

# Phase diagram and fluctuations in two dimensional space charge doped Bi2Sr2CaCu2O8+x

Edoardo Sterpetti

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Présentée par

## Edoardo Sterpetti

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Sujet de la thèse :

# Phase diagram and fluctuations in two-dimensional Space Charge Doped $Bi_2Sr_2CaCu_2O_{8+x}$

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Soutenue le 24/09/2018

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"Heat is chaos and in the heart of matter electrons do not have the chance to know each other in such a confusion. But when temperature falls, calm arises and sometimes they coupled, running free, spin by spin, with no obstacles on their way. Superconductivity, after all, is a story of love."

E.S.

#### Abstract

#### **English version**

The phase diagram of hole-doped high critical temperature superconductors as a function of doping and temperature has been intensively studied with chemical variation of doping. Chemical doping can provoke structural changes and disorder, masking intrinsic effects. Alternatively, electrostatically doped ultra-thin samples can be used through Field-Effect Transistor (FET) devices. The electrostatic modulation of charge carrier density in 2D materials is an elegant and clean approach, at the crossroads between fundamental condensed matter physics, the chemistry of phase transitions and device based micro and nano-electronics. It has long held the promise of providing an ideal test bench where one would take any material and transform it into different phases, changing only carrier densities without changing stoichiometry or defect concentrations. However it presents many technological challenges when high temperature superconductors are concerned. Firstly, the short screening length of these materials of the order of 1 unit cell, implies the requirement of perfect two-dimensional samples in complex structures, in order for the field effect to be homogeneously effective. Secondly, to probe the phase diagram, huge electric fields as high as  $10^9 - 10^{10}$  V/m are necessary to induce carrier density modulation of the order of  $10^{14} - 10^{15}$  cm<sup>-2</sup>, far above the possibilities of standard FET devices. Lastly, transport measurements performed over a large temperature range are needed.

In this thesis we overcome these technological obstacles by using proprietary techniques developed in our laboratory for the study of 2D materials, and we focus on the high temperature superconductor BSCCO-2212, whose phase diagram has so far never been studied via electrostatic effect.

Notably we fabricate ultra-thin high quality superconducting BSCCO-2212 devices and use an original electrostatic method called space charge doping to measure transport characteristics from 330 K to low temperature. We extract parameters and characteristic temperatures over a large doping range and establish a comprehensive phase diagram for one-unit-cell-thick BSCCO-2212 samples as a function of doping, temperature and disorder. We also identify the critical doping range where a quantum phase transition is predicted. Finally we take a closer look at the superconducting transition in the two dimensional limit. Fluctuations and extrinsic effects are accounted for using appropriate theoretical formalism and the two dimensional character of the superconducting transition of BSCCO-2212 is analysed.

#### Keywords

Superconductivity, high temperature superconductors, phase diagram, electrostatic doping, fluctuations.

#### Version française

Le diagramme de phase des supraconducteurs à haute température critique en fonction du dopage et de la température a été étudié de manière intensive avec une variation chimique du dopage. Le dopage chimique peut provoquer des changements structurels et du désordre, masquant les effets intrinsèques. Alternativement, des échantillons ultraminces dopés électrostatiquement peuvent être utilisés à travers des dispositifs de type transistors à effet de champ (FET). La modulation électrostatique de la densité de porteurs de charge dans les matériaux 2D est une approche élégante et propre, à la croisée des chemins entre la physique fondamentale de la matière condensée, la chimie des transitions de phase et la micro et nanoélectronique. Elle a longtemps tenu la promesse de fournir un banc d'essai idéal où l'on prend n'importe quel matériau et le transforme en différentes phases, en changeant seulement les densités de porteurs sans changer la stoechiométrie ou les concentrations de défauts. Cependant, cela présente de nombreux défis technologiques à affronter lorsque des supraconducteurs à haute température sont concernés. Premièrement, la courte longueur d'écrantage de ces matériaux de l'ordre de 1 u.c. implique l'exigence d'échantillons bidimensionnels parfaits dans des structures complexes, afin que l'effet de champ soit efficace de manière homogène. Deuxièmement, pour sonder le diagramme de phase, d'énormes champs électriques aussi élevés que  $10^9 - 10^{10}$  V/m sont nécessaires pour induire une modulation de densité de porteurs de l'ordre de  $10^{14} - 10^{15}$  cm<sup>-2</sup>, bien au-dessus des possibilités des dispositifs FET standard. Enfin, des mesures de transport effectuées sur une large plage de température sont nécessaires.

Dans cette thèse nous surmontons ces obstacles technologiques en utilisant des techniques développées dans notre laboratoire pour l'étude de matériaux 2D et nous nous concentrons sur le supraconducteur à haute température BSCCO-2212 dont le diagramme de phase n'a jamais été étudié par effet électrostatique.

Notamment, nous fabriquons des dispositifs supraconducteurs de BSCCO-2212 de haute qualité et utilisons une méthode électrostatique originale appelée dopage de charge d'espace, et mesurons les caractéristiques de transport de 330 K à basse température. Nous extrayons les paramètres et les températures caractéristiques sur une grande plage de dopage et établissons un diagramme de phase complet pour les échantillons BSCCO-2212 d'épaisseur 1 u.c. en fonction du dopage, de la température et du désordre. Nous identifions aussi la plage critique de dopage où une transition de phase quantique est prédite. Enfin, nous examinons de près la transition supraconductrice dans la limite de la bidimensionnalité. Les dispositifs BSCCO-2212 à 1 maille cristalline d'épaisseur. Les fluctuations et les effets extrinsèques sont décrits par des formalismes théoriques appropriés et le caractère bidimensionnel de la transition supraconductrice de BSCCO-2212 est analysé.

#### Mots-clefs

Supraconductivité, supraconducteurs à haute température, diagramme de phase, dopage électrostatique, fluctuations.

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#### Italian version

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#### English version

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# Chapter 1

# Superconductivity and High Temperature Superconductors

Superconductivity and high temperature superconductors have been extensively studied and reviewed. In this chapter we briefly present the theoretical background and stateof-the-art of some related aspects so as to motivate and lay the foundations for the work described in this thesis. After a brief description of the general concepts related to superconductivity, we introduce high temperature superconductor materials. We present the complexity of their generalized phase diagram as well as the doping methods developed in order to explore it. We then focus on the high temperature superconductor compound studied in this thesis, namely  $Bi_2Sr_2CaCu_2O_{8+x}$  (BSCCO-2212), by describing some of its physical properties and the experimental endeavor of several groups to unveil its temperature vs. doping phase diagram.

#### 1.1 Superconductivity

Superconductivity was discovered in 1911 by Heike Kammerling Onnes while measuring the resistivity of solid mercury at cryogenic temperatures [1]. Onnes was awarded the Nobel Prize for helium liquefaction in 1913, the breakthrough that lead to the discovery of superconductivity. Notably, Onnes observed that below 4.2 Kelvin, the resistivity of mercury abruptly collapsed to zero. This meant the existence of a new state, subsequently called "superconductive state" where a large amount of current could flow through a metal without dissipating any power. Some years after Onnes's discovery it was shown that superconductivity depends not only on the critical temperature ( $T_c$ ) but also on two other critical parameters namely the critical magnetic field ( $H_c$ ), and the critical current density ( $J_c$ ).

In 1933 the basic physics for the understanding of superconducivity was developed by Meissner and Ochsenfeld. They showed how perfect diamagnetism occurred in these metals in the superconducting state, i.e. the complete absence of magnetic permeability (magnetic susceptibility  $\chi_v$ =-1) as well as the ejection of magnetic field from its interior [2, 3], now known as the Meissner effect.



Figure 1.1: Resistance vs temperature measurement of a mercury wire by H.K. Onnes [1].

#### 1.1.1 General aspects of BCS theory

The complete microscopic theory of (conventional) superconductivity, namely the BCS theory, was finally proposed in 1957 by Bardeen, Cooper and Schrieffer [4]. The BCS theory relies on the assumption that superconductivity arises at sufficiently low temperature when the attractive Cooper pair interaction between electrons dominates over repulsive Coulomb forces. A Cooper pair is a weakly bound pair of electrons with opposed spin and momentum formed via lattice distortion. The interaction proposed by Frölich is related to electron movement in a lattice of polarisable ions at low temperature. A lattice distortion may take place through low energy lattice vibrations (phonons) increasing the density of positive charges around the electron and reducing the repulsive interaction with a second electron. This effective attractive interaction between two electrons with opposite spin and momentum forms Cooper pairs which "behave" like bosons allowing condensation in the same quantum ground state. The probability that such a pair is destroyed by thermal fluctuation obeys the Maxwell-Boltzmann distribution, and is therefore proportional to :

$$e^{-\frac{E_{\text{pairs}}}{K_{\text{B}}T}} \tag{1.1}$$

Where  $E_{\text{pairs}}$  is the binding energy of the pairs, i.e. the amount of energy gained through pairing.

#### 1.1.2 Ginzburg-Landau Theory

A phenomenological description of superconductivity was proposed by Ginzburg and Landau in 1950 [5], prior to the microscopic description of the BCS theory. The Ginzburg-Landau theory asserts that the superconducting transition can be described in term of a complex order parameter field  $\psi(r) = |\psi(r)|e^{i\chi r}$ , which can be considered as the wave amplitude of the center-of-mass motion of the Cooper pairs and such that the square of its real part  $|\psi(r)|^2$  is proportional to the pairs density. This order parameter is zero in the normal state, before the phase transition, and non-zero in the superconducting state. In the proximity of the critical temperature, the free energy F can be expressed as a function of  $\psi$  and of the vector potential  $\vec{A}$ :

$$F = F_n + \alpha |\psi|^2 + \frac{\beta}{2} |\psi|^4 + \frac{1}{2m^*} \left| \left(\frac{\hbar}{i} \nabla - \frac{e^*}{c} \vec{A}\right) \psi \right|^2 + \frac{\hbar^2}{8\pi}$$
(1.2)

By minimizing the free energy with respect to variations of the order parameter  $\psi$  and the magnetic vector potential A and assuming a homogeneous superconductor where no superconducting current is circulating the G-L equations can be expressed as:

$$\alpha \psi + \beta |\psi|^2 \psi = 0 \tag{1.3}$$

where  $\alpha$  and  $\beta$  are phenomenological parameters [6]. Assuming as temperature dependence of  $\alpha$ :  $\alpha(T) = \alpha_0(T - T_c)$ , equation 1.3 has the following solutions:

$$\psi = 0 \qquad \qquad T > T_{\rm c} \tag{1.4}$$

$$|\psi|^2 = -\frac{\alpha_0 (T - T_c)}{\beta} \qquad T < T_c$$
 (1.5)

where  $\alpha_0/\beta$  is assumed positive. The change in the order parameter  $\psi$  from a nonzero value to zero as T gets closer to  $T_c$  from below, is a behavior typical of a second order phase transition [7].

Another important contribution from the Ginzburg-Landau theory is the prediction of two characteristic length parameters, namely the coherence length  $\xi$  and the magnetic penetration depth  $\lambda$ , defined as:

$$\xi = \sqrt{\frac{\hbar}{4m|\alpha|}} \tag{1.6}$$

$$\lambda = \sqrt{\frac{m}{4\mu_0 e^2 \psi_0^2}} \tag{1.7}$$

where  $\psi_0$  is the equilibrium value of the order parameter in the absence of an electromagnetic field. Notably,  $\xi$  can be thought as a measure of the spatial coherence of the superconducting condensate, whereas  $\lambda$  characterizes the exponential law according to which an external magnetic field H decays inside a superconductor.

Both  $\lambda(T)$  and  $\xi(T)$  depend on temperature as  $(1 - T/T_c)^{-1/2}$  and G-L defined a dimensionless parameter  $\kappa = \lambda/\xi$ , now called the Ginzburg-Landau parameter. Depending on its value, as proposed by Landau, two families of superconductors are distinguished : Type I ( $\kappa < 1/\sqrt{2}$ ) and Type II ( $\kappa > 1/\sqrt{2}$ ).



#### 1.1.3 Type I and Type II superconductors

Figure 1.2: Qualitative phase diagram of the critical magnetic field vs critical temperature for Type I (panel a) and Type II (panel b) superconductors.



Figure 1.3: Schematic illustration from reference [8] of the the coherence length and penetration depth at the boundary between a normal metal and a type I (a) and type II (b) superconductor.

Type-I superconductors entirely repel magnetic flux (Meissner-Ochsenfeld effect) in the superconductive state whenever the external magnetic field H is below a critical field called  $H_c$  exhibiting perfect diamagnetism. For H bigger than  $H_c$ , superconductivity is destroyed. A schematic of the magnetic field versus temperature phase diagram of type I superconductor is illustrated in figure 1.2a. The universal relation between magnetic critical field and temperature is:

$$H_c = H_{c_0} \left[ 1 - \left(\frac{T}{T_c}\right)^2 \right] \tag{1.8}$$

where  $H_{c_0}$  is the critical field at 0 K.

Type-II superconductors have two different critical fields: the low critical field  $H_{c1}$ and the high critical field  $H_{c2}$  [9]. Below  $H_{c1}$ , they are perfect Meissner diamagnets. However for fields higher than  $H_{c1}$  and lower then  $H_{c2}$  magnetic flux penetrates the material in the form of cylindrical quantized flux lines, called vortices ([10, 11]). In this state the magnetic field is not ejected completely, but is constrained in fluxoid quanta (fluxon)  $\phi_0 = hc/2e$  (where h is the plank constant and c the speed of light), surrounded by vortices of superconducting currents as shown in figure 1.2b. The penetration profile of the magnetic field H(x), as well as the distribution of the Cooper pair density  $n_c(x)$ , are illustrated schematically in figure 1.3 for Type I and Type II superconductors, together with the coherence and magnetic penetration lengths  $\lambda(x)$  and  $\xi(x)$ , respectively [8].

#### **1.2** High critical temperature cuprate superconductors

In 1986, Georg Bednorz and Alex Mueller while working at IBM in Zurich Switzerland, were experimenting with a particular class of metal oxide ceramics called perovskites. They surveyed many different oxide compounds and finally found indications of superconductivity at 35 K in a ceramic of Lanthanum, Barium, Copper, and Oxygen (La<sub>2-x</sub>Ba<sub>x</sub>CuO<sub>4</sub> [13]), that was 12 K more than the record for a superconductor and above the limit of 30 K imposed and predicted by BCS theory in the weak coupling limit. This was the discovery of a new class of superconductors, later called high temperature superconductors (high-T<sub>c</sub>, Hi-T<sub>c</sub> or HTSCs) whose astonishing properties have triggered a huge amount of scientific research over the last three decades. New materials with higher critical temperature have been sought and found and figure 1.4 reports the growth of superconducting transition temperatures with time for various classes of superconductors.

HTSCs can be classified in two main groups, copper-oxide superconductors (or cuprates) and the recently discovered iron based superconductors. They can be doped by electrons or holes depending on the system. In this thesis we focus only on the hole-doped copper-oxide superconductor  $Bi_2Sr_2CaCu_2O_{8+x}$  (BSCCO-2212 or Bi-2212). A cuprate loosely refers to a material that can be viewed as containing copper anions. Figure 1.5 shows unit cell structures of some HTSC cuprates. Despite differences in terms of atoms and structures they are characterized by a common feature, that is the presence of copper and oxygen atoms arranged in two-dimensional planes. These planes are the seat of superconductivity. Neighboring layers containing ions such as lanthanum (La), barium (Ba), strontium (Sr), (etc.) act as electronically inert buffer layers whose main role is stabilizing the structure and furnishing charge for doping the  $CuO_2$  layers.



Figure 1.4: Superconducting transition temperatures vs year of discovery of several classes of superconductors. Conventional superconductors are plotted in yellow (highest  $T_c=39$  K for MgB<sub>2</sub>), heavy fermion superconductors in green (highest  $T_c=18$  K for PuCoGa<sub>5</sub>)Iron based superconductors in purple (highest  $T_c=56$  K for SmFeAsO)and cuprate superconductors in red (highest  $T_c=135$  K for HgBaCaCuO). The maximum  $T_c$  of 165 K was found in a 'mercury' copper oxide under pressure (dashed red line). Image reprinted from reference [12], with permission of Springer Nature, copyright 4421970172296.

Introducing charge carriers into copper oxygen planes does not result in a simple metallic behavior due to a complex and still not completely understood strongly correlated nature of these compounds. Unusual phases are observed for different doping levels and temperatures resulting in a rich phase diagram as will be discussed later.

Focusing on the electronic structure of the CuO<sub>2</sub> planes, without considering the charges added by the buffer layers, each atom of oxygen (electronic configuration of O:  $1s^2 2s^2 2p^4$ ) nominally attracts two electrons from the copper (electronic configuration of Cu: [Ar]  $3d^{10} 4s^1$ ). The resulting electronic configuration is therefore Cu: [Ar]  $3d^7$ . Given the odd number (seven) of electrons in the d-orbitals, metallic behavior is expected according to conventional band theory. Cuprates instead are insulators in normal conditions which is ascribed to the existence of strong electronic correlations [14]. Roughly speaking this is because the movement of an electron required for conduction is hampered by the energy barrier constituted by the repulsion between two electrons on the same atomic site (the basis assumption of the Mott-Hubbard theory [15, 16]).

The opening of a correlation gap in half-filled correlated systems is indeed ascribable to the on-site electron-electron Coulomb repulsion U, which being higher than the bandwidth W induces a split of the conduction band into two sub-bands called upper (HUB) and lower (LUB) Hubbard bands as described in figure 1.6 from ref. [17]. Depending on the amount of the Coulomb repulsion U with respect to the charge transfer energy  $\Delta$ , a



Figure 1.5: Unit cell structures of four different cuprates. For Hg-1201, YBCO, and Tl-2201, the hole concentration in the CuO<sub>2</sub> sheets is altered by varying the density of interstitial oxygen atoms (each interstitial oxygen introduces up to two holes into nearby CuO<sub>2</sub> sheets), whereas in LSCO holes are introduced by replacing La<sup>3+</sup> with Sr<sup>2+</sup> (p = x in this case). Below is illustrated the universal building block of cuprates, that is the CuO<sub>2</sub> sheet where the most important electronic orbitals, Cu d<sup>x2-y2</sup> (blue) and O p<sub> $\sigma$ </sub> (red), are shown.

Mott-  $(W < U < \Delta)$  or Charge transfer-  $(W < \Delta < U)$  insulator is found. In cuprates the Cu-O charge transfer energy  $\Delta$  is known to be smaller than the Coulomb repulsion U. Nevertheless, they are considered Mott-Insulators due to the finite hybridization between the correlated Cu (HUB) and the noninteracting-like O orbitals, with the formation of the O-derived Zhang-Rice singlet band (LHB) [18]. In the 'undoped' condition then, though nominally metallic from simple chemical considerations, cuprates are both insulators and antiferromagnetic (fig 1.7). Superconductivity is achieved at low temperatures when the material is chemically doped. Such doping can occur through a change in stoichiometric ratios, or through chemical substitution. In this way holes (lack of electrons) are introduced in the system, specifically on the CuO<sub>2</sub> planes thus weakening electronic correlations and emphatically changing physical properties.

#### 1.2.1 Phase Diagram

The electronic state or phase of a HTSC depends on the carrier concentration as well as on the temperature. A universal HTSC phase diagram locates these phases as a function of doping level (abscissa) and temperature (ordinate) and is still the subject of sustained scientific endeavor and requires fundamental physical understanding. Unconventional superconductivity, a variety of collective fluctuations, competing orders and exotic electronic phases are some of the unsolved issues that arise when studying cuprate phase diagrams [12]. Figure 1.8 shows a simplified universal phase diagram developed for



Figure 1.6: Schematic illustration of the energy levels for (a) a MottHubbard insulator and (b) a charge-transfer insulator generated by the d-site interaction effect. Image reprinted from reference [17] with permission of APS, copyright RNP/18/SEP/007473.



Figure 1.7: Sketch of a 2D  $CuO_2$  plane. When undoped it contains one electron per site with antiferromagnetic ordering and insulating nature. By adding holes (removing electrons) the antiferromagnetic order is suppressed and conductivity enhanced.

the most common *p*-doped cuprates. In this type of diagram we can distinguish five different principal phases, namely: Anti-ferromagnetic-insulator, pseudogap, strange metal (frequently called Non-Fermi Liquid), metal (or Fermi liquid) and superconductor. It is not the purpose of this thesis to discuss these in detail. Nevertheless, a brief overview on some generalities and the state of the art of the cuprate phase diagram is given in the following.



Figure 1.8: Schematic universal phase diagram of hole-doped high temperature superconductors.

#### Antiferromagnet Insulator (AFI)

HTSC parent compounds are known to be strongly correlated with antiferromagnetic ordering at low temperatures. To remove the magnetic ordering thermal energy is required and a diamagnetic-paramagnetic transition takes place at the Néel temperature  $T_N$ . Suppression of the magnetic ordering can also be achieved by increasing the hole concentration. A small amount of doping is required. Dopant holes on oxygen ions located between copper atoms, drastically affect the local spin orientation and ordering (fig.1.7) [9].

#### Pseudogap regime

The pseudogap phase in cuprates is a highly studied but not well-understood phase. It refers to the depletion of electronic Density Of States (DOS) at the Fermi level. This depression or minimum of the DOS at the Fermi level has been investigated in several high- $T_c$  compounds with spectroscopic techniques among which tunneling spectroscopy [19], Angle Resolved Photo-Emission spectroscopy (ARPES) [20] and Raman spectroscopy [21]. In this regime in the momentum space, the Fermi surface is incomplete, meaning that it is gapped at certain points, specifically at the antinodal points.

The ungapped parts of the Fermi surface are called Fermi arcs due to their shape in momentum space. Through its symmetry the pseudogap resembles the d-wave superconducting gap. In one interpretation Cooper pairs may form in the pseudogap phase although phase fluctuations prevent superconducting order until lower temperatures are reached [22].

However to establish the phase diagram, determining the temperature crossover below which the pseudo gap regime occurs is not trivial. Besides spectroscopic techniques transport measurements are a valid alternative to identify this state. The change of the electronic phase causes a substantial variation in the scattering regime and thus in the temperature dependence of resistivity. Several studies have established pseudogap temperature crossovers  $T^*$  as a function of doping in high-T<sub>c</sub> [23, 24].  $T^*$  is defined as the temperature below which the in-plane resistivity  $\rho_{ab}$  starts to deviate from the linear-Tbehavior expected at high temperature (strange metal regime). This deviation can be upward (LSCO) or downward (YBCO, BSCCO) depending on the relative magnitude of inelastic and elastic (disorder) scattering at  $T^*$  [25].

#### Strange metal

Another mysterious part of a cuprate superconductor phase diagram is the strange metal regime. A strange metal differs from a conventional Fermi-liquid metal in many aspects. From the transport measurement point of view resistivity shows a linear T dependence rather than the expected metallic  $T^2$  dependence and does not saturate at high temperature as expected for a conventional metal when the mean free path  $l_{\rm m}$  becomes smaller than the de Broglie length  $\lambda_L$  [12]. Furthermore its absolute value is several orders higher than in conventional metals meaning that in this regime cuprates are 'bad metals' in terms of electronic properties.

#### Metal (Fermi-liquid like)

When hole doping is high enough to suppress electron correlation effects in the  $CuO_2$  planes standard metallic behavior is observed and for very high doping superconductivity is suppressed. ARPES spectroscopy reveals a large closed Fermi surface and the Fermi-liquid approach is valid in this regime.

#### Superconductor

The superconducting phase is reached when temperature decreases below  $T_c$  and the intriguing aspect of this region is its shape in the phase diagram.  $T_c(\delta)$  where  $\delta$  refers to the holes per copper site is dome shaped so that  $T_c$  can be varied by controlling the doping level  $\delta$ . The doping range relative to the superconductive state is often divided into three different regions called "optimal, overdoped and underdoped" as shown in fig.1.8. The maximum transition temperature  $(T_{cmax})$  is found at the center of the optimal doping region at  $\delta \approx 0.16$  holes/Cu; when moving away from this point in either the overdoped or the underdoped direction,  $T_c$  decreases symmetrically to zero such that

superconductivity is found for  $\approx 0.05 \leq \delta \leq 0.27$ .  $T_c$  varies for different cuprates, but all have a dome shaped superconducting region well described by an empirical formula found by Tallon et *al.* [26].

$$\frac{T_c}{T_{cmax}} = 1 - 82.6(\delta - 0.16) \tag{1.9}$$

where  $T_{cmax}$  is the superconducting critical temperature at optimal doping or the maximum of the superconducting dome. However, it is important to point out that both shape and the position of the boundaries between the different phases, including the  $T_{\rm c}(\delta)$  one, might depend on the particular cuprate.

As for the symmetry of the superconducting gap, it is well established that cuprates show d-wave superconductivity, specifically  $d_{x^2-y^2}$ . This is distinct from conventional s-wave superconductors where the superconducting gap is isotropic. The unconventional d-wave superconducting gap is anisotropic and identically zero at four nodal lines corresponding to the diagonals of the Brillouin zone [27, 28]. Concerning the pairingmechanism several theories have been proposed but a consensus is still far from being found [29, 30, 31].

#### **1.3** Doping high temperature superconductors

Electronic properties of materials are most easily changed through a change in their carrier concentration or alternatively the Fermi level. The most simple and common method for achieving this is chemical doping, both substitutional and interstitial. This method however often changes structural properties as well and electronic phase transitions may be inextricably linked with structural ones. Electrostatic doping, naturally applicable to 2D materials is a way around this problem. The easy way to apply this technique is through a Field Effect Transistor (FET) device, well known in the microelectronics field, where the gate potential is used to apply an electric field which electrostatically changes the Fermi level and the carrier concentration. In the next sections, after a brief overview on chemical doping of cuprates, we will focus on the state of the art of electrostatic doping methods developed so far for controlling the charge carrier density on HTSC cuprate compounds.

#### 1.3.1 Chemical doping

The effect of chemical substitution on the electronic proprieties of high- $T_c$  cuprates such as LSCO, YBCO, TBCO and BSCCO has been extensively investigated [32, 33, 34, 35, 36, 37]. These studies were motivated by the desire to strongly vary the density of charge carriers in order to modulate superconductivity and eventually induce phase transitions. As previously mentioned, carrier density in HTSC cuprates can be modulated, by controlling oxygen concentration, by modifying the stoichiometry of the compound or by introducing foreign species. All these methods change the chemical makeup of the interleaved buffer layers which act as 'charge reservoirs' and allow the doping of  $CuO_2$  planes by electron removal.



Figure 1.9: Resistivity in the a-b plane  $(\rho_{ab})$  from reference [38], as measured after heat treatment in various oxygen pressures is shown as a function of temperature. Permission to reproduce this image has been granted by APS, copyright RNP/18/SEP/007470.

Chemical doping is the standard way to modify charge carrier density in HTSC cuprates and has been used to explore several parts of the phase diagram in these compounds. In BSCCO-2212, studies have concentrated on the underdoped regime (left side of the dome) with few works studying the overdoped region. This is due to strong experimental limitations and obstacles to increase the oxygen concentration up to values required for the overdoped regime to occur. Kendziora et al. [38], proposed an efficient way to achieve wide-range oxygen doping of bulk  $Bi_2Sr_2CaCu_2O_{8+x}$  samples by heat treatment in controlled oxygen atmosphere at different pressure values. Such studies have been performed at temperatures ranging from 400 to 600 °C with pressures from few  $\mu$ bar to  $2 \times 10^3$  bar (figure 1.9). They show that at a given temperature the oxygen content of the sample increases for higher oxygen pressures and decreases for lower ones, while the composition remains otherwise unchanged.

Although chemical doping allows for a wide doping range in HTSC cuprates, change of the stoichiometry or the introduction of foreign species inevitably affect the structural properties of the compounds. The change of the crystal structure may induce structural phase transitions as in YBCO where a tetragonal-orthorhombic transition occurs with increasing oxygen content [39]. Moreover chemical doping introduces chemical inhomogeneity and disorder which may degrade the critical temperature  $T_c$  [40] in extreme cases. Thus when inducing phase transitions via chemical doping it is difficult to disentagle the effects of correlations, disorder and structural changes. A long-standing goal is to tune the carrier density electrostatically in a reversible manner. Electrostatic-doping via field effect transistor devices is the simplest and cleanest approach possible in order to attain such a purpose.



#### 1.3.2 Electric Field effect

Figure 1.10: **a** Schematics of a typical field effect transistor device. **b** Energy band diagrams of the metal-oxidesemiconductor junction. The voltage controls the band bending at the oxide-semiconductor interface. Assuming a n-doped semiconductor, accumulation (depletion or inversion) of charge is obtained by applying positive (negative) gate voltage. This effect develops over a thickness comparable with the Thomas-Fermi electrostatic screening length  $\lambda_{\rm el}$ , above which electric field is screened by the space charge.

Modern microelectronics is dominated by semiconductor field-effect transistor devices. Every single electronic apparatus is based on microscopic switches controlled by electric field so that the electrostatic field effect can be considered as the heart of the microelectronic industry and technology. The general principle is the modulation of the electrical charge carrier density, therefore the electrical resistance, on a thin conducting channel of a semiconductor upon the application of electric field. Metal-Oxide-Semiconductor Field Effect Transistors (MOSFETs) are the most common electronic devices both in analog and digital circuits. The schematics of a MOSFET are reported in figure 1.10. It consists of a semiconductor with an oxide dielectric deposited on its top surface. This surface of the semiconductor becomes a conducting channel in the conducting state of the device. Two metallic leads, namely the drain (D) and the source (S) contact the edges of the channel, with a third contact called the gate (G) placed on top of the oxide. The gate electrode allows the modulation of charge carrier density within the channel, which results in an accumulation or depletion of charge at the semiconductoroxide interface controllable reversibly by means of the external gate voltage  $V_{\rm G}$ . The channel and the gate electrode behave like the two conducting faces of a parallel plate capacitor with the internal electric field responsible for the shift in the energy bands of the semiconductor at the interface with the oxide. The schematics in figure 1.10b show the energy band diagram of a metal-oxide-semiconductor device upon the application of the external gate voltage. Depending on voltage polarity, the Fermi level  $E_{\rm F}$ shifts up or down with respect to the conduction band. This local change in the energy levels of semiconductor's band structures is called band bending. Typical modulation of charge of the order of  $10^{17-18}$  cm<sup>-3</sup> is easily achieved over a thickness comparable with the electrostatic screening length  $\lambda_{el}$  which in low-carrier-density systems such as semiconductors can be of the order of several nanometers.

When applied to novel strongly correlated electron systems, electrostatic doping is a powerful tool both for fundamental physics and for innovative device applications as it provides a means to alter carrier concentration independently of other parameters. In a strongly correlated system the standard approximations leading to electronic structure may not be applicable due to the strong interactions between electrons, especially when dimensionality is reduced. Electronic phase transitions such as the change of magnetic ordering (antiferromagnetic-ferromagnetic) in Colossal Magnetic Resistance (CMR) manganites and ground state (insulating-superconductor) in HTSCs are brought about by a change in carrier concentration. Figure 1.11 from ref. [41] provides a schematic view of the ground state evolution of various correlated materials as a function of their sheet charge density and hence the potential of the electrostatic doping method.

From the experimental point of view, field effect devices with 2D materials or strongly correlated electron systems such as HTSCs are difficult to achieve due to the complex structures required. The two main challenges they pose are the the fabrication of ultrathin materials and the requirement of a huge local electric field in order to sufficiently dope these systems and eventually induce phase transitions. In particular, cuprates require an electric field as high as  $10^9$ - $10^{10}$  Vm<sup>-1</sup> and charge modulation of the order of  $10^{14}$ - $10^{15}$  cm<sup>-2</sup> [42]. Such huge fields can be reached at the oxide-material interface by extreme polarization of the oxide by the application of high V<sub>G</sub> or by decreasing the thickness of the insulating dielectric. Both cases require oxides that are tailored for very large breakdown electric fields (E<sub>b</sub>) and dielectric constant ( $\epsilon_r$ ). The polarization charge density is given by  $\sigma = \int_0^{V_G} \epsilon_0 \epsilon_r(V)/tdV$ , where  $\epsilon_0$  is the vacuum permeability and tthe oxide thickness. The need for ultra-thin samples derives from their short Thomas-Fermi screening length which varies from 0.5 to ~3 nm depending on cuprate compound [43, 44, 45].



Figure 1.11: Illustration of the zero-temperature behavior of various correlated materials as a function of sheet charge density  $(n_{2D})$  from ref.[41]

#### Field effect transistors for doping HTSCs

Modulations of superconductivity via the electrostatic effect has been achieved by using field effect transistor devices in a classical FET configuration. Here the dielectric is an insulator such as SrTiO<sub>3</sub> (STO) ([43, 46]) with high dielectric constant capable of sustaining a high interface electric field. In the late nineties, carrier density modulation as high as  $10^{13}$  cm<sup>-2</sup> was reached and notably several K shift of the transition temperature was observed in 8 nm YBCO systems as shown in the figure 1.12, by using ~ 300 nm thick STO gate insulator ([47, 48]). These techniques however did not provide the high carrier modulation range needed to sample large portions of the cuprate phase diagram though they were important milestones in the electrostatic doping of HTSCs .

#### 1.3.3 Ferro-electric Field Effect

Ferro-electric field effect hetero-structures based on HTSCs and ferroelectric materials have been fabricated to electrostatically modulate the carrier density of the superconducting layer in a reversible and non-volatile manner. Ferroelectricity is a property of certain materials that exhibit electric polarization and whose polarity can be reversibly controlled by external electric field application. This possibility to switch the polarization of a material by a temporary electric field has led to the investigation of the effect of electrostatic doping on the superconducting phase of the HTSCs [49, 50, 51]. In 1999, Ahn et al. used a ferroelectric field effect in hetero-structures based on superconducting GdBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> and ferroelectric Pb (Zr<sub>x</sub> Ti<sub>1-x</sub>) to modify the superconducting critical temperature. They achieved variation of  $T_c$  of several Kelvin by reversing the polarization P and notably they were able to drive the superconducting-insulating transition for



Figure 1.12: **a** Image reprinted from reference [47] with permission of APS, copyright RNP/18/SEP/007474. Temperature dependence of the drain–source resistance ( $R_{DS}$ ) of an 8 nm-thick-YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> with a gate insulator 300 nm thick, for varying gate voltages V<sub>G</sub>. **b** Resistance versus temperature for a 3–4 unit cell thick NBCO film (sample 1) for varying applied gate voltages; the right scale is the corresponding resistivity. The lower inset shows the resistance as a function of temperature of another sample, which is also 3–4 unit cells thick, for different applied gate voltages. The upper inset is a sketch of the field effect device, based on a thinned STO single crystal gate insulator. Image reprinted from reference [48] with permission of APS, copyright RNP/18/SEP/007471.

more underdoped thin films [49]. Later in 2011, Crassous et *al.* using hetero-structures that combine a large-polarization ferroelectric (BiFeO<sub>3</sub>) and a high-temperature superconductor YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub>, were able to obtain large modulation of the superconducting condensate at the nanoscale, via the ferroelectric field effect [52]. Notably shifts of the  $T_c$ up to ~ 30 K were achieved for a 3 u.c. thick channel of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$ </sub> via ferroelectric field effect [53] (Figure 1.13).

#### 1.3.4 Ionic-liquid gating method

In the following we cite [54, 55, 56] for the description of the Electric-Double-Layer transistor. An Ionic Liquid (IL) is an ionic compound that is in a liquid state. It is different from a typical electrolyte where the solvent is usually water that contains only a small fraction of ionic compounds as solutes. Ionic liquids have many applications. They are powerful solvents and electrically conducting fluids, and they are used in electrochemical capacitors to store large amounts of energy. An electrochemical capacitor can be qualitatively modeled as two capacitors connected in series through an IL, which forms two layers of opposite charges, called an electric double layer (EDL), at each electrode interface. EDL refers to two parallel layers of electronic charges surrounding the electrode when voltage is applied. A schematic diagram of EDL formation in an ionic liquid electrochemical capacitor is illustrated in figure 1.14.

Upon the application of an external voltage, mobile cations and anions within the ionic liquid dielectric move toward the surface of the two electrodes, which is the charging process. The charge on the electrode and the space charge of the ionic liquid of the ion



Figure 1.13: **a**, Sheet resistance normalized to the resistance at T = 150 K of a hetero-structure with 3 u.c. thick YBCO in which the BFO polarization points down (left-hand blue curve) and up (right-hand red curve). The inset shows schematics of the charge carrier depletion or accumulation induced in the YBCO by the ferroelectric polarization (white arrows). **b**  $T_c$  versus charge carrier density n (holes cm<sup>-3</sup>) for samples with different thickness, for the 'depleted' (empty symbols) and 'doped' (solid symbols) states. Images reprinted from reference [52] with permission of APS, copyright RNP/18/SEP/007472.



Figure 1.14: Schematics from ref. [55] of the charging and discharging process of the electric double layer capacitor.

accumulation layer in the electrolyte, from the double layer. The accumulation of charge at the electrode-electrolyte interface results in a very high capacitance and indeed EDL capacitors are considered as promising super-capacitor devices [57]. Concerning the discharging process, by removing the external voltage when a load resistance is added, ions will drift back away from the electrodes thus restoring the charge neutrality within the electrolyte.

If one of the electrochemical capacitor electrodes is replaced by a semiconductor or an insulator equipped with source and drain electrodes, the system works as a FET with the other electrode acting as a metal gate. This configuration is called electric double layer transistor (EDLT). The EDLT functions and operates the same way as a conventional FET, with the only difference of having an IL as the gate dielectric instead of a solid oxide insulator in a conventional FET.

A schematic diagram of an example EDLT with ionic liquid as gate dielectric from reference [58], is depicted in figure 1.15.



Figure 1.15: Schematic diagram of an example EDLT with ionic liquid as gate dielectric. Image reprinted from reference [58] with permission of Springer Nature, copyright 4421970710970.

Using an EDLT device, ultrahigh density carrier accumulation has been reported in several studies such as the one by Yuan et *al.*, in a ZnO field-effect transistor gated by electric double layers of an ionic liquid [59] where a carrier density up to  $\sim 8 \times 10^{14}$  cm<sup>-2</sup> at 220 K has been reached. Much of the effort and research has addressed electric-field-induced superconductivity in insulator materials [60, 58] and the Superconducting-Insulator (SIT) quantum phase transition driven by electric field in strongly correlated systems such as high temperature superconductors.

In 2008, the group of Iwasa published the first report of a study of the SIT in strontium titanate (STO) using the EDLT technique [60]. They used a polymer–electrolyte, namely polyethylene oxide containing KClO<sub>4</sub>, as the gate dielectric, and fabricated a top-gate FET using undoped STO single crystals. Sheet carrier density was enhanced to  $10^{14}$  cm<sup>-2</sup> by applying a gate voltage of up to 3.5 V to a pristine STO channel (figure1.16) finding evidence of superconductivity at low temperature. Such high carrier density modulation approaches that obtained for chemically doped bulk crystals confirming this method as promising for new superconducting materials.

In recent years, pioneering efforts have been made using ionic liquids as dielectrics to investigate high temperature superconductors physics and notably the superconductinginsulator phase transition. In the following section, some of these important achievements are briefly summarized.



Figure 1.16: Electrical properties of accumulated SrTiO<sub>3</sub> surface layer. **a** R<sub>S</sub> of T dependence measured while applying different gate voltages V<sub>G</sub>. (b) The upper and lower panels respectively show the temperature dependence of the sheet carrier density,  $n_{2D} = -1/R_{\rm H}e$ , and mobility,  $\mu_{\rm H}$ , evaluated by Hall effect measurements. Image reprinted from ref. [60] with permission of Springer Nature, copyright 4421971007605.

#### 1.3.5 IL-gating doping of high temperature superconductors

Superconductivity in strongly correlated electron systems such as HTSCs arises when a parent insulator compound is doped with carriers beyond some critical concentration as previously described. What exactly happens at this superconductor-insulating transition (SIT) is a key open question and needs further studies and experiments. The aim is to tune the carrier density using the electric field effect to modulate the sheet resistance and investigate phase transitions such as the SIT in the underdoped region of phase diagram.

In 2011 Bollinger et al. generated a SIT in  $La_{2-x}Sr_xCu_4O$  (or LSCO), using the EDLT technique with an ionic liquid as the gate dielectric [42]. Upon applying a gate voltage  $(V_G)$ , large shifts were observed both in the normal state resistivity and in the critical temperature  $(T_c)$ . In particular the significant changes in surface carrier density they achieved, enabled shifts of the critical temperature up to 25 K as shown in figure 1.17a. The sample was initially underdoped, as it is possible to notice from the curve at 0 V. Decreasing voltage down to -2 V allowed increasing the superconducting critical temperature to its maximum value at optimal doping (maximum LSCO  $T_c=45$  K). In addition resistance versus temperature curves with nearly continuous modulation of the carrier density in the underdoped regime were recorded (figure 1.17b) and were shown to collapse onto a single functional form, as expected for a direct two dimensional SIT using a finite size scaling analysis. They found the transition resistance to be the quantum



Figure 1.17: **a**,  $R_{\rm S}(T)$  curves corresponding to different applied gate voltages. The sample is intrinsically underdoped (few K  $T_{\rm c}$ ) but under the influence of the gate voltage charge is accumulated at the sample-ionic liquid interface causing a shift of  $T_{\rm c}$  of about 25 K. **b**, Temperature dependence of normalized resistance  $R_N = R_{\Box}(n,T)/R_Q$  of an initially heavily underdoped and insulating film. The carrier density, fixed for each curve, is tuned by varying the gate voltage from 0 V to -4.5 V in 0.25 V increments; the insulating film becomes superconducting by increasing the carrier density. The inset highlights a separation independent of temperature below 10 K. The black dashed line is  $R_{\Box}(n_c, T) = R_Q = 6.45 \text{ k}\Omega$ . Images reprinted from ref. [42] with permission of Springer Nature, copyright 4421971221439.

resistance for electron pairs  $h/(2e)^2$ , indicative of a phase transition driven by quantum phase fluctuations and Cooper pair localization [61]. This change of the electronic phase takes place at 0 K. A phase transition occurring at 0 K upon variation of a tuning parameter is called Quantum Phase Transition (QPT) and the point in correspondence of which this criticality occurs is the Quantum Critical Point (QCP) [62, 63, 30, 64].

Xiang Leng et al. reported carrier-driven SIT transition and modification of critical temperature in ultra-thin films of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (YBCO) using an EDLT configuration employing the IL DEME-TFSI ([65, 66, 67]). A superconductor-Insulator transition was observed in nominally seven unit-cell-thick films as shown in Figure 1.18. Charge density was modulated in the underdoped part of the phase diagram and the critical temperature was lowered until the insulating phase transition occurred.

The electrostatic tuning of the charge carrier density via ionic liquid gating appears to be a valid alternative to chemical doping, allowing to reach comparable results in terms of charge modulation in high- $T_c$  cuprates. The possibility of controlling the doping electrostatically without affecting crystals structure or chemical makeup, is a long-standing goal in high- $T_c$  physics, in order to disentangle the effects stemming from disorder from the ones related to electronic correlations. However, the debate is still open about the nature of doping when involving IL-gating. Intercalation and electrochemical reactions cannot be ruled out. Some recent studies showed how the control of carrier density via IL based devices, would be due to oxygen vacancy formation rather than to electrostatic doping [68, 69] and put a question on the true nature, electrostatic vs. electrochemi-



ical, of the doping of cuprates with ionic liquids.

Figure 1.18: Sheet resistance  $R_{\rm S}$  vs. temperature T with gate voltage  $V_{\rm G}$  varying with 0.1-0.2 V increments from 0 to 1.52 V, from bottom to top. The inset shows an enlarged low temperature region near the transition between the superconducting and insulating regime. Image reprinted from ref.[67] with permission of Springer Nature, copyright 4421971395794.

### 1.4 $Bi_2Sr_2CaCu_2O_{8+\delta}$

The high-T<sub>c</sub> compound studied in this thesis belongs to the Bi-based Copper oxide materials having the generalized chemical formula Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>n-1</sub>Cu<sub>n</sub>O<sub>2n+4+ $\delta$ </sub> with n=2, which is commonly referred as BSCCO-2212. Discovered in 1988 by Maeda et al. [70] BSCCO compounds were the first high-temperature superconductors that did not contain any rare earth element. Figure 1.19 illustrates the unit cell structure of BSCCO-2212, that is the smallest building block of the crystal, consisting of five chemical elements (Bismuth, Strontium, Calcium, Copper, Oxygen), whose geometric arrangement defines the orthorhombic crystal symmetry and whose repetition in space produces the crystal lattice. The dimensions of the cell are: a=b=5.4 Å, c=30.6 Å [71]. The superconducting CuO<sub>2</sub> bilayer planes with a thickness of ~0.3 nm are separated by the insulating BiO and SrO layers, which are ~1.2 nm thick. Bi-O planes are the cleaving planes because of the weak chemical bond between them. The crystal cleaves along these planes and therefore the c-axis is perpendicular to all the planes (Bi-O, Sr-O, Cu-O, Ca)of which the unit cell of BSCCO is composed.



Figure 1.19: Unit cell structure of  $Bi_2Sr_2CaCu_2O_{8+x}$ .

#### **1.4.1** Electronic and structural proprieties

A key feature that follows from the complex layered unit cell structure of BSCCO, is the strong electric transport anisotropy. Two main directions are defined for transport, that is along the CuO<sub>2</sub> planes (*ab*-direction) and perpendicular to them (*c*-direction). Superconductivity develops in the CuO<sub>2</sub> planes (*ab*-direction) whose resistivity ( $\rho_{ab}$ ) is several order of magnitude lower than the out-of plane one ( $\rho_c$ ). When measuring the temperature dependence of  $\rho_{ab}$  and  $\rho_c$ , two different behaviors are observed for doping levels corresponding to the optimal doping part of the superconducting dome. While  $\rho_{ab}$ decreases when temperature is lowered before before the transition,  $\rho_c$  increases showing insulating behavior until an abrupt superconducting transition takes place at  $T_c$ . When considering the out-of plane transport, an electron moving along the c-axis experiences several barriers due to the layered structure [72].

Typical values of resistivity of bulk BSCCO at room temperature (T<sub>R</sub>) are between 1-8 m $\Omega$ ·cm depending on texture and Oxygen content. Specifically these values come from the combination of the  $\rho_{ab}$  and  $\rho_c$  components, with  $\rho_c$  (T<sub>R</sub>)  $\approx 10 \ \Omega$ ·cm and  $\rho_{ab}$ (T<sub>R</sub> )≈ 1 mΩ·cm. Some studies report the  $\rho_c(T)$  and  $\rho_{ab}(T)$  behavior with respect to the doping (Oxygen) concentration of bulk Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+ $\delta$ </sub> [73]. In particular, they show how the  $\rho_c(T)$  insulating behavior can be described using a model that assumes two different transport mechanisms, namely thermal activation and incoherent tunnelling [74].

#### 1.4.2 BSCCO thin films

Although it is believed that in many cuprates the electronic coupling along the c-axis plays a role in terms of superconducting and magnetic properties, BSCCO systems are considered quasi-two-dimensional (2D) due to the strong anisotropy between the in-plane and the out-of-plane resistivity [72, 75, 73]. In this framework studying a sample whose thickness is 1 u.c. or 0.5 u.c., would give a direct probe to elucidate the 2D-physics of high temperature superconductors. High Temperature Superconductor (HTSC) thin films are thus promising materials both for fabricating novel electronic devices and for fundamental physics in low-dimensional strongly correlated electron systems. However, the quality of HTSC thin films is still a limiting factor for device performances and yields. This is usually due to the inevitable defects caused by substrate mismatch, dislocations, and grain boundaries [76].

The popular techniques for fabricating HTS thin films, such as molecular beam epitaxy (MBE) ([77, 78]) and pulsed laser deposition (PLD) [79], can produce high quality thin films, but are however very demanding [80, 81]. Mechanical exfoliation is an alternative method for producing thin-film-like single crystals. Various 2D materials from layered precursors are made by this technique [82]. The strong bonds and the weak Van Der Waals coupling between layers of these materials make them good candidates for studying the low-dimensional proprieties. For highly anisotropic BSCCO (Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+ $\delta$ </sub>, Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>) single crystals, it is therefore possible to obtain thin films by means such as simple method [83].

From both scientific and technological points of view it is important to study how the superconducting transition temperature varies with the thickness of the samples, and also to examine the minimum thickness for the occurrence of superconductivity. Several studies imply that the critical temperature of BSCCO-2212 thin films is lower than the bulk one and drastically drops when a certain critical thickness is reached until disappearing for few-unit cell samples [84]. Ref. [83] reports that this thickness effect begins to appear for samples thinner than  $\sim 10$  unit cell in BSCCO-2212 and BSCCO-2223. You et al. showed a similar behavior, by measuring the critical temperature of samples with same doping level and different thickness. They observed a small reduction of  $T_{\rm c}$  between 10 and 4 u.c. (from 87 to 84 K) followed by an abrupt depression of  $T_{\rm c}$  in 2 u.c. thick samples  $(T_c = 58 \text{ K})$  and eventually a complete suppression of superconductivity for 1 u.c. thick samples. This depression and eventual loss of superconductivity in ultrathin films of BSCCO is thought to be related to oxygen depletion from BSCCO surfaces. It is well-established that the escape of interstitial oxygen causes a region near the surface to become insulating [85, 86, 87]. Such an extrinsic effect is negligible for bulk or thick samples but plays a dominant role as much as the thickness is reduced. [82]. In addition,


Figure 1.20: **a**, Comparison between  $T^*$  determined by Raman (filled red circles and other spectroscopic probes. Image reprinted from ref.[21]) with permission of APS, copyright nd other spectroscopic probes. The references are (i) tunneling : R. M. Disapusil et al. [89], L. Ozyuzer et al. [90], N. Miyakawa et al., [91]. (ii) c-axis resistivity : T. Watanabe et al.[92]; ARPES: I.M. Vishik et al. [93]. (iv) neutron scattering: L.Mangin-Thro et al. [94]). **b** Figure from ref. [94]. hole doping dependencies of  $T^*$  measured by I.M. Vishik et al. [93] with ARPES in BSCCO-2212 compared with the characteristic temperature  $T_{mag}$  associated with the appearance of the intraunit-cell magnetic phase, as determined by polarized neutron scattering technique. Image reprinted from ref. [94] with permission of APS, copyright RNP/18/SEP/007477.

BSCCO-2212 crystals are also known to be highly sensitive to water and air moisture, so that ambient conditions can also play an important role in degrading the surface of ultra-thin samples [88].

As we shall discuss in chapter 4, understanding and disentangling the different factors that can affect the superconducting transition temperature such as disorder, dimensionality (reduction of inter-cell coupling and fluctuations) and doping is of crucial importance.

## 1.4.3 BSCCO Phase Diagram

The phase diagram of cuprates is thought to be universal in the sense of a common general behavior or evolution of the electronic phases when charge carrier density or temperature are varied. As previously described, the copper oxide planes that are present in these compounds are responsible for this universality due to the dominant role that they play in the physics of cuprates. Nevertheless several differences are observed between different compounds. For instance the superconducting dome might not be symmetric (YBCO [95]), the pseudogap or Fermi liquid crossovers may change their frontiers and the critical doping associated with the 0 K quantum phase transition (quantum critical point) may change as well [20, 64]. The phase diagram of BSCCO-2212 has been less studied with respect to other HTSCs and most studies have concentrated on the low doping part. Both the pseudogap temperature crossover as well as the Fermi liquid phase boundary along the overdoped regime are not well-established with the latter being barely studied due to technical obstacles that prevent the fabrication of sufficiently overdoped samples. Several methods have been used to investigate and detect the opening of the pseudogap phase (occurring at  $T^*$ ) for varying doping. Figure 1.20a reports a comparison of the results from: Angle Resolved PhotoEmisson Spectroscopy (ARPES) [93], Raman spectroscopy [21], tunneling spectroscopy [89, 90, 91], c-axis resistivity transport [92] and Inelastic Magnetic Neutron Scattering (MI-NS) [94].



Figure 1.21: Fermi surface resulting from a tight-binding fit to data through the Brillouin zone: **a**, For moderately overdoped samples with  $T_c$ =80 K; **b**, For heavily overdoped samples with  $T_c$ =55 K. **c** schematic phase diagram to illustrate where the Fermi surface is hole-like and where electron-like for varying doping. Images reprinted from ref. [96] with permission of APS, copyright RNP/18/SEP/007479.

These studies, carried out on bulk samples with carrier density varied by controlling oxygen doping seem to reveal a linear decrease of  $T^*$  with doping from the underdoped side to the optimal central part of the dome (p=0.16 holes/Cu), within the substantial lattitude permitted by large error bars. A subsequent flattening on the slightly overdoped side is followed by an abrupt vanishing at larger doping with a re-entrant behavior, as shown in figure 1.20b.

However, one interesting common observation is the possible indication of a quantum critical point, namely the critical carrier density at which the pseudogap-metal phase transition occur at 0 K, predicted at about 0.19 holes/Cu. In addition a Van Hove singularity is expected at this doping level [21]. This is a singularity of the density of states. In this scenario, the critical point would coincide with a Lifshitz quantum phase transition where the active hole-like Fermi surface becomes electron-like [21, 98],



Figure 1.22: Phase diagram showing superconducting and pseudogap crossovers  $T_c$  and  $T^*$  versus the conductivity normalized to its value corresponding to the optimal doping at 300 K for bulk Bi-2212 (triangles) and Bi(La)-2201 (circles) phase. Doping is varied chemically by controlling oxygen content. Image reprinted form ref. [97] with permission of Elsevier, copyright 4421981231560.

as illustrated in 1.21 from reference [96]. It is important to point out that the cuprate phase diagram is complex and the identification of crossovers is not trivial. Furthermore given the multiplicity and specificity of investigation techniques, their comparison is a fundamental factor in order to unveil and understand the physics of cuprates. Electronic transport is a valid alternative to detect changes in electronic phases. Kostantinovic et. al. [37, 97] established a temperature versus doping phase diagram of bulk BSCCO-2212 via transport measurements, determining the psuedogap temperature crossover  $T^*$  as well as the superconducting dome by analyzing the change in temperature dependence of resistivity and linking it to the electronic phase [23, 24]. A technical explanation about the determination of phase diagram crossovers by electronic transport is given in chapter 3. Figure 1.22 reports the characteristic temperatures  $T^*$  and  $T_c$  as a function of  $(\sigma/\sigma_{\rm op})_{300\rm K}$ , namely the conductivity at 300 K for varying Oxygen treatments (varying doping), normalized to the one corresponding to the optimal doping level. When comparing these results with the one reported in figure 1.20 one notices a different behavior of  $T^*$  on overdoped side. Indeed the low doping linear part is not followed by a plateau at 0.16 and no further presence of pseudogap phase in the overdoped regime is observed, but rather a drastic drop of  $T^*$  at around the optimal doping. However, open questions remain about the possibility of determining  $T^*$  closer to the optimal doping regime by transport measurements[36, 99].

## 1.5 Conclusions

From this introduction it can be seen that investigating the phase diagram of high temperature superconductors is of critical relevance. Notably, establishing this phase diagram for perfectly two dimensional samples is yet to be accomplished. Achieving this with electrostatic doping is equally important and new. Since this investigation combines the particularities of high- $T_c$  superconductivity and physics in two dimensions, it is all the more interesting. This is the aim of this thesis which seeks to use the high temperature superconductor BSCCO-2212 to attain this purpose using proprietary techniques developed in our laboratory for the study of 2D materials.

# Chapter 2 Experimental

This chapter presents the technical and experimental aspects of this thesis. The considerable problems faced during fabrication and characterization of 1 unit cell thick two-dimensional BSCCO-2212 samples are enumerated and the solutions and methods that permitted us to achieve superconducting two-dimensional BSCCO-2212 devices are explained. A detailed description of electronic transport measurements and our electrostatic doping method (Space Charge Doping) is provided.

## 2.1 Sample fabrication

In this section we describe the method we use to fabricate few-nanometer thick BSCCO samples. This method, developed in our laboratory and called the anodic bonding technique, involves the use of glass as substrate. An insight about the glass substrate, the fabrication method and the protocol we use is given here.

#### 2.1.1 Glass substrate

All devices of this thesis have been fabricated on glass substrates by anodic bonding technique (sect. 2.1.3) and electrostatically doped on the same substrates using space charge doping (sect. 3.2). Different glass types and suppliers have been considered in this work: borosilicate glass (SCHOTT<sup>TM</sup> D263T), and soda-lime glass (University Wafer, and Valley Design). Silicate glasses are mainly composed of an amorphous network of silicon dioxide (and boron oxide B<sub>2</sub>O<sub>3</sub> in borosilicates). Other oxides, such as sodium oxide (Na<sub>2</sub>O) and calcium oxide (CaO) are commonly added to glass in order to enhance some properties. From the structural point of view, introducing these species results in the breaking of some Si-O-Si bridges. Consequently, non-bridging oxygen atoms serve as anions for sodium cations (Na<sup>+</sup>) and Calcium cations (Ca<sup>2+</sup>) bound to them with ionic bonds. These bonds are weaker in comparison to the covalent bonds between oxygen and silicon. The mobility of Na<sup>+</sup> is also high with respect Ca<sup>2+</sup>. Consequently Na<sup>+</sup> is by far the most mobile species in the structure with the ionic conductivity activated by thermal energy.



Figure 2.1: **a** Schematics of the glass structure at the atomic level. Si-O-Si network is broken by  $Na^+$  ions. **b** Creation of the surface space charge. Heating: The glass is heated and an external voltage is applied;  $Na^+$  mobility is activated and a drift of ions due to the internal transverse electric field (red arrow) is achieved. Quenching: voltage is kept constant and the system is cooled down to room temperature. Frozen charge: voltage is removed, the charge is frozen at the interface.

Once ionic mobility is activated, an external potential difference applied across the glass slab generates an internal electric field causing the drift of sodium ions. As shown in Fig.2.1b, an accumulation or depletion layer of  $Na^+$  is formed at the surface, depending on voltage polarity. This build-up of charge is frozen once the system is cooled down to room temperature and results in a high electric field at the interface [100, 101]. Sodalime glass substrates with a relatively high Na<sup>+</sup> concentration of  $\sim 3.4 \times 10^{18}$  cm<sup>-3</sup> compared with borosilicates are used for this purpose. Another important parameter is the surface roughness, which is known to strongly affect the mobility of carriers in the material laying on its surface as in the case of Graphene, although the thin crystalline layers may ultimately have lower roughness than the substrate after the bonding process [102, 103, 100]. By using atomic force microscopy we measured the surface roughness (peak to valley variation), and calculate its root mean square (RMS). We measured RMS roughness of 0.2 nm for SCHOTT<sup>™</sup> D263T (borosilicate glass), 1 nm for commercial soda-lime (University Wafer) and 0.5 nm for polished soda-lime (Valey Design). The substrates used in this thesis are soda-lime glass and have a RMS roughness of 0.5 to 0.8 nm.

#### 2.1.2 Anodic Bonding technique

Anodic bonding is a technique commonly used in the microelectronics industry to seal metals, alloys, semiconductors or insulator to glass, without using an intermediate layer like glue. This technique, introduced by Wallis and Pomeranz in 1969 [104] leads to efficient bonding of glass to silicon [105]. Anodic bonding exploits the possibility of thermally activating sodium ionic mobility in glass substrates to create a strong electric field at the surface. Figure 2.2 reports a schematic view of the anodic bonding method. The interface between glass and the material is depleted of Na<sup>+</sup> and a space charge of uncompensated and fixed oxygen ions ( $O^{2-}$ ) is left at the surface creating strong electrostatic attraction between the glass and the sample. Typical temperature and voltage values are in the range of 200-400 °C and 1000-1700 V respectively [106]. The bonding time is between 15 and 30 minutes.

The anodic bonding technique is a useful and versatile method that can be used for fabricating two dimensional flakes from layered van der Waals materials [107]. The apparatus consists of two anvils (grey trapezoids), between which is placed the glass substrate and the material to be bound, in our case a bulk piece of layered material called the "precursor". The top anvil, touching the small layered material, can be replaced by a metallic tip positioned by a micromanipulator and connected to the voltage source to accurately make contact with very small precursors. The temperature and the voltage of the bottom anvil is regulated by an external controller whereas the anode is grounded. Graphene and other 2D materials such as MoS<sub>2</sub>, GaSe, InSe are routinely fabricated in our lab starting from layered bulk precursors [108, 109, 101, 100, 110]. The choice of the bulk precursor, the quality of the glass-material interface and the external parameters applied are crucial factors when fabricating thin samples by anodic bonding technique. A detailed explanation of these aspects is given in the following section where the fabrication of ultra-thin BSCCO-2212 samples is discussed.

#### 2.1.3 Ultra-thin BSCCO-2212 sample fabrication

BSCCO-2212 two-dimensional (2D) crystals with lateral size of ~ 100  $\mu$ m and thickness ranging from 1 to 2.5 unit cells (u.c.) are fabricated by the anodic bonding method on 0.5 mm thick soda-lime glass substrates using a bulk single crystal precursor with stoichiometry Bi<sub>2.1</sub>Sr<sub>1.9</sub>CaCu<sub>2</sub>O<sub>8+x</sub>. Figure 2.3 illustrates the main steps required to obtain atomically thin BSCCO-2212 flakes on a glass substrate.

The substrate is cleaned in an ultrasound bath at 40°C first in acetone and then in ethanol for 5 minutes each and dried in a nitrogen flow.

Thin flakes of 1-2 mm are cleaved from a thick bulk crystal with the help of adhesive tape and immediately placed on a  $\sim 1 \text{ cm}^2$  glass substrate. The substrate-precursor couple is then placed between the two electrodes of the anodic bonding machine, which may be in anvil or tip form and heated at 180 °C to activate Na<sup>+</sup> mobility. The tip allows higher precision of sample-glass contact area than the anvil and notably rules out the possibility of anode-glass contact that could arise when using the anvil (surface area



Figure 2.2: Schematics of anodic bonding for fabricating 2D materials from bulk layered Van der Waals materials. The bottom plate is heated in order to activate  $Na^+$  mobility. An external high voltage is applied between the precursor and the glass to create the interface charge for the electrostatic bonding.

of the anvil of the order of  $cm^2$ ). A negative voltage is then applied at the cathode, thus attracting Na<sup>+</sup> towards the bottom surface of the glass substrate. The depletion layer left at the glass-precursor interface is the space charge which induces a mirror charge in the sample creating a field and electrostatic bonding of the flake to the substrate. After 10-15 min the bonding process is complete and the voltage can be removed and the substrate cooled to room temperature. After mechanical peeling of the precursor with adhesive tape, few-layer thick BSCCO flakes are left onto the glass substrate. Table 2.1 reports the parameters used in this thesis for fabricating BSCCO-2212 ultra-thin samples via anodic bonding method on both Borosiliate and Soda-lime glass substrates for the case of tip and anvil anode.

Glass substrate	Anode	$V_G(V)$	$T (^{\circ}C)$	t (min.)
Borosilicate	Anvil	800 - 1000	200 - 225	10 - 20
Borosilicate	Tip	500 - 800	200 - 225	10 - 20
Soda-lime	Anvil	600 - 800	170 - 190	10 - 15
Soda-lime	$\operatorname{Tip}$	400-500	170-190	5-10

Table 2.1: BSCCO-2212 anodic bonding parameters



Figure 2.3: Anodic bonding of few-nm BSCCO-2212 samples. 1 A thin bulk BSCCO-2212 flake is placed on a glass substrate. 2 The system is heated and a high voltage of about 400-800 V is applied between the anode and the cathode. 3 As the anodic bonding process ends, a final exfoliation is carried out in order to remove the un-bonded thick part of the material. 4 Few-nm BSCCO-2212 samples bonded electrostatically to the substrate are obtained.

## 2.2 Sample characterization

The as-fabricated samples are first quickly observed and chosen by optical microscope according to color contrast. The thickness measurement is subsequently carried out by atomic force microscopy (AFM). When possible, Raman spectroscopy is carried out.

#### 2.2.1 Optical microscopy

Optical microscopy is an easy and fast characterization method allowing a good estimate of thickness of the as-fabricated samples via optical contrast. In this thesis all the images of the samples have been recorded with a Leica DM2500 and a CCD camera with objectives of  $5\times$ ,  $10\times$ ,  $50\times$  and  $100\times$  in the bright field imaging mode. Although utilizing glass substrate implies lower contrast than other substrates such as Si/SiO<sub>2</sub>, it is still possible to easily identify few-layer or monolayer samples. As discussed in chapter 1, BSCCO-2212 cleaves at the BiO layer so that the as-fabricated samples are expected to be multiples of 0.5 u.c. Fig.2.4 shows as an example 0.5 u.c. and 1 u.c. flakes with lateral size bigger than 100  $\mu$ m.



Figure 2.4: Optical picture of ultra-thin BSCCO samples fabricated via anodic bonding technique. Samples with thickness of 1.5-3 nm (0.5-1 unit cell) and lateral size of  $\approx 100-200 \ \mu m$  are easily obtained.

## 2.2.2 Raman spectroscopy

Raman spectroscopy is a powerful non-invasive technique, based on inelastic scattering of incident radiation through its interaction with excitations in the sample [111]. The sample is typically illuminated with a laser whose photons are absorbed by the material. The frequency of the re-emitted photons increases or decreases in comparison with the original monochromatic frequency and the shift provides information about vibrational, rotational and other low frequency transitions in condensed matter [112]. In the 2D material field, Raman spectroscopy is extensively used to identify and characterize monolayer or few layer materials like Graphene [113]. These studies show how thickness, quality, doping, strain as well as other properties of 2D materials can be investigated via the Raman effect [114, 115, 109]. A study of the evolution of the Raman spectra of BSCCO-2212 as a function of sample thickness was carried out in order to evaluate its pertinence for the 1-2 u.c. thick samples used in this work of thesis.

Specifically, a sample with flakes of different thickness (figure2.5b) ranging from 78 nm (26 u.c.) to 3 nm (1 u.c.) was analyzed. Because of the weak Raman signal of few-layer BSCCO one needs to evaluate the signal from the glass substrate and subtract it from the measured spectrum. Figure 2.5a shows the result of this procedure on the samples reported in the optical image of 2.5b.

These spectra were recorded with low intensity in the incident beam to prevent radiation damage. Reasonable statistics can be obtained for sample thickness equal or higher than 5 u.c. but for thinner samples such as those used in this thesis Raman spectroscopy is not applicable and was thus not used.



Figure 2.5: Raman spectra of BSCCO-2212 flakes with different thickness, ranging from 78 nm (26 u.c.) down to 3 nm (1 u.c.), according to AFM. The optical image of the corresponding sample is shown in the right panel.

## 2.2.3 Atomic Force Microscopy (AFM)



Figure 2.6: a Sketch of the AFM set-up. b Force-Distance curves.

Atomic Force Microscopy (AFM) is a scanning probe microscopy with vertical resolution of the order Amstrongs, that is 1000 times higher than the optical diffraction limit and lateral resolution of the order of nanometers. Invented in 1986 [116], it allows imaging, measuring, and manipulating matter at the nanoscale. Unlike Scanning Tunneling Microscopy (STM), which allows atomic-scale resolution topography studies on conductive samples by probing tunneling current, the AFM is based on the mechanical measurements of forces at the atomic scale, thus not depending on the electrical properties of the sample. Our setup is the Scanning Probe Microscope SmartSPM-1000 instrument (AIST-NT).

The heart of the AFM is a cantilever with a micro-fabricated tip that deflects when interacting with the sample surface (Fig.2.6a). Provided the sample can be scanned by means of piezo-actuators, the cantilever deflection may be measured in different ways in order to reproduce the sample topography. The most common methods to detect cantilever deflections are the interferometric method, the electronic tunneling method, or in our case the optical lever method [117].

The sample is scanned by means of a piezo-actuators that are able to perform minimal displacements of the order of 1 Å with high precision up to displacements of the order of 100  $\mu$ m. The AFM is able to acquire force-distance curves (Fig.2.6b) on most surfaces and in various environments, with high lateral, vertical and force resolution. When acquiring force-distance curves, the piezo must be ramped along the z-axis, i.e., the axis perpendicular to the surface. The z-displacement, as a function of the coordinates in the x - y plane ranges from 1  $\mu$ m to 0.1 Å, whereas the order of magnitude of the measured forces ranges from 10<sup>-6</sup> to 10<sup>-11</sup> N, thus making possible a non-destructive scan of the surface [118].

Three different operating modes are employable: the contact mode, the non-contact mode and the tapping mode, also called AC mode. The contact mode allows to achieve atomic resolution, by operating with a sample-tip distance of few A, which makes the tip sensitive to the ionic repulsive forces. This method is suited for hard samples, and low stiffness cantilevers are preferable to avoid damaging the sample as the tip is "dragged" onto the surface. In the non-contact mode, the cantilever is kept around 10 - 100 nm above the sample and oscillate around its resonance frequency with a small amplitude (few nm). In this mode, the topography is mapped by keeping the amplitude (or sometimes frequency) of the oscillation constant through a retro-feedback loop controlling the piezo-actuator along the z-axis. This method is preferred for soft materials, and uses stiff cantilevers. The phase of the oscillation measured at the same time as the amplitude is related to the properties of the material below the tip, so phase shifts during scans can be used to determine material boundaries (e.g. from substrate to thin layered sample). However, this method is sensitive to the wet layers that can form at the surface of the sample in normal atmospheric conditions and thus is preferrably used under high vacuum.

The tapping or AC mode is similar to the non-contact mode, but with a larger amplitude, so that the tip is getting closer to the sample during the oscillation. This method is best suited for the materials studied here as it is less damaging than contact mode, and can be operated in atmospheric conditions. Hence AC tapping mode has been used in this thesis for measuring both the thickness and surface topography of our superconducting BSCCO-2212 devices.

In figure 2.7 the identification via AFM of a 1 u.c. thick sample measured in this work is reported as an example. Two steps, each corresponding to a thickness of 1.5 nm



Figure 2.7: Atomic force microscopy on a BSCCO sample measured in this thesis. On the left the step profiles corresponding to the two scans indicated on the AFM image on the right. Step a (1.5 nm) is from the glass substrate to the thinnest possible BSCCO-2212 layer (0.5 u.c.) and Step b (also 1.5 nm) is from this layer to the surface of the 1 u.c. (3 nm) thick sample.

or 0.5 u.c. are measured. The first step (step a) on the edge of a small circular hole is from the glass substrate to the thinnest possible BSCCO-2212 layer (0.5 u.c.) since a substantial change in the phase is observed between the two surfaces of the step. The second step (step b) is from this layer to the surface of the 1 u.c. thick sample.

As done for the glass substrate (sect. 2.1.1), we measured the surface roughness of these thin samples. An RMS roughness of 0.2-0.4 nm is found, which is less than a tenth of the thickness of their unit unit cell.

## 2.3 Electronic transport measurement set-up

The space charge doping dependent electronic transport measurements of this thesis were carried out with the set-up shown in fig.2.8. It consists of a custom made liquid helium flow Oxford cryostat coupled with a 2 T electromagnet. The chamber pressure is lowered by an external vacuum pump to at least  $10^{-6}$  mbar. The temperature is measured with a calibrated Cernox Lake Shore resistive temperature sensor and a Lake Shore 331 temperature controller. The sensor is tightly connected to the sample holder receiver made from solid copper, which is itself screwed to the copper cold finger of the crysotat. The samples are mounted on a removable sample holder also made from copper and tightly screwed to the receiver. Copper allows an optimal exchange of heat between cryostat and sample so we can assume the temperature measured by the sensor is the same as the sample. A resistive heater is also mounted on the cold finger of the cryostat. Cooling can be adjusted by controlling the helium (He) flux within a transfer

tube inside the cryostat, while heating is controlled by the temperature controller. In this thesis we measured curves down to 3 K. Lowering the temperature below the boiling point of liquid He (4.2 K) is achieved by shutting the He flux once T is stabilized at 4.2 K, thus pumping from the liquid helium pot starting from a fixed quantity of helium. The diminution of pressure forces the boiling point of helium to go down following the liquid-vapor boundary in the Clapeyron diagram. The temperature goes down to 2.8-3 K, which is limited in our case by the residual pressure of the pump. The cooling last a few minutes as the helium is quickly evaporated. After total evaporation, heat exchange from the cryostat starts to increase temperature.

Measurements are coordinated by a LabVIEW interface and carried out using a cluster of Keithley multimeters, specifically two source-meters Keithley 2400 and one Digital multimeter Keithley 2700. One K2400 is used as the current source to apply excitation signals to the sample (of the order of  $\simeq 10$  nA-1  $\mu$ A depending on sample resistivity) during resistivity measurements. The other K2400 is used as the gate voltage source, by biasing the glass substrate during the doping process with high voltages from 0 to  $\pm 285$  V. Digital multimeter Keithley 2700 is a precision data acquisition system, which is used as voltmeter for 4-wire resistance measurements. This particular model is using a matrix of programmable relay switches that allows our setup to measure different parts of the sample consecutively (e.g. two different directions in a Hall bar configuration).

The magnetic field is applied by a vintage Varian 2 T electromagnet (originally used for electron paramagnetic resonance measurements) with its original console and power source. The magnetic field is measured with a Lakeshore 425 Gaussmeter and a Hall probe.

Different measurement modes are used:

- Low temperature transport measurement (3-300 K): 2- and 4- wires resistance measurement while the system is cooled down to few Kelvins ( $\sim$ 3 K) by controlling the flux of liquid He with the manual controller indicated in figure 2.8. Cooling rate in this thesis has been kept as low as possible, specifically at 0.2-1 K/minute in order to get high quality data set when measuring the resistivity vs temperature characteristics.
- High temperature transport measurement (300-420 K): Annealing and space charge doping of the samples. Heating rate as been kept at 1.5-2.5 K/minute.
- Hall measurement: Estimation of doping level. The magnetic field intensity is swept in the  $\pm$  2 T range by the electromagnet controller while temperature is kept at a stable value. A detailed description of the Hall measurements carried out in this thesis is provided in chapter 3.

## 2.4 Four-wire measurements

In order to investigate the electronic properties of the BSCCO-2212 thin films transport measurements were carried out with the possibility both to control temperature in the



Figure 2.8: Set-up used in this thesis for the electronic transport measurements, Hall measurements and space charge doping.

3-420 K range and apply perpendicular magnetic field for Hall measurements. Notably, we measured four-wire transport with the van der Pauw method explained below for measuring both sheet resistance and the Hall effect.

#### 2.4.1 Sheet resistance and Hall effect measurement

Sheet resistance  $(R_{\rm S})$  or resistance per square (measured in  $\Omega/\Box$ ) is a measure of resistance of thin films that are nominally uniform in thickness. The utility of sheet resistance as opposed to resistance or resistivity is that it is independent of the size of the sheet considered. A four-point (or alternatively called four-wires) measurement of  $R_{\rm S}$  is also independent of wires and contact resistance. Typically constant current is applied to two outer probes and the potential between the other two inner probes is measured with a high impedance ( $\geq 10^{12} \Omega$ ) voltmeter. Sheet resistance measurements are suitable for two-dimensional systems such as our samples. In a regular three-dimensional conductor, the resistance can be written as  $R = \rho L/Wt$  where  $\rho$ , L, W, t are resistivity, length, width and thickness of sample, respectively. Upon combining the resistivity with the thickness, the resistance can then be written as

$$R = \frac{\rho L}{tW} = R_{\rm S} \frac{L}{W} \tag{2.1}$$

where  $R_{\rm S} = \rho/t$  is the sheet resistance. If the thickness is known, the bulk resistivity is calculated by simply multiplying  $R_{\rm S}$  with the film thickness. This is true in isotropic bulk materials. In high temperature superconductor cuprates, the presence of CuO<sub>2</sub> planes that dominate the planar current flow in doped samples means that the planar resistivity of a bulk crystal can be considered as the resistivity per CuO<sub>2</sub> sheet.

The Hall effect is the appearance of a potential difference across an electrical conductor, perpendicular to the electric current I when an external magnetic field H is applied. The Lorentz force deflects moving charge carriers to one edge of the sample and generates an electric field perpendicular to both the current density and the applied magnetic field. By equating the transverse electrostatic force and the Lorentz force, one obtains the Hall coefficient:

$$R_{\rm H} = \frac{E_y}{J_x H_z} = \frac{1}{q n_v} \tag{2.2}$$

Where  $n_v$  is the charge concentration per unit volume of space,  $H_z$  is the perpendicular magnetic field,  $J_x$  the primary current and  $E_y$  the electric field corresponding to the transverse Hall voltage  $V_H = IB/qn_v d$ , where I is the applied current, d is the sample thickness, and q  $(1.602 \times 10^{-19} \text{ C})$  is the elementary charge. In 2D samples it is appropriate to directly use the layer or sheet charge density  $(n_s = n_v d)$  and therefore:  $V_{\rm H} = IB/qn_s$ . With eq.(2.2) one gets:

$$R_{\rm H} = \frac{V_{\rm H}}{I} = \frac{B}{qn_H} \tag{2.3}$$

where  $n_{\rm H}$  is the Hall sheet charge carrier density. The voltage sign is given by the charge polarity since the voltage, the current and the magnetic field form a direct trihedron. Therefore, when sweeping the magnetic field while measuring  $V_{\rm H}$ , the sign and the magnitude of  $n_{\rm H}$  can be easily calculated using eq.2.3.

From  $n_{\rm H}$  and  $R_{\rm S}$ , the Hall mobility is subsequently calculated as  $\mu_H = 1/(q n_H R_{\rm S})$ .

Experimentally, the measurement of the transverse voltage can be modified by residual parasitic resistance whose origin is usually related to sample geometrical asymmetry. In order to remove this contribution, the Hall resistance is measured as a function of positive and negative perpendicular magnetic field and the symmetric part of the measurement is removed, as the Lorentz force is anti-symmetric with field direction. In cuprates the  $R_S$  vs  $n_H$  relation is not as simple as in equation 2.3 due to the complex physics of these materials. Nevertheless, as will be explained in chapter 3, Hall measurements result to be a useful mean to get indications of carrier density modulation when carried out at low temperature.

#### 2.4.2 Van der Pauw method



Figure 2.9: Sketch of the van der Pauw configuration for sheet resistance and Hall effect measurements.

The van der Pauw method is an efficient and widely used four-wire measurement method for determining resistivity and Hall effect in materials in the form of thin films. Introduced by van der Pauw in 1958 [119], it is used to measure the resistivity of a flat sample of arbitrary shape without knowing the current pattern, if the following conditions are met: the contacts need to be small and at the circumference of the sample, the sample has to be uniformly thick and the surface of the sample needs to be singly connected, i.e., the sample should not contain any isolated holes. Considering a flat sample of a conducting material of arbitrary shape, with contacts 1, 2, 3, and 4 along the periphery as shown in fig.2.9 to satisfy the conditions above, the resistance  $R_{12.43}$  ( $R_V$ ) is defined as:

$$R_{12,43} = \frac{V_{34}}{I_{12}} \tag{2.4}$$

where the current  $I_{12}$  enters the sample through contact 1 and leaves through contact 2 and  $V_{43} = V_4 - V_3$  is the voltage difference measured between contact 3 and 4.  $R_{23,14}$   $(R_L)$  is defined similarly. The sheet resistance  $R_S$  is given by:

$$R_{S} = \frac{\pi}{\ln(2)} \frac{R_{V} + R_{L}}{2} f$$
(2.5)

where f is a correction factor which takes into account the shape of the sample through the ratio r, which is defined as  $R_V/R_L$  if  $R_V < R_L$  or  $R_L/R_V$  if  $R_L < R_V$ . The

correction factor f is given by the following equation:

$$\cosh\left(\frac{r-1}{r+1}\frac{\ln(2)}{f}\right) = \frac{1}{2}\exp\left(\frac{\ln(2)}{f}\right) \tag{2.6}$$

The f correction factor is smaller than 1 (it is 1 when r = 1, hence in the ideal case of perfect homogeneous square) and cannot be calculated analytically but it can be derived by using a polynomial approximation.

Hall carrier density and the Hall mobility can also be measured in the van der Pauw geometry. The configuration is sketched in Fig2.9. The excitation current I is applied between two diagonally opposite contacts of the sample  $(I_{13})$  and the transverse Hall voltage  $V_{\rm H}$  is measured between the other two while the magnetic field B is applied perpendicularly to the sample. As described in section 2.4, the sheet carrier density  $n_{\rm H}$ is easily calculated via eq.2.3. Specifically for the van der Pauw configuration, the Hall coefficient can be extracted from the anti-symmetric part of the measured transverse voltage with only positive magnetic fields by measuring the two transverse voltages on the sample ( $R_{13,24}$  and  $R_{24,31}$  and taking their average. However, the magnetic field was still reversed whenever possible in our experiments to increase the magnetic field range and thus the precision of the Hall coefficient.

## 2.5 Device fabrication

After the anodic bonding process and the characterization methods described above, the device used for the transport measurements and space charge doping is fabricated. This involves two main steps: deposition of contacts and sample shaping to avoid undesired conducting paths between the leads. In the following section all aspects related to sample patterning, contact deposition and the shaping of samples are discussed.

#### 2.5.1 Electron-beam lithography

Electron-beam lithography (EBL) is a technique used for the fabrication of micro- and nano- structures, based on the chemical modification of polymer resist films caused by electron irradiation [120] and used here for contacting the few-layer samples. The primary advantage of EBL with respect to photo-lithography is its possibility to overcome the diffraction limit of light to reach resolutions of few nanometers. The time to expose a certain area for a given dose is obtained by the following formula:

$$D \times A = t \times I \tag{2.7}$$

where t is the time to expose the resin, I is the electron beam current, D is the dose and A is the area exposed. In this thesis, I used E-beam lithography in a class 10000 clean room achieving devices from pre-contacted glass substrates [121]. The whole process can be summarized in the following steps:



Figure 2.10: Images from optical microscope camera of contacted devices in Hall bar  $\mathbf{a}$  and Van der Pauw  $\mathbf{b}$  configuration, after electron beam lithography.

- 1. Heating the Sample for 5 minutes at 180 °C
- 2. Spin coating of PMMA resin for 30 seconds at 4000 rpm/s, resulting in a thickness of  $\approx 246 \ \mu m$ ;
- 3. Evaporation of 35 nm Al in a  $\approx 10^{-6}$  mbar vacuum.
- 4. Exposition of the resin with Raith E-Line electron beam lithography setup. The parameters we have used are: 10  $\mu$ m and 60  $\mu$ m of aperture (depending of the resolution we needed), acceleration of beam of 20 kV and a dose of  $380\mu$ C/cm<sup>-2</sup>;
- 5. Development of Al and PMMA exposed in a bath of KOH for 100 seconds and methyl isobutyl ketone (MIBK) for 1 minute before, with subsequently cleaning in isopropanol for 30 seconds;

The use of an Al layer is mandatory because of the insulating glass substrates. The Al layer prevents the static charging of the glass and consequent defocusing of the electron beam. The lithography involves scanning the focused beam of electrons to expose the pre-designed mask on the resist layer. After the lithography and development, we deposit a 5 nm chromium sticking layer and 70 nm of gold by thermal evaporation. Samples with both van der Pauw and Hall bar geometry were made (Fig. 2.10).

Although lithography successfully allows to pattern samples with lateral dimensions as small as 10-20  $\mu$ m, it also involves heating of samples (causing oxygen loss), chemical degradation and surface damage that in our experience irreversibly degrades ultra-thin BSCCO-2212. This makes it unsuitable as a process for making devices for DC electronic transport measurements as the resulting devices are insulating with high resistivity  $(R_{\rm S} \sim 100 - 500 \text{ M}\Omega)$ . This led us to seek a cleaner procedure for depositing contacts on our samples using shadow stencil masks.



#### 2.5.2 Contact deposition via shadow stencil masks

Figure 2.11:  $\mathbf{a}$ , Alignment of a shadow stencil mask on a sample.  $\mathbf{b}$ , Deposition of contacts via thermal evaporation of gold.

Contact deposition on the few-nm thick BSCCO samples measured and studied in this thesis has been carried out exclusively by thermal evaporation of metals using shadow stencil masks. The masks were designed in the lab and fabricated by external supplier (Steec, Laser Micro Machining). We chose a van der Pauw configuration with contacts 10  $\mu$ m wide at the corner of a square of 50  $\mu$ m diagonal. This procedure requires much bigger samples than the ones for the e-beam lithography, due to the larger dimension of the laser-etched features of the mask. However, since the anodic bonding technique allows us to fabricate samples with lateral dimensions of the order of 100  $\mu$ m as previously described, the use of stencil masks was possible as the contact deposition method for BSCCO samples. The alignment is carried out in a probe station with the help a micromanipulator. The sample is placed on the stage of the probe station, with the possibility of moving it along the z-axis. The mask is held by the micromanipulator arm, and is moved in the x-y plane for aligning it with the sample. Double-sided adhesive tape is put on the edges of the backside of the mask in order to stick it with the glass substrate once in contact. As soon as the target position is reached, the stage is lifted up to attach the mask to the glass.

Once the mask is aligned on the sample, the thermal deposition of contacts takes place in a Joule Edwards evaporator. The Edwards evaporator is a vacuum chamber (base pressure:  $\approx 1 \times 10^{-6}$  mbar) of about 40 cm in height equipped with a tungsten crucible in which a current can flow in order to resistively heat and evaporate a metal contained in it. The area of the crucible is less than one square centimeter so that the solid angle subtended on the device is small, reducing parallax error. The samples are held on a metal plate which can heat up by absorbing radiation from the evaporation crucible. Heating can cause oxygen loss in ultra-thin samples even during the short interval of the contact deposition process. In order to avoid oxygen loss, radiation shielding of the metal plate with aluminum paper has been successfully used. We use 70-100 nm of gold directly on BSCCO for the best result in terms of contact resistance. In our experience a buffer layer of chromium results in a a Schottky barrier with contact resistance as high as hundreds M $\Omega$  at very low temperature, thus strongly affecting the low temperature transport measurement. Gold contacts with or without a buffer silver layer have been shown to form ohmic contacts on BSCCO as well as other high temperature superconductor compounds [122, 123, 124]. The typical contact resistance measured in the Au-patterned BSCCO samples fabricated in this thesis, were of the order of  $\approx 10-50 \Omega$ .



Figure 2.12: Optical image of a 1-u.c.-thick BSCCO-2212 device. The red dashed lines highlight the scratches made mechanically by micromanipulator tip in order to shape the sample for the van der Pauw geometry. The green circle delineates the effective final sample after the shaping.

An example of contact deposition using shadow stencil masks on a 1 u.c.-thick BSCCO-2212 sample measured in this thesis is shown in figure 2.12. Some shaping of the sample is required in order to ensure a shape compatible with van der Pauw measurements and to remove unwanted material that could short circuit contacts. This is done by mechanically scratching the surface with a probe station micromanipulator tip. The red dashed lines trace the scratches whereas the green circle shows the approximate effective area of the final sample to be measured.

## 2.6 Electrical properties of the as fabricated devices

Many studies report degradation of transport properties in few layer high temperature superconductors [125]. Few unit cell BSCCO-2212 samples in general exhibit lower crit-

ical temperatures than the bulk crystal. Drastic lowering of  $T_c$  has also been reported below a critical thickness of 2 u.c. [84, 126]. When thickness is reduced many factors can play a role in lowering the critical temperature, namely oxygen loss [87], increase of fluctuations due to low dimensionality, surface contamination, ageing [85], chemical inhomogeneity and disorder [40, 126]. In order to fabricate few-nm-thick superconducting BSCCO devices all these aspects need to be considered. Our fabrication protocol has been developed in this perspective.

- Oxygen loss: the heating of the sample at 180°C before spin-coating it with PMMA for e-beam Lithography, and deposition of the contacts in high vacuum were the two steps where oxygen loss could have taken place. We substituted lithography with direct deposition via physical masks and we avoid the heating of the samples in the high vacuum Joule evaporator with Al shielding, as explained before.
- Disorder: We fabricated our samples using the anodic bonding technique with the lowest values possible for temperature and applied voltage, limiting oxygen loss and sample-substrate strain.
- Surface Contamination and aging time: All devices are stored in primary vacuum and measured and characterized immediately after fabrication. The typical time that elapses between sample fabrication and insertion into the cryostat for measurements is 2-3 days.

With this protocol we find good superconducting quality above for 1 u.c and thicker films. However, 0.5 u.c. films consistently show insulating behavior and high resistivity. Figure 2.13 reports 3 different curves corresponding to samples with different thickness, specifically 1.5 nm (0.5 u.c.), 3 nm (1 u.c.) and 15 nm (5 u.c.) as measured by AFM. Differences in the superconducting transition temperature and the contributions of doping, disorder and electronic inhomogeneity will be discussed in detail later, as we focus here on the transport characteristics of the devices after fabrication. The 5 u.c and the 1 u.c. samples show high temperature superconductivity with  $T_c$  of 84 K and 87 K, respectively, close to the  $T_c$  measured in the bulk precursor (bulk  $T_c = 89$  K).

The 1.5 nm (0.5 u.c.) samples are insulating (red curve in fig 2.13). In a previous work [127] superconductivity in 1 and 0.5 u.c. samples is only seen with graphene encapsulation.

## 2.7 Space charge doping

Space Charge Doping (SCD) is a technique introduced in 2015 by our group to electrostatically dope two-dimensional materials with the aim to control and modulate charge carrier density in a reversible manner [100, 101, 128, 110] and provide an alternative for extreme electrostatic doping. When doping correlated electron systems and specifically HTSCs, charge modulation as high as  $10^{15}$  cm<sup>-2</sup> may be required in order to induce phase transitions and explore the phase diagram. In the following we describe the SCD



Figure 2.13: Sheet resistance versus temperature characteristic of three different as-fabricated samples with different thicknesses: 0.5 u.c (red curve), 1 u.c. (green curve) and 5 u.c. (blue curve). Critical temperatures  $T_c$  vary due to disorder and oxygen content.

method by first explaining its working principle and then providing an example of its application to a BSCCO-2212 device measured in this thesis.

#### 2.7.1 Principle

The space charge doping technique is a natural extension of the anodic bonding method, since both are based on the creation of a space charge at the sample-substrate interface, generating an extreme electric field as described in Fig. 2.14. The set-up is composed of a glass substrate, a 2D material device contacted with metal leads and a gate electrode (metal contact at the bottom surface of the glass substrate). At high temperature, glass can be seen as a negatively charged static matrix (mainly SiO<sub>2</sub> units) with mobile positively charged Na<sup>+</sup> ions. By applying a positive (negative) voltage on the back gate electrode, a drift current of mobile Na<sup>+</sup> towards (away from) the sample is generated. Consequently, an accumulation (depletion) layer at the glass-sample interface is created. Depending on voltage polarity and amplitude, this space charge can be modulated and 'frozen' when the system is quenched to room temperature. It induces a mirror charge within the device, thus changing its electronic properties.

A key factor when carrying out this doping technique is the control of the charging process which is related to  $Na^+$  mobility and drift velocity. In our experimental condi-



Figure 2.14: Illustration of the space charge doping principle. The temperature is raised in order to increase glass conductivity through the activation of Na<sup>+</sup> ions. When no gate voltage is applied (V<sub>G</sub> = 0) no space charge or interface field exists. By biasing the device through the application of an external voltage between the sample and the back-gate, the space charge at the interface is created. A positive V<sub>G</sub> applied to the back-gate will induce Na<sup>+</sup> accumulation at the sample substrate interface (n-doping of the sample) whereas a negative V<sub>G</sub> will induce Na<sup>+</sup> depletion at the sample substrate interface (p-doping of the sample).

tions, Na<sup>+</sup> mobility remains small, thus allowing us to finely control and measure the building-up of charge in real time. The dependence of the Na<sup>+</sup> mobility on temperature in soda-lime glasses is exponential [129] and the threshold to effectively measure the ionic drift is above 320 K. Thus by heating and simultaneous application of a gate voltage, space charge builds up until the internal voltage drop due to the  $Na^+$  and  $O^{2-}$  space charge accumulated at the opposite faces of the glass compensates the applied external potential. If the high temperature is maintained and the applied external voltage is removed, the Na<sup>+</sup> ions will drift back in the opposite direction. However by quenching the system to room temperature with the voltage applied, ion mobility is suppressed and the space charge is frozen at the two opposite faces of the glass even if the applied voltage is turned off. The glass-sample interface acts as a parallel plate capacitor with its capacitance amplified by the nanometric dimensions of the space charge layer. Considering a typical concentration of Na<sub>2</sub>O of  $10^{21}$  cm<sup>-3</sup>, for an accumulation layer of 1 nm a charge imbalance at the surface of  $10^{14}$  cm<sup>-2</sup> is created inducing the equivalent mirror charge. Carrier density modulation in the range of  $2 - 8 \times 10^{14}$  has been achieved in our group via space charge doping in Graphene [100], MoS<sub>2</sub> [101] and ZnO [128].

## 2.7.2 Space charge doping of ultra-thin BSCCO samples

In figure 2.15, the dynamics of the space charge doping technique is described in detail by considering the doping in a 1 u.c. BSCCO-2212 device. The figure shows the time dependence of the quantities involved in the doping process:  $V_{\rm G}$  (gate Voltage), T (temperature)  $R_{\rm S}$  (sheet resistance) and  $I_{\rm G}$  (gate current). The gate current  $I_{\rm G}$  is related to the variation of charge within the glass due to ion drift.  $V_{\rm G}$  and T can be considered as the doping parameters, whereas  $R_{\rm S}$  and  $I_{\rm G}$  are the two quantities monitored during the doping process. At the beginning a negative voltage of -150 V is applied so as to p-dope the sample. Doping takes place in the zone highlighted in orange in figure 2.15. The process begins once the temperature is sufficiently high to activate the Na<sup>+</sup> mobility



Figure 2.15: Space charge doping dynamics. **a**, Sheet resistance (green line, left axis) of the 1 u.c. BSCCO-device as a function of doping time. Temperature (red line, right axis) is increased up to 345 K and then quenched. **b**, Applied gate voltage (blue line, left axis) and measured gate current (orange line, right axis).

 $(T \simeq 320 \text{ K})$  shown by the fast increase of  $I_{\text{G}}$ . An exponential growth (bottom panel, fit to data in cyan) of  $I_{\text{G}}$  (bottom panel, orange curve) with temperature is expected. At the same time, a decrease of  $R_{\text{S}}(\text{T})$  (top panel, green curve) is observed. Once the temperature is stabilized at the doping temperature  $T_{\text{d}}$  (here 340-350 K), further decrease in  $R_{\text{S}}(\text{T})$  is achieved by increasing  $V_{\text{G}}$ . When the desired value of  $R_{\text{S}}(\text{T})$  is reached, the process is quenched by cooling the system thus freezing the space charge in the proximity of the glass-material interface. Increasing the voltage or temperature could accelerate the charging process. Limiting values of  $V_{\text{G}}$  and T are defined by the choice of glass and the material to be doped. The voltage in our case could be increased but the temperature is limited to limit the risk of oxygen loss.

## 2.8 Conclusions

In conclusions we fabricate ultra-thin BSCCO-2212 samples on glass substrates via anodic bonding technique. Flakes with thickness ranging from one to few unit cell and lateral dimension of order of 100  $\mu$ m are connected by thermally evaporating 70-100 nm Au trough shadow stencil masks previously aligned on the sample. We thus avoid chemical pollution and surface contamination from standard lithography techniques, which in our experience can irreversibly degrade the quality of BSCCO-2212 2D crystals. Transport measurements show superconductivity as high as 80-84 K for the best as fabricated 1-unit-cell-BSCCO-2212 devices, making them a perfect candidate for electrostatic doping experiments.

## Chapter 3

## Comprehensive Phase Diagram of two-dimensional space charge doped $Bi_2Sr_2CaCu_2O_{8+x}$

This chapter is partially based on our publication: E. Sterpetti, J. Biscaras, A. Erb and A. Shukla, Comprehensive Phase Diagram of two-dimensional space charge doped  $Bi_2Sr_2CaCu_2O_{8+x}$ , Nature comm., 8, 2060 (2017) [110].

In this chapter we show detailed results from the low temperature and magnetic field measurements of transport properties resulting from the electrostatic modulation of charge density in two-dimensional BSCCO-2212 devices using the space charge doping method[101, 100]. We extract parameters and characteristic temperatures over a large doping range and discuss the analysis that led us to establish the first comprehensive temperature-doping phase diagram of perfectly 2D BSCCO-2212, as thin as a unit cell. Furthermore we argue the influence of disorder on the electrical and physical properties of 2D BSCCO-2212 and carry out investigations of quantum criticality in the two dimensional limit.

## 3.1 Introduction

High temperature cuprate superconductors display a rich phase diagram, explored using a variety of techniques including transport [24, 130, 131, 132], by varying chemical doping. Their parent compounds are known to be strongly correlated with antiferromagnetic ordering at low temperatures. As doping is increased this ordering temperature falls, eventually giving place to fluctuations, as superconductivity sets in at lower temperatures. The superconducting temperature increases with doping until an optimal value and then falls, following a dome-like shape, until superconductivity is suppressed. Meanwhile at higher temperatures the non-superconducting state remains intriguing. In the underdoped regime a pseudogap in the electronic excitation spectrum, possibly related to the formation of superconducting pairs, has been shown to exist. The temperature below which this pseudogap state opens decreases with doping. Near the optimal doping level and above the superconducting temperature the material is thought to exist in a 'strange' metallic phase in the sense of a deviation from Fermi liquid behavior as seen from the linear dependence of resistivity on temperature. Finally as doping is further increased and superconductivity suppressed, Fermi-liquid behavior is progressively established.

As chemical doping is a source of disorder and structural change, alternative doping methods have been sought. To match chemical doping levels with electrostatic doping, intense electric fields ~  $10^9 \text{ V} \cdot \text{m}^{-1}$  and high carrier density modulation are required. In recent years pioneering efforts have been made using ionic liquids [133, 134] or ferro-electrics as the dielectric to investigate the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  families of materials [135, 42, 65, 52]. Considerable change in the doping and the critical temperature have been obtained and the insulator-superconductor transition in these materials investigated through transport measurements. However for transport measurements the ionic liquid method is only relevant well below room temperature because of the conductivity of mobile ions in the liquid state. This precludes its use for establishing a temperature versus doping phase diagram. Furthermore, intercalation and chemical reactions can occur when using this technique, interfering and possibly modifying a purely electrostatic effect.

## 3.2 Space charge doping of 2D BSCCO-2212 samples

The electrostatic tuning of charge carrier density in 2D BSCCO-2212 devices is explained in this section.

## 3.2.1 Sample characterization

BSCCO-2212 two-dimensional (2D) crystals with lateral size of ~ 100  $\mu$ m and thickness ranging from 1 to 2.5 unit cells (u.c.) were fabricated by the anodic bonding method on 0.5 mm thick soda-lime glass substrates [107, 108], using a bulk single crystal precursor with stoichiometry Bi<sub>2.1</sub>Sr<sub>1.9</sub>CaCu<sub>2</sub>O<sub>8+x</sub> and a critical temperature of 89 K determined by magnetic susceptibility measurements.

Contacts were deposited by evaporating 100 nm of gold through stencil shadow masks previously aligned on the sample. We thus avoid chemical pollution and surface contamination from standard lithography techniques which in our experience can irreversibly degrade the quality of BSCCO-2212 2D crystals. We performed transport measurements with the 4-wire van der Pauw geometry in a high vacuum cryostat coupled to an external 2 T electromagnet for Hall measurements. Details of fabrication and characterization can be found in chapter 2.

In the following, we show results for four different devices with thickness varying from 3 nm (1 u.c.) to  $\sim$ 7 nm (2.5 u.c.) as established by Atomic Force Microscopy

(AFM) and optical contrast. BSCCO-2212 cleaves at the BiO layer so that ultra thin samples are expected to be multiples of 0.5 u.c. with one pair of CuO<sub>2</sub> planes per half unit cell. The thinnest samples fabricated were 0.5 u.c. and were systematically insulating. All devices shown in this work were superconducting at the outset including the 1 u.c. device. The initial magnitude of resistivity varied, ranging from  $5 \times 10^{-4} \ \Omega \cdot cm$  to  $5 \times 10^{-3} \ \Omega \cdot cm$  depending on the device. We attribute this variation to the fabrication process which can induce mechanical disorder caused by substrate roughness and eventually varying doping due to partial oxygen loss. At the start of the measurements each device was annealed at 340-350 K (the temperature  $T_d$  at which devices are doped) for a few hours at  $10^{-6}$  mbar causing a decrease of the monitored sheet resistance  $R_S$  probably due to removal of eventual surface contamination. An increase of  $R_S$  would have indicated oxygen loss, not observed at this temperature. We thus control carrier density exclusively by our electrostatic doping mechanism with no change in stoichiometry or disorder during the doping process.

#### 3.2.2 Charge transfer and carrier density estimations

During the charging process, as explained in chapter 2, we also monitor the gate current  $I_{\rm G}$  measured through the glass, which gives the displacement of charge over time. Therefore  $I_{\rm G}$  is in principle a direct indication of Na<sup>+</sup> accumulation (or depletion, depending on voltage polarity) at the glass/sample interface and potentially provides an estimation of the charge transfer, once integrated over time.

Figure 3.1 shows how the gate current varies during the charging process in a typical device, that is when an external constant gate voltage is applied and temperature is raised and lowered in a controlled manner. Integrating  $I_{\rm G}$  would therefore allow to determine the charge induced within the sample.

We have made systematic calibration measurements with a standard sample and Hall measurements to test this possibility. Two difficulties prevent us from arriving at a result. Firstly the typical sample  $(10^4 \ \mu m^2)$  represents a small fraction of the area where charge is transferred when compared to the contact leads and pads (few mm<sup>2</sup>). This difficulty could in principle be overcome by assuming uniform charging and very precise gate current measurement. However minute current leaks which persist in the path through the cryostat between the electronics and the sample, despite insulated leads, make this difficult at present. This is the reason why we estimate charge carrier density using Hall measurements as well as the well known empirical formula commonly used for establishing high-T<sub>c</sub> cuprate phase diagrams [26]. Hall measurements are reliable, as will be discussed below, if not quantitatively exact. Details about the estimation of the doping level by means of these two approaches will be given in the following sections.

#### 3.2.3 Electrostatic tuning of the charge carrier density

As explained in chapter 2, doping is tuned by monitoring  $R_{\rm S}$  at the temperature  $T_{\rm d}$  while applying a gate voltage  $V_{\rm G}$  of the order of 100-280 V between the device and



Figure 3.1: Monitoring of the charging process. Time dependence of the temperature T (blue left y-axis) and the gate current  $I_{\rm G}$  (magenta right y-axis). Charging occurs in the zone where  $I_{\rm G}$  is non-zero.

a metallic electrode on the opposite face of the glass substrate, thus creating an ionic space charge at the glass-device interface. Lowering the temperature below  $T_{\rm d}$  freezes the accumulated space charge at the interface by annulling ionic mobility in the glass substrate, thus fixing the carrier density. For a given carrier density the temperature dependence of  $R_{\rm S}$  is measured from 330 K down to well below  $T_{\rm c}$ , defined here as the temperature below which the resistivity is zero.

A central question is the evaluation of the carrier concentration  $n_{\rm s}$ . We perform Hall effect measurements and use  $1/qR_{\rm H}$  to approximately evaluate  $n_{\rm s}$ . This value is indicative of the change introduced by doping and not an absolute measure of the carrier density since the electronic structure at the Fermi surface and its evolution with doping and temperature is complex and cannot be approximated by a single parabolic band. The Fermi surface evolves from hole-like to electron-like with doping and the contributions of these surfaces to the Hall coefficient are temperature dependent [23, 21]. To minimize errors related to this dependence we consider  $R_{\rm H}$  values at the fixed, low temperature of 120 K [97, 136] for all doping values. Next we discuss the doping range explored in the four samples of this study. These 2D devices are delicate and tend to fail after a certain number of measurements and temperature cycles, especially if the highest possible doping levels are sought. While samples B and C were measured for carrier concentrations on either side of the optimal doping level, samples A and D were preferentially measured for concentrations as high as could be reached on the overdoped side to compensate for a lack of similar data in literature on BSCCO. Measurements on either side of the optimal doping level, which has the highest superconducting transition temperature is needed to determine the carrier concentration from an empirical formula [26]. The  $n_{\rm s}$  calculated from Hall measurements is a reliable indicator for optimal doping. Measurements on samples B and C showed that the  $n_{\rm s}$  estimated using the 120 K



Figure 3.2: Overview of space charge doped BSCCO-2212 2D crystals.  $R_{\rm S}(T)$  for the four devices of this study at varying doping levels controlled by the gate voltage  $V_{\rm G}$ . Curves corresponding to the initial doping are indicated with stars; the underdoped region corresponds to cyan-blue curves whereas the overdoped region corresponds to yellow-brown curves;  $R_{\rm S}$  curves corresponding to the optimal doping level are plotted in thick green lines. Though samples A and D have not been swept through the optimal doping point, the fact that their initial doping is optimal is confirmed by the Hall coefficient measured in these samples as shown in the table reported in Fig. 3.3.

Table 1 BSCCO-2212 device characteristics							
Sample name	Thickness (nm)	$\mu_{\rm H}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Initial doping (cm <sup>-2</sup> )	T <sub>cinit</sub> (K)	T <sub>cinit</sub> (K)	T <sub>c</sub> (p <sub>opt</sub> ) (K)	T <sub>c</sub> variation (K)
A	7.0 (2.5 u.c.)	9.4	8.0 × 10 <sup>14</sup>	65	38	65	27
В	4.5 (1.5 u.c.)	8.7	7.0 × 10 <sup>14</sup>	70	59	71	12
C	4.5 (1.5 u.c.)	2.8	3.8 × 10 <sup>14</sup>	30	18	51	33
D	3.2 (1.0 u.c.)	10.7	8.3 × 10 <sup>14</sup>	81	51	81	30

Figure 3.3:	BSCCO-2212	Device	characteristics	summary
0				

Hall coefficient is  $\sim 8 \times 10^{14} cm^{-2}$  for optimally doped BSCCO. In the table reported in figure 3.3 one can notice as samples A, B and D are very similar in terms of initial doping, being this latter optimal or near optimal, while C is clearly not. This fact is explained because A, B and D were measured immediately after sample and device fabrication (a duration of about 2-4 days in primary vacuum except when being processed), while sample C was stored in primary vacuum for more than one month before measurements, probably resulting in oxygen loss during storage.

Fig. 3.2 shows an overview of the  $R_{\rm S}$  vs T characteristics as a function of space charge doping for the four devices of this study. We achieve a large, reversible variation in carrier density and hence in  $R_{\rm S}$  and  $T_{\rm c}$  by applying positive and negative  $V_{\rm G}$  to our devices, accessing both underdoped and overdoped regions of the phase diagram. At the outset the intrinsic carrier concentration  $(1/qR_{\rm H})$  as well as the sheet resistance  $R_{\rm S}$  and the Hall mobility  $\mu_{\rm H} = R_{\rm H}/R_{\rm S}$  were measured for each sample. The table reported in Fig. 3.3 shows these values along with the thickness,  $T_{\rm c_{init}}$  (initial  $T_{\rm c}$ ),  $T_{\rm c_{min}}$  (minimum  $T_{\rm c}$ ),  $T_{\rm c}(p_{\rm opt})$  ( $T_{\rm c}$  at the optimal doping level) and variation in  $T_{\rm c}$  achieved through doping in each sample.

In previous work thin samples have been known to show higher  $R_{\rm S}$  and lower  $T_{\rm c}$  than thicker ones and superconductivity in 1 u.c. or thinner samples is only seen with graphene encapsulation [82, 127, 84]. Our unprotected 1 u.c. BSCCO-2212 devices are superconducting and we do not find a direct correlation between thickness and mobility leading us to conclude that the degree of disorder is the important parameter. This result can be attributed to our sample fabrication method [107, 108] as well as the avoidance of lithography during device fabrication. We note that disorder can have significant impact on superconducting properties including  $T_{\rm c}$  suppression [137, 125, 138], localization of Cooper pairs [139] and broadening of the superconducting transition due to spatial inhomogeneity of the superconducting condensate [140, 141].

### 3.2.4 Reversibility of the doping method

In Figure 3.4 we show an example of reversible modulation of carrier density across the phase diagram. Fig. 3.4a shows a sequence of measurement from initial doping (0) to a final doping (5). Fig. 3.4b highlights the reversibility of the doping process by plotting  $T_c$  and the slopes (see sect. 3.3.5) of the linear part of the resistivity curve as a function of doping. The doping was changed in a non-monotonic manner. The coherence and



Figure 3.4: Reversibility of the doping method. **a**, Sheet resistance vs temperature characteristics of sample B, where carrier density is modulated in a non monotonic fashion by space charge doping by applying positive (blue arrows) and negative voltages (red arrows)  $V_{\rm G}$ . **b**, Tc (upper panel) and the slopes  $A_{\rm N}$  (lower panel) of the linear part of  $R_{\rm S}({\rm T})$  at the different doping levels

monotonic nature of these quantities again validates the reversibility of the process. Similar and further measurements of reversibility have been obtained on graphene [100] or  $MoS_2$  [101] among others. We have not observed any electrochemical effect to date on any sample or measurement.

#### 3.2.5 Limiting thickness

An important consideration is the screening length  $\lambda_{el}$  of the electrostatic field as compared to the thickness of the sample. The electrostatic field does not penetrate significantly beyond the screening length which means that if the sample is thicker, the parts not influenced by the electrostatic field will also determine transport properties and complicate meaningful interpretation of transport data. This is especially true for conducting samples like BSCCO and sample thickness is a critical aspect when homogeneity of electrostatic doping is sought. Some estimations concerning screening length in cuprates for electrostatic doping exists in the literature. For instance, references [45, 42] indicate that in LSCO compounds the screening length is sub nm, whereas references [43, 44] indicate that in YBCO it is of the order of 1-1.5 nm, and that it should be twice as much in BSCCO (~3 nm).

Several samples with different thickness were doped and the effect of doping compared. Figure 3.5 shows 4 samples with thickness of 15 nm (5 u.c., sample F), 7.5 nm (2.5 u.c., sample A), 4.5 nm (1.5 u.c., sample C) and 3 nm (1 u.c., sample D), all initially very close to the optimal doping level (darkest and boldest curves in each panel). We examine the shift in the sheet resistance and in the critical temperature  $T_c$  with maximum possible over-doping in each sample. This is done by doping holes into the device with



Figure 3.5: Space charge doping effect dependence on sample thickness.  $R_{\rm S}({\rm T})$  characteristics of samples with different thickness, specifically: **a** 15 nm (5 u.c.), **b** 7.5 nm (2.5 u.c.), **c** 4.5 nm (1.5 u.c.) and **d** 3 nm (1 u.c.). While change in  $T_{\rm c}$  obtained through doping (parameters used are similar) will depend on the initial  $T_{\rm c}$ , it is obvious that part of the 5 u.c. is unaffected by the field as the  $T_{\rm c}$  does not change while the  $R_{\rm S}$ .

maximum negative gate voltage  $V_{\text{G-max}} = -280$  V at temperature  $T_{\text{d-max}} = 350$  K until the change in sheet resistance saturates.

Going from the initial doping to an over-doped state we expect:

- A decrease of the sheet resistance due to increase of charge carrier density.
- A decrease of the critical temperature since the initial doping is optimal.

In figure 3.5 all curves are normalized to the initial undoped sheet resistance at 250 K in each device. We observe a change in the sheet resistance in all samples due to the gating effect. A decrease of  $R_{\rm S}$  of about 40-45% was observed in the 2.5, 1.5 and 1 u.c. samples whereas the 5 u.c. one showed a reduction of only 15%. No change in the critical temperature was found in the 5 u.c. sample, indicating that the electrostatic



Figure 3.6: Extraction of characteristic temperatures and parameters. **a**, Sheet resistance as function of temperature for an underdoped device (overdoped in the inset). **b**, Maximum  $T_c$  of each device as a function of resistivity;  $T_c(p_{opt})$  is the  $T_c$  at the optimal doping level or the peak of the superconducting dome. **c**, Dependence of the scaling factor Z on  $T_c(p_{opt})/T_{c_{max}}$ , where  $T_{c_{max}} = 84$  K is the maximum  $T_c$  measured by us to date in 2D BSCCO-2212 devices. The black line is a fit to the data (black squares) of the measurements of Naqib et al.  $(Z_{ref.})$  [131], while the magenta dots are the calculated values for the four devices of this work ( $Z_{exp.}$ ).

effect was screened from the topmost layers where the initial charge carrier density and corresponding critical temperature persist. Coherent and bigger shifts of  $T_c$  to lower temperatures (35-37%) were observed in sample C and D, whereas a broader superconducting transition and a smaller shift (30%) was found in sample A. Sample A is 2.5 u.c. thick and the doping profile is probably not homogenous over the whole sample with the electrostatic effect decreasing in the upper layers of the film resulting in smaller change in the critical temperature with respect to the lower layers. We found this effect only in sample A which also shows some discrepancy in the Hall coefficient estimated doping value (see below). The critical thickness for homogeneous doping is thus established at 2 u.c. or 6 nm for BSCCO.

## 3.3 Phase diagram

#### 3.3.1 Determining the temperature crossovers

The  $R_{\rm S}(T)$  curves obtained at various doping levels depend on the electronic structure of the corresponding phase. Variations in the temperature dependence of  $R_{\rm S}$  have been successfully used to demarcate different regions of the cuprate phase diagram [18, 24, 130]. It is known that the normal state in the cuprates around optimal doping is characterized


Figure 3.7: Extraction of the characteristic temperatures, further analysis. **a**, **c** First order derivative of  $R_{\rm S}$  versus T for an underdoped and overdoped sample respectively.  $T^*$  (blue dot) and  $T_{\rm m}$  (red dot) are found as the intersection between high temperature strange metal behavior (orange dashed lines) and the low temperature normal states (green dashed lines). **b**, **d**, Sheet resistance versus temperature curves corresponding to **a**, **c**.  $T^*$ ,  $T_{\rm m}$  determined as described in **a**, **c** coincide with the deflection and inflection points of low temperature normal states (green lines) with respect high temperature strange metal behavior (orange lines) respectively.

by a linear dependence of resistivity on temperature, generally called the 'strange metal' phase. At higher doping and lower temperatures this dependence assumes the normal metallic power law dependence in the 'Fermi liquid' phase. At lower doping and lower temperatures the dependence again deviates from linearity in a different manner in the region known as the 'pseudogap' phase. The temperatures corresponding to deviations in linearity (Fig. 3.6a) can be used to determine the domain of existence of the different phases. It is to be seen if a single, coherent, doping vs. temperature phase diagram of BSCCO-2212 emerges from these measurements of devices with differing intrinsic disorder and  $T_{\rm c}$ .

For each  $R_{\rm S}(T)$  curve we use a linear fit for the 'strange metal' high temperature region (290 K< T < 330 K) with  $\rho_{\Box}(T) = \rho_0 + A_{\rm S}T$ , where  $\rho_0$  is the residual square resistivity and  $A_{\rm S}$  is the slope [24].  $T_{\rm m}$  (temperature of crossover into the Fermi liquid phase) and  $T^*$  (temperature of crossover into the pseudogap phase) are determined respectively as the temperature of upward and downward deviation (green curves) from the linear behavior (orange straight lines).

The downward deviation below  $T^*$  in BSCCO-2212 is ascribed to the reduction of inelastic scattering rate of electrons in the pseudogap phase, when temperature is lowered [25]. This characteristic  $T^*$  may however be different [130] from the temperature of crossover into the pseudogap phase, commonly detected by photo-emission, Raman or tunneling spectroscopy [20, 21, 19].

It is well established in cuprates that in the Fermi-liquid phase the upward deviation of  $R_{\rm s}(T)$  below  $T_{\rm m}$  follows the power law  $\rho_{\Box}(T) = \rho_0 + BT^m$ , where the exponent m is expected to increase with doping from 1 to 1.5-2 depending on the material [132, 36, 131]. In our overdoped devices we observed an m(p) dependence, with a maximum m=1.35 at the doping level of  $1.6 \times 10^{15}$  cm<sup>-2</sup> (~0.21 holes/Cu). Where possible, similar estimations were found for  $T_{\rm m}$  and  $T^*$  by identifying the temperature at which  $dR_{\rm s}/dT$  deviates upward (respectively downward) from its high temperature constant value [24, 130], as shown in Fig. 3.7. The accessible range (up to 330 K) where linear behavior is found at high temperature ensures a reliable determination of  $T^*$  and  $T_{\rm m}$ .

#### 3.3.2 Doping estimation from empirical formula

The construction of the phase diagram for BSCCO-2212 also requires the determination of the carrier concentration for each device. We use two methods, the Hall carrier density from the measured Hall coefficient  $(1/qR_{\rm H})$  and an estimation of holes per copper atom (holes/Cu) obtained by an empirical and commonly used  $T_{\rm c}(p)$  relation [26].

$$T_{\rm c}(p)/T_{\rm c}(p_{\rm opt}) = 1 - Z(p - p_{\rm opt})^2$$
 (3.1)

where  $T_c(p_{opt})$  is the maximum critical temperature measured for each device corresponding to the optimal doping level and Z is a scale factor. In bulk material with minimal defects Z is empirically determined to be 82.6 [142, 132, 66] and superconductivity exists in the region p = 0.05 to p = 0.27 holes/Cu. Disorder reduces  $T_c$  and constrains superconductivity to a smaller region in p [131] with a scaling of the superconducting dome. The lowering of  $T_c$  due to disorder also corresponds to a higher normal state  $R_S(T)$ , ascribed both to Coulomb interactions and scattering by impurities [137]. In our 2D crystals this behavior can be expected as shown qualitatively in Fig. 3.6b. The empirical relation for obtaining p from  $T_c$  is modified in the presence of disorder [131] by modifying the scaling parameter Z as shown in Fig. 3.6c. Thus characteristic temperatures are obtained as a function of doped holes/Cu allowing us to construct phase diagrams for our samples with varying intrinsic disorder.

### 3.3.3 Phase Diagram of 2D BSCCO-2212 for varying disorder

The resulting phase diagram with doping p determined from  $T_c$  by equation (3.1) is shown in Fig. 3.8. The characteristic temperatures ( $T_m$  and  $T^*$ ) and their dependence



Figure 3.8: Phase diagram of 2D space charge doped BSCCO-2212. Of the 32 measured  $R_{\rm S}(T)$  curves, 26 were of the quality needed for extracting characteristic temperatures. The characteristic temperatures  $T^*$  (filled symbols),  $T_{\rm m}$  (open symbols) and  $T_{\rm c}$  (filled symbols on the domes) extracted for the four devices of this study are plotted as a function of doping (holes/Cu). They demarcate the boundaries of the pseudogap region (PG), the strange metal region (SM), the Fermi liquid region (FM) and the superconducting dome (SC). The different colors of the domes reflect the shrinking of the dome with disorder. The error on characteristic temperatures is estimated during their extraction while that on doping depends on  $T_{\rm c}$  through eq. 3.1 and is significant around optimal doping. Where not shown it is of the size of the data point or smaller.

on p for the four devices establish remarkably coherent and well-demarcated domains corresponding to the cuprate phase diagram. The superconducting dome, as determined from the empirical formula of equation 3.1, shrinks with increasing disorder as  $T_{\rm c}$  is suppressed. We thus establish a complete phase diagram for ultra-thin BSCCO-2212 extending well into the underdoped and overdoped regions and explored entirely using electrostatic doping. In particular we provide data in the overdoped region where scant information exists for BSCCO-2212 [97, 142].

The extracted phase boundary, notably between pseudogap region and the strange metal region is not linear. Extrapolating this phase boundary to the doping axis would indicate a critical doping close to the optimal value, but higher values can be obtained by extrapolating segments of the phase boundary on the underdoped side. Two shortcomings of the phase diagram in Fig. 3.8 are worth noting and shall be addressed in



Figure 3.9: Hall measurements. **a**, Temperature dependence of the Hall coefficient  $R_{\rm H}$  for different doping levels tuned by external gate voltage  $V_{\rm G}$ . The four points on the violet dashed line correspond to the four doping measured at T = 120 K.**b**, Transverse anti-symmetrized resistance  $R_{\rm xy}$  as a function of magnetic field at T = 120 K.

section 3.4. Firstly, to accurately determine the pseudogap to strange metal crossover we need data points close to optimal doping and at temperatures below 200 K. This is difficult because near optimal doping the critical temperature is high and the crossover temperature low, so detecting a change from the linear strange metal dependence becomes delicate. However in Fig. 3.8 we have only one data point below 200 K on this crossover line which makes it difficult to extend this line to the vicinity of the superconducting dome. Secondly, a careful observation of the strange metal to Fermi liquid crossover shows a greater dispersion of data with respect to the pseudogap to strange metal crossover. In particular, the disordered sample data (empty green diamonds) shows a crossover line closer to the optimal doping with respect to the low disorder sample (empty blue circles). This would indicate that while the pseudogap to strange metal crossover is independent of disorder, the strange metal to Fermi liquid crossover is influenced by disorder. The strange metal region, notably just above the superconducting dome, at the confluence of these two crossover lines is indicative of the nominal doping region where a quantum critical point could exist at zero temperature inside the superconducting region. An accurate determination of this is therefore desirable and which we will detail in section 3.4 with low disorder samples.

### 3.3.4 Doping estimation by Hall effect measurements

We performed Hall measurements at different temperatures in order to confirm the anomalous dependence on temperature of the Hall coefficient  $R_{\rm H}$  [23] in our BSCCO-2212 thin films, as reported in the literature [136]. In Fig. 3.9a the  $R_{\rm H}$  vs T curves corresponding to different doping levels are shown. The maximum of  $R_{\rm H}(T)$  is found at

T = 120 K, and we consider these values of  $R_{\rm H}$  to estimate qualitatively the variation in carrier density after each doping performed, being aware that a rigorous quantitative estimation of doping is not possible by simply considering the Hall number in the free electron relation [?], due to the correlated character of these compounds where spin fluctuation exchange can make the quasiparticle current different from the quasiparticle bare velocity. Fig. 3.9b shows the anti-symmetrized transverse resistance  $R_{\rm xy}$  as a function of applied magnetic field B at T = 120 K.

### 3.3.5 Phase Diagram with doping inferred by Hall coefficient

Finally we construct the same phase diagram using carrier density estimated by  $1/qR_{\rm H}$  (Fig. 3.10a) and reach two conclusions. Firstly the relation between p determined using equation (3.1) and  $1/qR_{\rm H}$  is non-linear. This is confirmed in Fig. 3.10b where an exponential dependence is found between the two quantities [97] and in Fig. 3.10c where the horizontal  $1/qR_{\rm H}$  axis is plotted in logarithmic scale yielding a result very similar to the phase diagram obtained in Fig. 3.8. However we must keep in mind the limitations in the use of  $R_{\rm H}$  for estimating doping discussed above and note only the qualitative similarity between the phase diagrams of Fig. 3.8 and Fig. 3.10c.

Secondly the data corresponding to the 2.5 u.c. device appears incoherent with the thinner devices while this was not the case in Fig. 3.8, where p is determined from the  $T_{\rm c}$  using equation (3.1). The probable reason is that in our 2.5 u.c. device the doping is not homogeneous over the total thickness (see sect. 3.2.5) given the small screening length of cuprates ( $\lambda_{\rm el} \sim 1$  u.c.) [45, 42] introducing an error in the determination of carrier density from  $1/qR_{\rm H}$ .

We conclude our analysis on these  $R_{\rm S}(T)$  as a function of doping by examining the normal state behavior in greater detail. In the normal state, it has been shown that the slope  $A_{\rm S}$  of the linear part of the  $R_{\rm S}(T)$  curve (Fig. 3.11) is inversely proportional to the doping with a simple, universal 1/p power law behavior [24, 32]. We confirm this finding as shown in Fig. 3.10d where we have accounted for the varying disorder in our devices by normalizing the measured slope  $A_{\rm S}$  of the  $R_{\rm S}(T)$  curve by  $A_{\rm N}=A_{\rm S}\mu_{\rm H}/\mu_{\rm Hmax}$ , where  $\mu_{\rm H}$  is the measured mobility of each device at T = 120 K and  $\mu_{\rm Hmax}$  is the highest measured mobility of our devices (in sample D, 1 u.c.).

# 3.4 Phase diagram: Precise determination of the critical region in low disorder 1 u.c. BSCCO-2212

The determination of the phase diagram of 2D BSCCO and in particular the crossover lines in the vicinity of the superconducting dome are important because of the possible existence of a Quantum Critical Point (QCP) which demarcates a Quantum Phase Transition (QPT) occurring at 0 K inside the dome and sampled by the variation of a tuning parameter other than temperature [62, 63, 30, 64]. The tuning parameter here is the charge carrier density. Transport data cannot directly access such a point masked by the



Figure 3.10: 2D BSCCO-2212 phase diagram with carrier density from measured Hall coefficients. a, Characteristic temperatures as in Fig. 3.8 with  $T^*$  (filled symbols),  $T_{\rm m}$  (open symbols) and (filled symbols below 100K) of the four devices as a function of  $1/qR_{\rm H}$  and the resulting phase diagram. **b**, Doping calibration: Exponential dependence of  $1/qR_{\rm H}$  on the calculated holes/Cu. c, Same as a but accounting for the exponential functional dependence found in b. The vertical green band indicates the region of optimal doping. Though limitations in the use of  $R_{\rm H}$  for estimating doping preclude quantitative conclusions a qualitative similarity with Fig. 3.8 can be seen. d, Doping dependence of normalized slope  $A_N$  of the linear part of  $R_S(T)$  in the strange metal phase  $(T > T^*, T_m)$ .  $A_N$  values for the four devices fall on a single curve (solid line) given by  $A_N \propto -b \times \ln(\text{holes/Cu})$ . Inset: doping dependence of the slope  $A_{\rm S}$  before normalization. Error bars in  ${\bf a}, {\bf b}, {\bf c}$  take into account uncertainty of determination of characteristic temperatures and  $R_{\rm H}$ .



Figure 3.11: Determination of the slopes  $A_{\rm S}$ . Fit of the linear part of the  $R_{\rm S}({\rm T}) = \rho + A_{\rm S}{\rm T}$  characteristics of sample C at different doping values indicated by different colours.

superconducting state unless superconductivity is completely suppressed by a very high magnetic field [143, 144]. Indirectly however, the crossover lines found above the superconducting dome can give an idea about the position of the QCP in the phase diagram. This requires several precise transport measurements around the optimal doping value and as close as possible to the superconducting region. As pointed out in section 3.3.3 disorder also seems to influence the strange metal to Fermi-liquid crossover. Therefore in this section we concentrate on a more precise determination of the critical region of the phase diagram using low disorder 1 u.c. samples.

These are the already discussed sample D (maximum critical temperature  $T_{\rm c}(p_{\rm opt}) = 81$  K) and a new device (sample E) with  $T_{\rm c}(p_{\rm opt}) = 80$  K.

Fig. 3.12 shows the sheet resistance of sample E as a function of temperature for varying charge carrier density controlled by space charge doping. The curve corresponding to the optimal doping level is marked by the star. Negative and positive gate voltages  $V_{\rm G}$  were applied to increase and decrease the charge density and therefore the critical temperature  $T_{\rm c}$ , allowing us to reversibly sweep between the overdoped regime and the underdoped regime as illustrated by the inset of Fig. 3.12. For these measurements the doping regime is tuned around the region where the T-linear behavior of  $R_{\rm S}(T)$  extends to the lowest temperatures narrowly separating the pseudogap phase and the Fermiliquid phase [145].

To determine the phase crossover boundaries we proceed as explained in section 3.3.1, by



Figure 3.12: Space charge doping of sample E.  $R_{\rm S}(T)$  curves of sample E at varying doping levels controlled by the gate voltage  $V_{\rm G}$ . The Curves corresponding to the initial doping is indicated with star; The  $R_{\rm S}$  curves corresponding to the optimal doping level is plotted in green line. The device has been subjected to both signs of bias, so that holes are reversibly added and subtracted.



Figure 3.13: Linear Fit of the  $R_{\rm S}({\rm T})$  characteristics. Sheet resistance vs temperature corresponding to three doping levels indicated at the top left. The green lines are the linear fit. The inset shows the difference between  $R_{\rm S}({\rm T})$ 's and the linear fit for each curve, thus focusing on the deviation points at  $T^*$  and  $T_m$ .



Figure 3.14: Phase diagram of the 1 u.c.-thick low disorder BSCCO-2212 samples. Doping dependence of the characteristic temperatures  $T^*$  (filled symbols),  $T_{\rm m}$  (empty symbols) and  $T_{\rm c}$  (filled symbols on the SC dome) of sample D and E.

detecting temperatures corresponding to deviations from the linear dependence of  $R_{\rm S}(T)$ . In Fig. 3.13 three  $R_{\rm S}({\rm T})$  curves at three specific point or doping values are shown. These correspond to the lowest  $T^*$  and  $T_m$  temperatures on the crossover boundaries as well as one point in the middle where the  $R_{\rm S}({\rm T})$  dependence remains strictly linear until the superconducting transition. The green lines are the linear fits to each curve and the inset shows the difference between  $R_{\rm S}({\rm T})$  and the linear fit. The blue curve corresponds to the highest doping level (p = 0.181 holes/Cu) where a downward deviation from linearity distinct from superconducting fluctuations is observed. The red curve corresponds to the lowest doping level (p = 0.195 holes/Cu) where an upward deviation from linearity is measured. The orange curve (p = 0.188 holes/Cu) remains linear until the superconducting transition as the downturn of  $R_{\rm S}({\rm T})$  observable at around 110 K can be attributed to the superconducting fluctuation regime.

The resulting phase diagram is shown in figure 3.14. The pseudogap to strange metal crossover  $T^*(\delta)$  appears linear and approaches the superconducting dome on the overdoped side of the phase diagram (about 0.181 holes/Cu). This recalls results found on bulk BSCCO-2212 in earlier work [21], as discussed in chapter 1 and shown in Fig. 1.20. The strange metal to Fermi liquid crossover is also correspondingly shifted to the over-



Figure 3.15: Phase diagram and QCP investigation for samples with varying disorder. Characteristic temperatures  $T^*, T_{\rm m}$  and  $T_{\rm c}$  as a function of sample C (green points) and E (magenta points) as a function of doping (holes/Cu). The green and magenta blurry windows, correspond to the doping interval enclosed by the lowest  $T^*$  and  $T_{\rm m}$  observed in sample C and E, respectively.

doped side of our lowest temperature point on this boundary being at a doping of 0.195 holes/Cu. Between these two doping values  $R_{\rm S}(T)$  dependence is linear and corresponds to the strange metal phase.

### 3.4.1 Phase Diagram: critical region and influence of disorder

An examination of Fig. 3.8 and then of figure 3.14 shows a discrepancy in the identification of the critical region which, when extended down to 0 K, indicates the doping value where a quantum critical point could exist as an extension of the linear-T strange metal phase. As mentioned above in section 3.3.3 the phase diagram of Fig. 3.8 has two shortcomings . However we lack data points close to optimal doping and at temperatures below 200 K. Furthermore there is sizable dispersion of data in the pseudogap to strange metal crossover between the disordered sample C (empty green lozenges) and the low disorder sample D (empty blue circles).

In Fig. 3.15 we compare  $T^*$ ,  $T_{\rm m}$  and  $T_{\rm c}$  which establish the crossovers for the phase diagram as determined from the high disorder sample C and the low disorder sample E. In both the doping has been swept over a large range of the phase diagram from the underdoped to the overdoped region. It can be seen that the measurements with the

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low disorder device (sample E) allow us to rectify these shortcomings and extend the boundaries of the phase diagram closer to the superconducting dome. Firstly, we have been able to distinguish the pseudogap and Fermi liquid related deviations of  $R_{\rm S}(T)$  from linear behavior to below 150 K. This is the result of precise measurements and very slow variation of temperature during the measurement at a stabilized rate of 0.3-0.5 K/min which allows for accurate determination of  $R_{\rm S}(T)$  dependence. Indeed, since we are measuring small quantities, slight changes in the experimental temperature variation rate during measurement can lead to artifacts in the  $R_{\rm S}({\rm T})$  dependence and data which cannot be interpreted reliably. Secondly, we detect systematic differences between the high disorder sample (green symbols) and the low disorder sample (magenta symbols). This is especially striking on the overdoped side, with disorder leading to a systematic shift in the estimated characteristic temperature  $T_{\rm m}$  of 30-50 K. This leads to a shift in the crossover line (not shown) linking the empty green lozenges for the disordered sample and the empty magenta circles for the ordered sample and a consequent shift in the identification of the critical region. This difference is not as marked for the pseudogap to strange metal crossover and this is also consistent with earlier findings which find that the pseudogap is not sensitive to disorder [146, 147, 148]. Both these facts account for the discrepancy mentioned above which in our opinion is not related to any intrinsic property but more to the method used for determining these crossovers. As we have stressed, the measurements need very careful and precise determination of the  $R_{\rm S}({\rm T})$ dependence but it would appear that sample quality is also crucial. Indeed, a look at the inset of Fig. 3.10d shows that the slope of the linear part of the  $R_{\rm S}({\rm T})$  depends on disorder. It is greater for the high disorder sample C than for the other samples and this clearly alters the determination, in particular of  $T_{\rm m}$ . We thus explain the earlier result and obtain in figure 3.14 a more precise determination of the phase diagram and the critical region (between 0.181 and 0.195 holes/Cu).

For a direct identification of the critical regime two important obstacles have been identified since the inception of such studies [149], and we have mentioned both earlier. Recalling them again, these are

- a precise determination of sheet carrier density
- measurement of the crossovers down to very low temperatures approaching 0 K

Following others before us, we have used an estimation based on an empirical formula [26] and  $T_{\rm c}$  measurement to estimate carrier density. We have alternatively used  $1/qR_{\rm H}$  as an estimation of the carrier density. As already mentioned, the Hall estimation does not give the real value of the carrier density but a quantity related to it, as shown in Fig. 3.10b. If we now use the  $1/qR_{\rm H}$  estimation the phase diagram obtained is shown in Fig. 3.16. As in section 3.3.5 we obtain a close correspondence with the phase diagram with the empirical carrier density of Fig. 3.15 and Fig. 3.16. The range of critical doping as estimated through  $1/qR_{\rm H}$  is  $[0.88-1.1] \times 10^{15}$ .

In BSCCO-2212, ground state electronic structure which is effectively masked in part by the superconducting state, could prove to be surprisingly complex. In some interpretations the quantum critical point is associated with a Lifshitz quantum phase transition,



Figure 3.16: Phase diagram of sample E and D with doping inferred from  $R_{\rm H}$ . Characteristic temperatures  $T^*$ ,  $T_{\rm m}$  and  $T_{\rm c}$  as a function of  $1/qR_{\rm H}$ .

where as a function of increasing doping the hole-like Fermi surface becomes electron-like [96, 21, 98] at a critical doping  $(p_{cr})$  of about 0.19 holes/Cu.

Finally we end this re-examination of the utility of the  $1/qR_{\rm H}$  estimation of carrier density by showing  $T_{\rm c}$  vs  $1/qR_{\rm H}$  in logarithmic scale in Fig. 3.17b for the high disorder sample C (green rhombus) and low disorder samples D (blue circles) and E (magenta squares). Again the superconducting domes obtained are coherent with the known level of disorder in the samples and reinforce the overall dependability of the results.

# 3.5 Conclusions

In this chapter we have presented ultra-thin superconducting (1-2.5 unit cell) BSCCO-2212 devices to which we apply a highly efficient electrostatic doping technique called space charge doping. Starting from the nominal optimal doping we obtain carrier density variations of the order of  $10^{15}$  cm<sup>-2</sup>, as estimated by Hall measurements, both in the overdoped and in the underdoped regions, entirely through space charge doping. We measure sheet resistance as a function of doping from 330 K to well below the superconducting transition. From these measurements we extract characteristic temperatures demarcating the various regions of the phase diagram. These measurements allow us to construct a comprehensive phase diagram as a function of doping, temperature and disorder in 2D Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+x</sub> and to analyze the influence of doping, disorder and



Figure 3.17: Superconducting dome for varying disorder as a function of Hall carriers.  $T_{\rm c}$  versus  $1/qR_{\rm H}$  dependence for sample C, D and E.

two dimensionality.

In order to identify the critical doping regime in 2D-BSCCO-2212, we explored the phase diagram for low disorder 1 u.c. samples by fine-tuning the carrier density in the slightly overdoped regime. By searching for the region in the normal state, above the superconducting dome, where the pseudogap and strange metal phases appear to meet, we found this critical region where a quantum critical point could be masked by superconductivity, to be confined in the range  $\sim 0.181 - 0.195$  holes/Cu . Our results demonstrate the potential of space charge doping to develop fundamental understanding of superconductivity and phase transitions in high-temperature superconductors and open new perspectives in the field of fundamental research.

# Chapter 4

# Superconductivity in two-dimensional $Bi_2Sr_2CaCu_2O_{8+x}$

In this chapter we take a closer look at the superconducting transition in our twodimensional BSCCO-2212 devices. Phase transitions are characterized by critical fluctuations and dimensionality plays an important part in the functional dependence on temperature of physical quantities such as conductivity. In the case of the Ginzburg-Landau theory used to describe the superconductivity, these can lead to an increase of the conductivity above the critical temperature due to the presence of fluctuating Cooper pairs. However, as long range order is forbidden in two-dimensional systems, 2D superconducting phase transitions have been described by Berezinskii, Kosterlitz and Thouless (BKT) as due to vortex and anti-vortex pairing, with characteristic fluctuations [150, 151, 152]. Resistivity data from two-dimensional BSCCO-2212 is a good candidate to test these predicted functional forms. In particular recent theoretical work combines the two approaches in different regimes of temperature and offers us a way to study and analyze our resistivity data as a function of doping, disorder and magnetic field.

# 4.1 Fluctuation phenomena and 2D superconductivity

In conventional clean bulk 3D superconductors fluctuations of the order parameter due to non equilibrium Cooper pairs above the critical temperature are considered negligible. The transition in temperature between a resistive normal state and a superconducting state is sharp with a vanishing width and no alteration of the conductivity in the vicinity of the critical temperature is observed. Any alteration can be ascribed to fluctuations and a numerical estimation of the range of temperature  $\Delta T$  where fluctuations occur, was given by Ginzburg and Landau (GL fluctuations) [153]:

$$\Delta T/T_{\rm c} \sim (\alpha/\xi_0)^4 \sim 10^{-13} - 10^{-16} \tag{4.1}$$

where  $\alpha$  is the inter-atomic distance and  $\xi_0$  is the coherence length.

In two dimensional superconductors however, this contribution cannot always be neglected. The short coherence length of HTSCs, their relatively low charge carrier density and the short coherence length can substantially increase  $\Delta T/T_c$  in eq. 4.1, thus making fluctuations observable. This is known as the Aslamazov-Larkin (AL) contribution to GL fluctuations [154, 155]. BSCCO-2212 is a special case due to its extreme anisotropy, weak interplane coupling and short coherence length [156] that make fluctuation phenomena relevant even in bulk samples [157, 158].

Moreover, the strong anisotropy of cuprates and BSCCO-2212 in particular has prompted many studies suggesting that the superconducting transition in these materials belongs to the Berezinskii, Kosterlitz and Thouless (BKT) class [159, 157, 160, 161]. Despite the arguments that low energy excitations forbid true long range order in 2D, the BKT theory explains how another type of "topological" order can form. The topological excitations for a 2D superfluid are vortices, and the transition occurs at  $T_{\rm BKT}$ , the temperature at which bound vortex-antivortex pairs dissociate [151, 152]. Experimentally, BKT transitions have been observed on superfluid helium films [162, 163]. In superconducting thin films, it was initially pointed out by Kosterlitz and Thouless that the cut-off of the logarithmic interaction by the 2D magnetic penetration length  $\lambda_{\perp}$  would prevent a vortex driven transition [151]. However, noting that in practice  $\lambda_{\perp}$  can sometimes be of the same order as the size of real crystals, the broadening of the transition in very thin superconducting films could reasonably originate from the same type of BKT fluctuations [164].

BKT and GL fluctuations differ in the way the coherence length diverges at the characteristic critical temperatures  $T_{\rm BKT}$  or  $T_{\rm GL}$ . The divergence is predicted to be exponential for the BKT transition and following a power law for the GL transition [165, 166]. The temperature dependence of the coherence length is reflected in measurable physical quantities among which the resistivity. Electrical transport measurements of two-dimensional samples with thickness of 1 u.c. is therefore a reasonable way to investigate the nature of the superconducting fluctuations and transition in BSCCO-2212.

# 4.1.1 Extrinsic effects in 2D superconductors: Finite-size effect and electronic inhomogeneity

Fluctuations, whether of the BKT or GL type, can be classified as intrinsic effects that smear the transition above the critical temperature. However in the experimental reality of two-dimensional superconductor materials, pronounced broadening and resistive tails are often encountered. Disorder, high current density or an applied magnetic field [168, 140] have all been previously cited as possible extrinsic factors that can prevent the observation of a BKT transition. However characterizing the broadening of the superconducting transition width and understanding the role played by such effects on the superconducting condensate is not straightforward, as discussed below. Two further effects can also intervene and contribute to altering the transition:



Figure 4.1: Gap maps of an underdoped BSCCO-2212 sample, showing an area of  $56 \times 56$  nm and colour scale spanning the range  $20 \pm 64$  meV. The sample is slightly underdoped, with critical temperature of 79 K. Image reprinted from reference [167] with permission of Springer Nature, copyright 4421990094549.

- Finite-Size Effect (FSE)
- Electronic Inhomogeneitiy (INH)

When considering FSE, one assumes a physical limiting length  $L_{FSE}$  for the system which constrains the superconducting coherence length ( $\xi$ ). This cut-off of  $\xi$  could lead to a resistive tail in  $R_{\rm S}(T)$  below the theoretical  $T_{\rm BKT}$  at which  $\xi$  should normally diverge resulting in  $R_{\rm S}(T)$  dropping to zero [169]. In clean homogeneous superconductors, the limiting length should be about the physical size of the sample (typically tens of microns to millimeters). However, it has been recognized that experimentally measured resistive tails would require much smaller length of the order tens of nanometer. In this picture, the system is characterized by homogeneous domains of size  $L_{FSE}$ . Sample size, dimensional constraints induced by a magnetic field H, and other extrinsic factors that affect the dimension of these homogeneous domains define the cut-off value of  $\xi$  so that  $L_{FSE} = min[L_{size}, L_{H}...]$  [170, 171, 168]. It has been argued in this framework that disorder doesn't affect the universal behavior of the BKT transition although non-universal parameters like  $T_{\rm c}$  may be affected [168].

The other proposed scenario is a broadening of  $R_{\rm S}({\rm T})$  due to inhomogeneity of the superconducting condensate on the mesoscopic scale. This is a very intensely investigated and debated point in the physics of HTSCs, with some recent observations concerning the spatial dependence of the superconducting gap [172, 173].

In BSCCO-2212, Scanning Tunneling Microscopy (STM) revealed striking electronic inhomogeneity on the nanometer scale. This manifests itself as the spatial variation of both the local density of states and the superconducting energy gap [174, 175]. This inhomogeneity in BSCCO-2212 could be due to:



Figure 4.2: Comparison between the INH approach (left panel) and the FSE one (right panel). Image reprinted from ref. [140] with permission of APS, copyright RNP/18/SEP/007480.

- Inhomogeneous introduction of charge on the CuO<sub>2</sub> planes by oxygen dopants located in the BiO layer, resulting in poor screening of the charge potentials associated with the oxygen ions left in the BiO plane after doping [174, 167].
- Disorder-induced inhomogeneity with superconducting islands connected to nonsuperconducting regions [176].

Independently of the purported cause and the nature of the electronic inhomogeneity, all these studies show a spatial variation of the energy gap as seen through STM mapping. In slightly underdoped BSCCO-2212 for example, superconductivity is clearly granular in nature, with homogeneous superconducting domains of  $\sim 3$  nm, as shown in Fig. 4.1 from [167]. These studies point to inhomogeneous patchy electronic systems in HTSCs in general and BSCCO-2212 in particular as well as inhomogeneous superconductivity [141]. Within each domain, fluctuations modulate the divergence of the coherence length (intrinsic effects) which can eventually be further cut-off by the extrinsic effects previously discussed. However for global superconductivity a percolation threshold needs to be attained. The net result is a distribution of domains with a corresponding distribution of  $T_{\rm BKT}$  corresponding to coherence length divergence. This effect could substantially broaden the superconducting transition masking the expected sharp transition at  $T_{\rm BKT}$  [140].

As a conclusion to this discussion we show figure 4.2 from [140], which gives a synthetic view of two scenarios. The first one is the BKT+FSE approach already mentioned above, which provides for BKT fluctuations above  $T_{\rm BKT}$  and a tail coming from finite size effects below  $T_{\rm BKT}$ . The second scenario [140] allows for more complex behavior with GL fluctuations at temperatures higher than  $T_{\rm BKT}$ , but a narrow window ( $T_{\rm GL} - T_{\rm BKT}$ )



Figure 4.3:  $R_{\rm S}({\rm T})$  of device C, normalized to  $R_{\rm S}(120 \text{ K})$ . Thick lines indicate the most underdoped (UD, blue), the optimally doped (OP, green) and the most overdoped (UD, brown) curves.

near  $T_{\rm BKT}$  where BKT fluctuations occur. In this scenario the broadening below  $T_{\rm BKT}$  is generated by inhomogeneity.

# 4.2 Superconducting transition width dependence on electrostatic doping : Preliminary study

Before doing detailed analysis of the origins of the fluctuations and broadening of the superconducting transition, we start with a simple study, based on first determining the superconducting transition width for the five samples discussed in chapter 3 and subsequently probing its variation as a function of the electrostatic space charge doping.

In the following sections superconducting fluctuations, finite size effect and inhomogeneity, will be invoked through appropriate models applied to our transport data in the presence of varying doping, disorder and magnetic field.

In Fig. 4.3 the superconducting transition from the underdoped to the overdoped region is shown for device C (1.5 u.c.). A strong reduction of the transition width with doping is clearly visible. Since doping affects both the superconducting transition width and the normal state behavior, we first normalize each  $R_{\rm S}(T)$  curve by  $R_{\rm N}(T)$ , its normal state component, fitted by  $R_{\rm N}(0) + BT^{\rm m}$  in the overdoped region, or by  $R_{\rm N}(0) + aT - bT^2$  in the underdoped region.

To estimate an intrinsic superconducting transition width we must eliminate extrinsic contributions, which tend to broaden the transition either at the onset or near  $T_c$ . This is done using the normalized  $R_S(T)/R_N(T)$  curves by fitting a linear component to the transition and extracting two limiting temperatures  $T_h$  and  $T_l$  [141], corresponding to the 'intrinsic' onset and critical temperature as shown in Fig. 4.4.

Fig. 4.5 shows in more detail the normal state fitting of  $R_{\rm S}({\rm T})$  and the corresponding



Figure 4.4:  $R_{\rm S}(T)/R_{\rm N}(T)$  (with  $R_{\rm N}(T)$  normal state resistance ) in the proximity of the superconducting transition.  $R_{\rm N}(T)$  is determined as  $R_0 + BT^{\rm m}$  or as  $R_0 + aT - bT^2$  according to whether the device is overdoped or underdoped respectively. A linear component is fitted to the superconducting transition with  $T_{\rm h}$  and  $T_{\rm l}$  extrapolated as the intersection with the dashed green line and the x-axis respectively.



Figure 4.5: SCT analysis. Normal state fitting of  $R_{\rm S}({\rm T})$  characteristics and the corresponding  $R_{\rm S}(T)/R_{\rm N}(T)$  obtained, showing the low disorder (sample D) and high disorder (sample C) cases as example.

 $R_{\rm S}(T)/R_{\rm N}(T)$  obtained, by showing the low disorder and high disorder case as examples. The transition width normalized to the critical temperature is then approximated as  $\Delta T/T_{\rm c} \approx (T_{\rm h} - T_{\rm l})/T_{\rm l}$ . In conventional 2D superconductors,  $\Delta T/T_{\rm c} \simeq (\alpha_0/\xi)^2$  (where  $\alpha_0$  is the inter-atomic distance and  $\xi$  the coherence length) is of the order of 0.02 and the broadening of the superconducting transition is ascribed to Aslamazov-Larkin fluctuations [141]. As previously mentioned, fluctuation phenomena are prominent in cuprates, mostly due to the short coherence length and  $\Delta T/T_{\rm c}$  is expected to be higher.

In Fig. 4.6 we show the variation of  $\Delta T/T_c$  for each device as a function of doping p (holes/Cu). They are significantly higher than for a conventional 2D superconductors and decrease strongly with doping in the underdoped region. Notably, for sample D and E we measured  $\Delta T/T_c$  as low as 0.07-0.08, close to the values measured in clean bulk BSCCO-samples (~ 0.05) [177] which is a further proof of the high quality and low disorder of these samples.

Concerning the other samples, devices A (2.5 u.c.) and C (1.5 u.c.) have a higher  $\Delta T/T_c$ . Device C has the lowest mobility and is probably the most disordered while the thickest device A can be expected to have a gradient in the doping over the total thickness, as discussed in section 3.2.5 of chapter 3. Thus extrinsic factors like disorder and inhomogeneity can lead to an increased  $\Delta T/T_c$ . However in all devices  $\Delta T/T_c$  decreases strongly with doping until the optimal doping is attained and then remains almost unchanged. This can be ascribed to a change in the inhomogeneity landscape [169, 168] which in turn increases the characteristic dimension of homogeneous superconducting domains and the spatial coherence of the superconducting state.

# 4.3 Analysis

In this section we present a more detailed analysis based on theoretical approaches and examine the adequacy and limitations of these when confronted with our experimental data.

In two dimensions, following BKT theory, the temperature dependence of resistivity near the transition or the paraconductivity due to vortices [178, 140], is related to the correlation length  $\xi(T)$  and the density of free vortices  $n_F$  by the following relation:

$$\frac{R(T)}{R_{\rm N}} = 2\pi\xi_0 n_F = \left(\xi/\xi_0\right)^2 \tag{4.2}$$

where  $\xi_0$  is the zero temperature coherence length, assumed equal to the vortex core radius. In equation 4.2,  $\xi(T)$  is calculated within BKT theory, and the Berezinskii-Kosterlitz-Thouless critical behavior is characterized by the following temperature dependence of  $\xi$  above  $T_{\rm BKT}$ :

$$\xi(T) = \xi_0 \exp[2\pi/(bt^{1/2})], \qquad t = |T/T_{\rm BKT} - 1|$$
(4.3)

where b is a non-universal constant related to the vortex core energy  $E_c$  [179, 180, 181]:



Figure 4.6: Doping dependence of the normalized superconducting transition width  $\Delta T/T_c$ , for varying thickness and disorder. Error bars take into account uncertainty of determination of transition width. The bright blue area highlights the underdoped side, where most of the reduction of  $\Delta T/T_c$  occurs, upon increasing charge density. The dashed black line is the magnitude of the superconducting transition width of a bulk sample at its optimal doping level, calculated from the data of ref. [177] and shown as a reference of minimum SCT-width in BSCCO-2212 system.

$$b = f[E_c/k_B T_c] \tag{4.4}$$

 $E_c$  can be considered in terms of the energy required to create a vortex core [182, 183, 184, 141], whereas b is related to the difference between  $T_{\text{BKT}}$  and  $T_{\text{GL}}$  by the following relation [140]:

$$b \simeq 2\alpha \sqrt{T_{\rm c}}$$
 (4.5)

where  $T_{\rm c} = T_{\rm GL}/T_{\rm BKT} - 1$  and  $\alpha$  is a scaling factor relating the vortex-core energy to the superfluid stiffness J:

$$E_c(T) = \frac{\alpha \pi^2}{2} J(T) \tag{4.6}$$

The superfluid stiffness J is the energy scale associate to the 2D superfluid density  $n_s^{2d}$ :

$$J(T) = \frac{\hbar n_{\rm s}^{2d}(T)}{4m^* k_B} \tag{4.7}$$

Combining eq. 4.5 with eq. 4.6 and eq. 4.7 we get:

$$b \simeq \frac{4}{\pi^2} \frac{E_c}{J} \sqrt{T_c} = C \frac{E_c}{n_s^{2d}} \sqrt{T_c}$$

$$\tag{4.8}$$

where C is a constant. Therefore it turns out that b, which is proportional to  $T_{\rm GL} - T_{\rm BKT}$ , is also proportional to the ratio  $E_c/n_s^{2d}$ .

It has been proposed that BKT critical behavior should be explicitly observable, since [185, 169]:

$$(dlnR/dT)^{(-2/3)} = (2/b_{\rm R})^{(2/3)}(T - T_{\rm BKT})$$
(4.9)

where  $b_{\rm R} = (4\pi\sqrt{T_{\rm BKT}})/b$ . An example of this scaling for data from a 1 u.c. BSCCO-2212 device at its optimal doping ( sample D,  $T_{\rm c(opt)}=81$  K) of this work, is shown in Fig. 4.7. Consistency of the data with BKT fluctuations should be seen if a linear dependence is detected, even over a range of a few Kelvin [48], as seen here between 89 and 92 K. In this analysis, the deviation from the linearity below 89 K may be ascribed to finite-size effects [169]. However similar analysis of our data always results in the extraction of unphysical parameters and incoherent fitting at higher temperatures. For example, from the data shown in Fig. 4.7, we extract a value of  $b_R = 1.45$  and, using eq. 4.9 we find b=80.3. Consequently we extract an impossible value of  $T_{\rm GL} = 10^7$  K. This is probably due to neglected effects that can have a preponderant bearing: the contribution of AL fluctuations, of finite size, or of inhomogeneous superconductivity.

In the following, we use theoretical approaches that try to describe paraconductivity by taking into account some or all of these contributions and confront them with our BSCCO-2212 transport data.

We first start by considering the Halperin-Nelson (HN) interpolation formula [186] between AL (GL) and BKT fluctuations [140, 141] for  $T > T_{\text{BKT}}$ . Some minimum finite length scale in the sample is assumed to prevent  $\xi$  increasing beyond a cut-off value and giving rise to a resistive tail when  $T \leq T_{\text{BKT}}$ . Under this assumption, the paraconductivity can be written as [140]:

$$\frac{R_{\rm S}(T)}{R_{\rm N}} = \frac{1}{1 + (\xi/\xi_0)^2} \tag{4.10}$$

where  $\xi/\xi_0$  in the Halperin-Nelson interpolating scheme assumes the form:

$$\frac{\xi}{\xi_0} = \frac{2}{A} \sinh \frac{b}{\sqrt{t}} \tag{4.11}$$

with  $t = T/T_{BKT} - 1$  and A a fitting parameter of order 1 [140]. Therefore on the assumption of finite-size effect provoking a cut-off in  $\xi$  we have:

$$\frac{R_{\rm S}(T)}{R_{\rm N}} = \frac{1}{1 + (\frac{2}{A}sinh\frac{b}{\sqrt{t}})^2} \qquad T > T_{BKT}$$
(4.12)

$$\frac{R_{\rm S}(T)}{R_N} = \frac{1}{1 + (\frac{L}{f_{\rm C}})^{\frac{2|t|}{T_{\rm C}}}} \qquad T \le T_{\rm BKT}$$
(4.13)

where L is the size of homogeneous domains in the system [168].



Figure 4.7: BKT fluctuations exploration by dynamic scaling of the sheet resistance in two dimensions.  $(d\ln R/dT)^{-2/3}$  versus T of the curve corresponding to the optimal doping level of sample D  $(R_S/R_N \text{ vs } T \text{ characteristic reported in the inset})$ . The blue line shows the consistency of data with the linear BKT relationship (4.9) between 92 and 89 K.  $b_R$  is determined from the slope of this line, that is  $(2/b_R)^{(2/3)}$ , whereas  $T_{\text{BKT}}$  is the temperature where  $(d\ln R/dT)^{-2/3}=0$ .

In Figure 4.8 we show fits to experimental data using as prototypical again the one corresponding to the optimal doping of sample D (1 u.c.,  $T_c(opt)=81$  K). The same analysis have been done on a few other samples to ascertain the results. These fits correspond to four different hypotheses:

- 1. HN: Standard Halperin-Nelson interpolation (eq. 4.11)
- 2. HN\*: Best-fit Halperin-Nelson (which results in unphysical parameters A and b in eq. 4.11
- 3. HN+FSE: Halperin-Nelson and finite-size effect (eq. 4.12 and 4.13)



Figure 4.8: Sheet resistance  $R_S$  normalized to its normal state  $R_N$  fitted using the HN formalism with additional contributions (see text). Data (black) are fitted by: **a**, standard HN (magenta); **b** best-fit HN or HN\*, with unphysical parameters (yellow); **c** HN+FSE ( $L/\xi = 1$ , red) which includes a cut-off at the coherence length; **c**, HN+INH (cyan) which supposes inhomogenous superconductivity.

### 4. HN+INH: Halperin-Nelson and electronic inhomogeneity (eq. 4.14, discussed below).

Each panel of fig. 4.8 shows a comparison between the data (black curves) and the fits (colored curves), with the residuals Err = Data - Fit reported in the inset of each panel in the corresponding color assigned for each fit.

In figure 4.8a the magenta curve represents the standard HN case with no additional contribution. The  $T_{\rm BKT}$  transition temperature is determined by the intersection of the fit with the x-axis (T~ 86 K), namely the temperature at which the BKT transition is supposed to occur in the absence of other effects. In this case this temperature coincides with the  $T_{\rm BKT}$  extracted in figure 4.7 where only BKT fluctuations were considered. AL fluctuations thus do not significantly affect the BKT transition since they account for the higher temperature paraconductivity. However, the long low temperature tail of  $R_{\rm S}$  is completely unexplained by this approach.

A better fit can however be found by allowing parameters to vary at will and we



Figure 4.9: INH fit results, example.  $R_{\rm S}/R_{\rm N}$  (right axis) and  $P(T_{\rm BKT})$  (left axis) as a function of T. Data are shown by the black bold circles whereas the HN+INH fit in cyan. This fit corresponds to the gray distribution (eq 4.14). The green curve is the standard HN transition corresponding to the 'mode' (green star), whereas the blue and red curves are the HN transitions corresponding to the blue and red stars on  $P(T_{\rm BKT})$  (HWHM of the distribution)

find b=1.2 and A=20. Both these values are about one order of magnitude higher than 'reasonable' values for these parameters [184, 140]. The residuals shown in the inset of figure 4.8b (yellow curve, HN<sup>\*</sup>), still show considerable structure  $\pm 2\%$ .

Finite-size effect are then considered as an additional contribution to HN interpolation (eq. 4.12 and 4.13). To approach experimental data we are forced to adopt the radical assumption that  $L/\xi_0 \simeq 1$ . This means homogeneous domains as small as the vortex core radius  $\xi_0$ , which is not very reasonable. However we keep in mind that in BSCCO-2212 homogeneous domains of only a few nm have been measured in STM experiments [167, 175]. The corresponding fit is shown in figure 4.8c by the red curve which results in a sharp transition and a pronounced tail at low temperatures. However the agreement is not satisfactory as seen in the inset of figure 4.8c, where substantial structure (as high as 10%) is seen in the residuals.

On this basis we find that bare HN interpolation or HN interpolation combined with finite-size effects is not sufficient to explain experimental data. On the other hand several experiments, in particular STM maps of spatial fluctuations of the energy gap  $\Delta$  and granular character of superconductivity in BSCCO-2212 [167, 175, 174] point to inhomogeneous superconductivity as proposed in previous works [140, 141].

We thus make the hypothesis of an inhomogeneous BKT transition due to a spatial distribution of superfluid density and hence varying  $T_{\rm BKT}$ . We remark that assuming a variation of  $T_{\rm BKT}$  is equivalent to considering a variation of the superfluid stiffness J, which in turn means variation of  $n_{\rm s}^{2D}$  (eq. 4.7), that is coherent with the experimental

STM observation of spatial-varying energy gap.

We start with the HN formalism (eq.4.11) for  $\xi(T)$  in eq.4.10 including GL and BKT fluctuations. The inhomogeneity leads to a statistical distribution of such transitions, each corresponding to a local  $T_{\text{BKT}}$ . The final  $R_{\text{S}}(T)$  corresponds to a sum of these, weighted by the statistical distribution  $P(T_{\text{BKT}})$ .

$$\frac{R_{\rm S}(T)}{R_{\rm N}} = \int_{T_{BKT_m}}^{T_{BKT_m}} \frac{P(T_{\rm BKT})}{1 + (\frac{2}{A}sinh\frac{b}{\sqrt{t}})^2} dT_{\rm BKT}$$
(4.14)

where  $T_{BKT_M}$  and  $T_{BKT_m}$  are the maximum and minimum  $T_{BKT}$  of the distribution. Strictly speaking the parameter *b* should vary with the  $T_{BKT}$  whereas in this procedure it remains fixed for technical reasons and is identified as the *b* corresponding to the 'mode' of the  $T_{BKT}$  distribution.

The functional form of  $P(T_{BKT})$  is of course important. Gaussian distributions quite accurately reproduce the  $R_{\rm S}(T)$  curves for varying doping and disorder but they fail to reproduce the pronounced tail which appears with magnetic field. Moreover Gaussian distributions do not have a finite maximum critical temperature which is unphysical. Bi-modal distributions have also been considered in previous work [141], so as to reproduce long-tailed behavior but more importantly non-zero resistance states occurring in superconductor-insulator transitions. While these distributions can account for very long tails, they also introduce more parameters in the fitting procedure.

The Gamma distribution chosen in this work for  $P(T_{BKT})$  combines a small number of fitting parameters with a possibility for asymmetry to account for resistive tails:

$$P(T_{\rm BKT}) = \frac{(T_{BKT_M} - T)^{k-1} e^{\frac{-(T_{BKT_M} - T)}{\theta}}}{\theta^k \Gamma(k)}$$
(4.15)

where k and  $\theta$  control the shape and the scale, respectively. Depending on the values of these two parameters the distribution assume high or low symmetry with Gaussian and exponential character as extreme cases. In particular the skewness and 'mode' can be determined directly from k and  $\theta$ :

$$mode = (k-1)\theta \tag{4.16}$$

$$skewness = 2/\sqrt{k} \tag{4.17}$$

We show an example of a fit with this distribution in figure 4.9 (cyan curve, left axis) where all the curves are normalized by the normal state. A very good correspondence

with the experimental superconducting transition is obtained by using the  $P(T_{\rm BKT})$  distribution shown in grey (right axis). To illustrate the process we also show in the figure the HN transitions at three different  $T_{\rm BKT}$ . These are incorporated in the fit with the weights given by  $P(T_{\rm BKT})$ . In Fig. 4.9 the green curve is the HN transition corresponding to the 'mode' (green star) or maximum of  $P(T_{\rm BKT})$  weighted by ~0.25 in the fit, whereas the blue and red curves are the HN transitions corresponding to the blue and red stars on  $P(T_{\rm BKT})$ , weighted by ~0.125 in the fit .

In the following we show the extracted local  $T_{\rm BKT}$  distributions using the fitting procedure and formalism explained above for varying charge carrier density (doping), disorder and magnetic field.

Let us note as a preamble that by using a  $P(T_{BKT})$  distribution, it is quite natural that we find a better fit to the data compared with a single  $T_{BKT}$ . However apart from a better fit to experimental data this procedure firstly allows us to maintain reasonable, physical values for fitting parameters; secondly it allows us to make some conclusions about the nature of the superconducting transition in BSCCO-2212 in two dimensions and its variation with doping, disorder and magnetic field; thirdly it is based on a plausible hypothesis of inhomogeneity, observed in other experiments and which it vindicates *a posteriori*. Most importantly, though bulk BSCCO-2212 is known to be highly anisotropic, the 2D formalism can be applied here without any reserves because our samples *are* perfectly 2D. This allows us to obtain physical parameters related to superconductivity, and their variation, using the phase transition formalism in two dimensions. However these can be obtained in a reliable manner only if the formalism describes data sufficiently well, or in other words if we are able to fit all our data with the same approach.

We also point out that though we obtain a  $P(T_{BKT})$  distribution, this cannot be directly linked to a spatial distribution of local  $T_{BKT}$ . Indeed a 2D grid of resistor network with randomly distributed  $T_{BKT}$  (RRN)corresponding to an extracted  $P(T_{BKT})$  would almost certainly *not* reproduce the measured  $R_S(T)$ . The resistivity obtained as a solution of the RRN in the effective-medium approximation (EMA) has no tails, unless one assumes that a fraction of the system is not SC [141]. This is true even if the inhomogeneities have no space correlations at all.

To solve the problem of the "missing" tails, inhomogeneities with space structures have been proposed and explored in previous works[141]. Furthermore to get such correspondence, very specific spatial distributions and percolation theory would need to be invoked as has been done for example in [187] where it has been noted that percolation of superconducting droplets in the presence of quenched disorder could produce observed broad transitions. In this picture superconductivity spreads topologically as temperature is lowered and macroscopic superconductivity sets in as superconducting droplets percolate.



Figure 4.10: Temperature dependence of the superconducting transition of 2D BSCCO-2212 as a function of : **a**, Doping. Charge density is modulated by space charge doping for sample D (1 u.c.), **b** Disorder. Varying disorder corresponds to samples with comparable thickness (1-1.5 u.c.) but different resistivity at 300 K, **c** Magnetic field. Varied from 0 to 2 T for sample D (1 u.c.). The bold blue curve shown in each panel corresponds to the optimal doping level of sample D (1 u.c.) at zero magnetic field.

# 4.4 The 2D superconducting transition with varying doping, disorder and magnetic Field

Figure 4.10 shows some specific cases picked from the general discussion which follows below, to illustrate the variation of the superconducting transition normalized at T = 100 K as a function of carrier density, disorder and magnetic field. The bold blue curve shown in each panel corresponds to the optimal doping level of sample D (1 u.c.,  $T_c=81$  K) at zero magnetic field. The variation as a function of carrier density and magnetic field are shown for this low disorder (high mobility) sample. The variation shown as a function of disorder includes three other BSCCO-2212 samples with comparable thickness (1-1.5 u.c.) at optimal doping ( $\sim 0.16$  holes/Cu), but different resistivity measured at 300 K (4-25 k $\Omega$ ), and critical temperatures at optimal doping  $T_{\rm c}(p_{\rm opt})$  varying between 81-51 K. We note some trends that can be detected in these and which will be analysed and discussed more in detail in the following sections. Figure 4.10a shows the evolution of the superconducting transition as doping is increased from optimal to considerably overdoped.  $T_{\rm c}$  decreases but the width of the transition does not vary perceptibly in this overdoped region. We will see below that this is not true in the underdoped region of the phase diagram. Figure 4.10b, where the doping is always optimal but disorder varies, shows that  $T_{\rm c}$  decreases with increasing disorder and the width of the transition increases as well. Finally in Figure 4.10c, as the applied magnetic field is increased, the resistive tail increases sharply but the onset of the transition is not visibly affected. In the following sections these trends will be confirmed and to some extent quantified by using the formalism described above.

# 4.5 **Results and Discussion**

### 4.5.1 Doping

We first discuss the variation of the superconducting transition with carrier density, obtained by space charge doping as seen in the sheet resistance normalized to 100 K. Figure 4.11a (data already seen in Figure 4.10a) shows the evolution of the superconducting transition in the low disorder sample D (1 u.c.,  $T_{c(opt)}=81$  K) as doping is increased from optimal to considerably overdoped. Figure 4.11b shows similar data for the high disorder sample C (1.5 u.c.,  $T_{c(opt)}=51$  K) for doping varying from the underdoped to the overdoped region. The doping values indicated are extracted from the empirical formula [26] as described in chapter 3.



Figure 4.11: Superconducting transition dependence on charge carrier density. Sheet resistance normalized to its value at 100 K for **a**, sample D and **b** Sample C. The corresponding  $P(T_{\text{BKT}})$  distributions obtained from the fit (eq.4.14), are shown in figure **c** and **d**, respectively.

Figures 4.11c and 4.11d show the  $P(T_{\rm BKT})$  distributions obtained from the fits as previously explained. These help us to quantify the visual observations made in the earlier section. In Figure 4.11d, we see that as doping increases from underdoped to overdoped, the maximum of the  $P(T_{\rm BKT})$  distribution follows the trend for  $T_{\rm c}$ , increasing then decreasing. However the width of the distribution decreases until the optimal



Figure 4.12: Superconducting transition dependence on disorder. (a), Normalized sheet resistances vs temperature of 5 different sample with varying resistivity at 300 K. The dashed curve corresponds to a 5-u.c.-thick sample we use as a reference for minimum disorder case. (b), corresponding  $P(T_{\rm BKT})$  distributions determined by our fits (eq.4.14).

doping and then remains constant in the overdoped state. This is confirmed in Figure 4.11c where doping is varied form optimal to overdoped in the low disorder sample without significant change in the width. It can be noted that the width of the  $P(T_{\rm BKT})$  is always bigger in the high disorder sample and the distributions are slightly more asymmetric indicating a bigger resistive tail. The remarkable change in width of the local  $T_{\rm BKT}$  distributions over the underdoped state shows that in 2D BSCCO-2212 there is considerable local inhomogeneity in the underdoped region and that electrostatic doping strongly diminishes this inhomogeneity as proposed by Schneider et. *al* [169] for the case of 2D electron gas at the LaAlO<sub>3</sub> SrTiO<sub>3</sub> interface. A different way to see this is that inhomogenity is triggered by disorder and for a fixed amount of intrinsic impurities, the decreasing of the charge density induces an effective increase of the disorder strength, due to reduced screening.

Chemical inhomogeneity and strong electrostatic-potential variation have been observed in BSCCO-2212 near the Mott-insulator phase. This can cause inhomogeneous carrier density in the CuO<sub>2</sub> planes and introduce disorder [40, 174, 167]. Thus the narrowing of the  $P(T_{\rm BKT})$  distribution on increasing hole doping can be explained by the enhancement in the spatial uniformity of the electrostatic potential (reduction of electronic inhomogeneity) whereas the shift towards higher temperature would reflect the change of the 2D superfluid density  $n_{\rm s}^{2d}$ .

#### 4.5.2 Disorder

Figure 4.12a shows the temperature dependence of the sheet resistance at the optimal doping normalized to the 100 K value for 4 samples (1-1.5 u.c.). These four samples show

different resistivity at 300 K, ranging from  $4.9 \times 10^{-4} \ \Omega \cdot cm$  to  $26.2 \times 10^{-4} \ \Omega \cdot cm$ . Since the carrier density is the same, differences in resistivity are due to different mobility which is a measure of the level of disorder. Increasing disorder lowers  $T_c$  from 81 K down to 51 K. However the width of the transition is also noticeably affected. The extracted  $P(T_{BKT})$  distributions are shown in Figure 4.12b. Clearly, with increasing disorder the distribution shifts to lower temperatures (corresponding to lower  $T_c$  and probably to a reduced effective superfluid density) and widens at the same time (corresponding to an increase in inhomogeneity).

STM experiments as well as calculations agree in finding strong spatial fluctuations of the amplitude of the local superconducting order parameter  $\Delta$  in the presence of disorder [188]. Note that here the order parameter is the gap function which is however related to the GL order parameter defined in chapter 1. For increasing disorder the spatial distribution  $P(\Delta)$  of the order parameter is seen to broaden considerably. This spatial inhomogeneity of the order parameter has been interpreted as Josephson coupled superconducting islands in a non-superconducting background [173]. Moderate disorder will suppress coherence between these islands and increase inhomogeneity [176] while high disorder can cause a substantial reduction of the superfluid stiffness lowering the critical temperature, eventually until the insulating state [189]. It should however be pointed out that in microscopic theory and mean field approaches, spatial variations of the order parameter can only be very smooth [189, 190].



#### 4.5.3 Magnetic Field

Figure 4.13: Superconducting transition dependence on magnetic field. Normalized sheet resistances vs temperature of (a) 1-u.c.-thick BSCCO-2212 (sample D) and (b) a 5-u.c.-thick one, at varying magnetic field H. (c), (d), Corresponding  $P(T_{\text{BKT}})$  distributions determined by our fits (eq.4.14).

The superconducting transition in the presence of a magnetic field in a 2D superconductor like 1 u.c. BSCCO-2212 is directly relevant to the vortices of the 2D phase transition [151, 160, 159]. Vortex-antivortex pairing drives the system to a superconductor state whereas free vortex motion causes dissipation and entropy flow, thus suppressing superconductivity. In two dimensions, free vortices can be thermally-activated above the Berezinskii-Kosterlitz-Thouless critical temperature  $T_{\rm BKT}$  or magnetically-activated by the application of external H field [191, 192]. Furthermore it is well-known that in cuprates and 2D superconductors, disorder induced pinning can strongly affect vortex dynamics and has been used as a strategy to limit this dynamics and hence dissipation [193]. The interplay of these phenomena can lead to complex and rich H vs T vortex phase diagrams [9].

Here we focus on  $R_{\rm S}(T)$  as a function of an applied perpendicular magnetic field H between 0 and 2 T. Figure 4.13a shows the effect of H on the low disorder 1 u.c. sample D. Increasing the magnetic field induces a strong resistive tail in the transition. This dissipative state is known as the mixed state due to the presence of different dissipation regimes [177, 194]. The  $P(T_{\rm BKT})$  distributions extracted for this data are shown in Figure 4.13b. In line with our earlier observation we find that the maximum of the distribution is nearly constant, decreasing very slightly with the magnetic field. On the other hand the distribution becomes increasingly asymmetric with increasing magnetic field mirroring the dramatic decrease in  $T_c$ . These tails of the  $R_S(T)$  due to applied perpendicular magnetic field is strictly related to vortex-motion dissipation as previously mentioned. Furthermore, in the presence of electronic inhomogeneity the magnetic field might act differently on each homogeneous domain. In this picture, the increase of the tails for increasing H-field would be justified by a bigger decrease of the critical temperatures corresponding to domains of the system with lower superfluid density  $n_s^{2d}$ . This is supported by recent experiments on YBCO samples, where a strong dependence of the upper critical field  $H_{c2}$  on doping has been observed [144].

Considerable research has been generated with the aim of investigating this dissipation regime in terms of vortex physics. The mixed state and its evolution as a function of applied magnetic field and temperature is related to the structure and dynamics of vortices in the material which can vary from an ordered lattice to viscous steady state flow, passing through activated regimes [195, 196, 197, 198?]. These regimes determine the dissipation and the transition resistance and considerable effort has been spent to investigate methods to suppress dissipation which impedes the use of these materials in technological applications. One solution is for example to use pinning centers introduced by defects which pin vortices and prevent a dissipating flowing regime [191, 9]. In 3D materials these defects need to be columnar and parallel to flux lines formed by the magnetic field inside the sample so as to pin them [199]. They are often introduced using heavy ion irradiation [200, 201]. It can therefore be interesting to study the case of perfectly 2D sample where in principle every defect is a columnar defect. However in the present work the magnetic field at our disposal is limited to 2 T so that we use and consider these measurements as a preliminary study. Figure 4.14 shows magnetoresistance measurements  $(R_{\rm S} \text{ vs } H)$  carried out on the 1 u.c. sample D in order to investigate these dissipation states in 2D BSCCO-2212. The dependence on magnetic field of the



Figure 4.14: Magneto-transport and vortex phase diagram of 2D BSCCO-22212. **a**, Dependence of the sheet resistance on perpendicular magnetic field for varying temperature (80-68 K). **b** the 77 K curve of panel **a** shows an example of extraction of the characteristic fields  $H_{irr}, H_K, H_{c2}$  in the way explained in the text. **c** Vortex phase diagram with vortex solid (VS), activated vortex liquid (VL<sub>act</sub>) and diffusive vortex liquid VL<sub>diff</sub> phases delimited by the characteristic fields.

sheet resistance is shown in Fig. 4.14a at different temperatures, ranging from 68 K to 80 K.

By increasing H, the vortex solid phase undergoes a melting transition at the irreversibility field  $H_{irr}$  associated with the depinning of single flux lines [202, 203].  $H_{irr}$ separates the superconducting vortex solid phase to the vortex liquid one [195] wherein vortex motion causes dissipation and resistance, thus destroying superconductivity. This dissipating phase is the vortex liquid state, where two different dissipation regimes or vortex phases are known to exist for cuprates [195, 196, 197, 198]: the activated regime, occurring in a range of low field and temperature where resistivity shows a strong temperature dependent activation energy U(T), and the diffusion-dissipation state in a high field and high temperature regime. A characteristic field  $H_K$  separates these two liquid phases [204, 205].

The change in the resistivity as a function of magnetic field is used to identify these fields and the boundaries between these three states and probe the vortex phase diagram in cuprates such as YBCO, LSCCO and BSCCO [194, 195?, 206, 207]. In figure 4.14b the determination of these three characteristic fields is shown. The  $R_{\rm S}({\rm H})$  characteristic corresponding to the curve measured at 77 K is considered as an example. We determine  $H_{\rm irr}$  as the field at which  $R_{\rm s}$  starts to be  $\neq 0$ ,  $H_{\rm K}$  as the field above which the sheet resistance shows a linear dependence (magenta line fit) on H [204, 195] and  $H_{\rm c2}$  as the field above which a downward deviation from this linearity is observed [194, 144]. The resulting phase diagram is reported in figure 4.14c where the characteristic fields  $H_{irr}$ ,  $H_K$  and  $H_{c2}$  separate the vortex solid (V<sub>S</sub>), the activated vortex liquid (VL<sub>act</sub>) and the diffusive vortex liquid (VL<sub>diff</sub>) phases [194, 144].

Our data, even though in a limited range of high temperature and low magnetic field, seems to confirm the existence in our 2D samples of the same different dissipation regimes or vortex phases observed in bulk BSCCO-2212 compounds. It would in effect be interesting to examine, firstly the coherence of these results in extended measurements at low temperature and high field, and secondly, if the resulting phase diagram in 2D could be different from the one found in 3D samples.



4.5.4 Quantitative analysis and parameter extraction

Figure 4.15: Parameter extraction. Skewness (left-y-axis, empty symbols) and Asymmetry (right-y-axis filled symbols) of the  $P(T_{\text{BKT}})$ 's distributions as a function of (a) doping, (b) disorder and (c) magnetic field. 'mode' and  $T_{\rm c}$  dependence on (d) doping, (e) disorder and (f) magnetic field.

Here we discuss the parameters extracted from (eq.4.14) from all the data analysed in the earlier sections. Fig. 4.15a, Fig. 4.15b and Fig. 4.15c, show the extracted  $P(T_{\text{BKT}})$ distribution skewness (left-y-axis, empty symbols) and asymmetry (right-y-axis filled symbols) and their dependence on doping (distributions of Fig. 4.11c), disorder (distributions of Fig. 4.12) and magnetic field H (distributions of Fig. 4.13b), respectively. The 'skewness' is determined by eq.4.17 from the parameters k and  $\theta$  of the gamma distribution (4.15) and its absolute value gives a measure of the asymmetry of the distribution. We define 'Asymmetry' by the ratio between the Half-Width at Half-Maximum (HWHM) on the low temperature of a  $P(T_{\rm BKT})$  distribution, and the HWHM on the high temperature so that: HWHM<sup>-</sup>/HWHM<sup>+</sup> = Asymmetry. With this definition, a symmetric curve has an asymmetry of 1 and a very tailed curve an asymmetry > 1. The variation as a function of carrier density and magnetic field are for the 1 u.c. low disorder sample D. The variation shown as a function of disorder includes three other BSCCO-2212 samples with comparable thickness (1-1.5 u.c.) and optimal doping (~ 0.16 holes/Cu), but different resistivity measured at 300 K (4-25 k\Omega), and critical temperatures at optimal doping  $T_{\rm c}(p_{\rm opt})$  varying between 81-51 K.

In Fig. 4.15a and Fig. 4.15b we observe that neither doping nor disorder change the symmetry of the distributions which stay symmetric with skewness close to 0 and asymmetry close to 1. However when the magnetic field is varied a substantial increase of the skewness and asymmetry for increasing H is observed. In figure 4.15d, 4.15e, 4.15f, the corresponding 'mode' and the critical temperature  $T_c$  are shown. The 'mode' is the temperature corresponding to the maximum of the  $T_{BKT}$  distribution, whereas  $T_c$ refers to the lowest critical temperature of the distribution below which the measured resistivity is zero. The difference between these two is proportional to the width of the distribution and that of the superconducting transition.

Figure 4.15d shows that on the overdoped side of the superconducting dome, the distribution rigidly shifts with doping to lower temperatures without changing shape or width. In figure 4.15e and 4.15f we can see that both disorder and magnetic field lower  $T_c$  in a similar fashion. While the 'mode' of the distribution also decreases with disorder it is nearly independent of the magnetic field indicating that the onset of pairing is barely altered.

We finally show the parameter b obtained from the fits when using eq. 4.14. Figure 4.16 shows the variation of b on doping, disorder and magnetic field. A monotonic decrease of b is found as the samples are tuned from the underdoped region through the optimal doping to the overdoped region. This behavior is similar to the one found for the superconducting transition width in Fig. 4.6. For example, the sample corresponding to higher disorder shows a higher value of b as well as a higher width. However the width in Fig. 4.6 does not decrease appreciably beyond the optimal doping, while b shows continuous decrease.

Figure 4.16b confirms the earlier observation that increasing disorder leads to a higher value of b. Figure 4.16c shows that the magnetic field increases the resistive tail rather than broadening the transition as such, since b is constant for low field.

From a theoretical perspective, b is related to the ratio between the vortex core energy  $E_{\rm c}$  and the superconducting stiffness J through eq. 4.8 as discussed in section 4.3 and



Figure 4.16: Dependence of the parameter *b*. **a** *b* as a function of doping in four different sample with thickness of 1-1.5 u.c. and varying maximum critical temperature  $T_c(opt)$  (indicated in brackets). **b**, Dependence of *b* on disorder for the distributions of Fig. 4.12**b**. **c**, Dependence of *b* on magnetic field for the distributions of Fig. 4.13**b** 

is proportional to the ratio  $E_{\rm c}t_c/J$ . This is a complex dependence and determining  $E_{\rm c}$  and J independently would be of great interest, though not possible with our data. These quantities are in principle accessible by measuring the temperature dependence of the magnetic penetration depth  $\lambda$  [183, 184], which is typically done by inductance measurement.

### 4.6 Conclusions

In conclusion, we have investigated superconductivity in two-dimensional BSCCO-2212 samples by comparing our data with different theoretical approaches and using the appropriate formalism for fitting experimental data to extract relevant parameters. Doping, disorder and magnetic field have been varied in order to disentangle intrinsic and extrinsic effects that are known to modify the superconducting transition in 2D systems.

We first consider the hypothesis of homogeneous macroscopic superconductivity in two dimensions with either Berezinskii-Kosterlitz-Thouless (BKT) or Berezinskii-Kosterlitz-Thouless as well Aslamazov-Larkin (AL) fluctuations occurring at  $T > T_{\rm BKT}$ . Consistency with BKT fluctuations is found in a range of a few K above  $T_{\rm BKT}$  with AL fluctuations found over a larger and higher temperature range. However the experimental superconducting transition is not well described even after considering finite-size effects which can limit the divergence of the coherence length. We therefore consider a phenomenological approach and inhomogeneous superconductivity within the Halperin-Nelson formalism with a distribution of  $T_{\rm BKT}$ . The functional form is taken to be the gamma distribution which allows for a possible asymmetric character for the distribution
of  $T_{\rm BKT}$ . We can thus reproduce our measured superconducting transitions, notably the width and the tail, when doping, disorder or magnetic field were varied. Finally we extract parameters related to this inhomogeneous superconductivity in 2D-BSCCO.

## Chapter 5 Conclusions and perspectives

In this thesis we investigated the physics of two-dimensional  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  using innovative techniques developed in-house for sample fabrication and electrostatic doping. We first focused on establishing a comprehensive temperature vs doping phase diagram and subsequently analysed the 2D character of superconductivity with the aim of investigating the role of fluctuations.

We began by fabricating ultra-thin superconducting BSCCO-2212 devices on glass substrates using anodic bonding, an original method of exfoliation developed in our laboratory for preparing high quality 2D crystals from layered bulk materials. Flakes with thickness ranging from one to few unit cells and lateral dimensions of the order of 100  $\mu$ m were then contacted in a van der Pauw configuration by thermally evaporating gold through shadow stencil masks previously aligned on the samples. This allowed us to avoid chemical pollution and surface contamination from standard lithography techniques, which in our experience can irreversibly degrade the quality of BSCCO-2212 2D crystals. Transport measurements showed superconductivity with critical temperatures as high as 80-84 K for the as fabricated 1-unit-cell-BSCCO-2212 devices, making them perfect candidates for electrostatic doping experiments.

We applied a highly efficient electrostatic doping technique which we call space charge doping to these ultra-thin superconducting BSCCO-2212 devices. Starting from the nominal optimal doping we obtained carrier density variations of the order of  $10^{15}$  cm<sup>-2</sup>, as estimated by Hall measurements, both in the overdoped and in the underdoped regions, and variations in critical temperatures up to 33 K. This was the first time that ultra-high electrostatic doping was applied to BSCCO. In particular we measured sheet resistance from low temperature up to 330 K. This allowed us to not only extract characteristic temperatures including the critical temperature related to superconductivity, but also to determine normal state parameters related to the pseudo-gap and the Fermi liquid phases requiring measurements up to room temperature and above. These measurements and the subsequent analysis allowed us to construct the first comprehensive phase diagram in 2D Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+x</sub> using the electrostatic effect. Furthermore we showed and discussed the effect of disorder in suppressing  $T_c$  and shrinking the superconducting dome, hence adding a further dimension to the phase diagram. In order to identify the critical doping regime in 2D-BSCCO-2212, we explored the phase diagram for low disorder 1 u.c. samples by fine-tuning the carrier density in the slightly overdoped regime. By searching for the region in the normal state, above the superconducting dome, where the pseudogap and strange metal phases appear to meet, we found this critical region where a Lifshitz quantum phase transition is expected to occur, to be confined in the range  $\sim 0.181 - 0.195$  holes/Cu.

Finally we took a closer look at the superconducting transition in these two-dimensional BSCCO-2212 devices, by fitting our data with different theoretical approaches accounting for superconducting fluctuations. Doping, disorder and magnetic field were varied in order to disentangle intrinsic and extrinsic effects, that modify the superconducting transition in 2D.

We first considered the hypothesis of homogeneous macroscopic superconductivity in two dimensions with either Berezinskii-Kosterlitz-Thouless (BKT) or Berezinskii-Kosterlitz-Thouless as well Aslamazov-Larkin (AL) fluctuations occurring at  $T > T_{\rm BKT}$ . Consistency with BKT fluctuations was found in a range of a few K above  $T_{\rm BKT}$  with AL fluctuations active over a larger and higher temperature range. However the experimental superconducting transition was not well described even after considering finite-size effects which limit the divergence of the coherence length. We therefore considered a phenomenological approach and inhomogeneous superconductivity within the Halperin-Nelson formalism with a distribution of  $T_{\rm BKT}$ . The functional form was taken to be the gamma distribution which allowed for a possible asymmetric character for the distribution of  $T_{\rm BKT}$ . We could thus reproduce our measured superconducting transitions, notably the width and the tail, when doping, disorder or magnetic field were varied. Finally we extracted parameters related to this inhomogeneous superconductivity in 2D-BSCCO.

Our results demonstrate the potential of space charge doping to develop fundamental understanding of superconductivity and phase transitions in high-temperature superconductors and open new perspectives in the field of fundamental research. This work could thus provide new impetus to the study of HTSC materials. Indeed in a special issue on high- $T_c$  superconductivity [208], Mohit Randeria expressed the following opinion in the article 'Towards a complete theory of high- $T_c$ ': "We need better samples of different sets of materials far from optimal doping. On the highly overdoped side this would help elucidate the extent to and the manner in which coherence is established and conventional Fermi-liquid behaviour is obtained. On the highly underdoped side, these would give more insights into the pseudogap phenomena. If doping could be varied in a controlled manner by gating or other means that does not introduce disorder it would greatly help disentangle disorder effects from strong correlation effects in the highly underdoped regime. Finally more experiments that suppress  $T_c$  down to zero would provide insights into the underlying non-superconducting state(s) and competing order parameters in the underdoped region."

We consider our work to be an effective response to this opinion opening a new window in the field of 2D materials and phase transitions. With further efforts to master device quality and the effects of disorder, it could be a precursor to a novel approach for studying Berezinskii-Kosterlitz-Thouless transitions as a function of carrier concentration in a single device and for applications based on high- $T_c$  superconductors. Moreover, the possibility to reversibly modulate charge carrier density in two dimensional high critical temperature superconductors using the electrostatic effect could be an even more powerful resource if combined with spectroscopy probes such as Raman spectroscopy, scanning tunneling microscopy or angle-resolved photo-emission. In this prospective, in-situ space charge doping experiments could allow a better understanding of the dependence of fundamental physical properties like Fermi surface, density of states and superconducting energy gap on carrier density.

Finally, we note that even though the thinnest samples studied here are one unit cell thick, they are still two times a half unit cell and each half unit cell is in principle the thinnest superconducting unit. In this sense, 0.5 u.c.-thick BSCCO-2212 crystals would be required to directly study a single pair of  $CuO_2$  planes. However this is still a difficult prospect because surface contamination and/or oxygen loss need to be avoided. Encapsulation methods could help in preserving the electrical properties of these ultra-thin samples so that space charge doping can be used to investigate their superconducting properties and phase diagram.

## List of abbreviations and symbols

2D	Two-dimensional
$\mu_{ m H}$	Hall mobility
ξ	Superconducting coherence length
$\lambda_{ m el}$	Electrostatic screening length
$\bigtriangleup$	Superconducting energy gap
$\lambda_{\perp}$	2D magnetic penetration length
AFI	Antiferromagnetic insulator
AFM	Atomic force microscopy
AL	Aslamazov-Larkin
ARPES	Angle-resolved photoemission spectroscopy
BKT	Berezinskii-Kosterlitz-Thouless
DC	Direct current
DOS	Density of states
$E_{\mathbf{c}}$	Vortex core energy
EDLT	Electric double layer transistor
FET	Field effect transistor
FSE	Finite-size effect
$\operatorname{GL}$	Ginzburg-Landau
HWHM	Half-width-half-maximum
HTSCs	High temperature superconductors
HN	Halperin-Nelson
IL	Ionic liquid
INH	Inhomogeneity
$I_{ m G}$	Gate current
$l_{ m m}$	Mean free path
MOSFET	Metal-oxide-semiconductor field effect transistor
$n_{ m S}$	Sheet carrier density
$n_s^{2d}$	2D superfluid density
$n_{ m H}$	Hall carriers
QCP	Quantum critical point
$R_{\rm H}$	Hall resistance
$R_{\rm S}$	Sheet resistance
RMS	Root mean square
SCD	Space charge doping
SIT	Superconductor-insulator transition
STM	Scanning tunneling microscope/microscopy
$T^*$	Pseudogap characteristic temperature
$T_{\rm m}$	Fermi-liqui characteristic temperature
$T_{\rm c}$	Superconducting critical temperature
$T_{\rm BKT}$	${\it Berezinskii-Kosterlitz-Thouless\ critical\ temperature}$
$V_{ m G}$	Gate voltage

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