence of the Raman spectra at low temperatures, the samples were placed at the cold finger of a cryostat cooled by liquid helium flow with a temperature stabilization better than 1 K. For a precise determination of the phonon frequencies and linewidths, a calibration spectrum of a nearby argon or neon line was measured after each YBCO spectrum.

The x-ray diffuse scattering measurements presented in subsec. 5.4 were conducted at the high energy wiggler beamline BW5 at the Synchrotronstrahlungslabor (HASYLAB) at the Deutsches Elektronen-Synchrotron (DESY). The energy of the x-ray beam was 100 keV. A closed cycle cryostat was used to reach temperatures as low as 8 K.

### Chapter 5

# **Results and Discussion**

### 5.1 $YBCO_{6.95}$ and $YBCO_{6.95}$ :Ca

### 5.1.1 ERS in xx versus yy Symmetries: Signature for s-wave Admixture to the d-wave Pairing Symmetry

Figures 5.1-5.3 show Raman spectra of detwinned YBCO<sub>6.95</sub> and YBCO<sub>6.95</sub>:Ca crystals measured at various temperatures. As in other high- $T_c$  superconductors [16, 154, 156, 83, 184], the normal-state spectra exhibit a flat electronic continuum with superimposed phonons. Below  $T_c$ , a significant fraction of the electronic spectral weight is transferred to higher energies, resulting in a broad pair-breaking peak in the continuum. In addition, the phonon lineshapes reveal characteristic changes. In B<sub>1g</sub> polarization this spectral-weight redistribution is most pronounced because electronic Raman scattering in this geometry is sensitive to the maximum of the SC gap along the anti-nodal direction of the two-dimensional SC gap. We therefore focus in this work on this geometry, along with the xx and yy polarization channels that provide direct information about the in-plane anisotropy of the electronic response.

Figure 5.2 gives an overview of the phonon modes of YBCO<sub>6.95</sub> in the xx and yy polarization geometries. As expected based on a group-theoretical analysis (sec.2.4) five phonons appear in both polarization channels. The lowest-frequency phonon at 113 cm<sup>-1</sup> ( $A_{1g}$ ) originates predominantly from vibrations of the barium atoms. The next lowest frequency phonon at 148 cm<sup>-1</sup> ( $A_{1g}$ ) corresponds mainly to the vibrations of copper (Cu2 ions). The vibrations of the apical oxygen ions (O4) appears at 501 cm<sup>-1</sup> ( $A_{1g}$ ). The two modes at 340 cm<sup>-1</sup> ( $B_{1g}$ ) and 446 cm<sup>-1</sup> ( $A_{1g}$ ) originate from out-of-phase and in-phase vibrations of the planar oxygen ions (O2 and O3), respectively [109]. Two additional defect-induced modes appear in the



Figure 5.1: Raman spectra of a detwinned slightly overdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub> single crystal in the yy symmetry taken with an Ar<sup>+</sup> laser line ( $\lambda$ =514.5 nm) at 20 K (black) and 100 K (red). The normal state spectrum reveal a flat electronic background. The arrow denotes the spectral weight transfer due to the opening of the superconducting gap, which is marked with the shaded area.

yy symmetry at 232 cm<sup>-1</sup> and at 579 cm<sup>-1</sup>. They originate from vibrations of the copper (Cu1) and the oxygen (O1) ions, respectively, in the Cu–O chains, which are aligned along the crystallographic *b*-axis [135]. In YBCO crystals with fully oxygenated chains, these two modes are Raman forbidden but infrared-allowed (B<sub>1u</sub> symmetry) [136, 137, 138]. They become Raman-active due to breaking of the translational symmetry by defects, *i.e.*, unoccupied oxygen positions in the Cu1-O1 chains [116, 135, 140]. The absence of the strong mode at 579 cm<sup>-1</sup> in the data with xx polarization confirms the high detwinning ratio of our crystal (~ 95%). In Ca-doped YBCO (Fig. 5.3), the Ca ions partially replace the Y ions at the center of inversion of the YBCO unit cell, thus the Raman activity of their vibrations, if any, should be very weak. Hence, the assignment of the phonon modes is identical. Again, the anisotropy of the phonon spectrum confirms the nearly perfect detwinning ratio of our YBCO<sub>6.95</sub>:Ca crystal.

We have employed a non-linear fit procedure with ten (six) independent fit parameters to the Raman spectra of YBCO<sub>6.95</sub> and YBCO<sub>6.95</sub>:Ca in the superconducting (normal) state.  $C_n$  and  $\omega_T$  describe the intensity and position of the maximum of the normal-state electronic background given by the square root of a rational function. In the superconducting state  $C_1/C_2$ ,  $\omega_{1,2}$ , and  $\Gamma_{1,2}$  describe amplitude,



Figure 5.2: Raman spectra of a detwinned slightly overdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub> single crystal in xx and yy polarization taken with an Ar<sup>+</sup> laser line ( $\lambda$ =514.5 nm). The mode assignment corresponds to Refs. [109, 112, 116, 135, 140]. The spectra were shifted by a constant offset with respect to each other. The intensity scales in left and right panels are the same.

position and width of a Lorentzian function reflecting the region of the pair-breaking peak. Finally,  $\Gamma_0$ ,  $\omega_0$ , and  $S_0$  effectively characterize amplitude, width, position, and asymmetry of a generalized Fano function (describing the  $B_{1g}$  phonon). Note that for not too strong frequency dependences of  $\rho(\omega)$  and  $R(\omega)$ , the renormalization of the Fano formula due to the electronic background can be simply viewed as an offset of the parameters entering in the Fano formula [cf. Eqs. (3.2), (3.3) and (3.8)].

The results of this fit procedure are shown in Figs. 5.4-5.6 together with the



Figure 5.3: Raman spectra of a detwinned overdoped  $Y_{0.85}Ca_{0.15}Ba_2Cu_3O_{6.95}$  sample in xx and yy polarizations taken with  $\lambda$ =514.5 nm at 80 K. For clarity, the yy spectrum was vertically shifted with the horizontal line indicates the corresponding baseline.

experimental data. Table 5.2 lists the corresponding fit parameters. Note that on general grounds the extracted  $\omega_0$  and  $\Gamma_0$  parameter values need to be identical at a given temperature for all measurements of a given phonon. In Table 5.2 we show, however, the parameter values that correspond to the best (non-linear least squares) fit to the data. The differences reflect the error bars of our procedure. It is important to emphasize that the Fano profile of the  $B_{1g}$ -mode shown in Figs. 5.4-5.8 results from the interaction with the electronic Raman signal; *both* electronic and phononic contributions and their interdependence can be described by Eqs.(3.8) and (3.10). The final result agrees well with the measured data. Thus, our model allows us to some extent to disentangle the electronic and phononic parts of the Raman response, and to identify the shape of the electronic background. However, strictly speaking, only a combination of parameters such as  $g^2\rho$  and  $g^2R$  can be extracted. This fit procedure is improved for the SC state by employing a microscopic description of the pair-breaking excitations (see below).



Figure 5.4: xx and yy Raman spectra of YBCO<sub>6.95</sub> ( $\lambda = 514.5$  nm) in the normal state at T = 100 K (a,c) and in the superconducting state at T = 20 K (b,d). Open circles show the experimental data. The solid curves represent the fitting result with formula 3.8 and four Lorentzians for the remaining  $A_{1g}$  phonons whereas the dashed curves depict the electronic background.

#### 5.1.2 $B_{1q}$ Raman Signals

To describe the combined electronic and phononic Raman response in the SC state, we use Eq. 3.8 together with the real and imaginary parts of the electronic Raman response in the SC state, Eq. 3.16. We have assumed the same band structure parameters as in Ref. [21] together with  $\Delta_d = 30$  meV,  $\Delta_s = 0$ , 3 and 6 meV, and  $\eta = 5$  meV. Furthermore, we assume that the bare fit parameters do not change as we go from the normal state to the SC state.

In Figure 5.7(a) we show numerical results obtained from our theoretical model and their comparison with the data on YBCO<sub>6.95</sub> obtained in  $B_{1g}$ -polarization. The calculations have been performed at T = 20 K and for various *s*-wave contributions. The best description for both the  $B_{1g}$ -mode and the electronic response is found if  $\Delta_s$  is assumed to be 10% of the maximum of the  $d_{x^2-y^2}$ -wave gap (short dotted



Figure 5.5: Same as Fig. 5.4 but for the overdoped sample  $YBCO_{6.95}$ :Ca.

YBCO <sub>6.95</sub>	$S_0$	$2\Gamma_0$	$\omega_0$	$\omega_0(INS)$	$\omega_0(\text{sqrt})$	$\omega_0(\text{lin.})$
$B_{1g}$ (100K)	1.5	15.3	343.1	343.9	342.8	341.9
XX (100K)	1.8	12.2	342.9	343.9	339.1	340.7
YY (100K)	1.8	12.2	342.9	343.9	339.5	338.7
$B_{1g}$ (20K)	2.6	14.8	338.6	338.4	335.8	335.7
XX (20K)	4.1	13.2	336.4	338.4	333.0	332.5
YY (20K)	2.1	13.8	336.3	338.4	334.2	334.2

Table 5.1: Extracted parameter values of the  $B_{1g}$  oxygen vibration in YBCO<sub>6.95</sub> measured at 20 K and 100 K, respectively. Left part: asymmetry parameter  $S_0$ , intrinsic phonon linewidth (FWHM)  $2\Gamma_0$ , and intrinsic phonon frequency  $\omega_0$  using the generalized Fano approach of Eq.(3.8). Right part:  $\omega_0$  extracted with Eq.(3.2) for different phenomenological electronic backgrounds [sqrt = first term in Eq.(3.10); lin. = linear background with offset at  $\omega = 0$ ]. For comparison we display in the middle part  $\omega_0$  obtained from inelastic neutron scattering (INS) experiments by Reznik *et al.* [96]



Figure 5.6:  $B_{1g}$  Raman spectra of YBCO<sub>6.95</sub> ( $\lambda = 514.5$  nm) in the normal state at T = 100 K (a) and in the superconducting state at T = 20 K (b). Open circles show the experimental data, the solid curve the fitting result with formula 3.8 and four Lorentzians for the remaining  $A_{1g}$  phonons. The insets show the corresponding data after phonon subtraction. Panels (c) and (d) show the phonon-subtracted spectra for the xx and yy channels, respectively. The vertical lines in (c,d) indicate the maxima of the electronic peak intensity at 450 cm<sup>-1</sup> and 480cm<sup>-1</sup>, respectively. (e-h) Same as (a-d) but for the overdoped sample YBCO<sub>6.95</sub>:Ca. The spectra were recorded at 80 K (normal state) and 12 K (SC state). The vertical lines in (g,h) indicate the maxima of the electronic peak intensity at 290 cm<sup>-1</sup> (XX) and 355 cm<sup>-1</sup> (YY), respectively.

line); this also accounts for the slight shift of the pair breaking peaks in xx and yy polarizations (Fig. 5.6 (c) and (d)). Furthermore, our numerical results solely for the



Figure 5.7: (a)  $B_{1g}$  Raman spectra of YBCO<sub>6.95</sub> in the superconducting state at T = 20 K ( $\lambda$ =514.5 nm). Open circles show the experimental data. The short dashed, short dotted, and short dash-dotted curves are the theoretical result obtained with Eq. 3.16. The  $B_{1g}$  phonon was also taken into account. We show results for various *s*-wave contributions  $\Delta_s/\Delta_d = 0$  (dashed); 0.1 (dotted); 0.2 (dash-dotted). The dashed, dotted, and dash-dotted curves show the calculated imaginary part of the electronic response,  $\chi''_{B_{1g}}(\omega)$ . (b) Subtracted spectra [20K (sc-state)-100K (n-state)] for the  $B_{1g}$  polarization channel of YBCO<sub>6.95</sub>. Before subtraction the spectra were divided by the Bose factor. The solid curve depicts the theoretical result for 10% *s*-wave contribution.

electronic response, *i.e.* the 2 $\Delta$ -pair-breaking peak, are also displayed in Fig. 5.7 (dashed, dotted and dash-dotted lines). They are obtained by setting all phononic parts and the corresponding interference terms in Eq. (3.8) to zero. Interestingly, we



Figure 5.8: (a)  $B_{1g}$  Raman spectra of YBCO<sub>6.95</sub>:Ca in the superconducting state at T = 12 K ( $\lambda = 514.5 \text{ nm}$ ). Open circles show the experimental data. The short dashed, short dotted, and short dash-dotted curves are the theoretical result obtained with Eq. 3.16. The  $B_{1g}$  phonon was also taken into account. We show results for various *s*-wave contributions  $\Delta_s/\Delta_d = 0.05 \text{ (dashed)}; 0.15 \text{ (dotted)}; 0.25 \text{ (dash-dotted)}$ . The dashed, dotted, and dash-dotted curves show the calculated imaginary part of the electronic response,  $\chi''_{B_{1g}}(\omega)$ . (b) Subtracted spectra [12K (sc-state)-80K (n-state)] for the  $B_{1g}$  polarization channel of YBCO<sub>6.95</sub>:Ca. Before subtraction the spectra were divided by the Bose factor. The solid curve depicts the theoretical result for 15% *s*-wave contribution.

find that the pair-breaking peak shifts to lower energies with increasing  $\Delta_s$ , a fact which has been discussed in a previous paper by Schnyder *et al.* [21]. In addition, the cubic low-energy response, *i.e.* its  $(\omega/2\Delta_0)^3$ -behavior found for  $\Delta_s = 0$  changes

if  $\Delta_s \neq 0$ : we obtain linear correction terms which are, however, proportional to  $\Delta_s/\Delta_d$ , and thus barely observable [3].

Figure 5.7(b) shows the differences  $(\chi''_S - \chi''_N)$ , which were obtained by subtracting the spectra at 20 and 100 K after dividing by the Bose factor. The solid line is obtained after subtracting the model function 3.10 for the normal state [see Fig. 5.6(a)] from the results for the SC state when  $\Delta_s/\Delta_d = 0.1$  [dotted line in Fig. 5.7(a)]. We find that the position of the pair-breaking peak at ~ 460 cm<sup>-1</sup> (and partly its shape) is well described by our theory. This confirms that 10% s-wave contribution [short dotted line in Fig. 5.7(a)] yields an excellent description of the electronic Raman response. Furthermore, the temperature-dependence of the related  $B_{1g}$  phonon is also reproduced (Fig. 5.7(b)). Note that the difference between experimental and calculated data at small energies is likely to be due to elastic impurity scattering which is not taken into account in our theoretical model. Here, we emphasize that the low-energy power laws in Figs. 5.6 and Fig. 5.7(a) are changed in the presence of an s-wave contribution while there exists no power law for the subtracted data in Fig. 5.7(b).

Finally, we return to the moderately overdoped sample. Raman data on YBCO<sub>6.95</sub>: Ca above and below  $T_c$  in several polarization geometries are displayed in Fig. 5.6. In the absence of specific information about the electronic band dispersions of this material, we modeled these data by scaling the magnitude of the energy gap  $\Delta_d$  by the ratio of transition temperatures (*i.e.*  $\Delta_d$ (YBCO<sub>6.95</sub>:Ca) = 25 meV and  $\Delta_s =$ 0, 2.5 and 5 meV), keeping all other model parameters identical to those used for YBCO<sub>6.95</sub>. The best fit was obtained for  $\Delta_s/\Delta_d = 0.15$  (however the estimated error bars are about  $\pm 0.05$ ), slightly larger than the corresponding quantity in YBCO<sub>6.95</sub>. Note that the quality of the fit is comparable to the one for YBCO<sub>6.95</sub>, although separate plane and chain subsystems were not introduced in the analysis [185, 186]. The previously observed difference between spectra in xx and yy geometry was confirmed (Fig. 5.6), but our model calculations suggest that this is a consequence of the *s*-wave admixture to the gap [3], obviating the need to introduce quantum interference between scattering from chains and planes[78, 185].

### 5.2 Temperature Dependent Phonon Lineshapes

#### 5.2.1 Anisotropic Fano Profile

Several phonons in YBCO display a pronounced asymmetric lineshape suggesting a strong interaction with the electronic continuum. As shown in Fig. 5.9 the asym-



Figure 5.9: Fano-analysis [Eq.(3.2)] of three different phonons measured at a temperature of 20 K ( $\lambda$ =514.5 nm). (a,b) The fit of the 340 cm<sup>-1</sup> mode, which corresponds to the outof-phase vibrations of the planar oxygen, along yy and xx polarizations, respectively.(c,d) same as (a,b) but for the in-phase planar oxygen mode around 440 cm<sup>-1</sup> and apical oxygen mode at 501 cm<sup>-1</sup>. Open circles show the experimental data. The dash-dotted lines are the results of the overall fit to the experimental data. The solid lines are the results of fits to Fano-profiles [Eq.(3.2)] as described in the text. The dotted lines correspond to a linear background. The intensity units are arbitrary but the same in the four vignettes.

metry is most pronounced for the 340 cm<sup>-1</sup> mode. Interestingly, the phonon peak reflecting the vibration of the apical oxygen at 501cm<sup>-1</sup> exhibits a strong asymmetry for a polarization of incident and scattered light along the *a*-axis, whereas along the *b*-axis the phonon appears to be almost symmetric (see Fig. 5.9). Two additional modes are present in this spectral range. The mode at 440 cm<sup>-1</sup> originates from an in-phase vibration of the oxygen atoms O2 and O3. Additional modes are present at about 472 cm<sup>-1</sup> and 480 cm<sup>-1</sup> for polarizations parallel to the *a*- and *b*-axis, respectively. As mentioned above, these modes are Raman forbidden, but correspond to IR allowed vibrations involving the Cu1-O1 chains [187]. Due to defects (oxygen vacancies) in the Cu1-O1 chains they become Raman active. Similar to previous temperature dependent Raman experiments on  $\text{YBCO}_{7-\delta}$  [140, 188, 189, 190] and  $\text{HgBa}_2\text{Ca}_3\text{Cu}_4\text{O}_{10+\delta}$ , [99] we have fitted the phonons of  $\text{YBCO}_{6.95}$  by using simple Fano profiles. The solid lines in Fig. 5.9 are the results of fits to the experimental data using Eq. 3.2, the dash dotted lines correspond to the resulting fitted lineshape of the entire spectrum. The calculated profiles agree well with the measured spectra.

In order to obtain estimates of the intrinsic phonon positions and linewidths, we have followed the procedure used in Ref.[20] and corrected the peak position and linewidth using Eq.(3.4). Figure 5.10 shows the apparent and intrinsic positions and linwidths of the B<sub>1g</sub> phonon in xx and yy polarizations. The apparent phonon positions (peak maxima) and linewidths are polarization dependent, *i.e.* different along xx and yy symmetries, whereas the intrinsic positions and linewidths are the same in both polarization geometries. The difference in the apparent parameters ( $\omega_p$  and  $\Gamma_p$ ) reflects the xy-discrepancy of the asymmetry of the phonon lineshapes, which contains valuable information about the xy-anisotropy of the 2 $\Delta$  gap (sec.5.2.3).

Fits to the simplified Fano profile of Eq. (3.2) are much less complicated than the fitting procedure to the full spectrum discussed above. This is a key advantage especially in situations in which several closely spaced phonons partially overlap as is the case, for instance, for the apical-oxygen vibration in Fig. 5.9. The multi-parameter, global fit [Eq. (3.8)] yields unstable results for these phonons. It is important to note, however, that the quantities extracted from simple Fano fits are renormalized by the electronic response function, and therefore deviate slightly from the intrinsic phonon frequency  $\omega_0$  and the bare linewidth  $\Gamma_0$  of Table 5.2. We will compare the results of both procedures in detail at the end of the next subsection.

Since the energy of the pair breaking peak in  $YBCO_{6.95}$ : Ca is lower than the one in  $YBCO_{6.95}$ , it coincides with the energy of the  $B_{1g}$  phonon mode. Therefore, fits using the simplified Fano profile (Eq. 3.2) are, however, barely achievable. Due to this reason, we will focus the discussion on the phonons of  $YBCO_{6.95}$ .

### 5.2.2 Superconductivity-Induced Changes in the Phonon Frequencies and Linewidths

Figure 5.11 shows the temperature dependence of the energies and linewidths of two particular phonons, the 340 cm<sup>-1</sup> and 501 cm<sup>-1</sup> modes, measured with light polarization along the crystallographic a- and b-axes. The spectra were taken at



Figure 5.10: Frequency and line width versus temperature of the 340 cm<sup>-1</sup> mode ( $\lambda$ =514.5 nm). Triangles and circles are the apparent values obtained using Eq.(3.2) (before asymmetry correction) for the xx- and yy-polarization, respectively. Squares and crosses are the corresponding intrinsic values using Eqs.(3.2) and (3.4) (after asymmetry correction). Inset displays the Fano analysis of the 340 cm<sup>-1</sup> mode for the xx (triangles) and yy (circles) polarizations.  $\omega_p$  and  $\omega_0$  correspond to the apparent and intrinsic phonon frequencies, respectively.

temperatures ranging from 20 to 300 K. The temperature dependence of the phonon energy and linewidth in the normal state arises from anharmonic phonon-phonon interactions, i. e., the decay of a high-energy optical phonon into two phonons of lower energy with opposite momenta [191, 192]. For simplicity, assuming the resulting phonons to have the same energy [191, 192] and using Bose-Einstein statistics, this decay process leads to

$$\Gamma_{anh.}(T) = \Gamma_{anh.}^{T=0}(1 + 2n(\omega_p/2)).$$
(5.1)

This process, implying decay through real transitions, is strictly valid for the line width, but has been also used for the frequency shift although, in this case, virtual transitions also play a role. In Fig. 5.11, both linewidth and peak position were fitted simultaneously for the temperature range above  $T_c$  (solid lines). Both of these quantities show abrupt changes at the SC transition temperature due to the opening of the superconducting gap, as previously observed in YBCO (see for example Refs. [140, 188, 189, 190]) and also other superconducting compounds like HgBa<sub>2</sub>Ca<sub>3</sub>Cu<sub>4</sub>O<sub>10</sub> [99, 120] and Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> [193, 194].

Within the error bars of ~ 0.8 cm<sup>-1</sup> in (a)-(c) and 2.0 cm<sup>-1</sup> in (d), the phonon peak position and linewidth of the 340 cm<sup>-1</sup> mode is the same for the xx and yy polarizations (see Fig. 5.11(a) and (b)). Taking the phonon positions and linewidths in the SC state as  $\omega_p^s$  and  $\Gamma_p^s$ , the maximum change in the phonon position and linewidth is obtained from  $\Delta \omega = \omega_p^s(\tilde{T}) - \omega_p(T = 100 \text{ K})$  and  $\Delta \Gamma = \Gamma_p^s(\tilde{T}) - \Gamma_p(T = 100 \text{ K})$ , where  $\tilde{T}$  denotes the temperature at which the maximum of the SC-induced changes occurs [195]. The additional softening below  $T_c$  due to the electron-phonon interaction is about -6 cm<sup>-1</sup>. The change in linewidth (FWHM) is +3 cm<sup>-1</sup>, reflecting a broadening. For the vibration of the apical oxygen, *i.e.* the 501 cm<sup>-1</sup> mode, the corresponding shift (hardening) and broadening are +3 cm<sup>-1</sup> and +5 cm<sup>-1</sup>, respectively. The SC-induced changes for the 340 cm<sup>-1</sup> and 501 cm<sup>-1</sup> modes are in good agreement with previous data obtained on twinned YBCO [140, 188, 189, 190, 195].

The SC-induced changes in the phonon linewidth and peak position (for a phonon labeled as  $\mu$ ) can be related to changes in the phonon self–energy  $\Sigma_{\mu}(\omega) = |g^{\mu}|^2 \Pi(\omega + i\eta)$  (with  $\eta \to 0$ ), resulting from the interaction between the phonons and the electronic system below  $T_c$  [21, 176, 194]. The induced frequency shifts  $\Delta \omega$  are related to the real part of the phonon polarization  $\Pi$  by [97, 176, 196]:

$$\frac{\Delta\omega}{\omega_0} = \frac{1}{N(0)} \,\lambda \,\mathrm{Re}\Pi(\omega_0),\tag{5.2}$$

while the induced changes in the linewidth can be calculated via:

$$\frac{\Delta\Gamma}{\omega_0} = \frac{1}{N(0)} \lambda \operatorname{Im}\Pi(\omega_0).$$
(5.3)



Figure 5.11: Frequency and line width (FWHM) obtained using Eqs.(3.2) and (3.4) versus temperature of the 340 cm<sup>-1</sup> mode and the 501 cm<sup>-1</sup> mode of YBCO<sub>6.95</sub> for the xx- and yy-polarization, respectively ( $\lambda$ =514.5 nm). Below  $T_c$  a comparison between calculations for  $s = \Delta_s / \Delta_d = 0$  (dashed line), 0.1 (dash-dotted line), and 0.2 (dotted line) is displayed. The solid line corresponds to the temperature dependence of pure phonon–phonon interaction (interpreted as Klemens decay into two phonons of equal frequencies).

Here, N(0) denotes the electronic density of states at the Fermi level and  $\lambda$  is the dimensionless electron-phonon coupling constant which can be given as [197]:

$$\lambda = 2\sum_{\mathbf{k}} \sum_{\mu} \int \frac{d\omega}{\omega} |g_{\mathbf{k},0}^{\mu}|^2 F_{\mathbf{k}}^{\mu}(\omega) \delta(\epsilon_{\mathbf{k}}).$$
(5.4)

 $F_{\mathbf{k}}^{\mu}(\omega)$  denotes the spectral function for phonon  $\mu$  under consideration [197]. Taking into account screening effects, *i.e.* the long-range Coulomb force, the self-energy is given by [21, 97, 176, 196]:

$$\Sigma_{\lambda}(\omega) = -\left\langle \left(g_{\boldsymbol{k},0}^{\mu}\right)^{2} \theta_{\boldsymbol{k}}(\omega) \right\rangle + \frac{\left\langle g_{\boldsymbol{k},0}^{\mu} \theta_{\boldsymbol{k}}(\omega) \right\rangle^{2}}{\left\langle \theta_{\boldsymbol{k}}(\omega) \right\rangle}, \tag{5.5}$$

where the angular brackets are defined by Eq. 2.13. The symmetry of the optical phonons is reflected in the matrix element  $g^{\mu}_{k,0}$ . The electron-phonon coupling of phonons of  $A_{1q}$  and  $B_{1q}$  symmetry are in a first approximation given by

$$g_{\mathbf{k},0}^{B_{1g}} = g_{B_{1g}}(\cos k_x - \cos k_y)/2,$$
 (5.6a)

$$g_{k,0}^{A_{1g}} = g_{A_{1g}}(\cos k_x + \cos k_y)/2,$$
 (5.6b)

with the electron-phonon coupling strength  $g_{B_{1g}}$  and  $g_{A_{1g}}$  (Note that there is more than one phonon of  $A_{1q}$  symmetry). Calculations of the superconductivity-induced phonon self-energy effects show that phonons below the energy of the superconducting gap  $2\Delta_{max}$  should soften below T<sub>c</sub> (*i.e.* they should shift to lower energies) [21, 176, 196], whereas phonons above  $2\Delta_{max}$  should harden (see fig. 5.12). This is confirmed in our experiments (not all data are shown here) and in previous work (see Refs. [19], [140], [188], [189] and [190]). The energy of the apical oxygen phonon (501 cm<sup>-1</sup> = 62.5 meV) is right at the gap energy and is therefore sensitive to small changes in the energy of the SC gap. The  $340 \text{ cm}^{-1}$  mode is well below the SC energy gap for  $T \ll T_c$ . With increasing temperature the energy of the  $2\Delta$  gap shifts to lower energies and moves through the energy of the 340  $\rm cm^{-1}$  mode. Changes to the phonon self-energy are predicted to be strongest when the phonon energy coincides with the energy of the  $2\Delta$  gap and to decrease with increasing the separation from the  $2\Delta$  gap. This explains the monotonic decrease and nonmonotonic behavior (maximum of the linewidth at 75 K) of the 501 and  $340 \text{ cm}^{-1}$  modes, respectively. A similar behavior was observed by Limonov *et al.* [18]. Again, the same reason can explain the weak superconductivity-induced line shape changes of the Ba vibrations near 115  $\rm cm^{-1}$ . Since the phonon frequency of the Ba-mode is considerably smaller than the amplitude of the superconducting gap, the coupling of this mode to the electronic continuum is much weak (Fig. 5.13).

Finally, we discuss the role of the s-wave contribution to the superconducting gap  $\Delta_k = \Delta_k/2(\cos k_x - \cos k_y) + \Delta_s$ . Our numerical results obtained with Eqs. (3.13)–(3.16) and Eqs. (5.2)–(5.6) using the fits reported in Sec. 5.1.2 and those displayed



Figure 5.12: The real part of the superconductivity-induced self-energy of the  $A_{1g}$  phonons calculated at zero temperature. Negative and positive values refer to softening and hardening, respectively. Inset (1) shows the corresponding imaginary part of the self-energy with negative (positive) values correspond to linewidth broadening (sharpening). Inset (2) displays schematic electronic density of states (full lines) in the normal and superconducting states interacting with phonons at energies below and above the  $2\Delta$ -gap. The arrows in inset (2) indicate the softening (shift to lower energy) and hardening (shift to higher energy) of phonons 1 and 2, respectively. This figure is obtained from [21].

in Fig. 5.11. We compare  $\Delta_s = 0$  (dashed line) with  $\Delta_s = 3$  meV (dash-dotted line) and  $\Delta_s = 6$  meV (dotted line). We find that the results obtained with 20 % s-wave contribution cannot describe our data. This is clearly visible in Figs. 5.11(a) and (c) which show the SC-induced changes  $\Delta \omega$  in the position of the corresponding phonon. In particular, for the 501 cm<sup>-1</sup>-mode which is known to be very sensitive to the superconducting gap [21], one predicts a softening for  $\Delta_s = 6$  meV, while instead a hardening is observed. Therefore, our data imply an upper limit of  $\Delta_s/\Delta_d = 0.2$ . The best agreement is obtained for 10% s-wave admixture.

At the end of this subsection, we are contrasting our generalized Fano theory [see Eq. (3.8)] with the standard Fano approach described by Eq. (3.2). The main difference between both approaches is the theoretical description of the electronic Raman response. While in the standard Fano approach the background is assumed either to be linear (see Fig. 5.9) or to follow a square-root behavior [first term in Eq. (3.10)] in both the normal and SC-state, our generalized Fano theory is able to take the rearrangement of spectral weight due to the opening of the superconduct-



Figure 5.13: Frequency, line width (FWHM) and asymmetry parameter  $(q^{-1})$  obtained using Eq. (3.2) versus temperature of the Ba-mode of YBCO<sub>6.95</sub> for the xx- and yypolarization, respectively ( $\lambda$ =514.5 nm). The solid lines represent the temperature dependence of pure phonon-phonon interaction (Klemens decay). The dotted vertical line denotes the T<sub>c</sub>.

ing gap into account. Within our microscopic description [Eqs. (3.13)–(3.16)] it is then possible to determine the ratio  $\Delta_s/\Delta_d$ . Another difference between both Fano theories concerns the asymmetry parameter q: in our generalized theory it becomes  $\omega$ -dependent which allows a self-consistent description of the  $B_{1g}$ -phonon and the electronic Raman response from 80 to about 1000 cm<sup>-1</sup>. Thus, in other words, no specific frequency interval close to the phonon peak position [see Fano lineshape analysis in Figs. 5.9(a) and (b)] needs to be selected.

We have summarized our comparison in Table I in which the intrinsic frequency of the  $B_{1g}$ -phonon extracted from both Fano theories is displayed:  $\omega_0$  obtained from Eq. (3.8) [left part, third column],  $\omega_0$  obtained from Eqs. (3.2) and (3.4) either for a square-root [ $\omega_0(\operatorname{sqrt})$ ] or linear background [ $\omega_0(\operatorname{lin.})$ ] (right part). These values have to be compared with  $\omega_0$  obtained from inelastic neutron scattering experiments [ $\omega_0(\operatorname{INS})$ ] (middle column). One clearly sees that the values for  $\omega_0$  obtained from our generalized Fano theory are similar to those measured in INS experiments. On the other hand, the values extracted from the standard Fano approach differ by 1.1 [ $B_{1g}(100\mathrm{K}), \omega_0(\operatorname{sqrt})$ ] to 5.9 [XX(20\mathrm{K}),  $\omega_0(\operatorname{lin.})$ ] wavenumbers. Note, however, that these values can be substantially modified if a specific frequency interval around the peak position of the  $B_{1g}$ -phonon is defined and the corresponding lineshape analysis is then restricted to this interval (see Fig. 5.9.) These improved values are shown in Fig. 5.11. In the case of the apical oxygen vibration analyzed in Figs. 5.9(c) and (d), a fit with Eq. (3.8) is hardly possible due to the multiple peak structure between
400 cm<sup>-1</sup> and 540 cm<sup>-1</sup>. Therefore, we have used Eqs. (3.2), (3.4), and (3.10). On the whole, we find characteristic differences between our self-consistent, generalized Fano theory and the standard Fano approach, but our conclusions about the ratio  $\Delta_s/\Delta_d$  are independent of the theory used provided that Eqs. (3.2), (3.4), and (3.10) are restricted (or strongly weighted) to an interval around the peak position of the phonon being investigated.

### 5.2.3 Temperature Dependence of the Asymmetry Parameter

Figure 5.14 shows the temperature dependence of the asymmetry parameters  $q_{xx}^{-1}$  and  $q_{yy}^{-1}$  in Eq. (3.2) as obtained from the fits of the Fano profile to the experimental spectra. We discuss these data in the framework of the approximate expression

$$q \approx \frac{T_{\sigma}/\gamma_{\sigma}}{g_{\sigma}\chi_{\sigma}''},\tag{5.7}$$

already applied in Raman work on other high  $T_c$  superconductors. [98, 99, 138] We first focus on temperatures above  $T_c$  and note that  $q_{xx}^{-1} \approx q_{yy}^{-1} \sim -0.12$  for the 340 cm<sup>-1</sup> mode, whereas a pronounced difference in the asymmetry parameters along in xx and yy geometries is observed for the 501 cm<sup>-1</sup> mode ( $q_{xx}^{-1} \sim -0.20$ ,  $q_{yy}^{-1} \sim -0.08$ ). As  $g_{\sigma}$  is a materials parameter independent of the light-field configuration and  $\chi_{\sigma}''$  is weakly  $\omega$ -dependent, the strong variation of asymmetry parameters must be attributed to differences in  $T_{\sigma}/\gamma_{\sigma}$ . Our results are in fair agreement with the phononic and electronic Raman efficiencies (proportional to  $|T_{\sigma}|^2$  and  $|\gamma_{\sigma}|^2$ , respectively) calculated in refs. [159, 198] using density functional methods. For instance, the calculated  $\frac{|\gamma/T|_{yy}}{|\gamma/T|_{xx}} (\sim \frac{q_{yy}^{-1}}{q_{xx}^{-1}})$  in the normal state is about 1.2 and 0.65 for the 340 cm<sup>-1</sup> and 501 cm<sup>-1</sup> modes, respectively. The changes of the asymmetry parameters with temperature in the normal state may reflect a temperature dependence of  $\gamma_{\sigma}$ , *i.e.* parameters in the electronic band structure as well as that of the anharmonic linewidth, but their detailed origin cannot be disentangled.

Moving to the superconducting state, we note that the only parameter in Eq. (5.7) expected to change significantly across  $T_c$  is the response function  $\chi''_{\sigma}$ . The temperature dependence of  $q_{xx}^{-1}$  and  $q_{yy}^{-1}$  below  $T_c$  therefore also reflects the *ab*-anisotropy in the 2 $\Delta$ -gap. Thus we have computed the temperature evolution of the asymmetry parameters in the superconducting state, using the same model parameters described in Sec. 3.2. The reasonable agreement with the data (Fig. 5.14) demonstrates the self-consistency of our approach. However, since the superconductivityinduced modification of  $q_{xx}^{-1}$  and  $q_{yy}^{-1}$  is relatively subtle (compared to that observed in the normal state), this analysis does not provide constraints on the ratio  $\Delta_s/\Delta_d$ 



Figure 5.14: Fano asymmetry parameter ( $\lambda = 514.5 \text{ nm}$ ) of both polarization channels for the 340 cm<sup>-1</sup> and 503 cm<sup>-1</sup> mode of YBCO<sub>6.95</sub>, respectively. Results of the theoretical calculations for different s-wave admixtures (0, 0.1, and 0.2) are also shown.

beyond those already discussed above.

It is interesting to note that other  $A_g$  modes also reveal a temperature-dependent asymmetry. In particular, we have observed that the Ba mode near 115 cm<sup>-1</sup> is symmetric (*i.e.*  $q^{-1} = 0$ ) for  $T \to 0$  and its asymmetry increases monotonically to  $q^{-1} = 0.25$  (see fig. 5.13). Its intensity, however, is rather weak compared with the  $B_{1g}$  mode (and this applies even more so to the Cu mode near 150 cm<sup>-1</sup>), so we have not used these modes further in our discussion. Their asymmetry has been analyzed in more detail in Refs. [153, 199], however without considering a possible *s*-component to the  $d_{x^2-y^2}$ -wave gap.



Figure 5.15: Raman spectra of a detwinned underdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> single crystal in xx and yy Raman channels taken with an Ar<sup>+</sup> laser line ( $\lambda = 514.5$  nm) at 20 K. The mode assignment corresponds to Refs. [138, 143, 142]. The horizontal dotted line shows the baseline of the yy spectrum.

### **5.3** Underdoped $YBCO_{6.6}$ and $YBCO_{6.45}$

#### 5.3.1 Mode Assignments

Oxygen-deficient YBCO<sub>6.6</sub> (YBCO<sub>6.45</sub>) crystallizes in an ortho–V (ortho–II) superstructure; hence its elementary supercell becomes  $5a \times b \times c$  ( $2a \times b \times c$ ) [93]. Figure 5.15 and 5.16 display the Raman spectra of a detwinned YBCO<sub>6.6</sub> crystal measured at various temperatures in xx and yy polarization geometries. Due to the formation of the oxygen superstructures, several modes in addition to the conven-

Atomic	YBCO <sub>6.6</sub>		YBCO <sub>6.45</sub>	
displacement	xx	yy	xx	yy
$\operatorname{Cu2}(z)$ - $\operatorname{Cu2'}(-z)$	109	110	_	—
$\operatorname{Ba}(z)$	120.7	122	_	_
mixed $\operatorname{Ba/Cu}(2)(z)$	145.3	144.6	142.7	142.7
$B_{2g}/B_{2g}$ symmetry	188.9	187.4	188.1	188.4
$\mathbf{Y}(x)$	203.6	—	_	—
Cu1 ( $B_{1u}$ symmetry)	-	232.7	_	230.7
O2-O3(z)	340	340	338.8	338.6
O2+O3(z)	453.7	452.7	450.8	450.4
Defect mode	464.3	—	_	—
O4(z)	487.2	489.7	484.2	484.9
Defect mode	-	547.9	-	545.7
O2(x)	562.1	—	552.5	—
O2(x)	594.9	_	_	—
O1 ( $B_{1u}$ symmetry)	-	579.7	-	580.4
O2(x)	594.9	_	588.5	—
O2(x)	612	-	_	—

Table 5.2: Phonon frequencies (in cm<sup>-1</sup>) of YBCO<sub>6.6</sub> and YBCO<sub>6.45</sub> measured in xx and yy polarization geometries at 20 K.

tional 4  $A_{1g}+1$   $B_{1g}$  phonons of YBCO<sub>7</sub> are observed. The phonon peaks near 121  $(A_{1g})$ , 145  $(A_{1g})$ , 340  $(B_{1g})$ , 453  $(A_{1g})$  and 486 $(A_{1g})$  cm<sup>-1</sup> are ascribed to vibrations of Ba, mixed Ba/plane copper Cu(2), O(2)-O(3) (out-of-phase), O(2)+O(3) (in-phase) oxygen and apical oxygen atoms, respectively [18, 45]. The frequency of the apical oxygen vibrations is highly dependent on the oxygen concentration in YBCO<sub>6+x</sub> [112]. The appearance of the apical oxygen mode at around 486 cm<sup>-1</sup> agrees with previous Raman measurements [112, 138] and confirms that our samples are underdoped with oxygen concentrations of O<sub>6.6</sub> (p = 0.1) (O<sub>6.45</sub> with p = 0.07).

We turn now to the phonon modes originating from the formation of the superstructures. Since YBCO<sub>6.6</sub> has a larger unit cell than YBCO<sub>6.45</sub>, one would expect the former to have more Raman lines than the latter. But as listed in table 5.2, both samples reveal the same number of Raman modes, which is similar to that of YBCO<sub>6.5</sub> in ref. [138]. Thus, we have based the assignment of the extra modes on the ortho–II structure, i.e., the conventional 4  $A_{1g}$ +1  $B_{1g}$  modes presented above plus the periodicity-induced 6  $A_{1g}$ + 4  $B_{1g}$  modes [138, 199].

Some of the periodicity-induced modes are seen in both xx and yy geometries.

This is the case, for example, for the  $A_{1g}$  mode at 109 cm<sup>-1</sup>, which is attributed to the z-polarized out-of-phase vibrations of plane copper atoms [Cu2(z)-Cu2'(-z)] as well as for the weak O4'(z) vibrations near 382 cm<sup>-1</sup> (the eigenvectors are shown in Fig. 2.4). The out-of-phase vibrations of the apical oxygen [O4(z)-O4'(-z)] expected to appear at 352 cm<sup>-1</sup> are hardly recognized because of the adjoining strong mode at 340 cm<sup>-1</sup>. The two modes near 233 and 580 cm<sup>-1</sup> in the *yy* scattering channel are usually assigned to vibrations of the Cu1 and O1 atoms of the symmetry-broken chains, i.e. defect-induced modes [138, 135]. The absence of the chain modes in the *xx* symmetry confirms a high detwinning ratio of our samples (~ 95%).

Most of the periodicity-induced modes appear only in the xx symmetry. The peak at 203 cm<sup>-1</sup> agrees in energy with that attributed to the x-polarized yttrium vibrations [138, 142, 143]. The phonon mode at 464 cm<sup>-1</sup> is attributed to vibrations involving the Cu–O chains [187, 45]. The modes recorded at 562, 589 ,and 612 cm<sup>-1</sup> originate from stretching vibrations of the O2 plane oxygen atoms along the x-axis [138, 139, 142].

As the z-polarized atomic vibrations are present in either xx or yy polarization geometries, the 203, 562, 589, and 612 cm<sup>-1</sup> vibrational modes appear only when light polarizations are parallel to the *a*-axis, i.e., the axis along which the unit cell is extended. These modes are thus excellent tools for investigating the xy-anisotropy of the electronic system of underdoped YBCO<sub>6+x</sub>. In YBCO<sub>6.45</sub> (Fig. 5.17), the phonon modes are similar to those observed for YBCO<sub>6.6</sub>; hence their assignments are identical.

#### 5.3.2 Temperature dependence of Phonons

Figures 5.16(a,b) and 5.17(a,b) show the Raman spectra of YBCO<sub>6.6</sub> and YBCO<sub>6.45</sub>, respectively, taken at various temperatures using the 514.52 nm laser line. The most striking observation in the spectra is the strong temperature dependence of the phonon intensities. For both dopings, some of the phonon lines present at the lowest temperatures are hardly detectable above ~ 200 K. The strongest effect is seen in phonons around 203 cm<sup>-1</sup> and in the group of phonons with an energies between ~ 400 and 650 cm<sup>-1</sup> in the xx polarization. By contrast, all the phonon modes present at low temperatures in the yy polarization geometry persist up to room temperature (Fig. 5.21).

In order to examine the possible existence of resonant effects here, we have carried out the same measurements using the red laser line ( $\lambda = 632.8$  nm). The results are presented in Figs. 5.16(c,d) and 5.17(c,d) for YBCO<sub>6.6</sub> and YBCO<sub>6.45</sub>,



Figure 5.16: Raman spectra of a detwinned, underdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> single crystal in xx and yy Raman channels taken with (a,b) an Ar<sup>+</sup> laser line ( $\lambda = 514.5$  nm) and with (c,d) a He<sup>+</sup>/Ne<sup>+</sup> laser line ( $\lambda = 632.8$  nm) at various temperatures. The intensity scales are the same in (a,b) and in (c,d). The insets show the 20 K(sc-state)-60 K(n-state) signal in the xx and yy symmetries.

respectively. We observed modifications of the relative intensities of phonons compared to the measurements performed using 514.53 nm laser light (Figs. 5.16(c,d) and 5.17(c,d)). This is clearly visible in the relative strength of the Y(x) and O(x) modes with respect to that of the B<sub>1g</sub> mode at 340 cm<sup>-1</sup> in both compounds. For instance, the observed ratio between the area enclosed by the three peaks at 561, 589, and 611 cm<sup>-1</sup> and that of the B<sub>1g</sub> mode at 60 K is about 0.8 when the sample is illuminated with green light ( $\lambda = 514.5$  nm), whereas this ratio increases to about 4 when the exciting light is changed to red ( $\lambda = 632.8$  nm).

However, the unusual disappearance of several phonon lines in the xx symmetry with increasing temperature above 200 K is still clearly observable in the two samples when changing the exciting laser line. This suggests that this giant anomaly in



Figure 5.17: Raman spectra of a detwinned underdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.45</sub> single crystal in xx and yy Raman channels taken with (a,b) an Ar<sup>+</sup> laser line ( $\lambda = 514.5$  nm) and with (c,d) a He<sup>+</sup>/Ne<sup>+</sup> laser line ( $\lambda = 632.8$  nm) at various temperatures. The intensity scales are the same in (a,b) and in (c,d).

the phonon intensities is indeed a material-associated phenomenon, and not merely the influence of resonance effects.

Furthermore, we have fitted the phonons of YBCO<sub>6.6</sub> using Lorentzian profiles (Eq. 3.12). The solid lines in Figs. 5.18(a,b) (spectra measured using  $\lambda = 514$  nm) and 5.19c(a,b) (spectra measured using  $\lambda = 632.8$  nm) are the results of fits to the experimental data, and the dash-dotted lines corresponding to the resulting fitted lineshape of the entire spectrum. The calculated profiles agree well with the measured spectra. Figures 5.18(c) and 5.19(c) display the temperature evolution of the integrated intensity  $A \times \Gamma$  of the 203, 462, 486, 560, 589 and 612 cm<sup>-1</sup> peaks of YBCO<sub>6.6</sub> extracted from the fits using Eq. 3.12. We notice, however, that the superconductivity-related changes in the phonon intensities below T<sub>c</sub> seems to be dependent on the incident photon energy.

We have fitted the phonon intensities in Figs. 5.18(c) and 5.19(c) for the tem-



Figure 5.18: (a,b) Analysis of the Raman phonon peaks of a detwinned, underdoped YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> single crystals between 360 cm<sup>-1</sup> and 720 cm<sup>-1</sup> measured at a temperature of 20 K in the *xx*-symmetry using a green laser line ( $\lambda = 514.5$  nm). The analysis was performed using Lorenzian profiles. The phonon assignment is discussed in the text. The intensity units in panels (a,b) are arbitrary but of the same scale. (c) Renormalized integrated intensity (I(T)/I(60 K)) versus temperature of various phonon modes. The mode assignment is discussed in the text. The solid line shows the fitting result using the  $a(T - T^*)^n$  formula with T<sup>\*</sup>=200 K.

perature range between 60 K and 200 K using the formula  $a(T-T^*)^n$ , with T\*=200 K. The best description (solid lines) for the temperature dependence of the phonon intensities is obtained if n is assumed to be ~ 0.5. The power-law behavior of the intensity is indicative of an underlying phase transition.

Similar analysis has been performed for the YBCO<sub>6.45</sub> spectra. Since the xx Raman spectra in the green light experiment reveal a complicated and weak phonon structure in the energy range between 520 and 650, reliable results were extracted only from the data recorded with the red line (Fig. 5.20). Interestingly, we notice



Figure 5.19: Same as fig. 5.18 but spectra are taken with a He<sup>+</sup>/Ne<sup>+</sup> laser line ( $\lambda = 632.8$  nm).

that the modes of both samples, which persist up to room temperature, are the conventional Raman modes of the ortho–I unit cell. However, before discussing the possible origins of the dramatic changes in the phonon intensities around 200 K, we will briefly describe in the following section the evolution of the electronic signals.

#### 5.3.3 Electronic Raman signals

Raman spectra of optimally- or overdoped HTSCs in the normal state are linear in  $\omega$  at small frequencies, becoming almost flat for large energies [45, 200]. As the slope at low frequency is inversely proportional to the scattering rate of charge carriers, it is expected to increase as the temperature is lowered in conventional metals [201, 202]. It is well established that the opposite occurs in underdoped cuprates, that is, the Raman response loses a fraction of the low energy spectral weight below a certain temperature. This is confirmed in our experiments (Figs. 5.16 and 5.17)



Figure 5.20: (a) Analysis of the Raman phonon peaks of a detwinned, underdoped  $YBa_2Cu_3O_{6.45}$  single crystals between 500 cm<sup>-1</sup> and 720 cm<sup>-1</sup> measured at a temperature of 20 K in the *xx*-symmetry using red laser line ( $\lambda = 632.8$  nm). The analysis was performed using Lorenzian profiles. The inset displays the folding of a phonon dispersion due to a periodic structure. (b) Renormalized integrated intensity (I(T)/I(20 K)) versus temperature of various phonon modes. The phonon assignment is discussed in the text.

and in previous work (see Refs. [29, 203]). We observe a suppression in the spectral weight between  $\omega_1 \sim 200 \text{ cm}^{-1}$  and  $\omega_2 \sim 800 \text{ cm}^{-1}$  in the spectra measured in the yy geometry as the temperature is lowered. The energy scale of the depletion in the electronic signal coincides with the energy of the pseudogap seen in ellipsometry measurements of the *c*-axis conductivity [31]. A precise determination of the temperature at which this suppression takes place is, however, not achievable here. Although the electronic redistribution is weaker in the spectra recorded using the red laser line, the effect is still visible.

Finally, when the sample is cooled below the superconducting transition, the Raman spectrum loses an additional fraction of the spectral weight at low energy (i.e., lower than  $\omega_1$  in figs. 5.16 and 5.17). This is again more pronounced in the yy geometry, as illustrated in the inset of fig. 5.16. Although no superconducting coherence peak is observed, this effect likely originates from the opening of the superconducting gap, whereas the earlier suppression is often tentatively associated with the opening of the pseudogap.



Figure 5.21: Renormalized integrated intensity [I(T)/I(20 K)] versus temperature of various z-polarized phonon modes in the xx and yy symmetries of (a) YBCO<sub>6.6</sub> and (b) YBCO<sub>6.45</sub> measured using  $\lambda = 632.8 \text{ nm}$ . All phonons were analyzed using Lorenzian profiles.

### 5.4 Possible Origins of the Phonon Anomalies

As shown in section 5.3.2, the most unusual effect observed in the temperature dependence of the phononic structure of the detwinned, underdoped YBCO<sub>6.6</sub> crystal is the disappearance of the yttrium and O2 vibrations along the a-axis above  $T^* \sim 200$  K. This observation is independent of the different photon energies used in the measurement. A similar trend is observed for YBCO<sub>6.45</sub> phonons. Interestingly, the temperature at which the phonons disappear essentially corresponds to that below which the depletion in the electronic response is seen.

The Y(x) and O2(x) modes are a direct consequence of the formation of oxygen superstructures in our samples, which result in folding of the Brillouin zone due to the new periodicity along the a-axis. Thus, the zone edge modes in the ortho-I cell (Raman-forbidden) become zone center Raman active in the ortho–II case (see inset in fig. 5.20(a)). This is well confirmed in our results. The combined width of the 562, 589, and 612 cm<sup>-1</sup> peaks agrees with the energy difference between the oxygen stretching mode at Q = 0 and that at  $Q = \pi/a$  of YBCO<sub>6.6</sub> measured by INS [42]. The same argument holds for the YBCO<sub>6.45</sub> sample. Besides that, a different number of peaks associated with the stretching vibrations of plane oxygens are observed in YBCO<sub>6.6</sub> and YBCO<sub>6.45</sub>, i.e., three and two, respectively (Figs. 5.19 and 5.20). This likely originates from the different Cu–O chain periodicities in both dopings, leading to different foldings.



Figure 5.22: Temperature dependences of the integrated intensity of (a) the  $(4.4 \ 0 \ 2.5)$  reflections in YBCO<sub>6.6</sub>, and (b) the  $(4.5 \ 0 \ 2)$  reflections in YBCO<sub>6.45</sub> samples which correspond to the ortho-V and ortho-II superstructure, respectively. The insets in (a) and (b) show the respective Q-scans along a<sup>\*</sup> at 10 K. For data analysis, the diffuse peaks were modeled using Lorenzian profiles and their integrated intensities were normalized at every temperature to the intensity of the  $(4 \ 0 \ 0)$  Bragg peak.

A first, natural explanation for the disappearance of these phonon modes above  $T^*$  is the disappearance of the superstructure (or, equivalently, the loss of the Cu–O chain periodicity). To examine this hypothesis, we have performed x-ray diffraction measurements on our samples. Figure 5.22 displays the diffuse peaks characteristic of the oxygen superstructures obtained for YBCO<sub>6.6</sub> and YBCO<sub>6.45</sub> samples as well as their integrated intensities at temperatures between 10 K and 300 K. The diffuse peaks of each superstructure persist up to temperatures well above T<sup>\*</sup>. Within the experimental error, the integrated intensities of the diffuse peaks exhibit a smooth decrease with no anomalies observed either at  $T_c$  or at T<sup>\*</sup>. This rules out any explanation of the singular behavior of phonon intensities based on structural phase transitions.

Since the superstructures of our samples are present above T<sup>\*</sup>, an alternative explanation for the giant enhancement of the extra mode intensities at low temperatures arises from modifications in the electronic system. In other words, breaking of



Figure 5.23: (a) The real part of the far-infrared c-axis conductivity of underdoped YBCO<sub>6.5</sub> (T<sub>c</sub>=52 K) single crystal at various temperatures. The arrows denote the planar oxygen bending phonon (320 cm<sup>-1</sup>) and the transverse optical Josephson plasmon (410 cm<sup>-1</sup>) modes. (b) Temperature dependence of the loss (gain) in the spectral weight of the 320 cm<sup>-1</sup>  $\Delta$  SW<sup>320</sup> (circles) (410 cm<sup>-1</sup> SW<sup>410</sup> (squares)). This figure is taken from Ref. [205].

the YBCO<sub>7</sub> (ortho-I) translational symmetry by the periodic rearrangement of the Cu–O chains, leads to the appearance of these modes at all temperatures, whereas their intensities are significantly enhanced through a strong *ele-ph* coupling below  $T^*$ . Correlation of the phonon anomaly with changes in the electronic channel is further supported by the apparent correspondence of the temperature scales extracted from both vibronic and electronic Raman responses.

Interestingly, infrared ellipsometric study of the *c*-axis conductivity of underdoped YBCO<sub>6.5</sub> [205] revealed a sizable anomaly in the spectral weight of both, the planar oxygen bending phonon mode at 320 cm<sup>-1</sup> (decrease) and the so-called "transverse optical Josephson plasmon" mode around 400–500 cm<sup>-1</sup> (increase) at around 150 K (Fig. 5.23), which is comparable to the onset temperature of our phonon anomalies. The ellipsometric results [205] showed that part of the gain in the spectral weight of the latter mode comes from electronic redistributions, and not merely from the the spectral weight loss of the 320 cm<sup>-1</sup> mode. Evidently, there exists an intimate relationship between the above mentioned findings and the strong phonon anomalies observed in our work. Again, this suggests an electronic origin for these observations.

Recent temperature-dependent IR ellipsometry studies of the *c*-axis [31] as well as in-plane conductivity of underdoped  $\text{YBCO}_{6+x}$  [206] point towards precursor superconducting fluctuations that develop within the pseudogap state at  $T_{onset}$  (with



Figure 5.24: Folding of a phonon dispersion around a periodic electronic structure. Q refers to the modulation wavevector. 1: Charge collective mode. 2: Unperturbed phonon. 3, 4, and 5: Phonons folded, respectively, around 2Q, 4Q, and 6Q via Umklapp processes. This figure is taken from Ref. [212].

 $T_c < T_{onset} < T^*$ ), i.e, phase-disordered superconductivity starts to develop below  $T_{onset}$  whereas long-rang phase coherence sets in below  $T_c$ . Evidence for superconducting fluctuations has also been found [207] in different families of high  $T_c$ superconductors by vortex Nernst experiments (the detection of an electric field  $E_y$ when a temperature gradient  $\nabla_x T$  is applied in the presence of a magnetic field  $H_z$ ). The temperature scale of the phonon anomalies we report here is compatible with the ellipsometry and Nernst effect measurements just mentioned. Precursor superconducting fluctuations picture agrees with our results since the temperature, at which the phonon anomalies happen, slightly decreases with decreasing hole density (i.e., T<sup>\*</sup> ~ 200 K (Fig. 5.19) and 175 K (Fig. 5.20) for YBCO<sub>6.6</sub> and YBCO<sub>6.45</sub>, respectively) whereas the pseudogap temperature is expected to increase with lowering the doping level.

Besides the superconducting fluctuations just mentioned, other effects may occur at this temperature scale. Since the phonon anomalies we observe exhibit a onedimensional anisotropy, key candidates which may cause such effect can be static stripes [32], a Pomeranchuk instability [208] or nematic states [30, 209].

INS measurements have revealed a sizable anomaly in the dispersion of the planar oxygen bond-stretching mode (at around 70 meV =562 cm<sup>-1</sup>) of YBCO<sub>6+x</sub> and La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4</sub> [42, 43, 210, 211] half-way to the BZ boundary. These observations



Figure 5.25: Temperature dependence of the amplitude of the superconducting ( $\Delta$ ) and CDW ( $\Phi$ ) order parameters for the hole doping  $\delta = 0.114$ . This figure is taken from Ref. [216].

have been interpreted as a consequence of the formation of charge stripes in cuprates. The influence of the formation of static charge stripes on the lattice dynamics of cuprates has been theoretically emphasized by E. Kaneshita et al [212]. In these calculations, the authors have shown that the formation of charge stripes allows for folding the phonon dispersion around the wavevector of the charge stripe via umklapp processes (Fig. 5.24). At first glance, these calculations can qualitatively explain the doping dependence of the multipeak structure observed for the O2(x)vibrations, if charge stripes exist in underdoped  $YBCO_{6.6}$  and  $YBCO_{6.45}$  with different modulation wavevectors. Although one-dimensional static charge/spin stripes have been reported in  $YBCO_{6+x}$  system [12, 40], debate about these results was later reopened [30, 41]. Rigid stripe arrays have never been observed in YBCO<sub>6+x</sub> by microscopical probes like, for example, NMR/NQR, neutrons scattering, or xray measurements. Due to these reasons, a static stripe scenario is less probable to cause the phonon anomalies we present here. However, our results cannot rule out the existence of fluctuating stripes which was reported by a previous Raman work on underdoped, twinned YBCO<sub>6+x</sub> [213] and/or local charge ordering in a checkerboard configuration observed by scanning tunneling microscopy (STM) measurements in variously doped  $Bi_2Sr_2CaCu_2O_{8+x}$  [34, 214].

The pseudogap is a rich state with a large variety of observations. Recently, d-charge-density waves (d-CDW) have been suggested as an origin for the pseudogap state (see for example Ref. [215, 216]). In this scenario, a competition between the superconducting and the d-CDW order parameters is expected. Although the temperature evolution of the phonon intensities we report here cannot be taken as a strong evidence for the formation of d - CDW in the pseudogap state, there exists similarities with the temperature evolution of the d - CDWs calculated by Zeyher and Greco [216] (Figs. 5.19 and 5.25). The phonon intensities (Fig. 5.19) show an increase with cooling the sample down until  $T_c$  and then a decrease (saturation in the green light experiment (Fig. 5.18)). This nonmonotonic behavior may arise from a competition between the pseudogap (with d - CDW) and the superconducting states. Despite these similarities, more work remains to be done in order to examine the possible existence of d - CDW in the pseudogap state.

The onset temperature of the phonon anomalies we present here coincides with pronounced rearrangement of the magnetic excitation spectrum observed by inelastic neutron scattering, which has been interpreted as evidence of an electronic liquid crystal state [30, 208, 209]. Therefore, the most likely scenario that can qualitatively explain our data is an unidirectional, nematic state involving charge degrees of freedom that develops below T<sup>\*</sup>. In this state, the rotational but not translational symmetry is spontaneously broken.

This scenario may hold for the phonon anomalies we observe. The orthorhombic distortion as well as the new periodicity of the Cu-O chains, which seem to be temperature independent (Fig. 5.22), induce several phonon modes (Sec.5.3.1). The nematic phase sets in at a temperature close to the pseudogap or onset of superconductivity temperatures affecting mostly the x-polarized yttrium and oxygen vibrational modes. Due to the interaction between the phonon modes and the electronic nematic order, the phonon intensities initially increase monotonically down to the superconducting transition and then they abruptly decreases (Fig. 5.19). This non-monotonicity indicates a possible competition between the nematic and superconducting states.

Within the framework of the nematic order scenario, nematicity is expected to diminish at hole dopings close to the optimal doping level [208]. This hypothesis cannot be examined by performing Raman experiments on optimally doped YBCO<sub>6.93</sub> single crystal, since the Y(x) and O2(x) phonons are prohibited by Raman symmetry considerations. Therefore, we have prepared a Y<sub>0.87</sub>Ca<sub>0.13</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> (YBCO<sub>6.6</sub>:Ca) single crystal ( $T_c = 82$  K,  $p \approx 0.13$ ), in which the Cu-O chain periodicity was kept the same as that of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.6</sub> but with a higher hole density due to the calcium doping. The Raman results are shown in fig. 5.26. It is clearly seen that the *x*-polarized phonon anomalies seen in Ca-free YBCO<sub>6.6</sub> (Fig. 5.19) are much less pronounced in the slightly underdoped YBCO<sub>6.6</sub>:Ca (Fig. 5.26(c)), suggesting that the nematic state weakens when approaching the optimal doping from below. Again, these observations support the nematic phase scenario.



Figure 5.26: (a,b) Raman spectra of a detwinned, slightly underdoped  $Y_{0.87}Ca_{0.13}Ba_2Cu_3O_{6.6}$  single crystal in the xx and yy Raman channels, respectively, taken with a He<sup>+</sup>/Ne<sup>+</sup> laser line ( $\lambda = 632.8$  nm) at various temperatures. The ellipse in (a) indicates the O2(x) vibrational modes. (c) Renormalized integrated intensity (I(T)/I(20 K)) versus temperature of various x-polarized phonon modes recorded in the xx and yy symmetries. All phonons were analyzed using Lorenzian profiles. The phonon assignment is discussed in the text.

Although the presence of the nematic order phase below T<sup>\*</sup> is generally consistent with the phonon anomalies we observe, more experiments have to be done before accepting or refuting this scenario.

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## **Publication List**

• M. Bakr, A. Schnyder, L. Klam, D. Manske, C.T. Lin, B. Keimer, M.Cardona, and C. Ulrich: Electronic and phononic Raman scattering in detwinned YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub> and Y<sub>0.85</sub>Ca<sub>0.15</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>6.95</sub>: s-wave admixture to the  $d_{x^2-y^2}$ -wave order parameter; Phys. Rev. B **80**, 064505 (2009).

• M. Bakr, M. Le Tacon, I. Zegkinoglou, J. Strempfer, C. Ulrich, D. Manske, C.T. Lin, M. Cardona, G. Khaliullin, and B. Keimer: Unusual phonon behavior in underdoped detwinned  $YBa_2Cu_3O_{6+x}$ , in preparation.

• M. Raichle, D. Reznik, M. Bakr, C. Ulrich, V. Hinkov, K. Hardil, D. Lamago, M. Brll, C.T. Lin and B. Keimer, Unusual electron-phonon interaction of the buckling mode in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, submitted.

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