The following individuals certify that they have read, and recommend to the Faculty of Graduate and Postdoctoral Studies for acceptance, the thesis entitled:

**Correlated phenomena studied by ARPES: from 3$d$ to 4$f$ systems**

submitted by **Marta Zonno** in partial fulfillment of the requirements for the degree of **Doctor of Philosophy** in **Physics**.

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Abstract

The physics of strongly correlated materials is at the heart of current condensed matter research. The inclusion of interactions in these materials between electron themselves or with other excitations intertwines various degrees of freedom (orbital, spin, charge and lattice), leading to a number of novel phenomena like Mott-Hubbard and charge-transfer insulators, high-temperature superconductivity and mixed-valence and Kondo physics. This thesis focuses on the study of two classes of correlated materials: copper-oxide high-temperature superconductors, whose correlated physics is driven by the localized nature of the half-filled Cu 3d-orbitals, and the rare-earth hexaborides, which are characterized by the strongly correlated 4f-shell.

Recently, it has been shown that the interplay between different mechanisms underlying the formation of the superconducting condensate in the hole-doped bi-layer Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ can be addressed in the time domain by means of time- and angle-resolved photoemission spectroscopy (TR-ARPES). Using this technique, the primary role of phase coherence has been established. By exploiting the same dynamical experimental approach, we show that such scenario also describes the ultrafast collapse of superconductivity in the single-layer compound Bi$_2$Sr$_2$CuO$_{6+\delta}$. Moreover, by performing a comprehensive study on different doping levels of both single- and bi-layer compounds, we provide new insights on the temperature evolution of the nodal quasiparticle spectral weight.

The second part of the thesis focuses on electron-doped cuprates, addressing the putative relation between the spectroscopically observed pseu-
dogap and the robust antiferromagnetic order. Employing TR-ARPES as a tool to perform a detailed temperature dependent investigation allows us to explicitly link the momentum-resolved pseudogap spectral features to the evolution of the short-range spin-fluctuations in the optimally-doped Nd$_{2-x}$Ce$_2$CuO$_4$.

Lastly, we make use of chemical substitution to investigate the mixed-valent character of the rare-earth hexaboride Sm$_x$La$_{1-x}$B$_6$ series. Our combined ARPES and x-ray absorption measurements reveal a departure from a monotonic evolution of the Sm valence as a function of $x$ and the possible emergence of a mixed-valent impurity regime.
Lay Summary

In many materials, electrons behave independently from other particles. However, for a wide class of quantum materials each electron cannot be considered as an independent particle, but it is instead strongly linked to the other electrons around and subjected to their interaction. This electronic connection gives rise to new quantum phenomena, including superconductivity where a material can conduct electricity without any loss. In this thesis, we study how the interplay between electrons affects the physics of two classes of materials: high-temperature superconductors and rare-earth compounds, by employing ultrafast laser excitations and chemical substitution, respectively. The results may contribute to a better understanding of the role of electron correlations in shaping the properties of quantum materials, which may play a vital role in future technologies and applications.
Preface

The work presented in this thesis is representative of the research activity I conducted at UBC during my time as graduate student. It consists of three projects for which I have been the primary investigator. However, experimental physics is a highly collaborative endeavor and all the work presented here was made possible thanks to involvement from numerous individuals as of sample growth, technical support and complementary experimental techniques. I will list here the specific contributions I and others have made for each of the experimental chapters.

Chapter 3. This chapter focuses on the analysis of the spectral function of hole-doped Bi-based cuprates, both single- (Bi2201) and bi-layer (Bi2212) compounds, by means of time-resolved and equilibrium angle-resolved photoemission spectroscopy (TR-ARPES and ARPES). The experiments were conceived by F. Boschini, A. Damascelli and me. All the TR-ARPES measurements were performed at UBC by me, with the help of F. Boschini and E. Razzoli. F. Boschini, E. Razzoli, R. P. Day, M. Michiardi, B. Zwartsenberg, P. Nigge, A. Sheyerman, M. Schneider, S. Zhdanovich, A. K. Mills, G. Levy and me provided technical support and maintenance for the ARPES setup at UBC. The equilibrium ARPES data were collected at the Canadian Light Source synchrotron facility in Saskatoon by me and F. Boschini, with assistance from S. Zhdanovich, T. Pedersen and S. Gorovikov. The Bi2201 and Bi2212 samples were provided by Y. Yoshida and G. D. Gu, respectively. Data analysis was done by me, with input from F. Boschini and A. Damascelli. A. Damascelli supervised the project and was responsible for the overall project’s direction, planning and management. These
results are currently being prepared for publication.

**Chapter 4.** The results in this chapter are largely based on the publication "Emergence of pseudogap from short-range spin-correlations in electron-doped cuprates" by F. Boschini*, M. Zonno* et al. (2020). F. Boschini and me performed the TR-ARPES experiments at UBC, with the assistance of E. Razzoli and M. Michiardi, and analyzed the data. F. Boschini, E. Razzoli, R. P. Day, M. Michiardi, B. Zwartsenberg, P. Nigge, A. Sheyerman, M. Schneider, S. Zhdanovich, A. K. Mills, G. Levy and me provided technical support and maintenance for the ARPES setup. The interpretation of the work was done by me, F. Boschini and A. Damascelli, with precious inputs from E. Razzoli, E. H. da Silva Neto, C. Giannetti and D. J. Jones. Single crystals of electron-doped NCCO were grown by A. Erb. A. Damascelli supervised the project. A. Damascelli was responsible for the overall direction, planning and management of the project. The manuscript summarizing the main results was written by me, F. Boschini, R. P. Day and A. Damascelli with input from all authors.

**Chapter 5.** This chapter investigates the evolution of the mixed-valence character in the Sm$_x$La$_{1-x}$B$_6$ series. The project was conceived by me, G. A. Sawatzky and A. Damascelli. I performed the ARPES experiments at UBC with 21.2 eV photon energy, with assistance from M. Michiardi. Additional ARPES data with 67 eV photon energy were collected by M. Michiardi in collaboration with the group of P. Hofmann in Aarhus at the ASTRID2 synchrotron facility, with support from K. Volkaert, D. Curcio and M. Bianchi. I analyzed all the ARPES data. X-ray absorption measurements were performed at the Canadian Light Source by R. Green and myself. R. Green analyzed the XAS data. M. Michiardi, F. Boschini, E. Razzoli, B. Zwartsenberg, P. Nigge, A. Sheyerman, R. P. Day, M. Schneider, G. Levy and me provided technical support and maintenance for the ARPES setup at UBC. Single crystals of Sm$_x$La$_{1-x}$B$_6$ were grown by P. F. S. Rosa and Z. Fisk. The interpretation of the work was done by me, R. Green, G. A. Sawatzky and A. Damascelli. G. A. Sawatzky and A. Damascelli supervised the overall project. These results are currently being summarized into a manuscript for publication.
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# Glossary

2D  two-dimensional

3D  three-dimensional

AFM  Antiferromagnetic

ARPES  Angle-Resolved Photoemission Spectroscopy

BCS  Bardeen, Cooper, and Schrieffer theory

Bi2201  \( \text{Bi}_2\text{Sr}_2\text{CuO}_6+\delta \)

Bi2212  \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8+\delta \)

Bi2223  \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta} \)

BZ  Brillouin zone

CFPs  Coefficients of Fractional Parentage

CO  Charge-Order

CSW  Coherent Spectral Weight

DFT  Density Functional Theory

dHvA  de Haas van Alphen oscillations

DOS  density of states

EDC  Energy Distribution Curve
<table>
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<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
</tr>
<tr>
<td>FEL</td>
<td>free electron laser</td>
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<tr>
<td>FL</td>
<td>Fermi-liquid</td>
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<tr>
<td>FS</td>
<td>Fermi Surface</td>
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<td>FWHM</td>
<td>full width half maximum</td>
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<td>HHG</td>
<td>high-order harmonic generation</td>
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<td>HTSC</td>
<td>High Temperature Superconductivity</td>
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<td>IPFY</td>
<td>Inverse Partial Fluorescence Yield</td>
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<tr>
<td>LHB</td>
<td>Lower Hubbard Band</td>
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<td>LSCO</td>
<td>La$_{2-x}$Sr$_2$CuO$_4$</td>
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<td>MDC</td>
<td>Momentum Distribution Curve</td>
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<tr>
<td>MFL</td>
<td>marginal-Fermi-liquid</td>
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<tr>
<td>MOs</td>
<td>molecular orbitals</td>
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<td>MV</td>
<td>Mixed-Valent state</td>
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<td>NCCO</td>
<td>Nd$_{2-x}$Ce$_2$CuO$_4$</td>
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<tr>
<td>NEXAFS</td>
<td>Near Edge X-ray Absorption Fine Structure</td>
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<tr>
<td>OD</td>
<td>overdoped</td>
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<tr>
<td>OP</td>
<td>optimal-doping</td>
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<tr>
<td>PEY</td>
<td>Partial Electron Yield</td>
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<tr>
<td>PFY</td>
<td>Partial Fluorescence Yield</td>
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<tr>
<td>PG</td>
<td>Pseudogap</td>
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<td>SC</td>
<td>Superconductivity</td>
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**SDW** Spin-Density Wave

**SEDC** Symmetrized Energy Distribution Curve

**TEY** Total Electron Yield

**TFY** Total Fluorescence Yield

**TKI** Topological Kondo Insulator

**TMOs** Transition Metal Oxides

**TM** Transition Metal

**TR-ARPES** Time- and Angle-Resolved Photoemission Spectroscopy

**UD** underdoped

**UHB** Upper Hubbard Band

**UHV** Ultra High Vacuum

**VB** valence band

**XAS** X-Ray Absorption Spectroscopy
Experimental physics is by nature a collaborative environment and, although this thesis has a single author, it could have never been possible without the help and support of numerous people around me.

The first and bigger thank you goes to my supervisor Andrea Damascelli for offering me the unique opportunity to move thousands of kilometers from my home-town in this beautiful place I quickly learned to call "home". Your deep understanding of physics, your enthusiasm and your guidance have helped me to sail through the exciting (and at times rough) waters of a PhD in condensed matter physics. I feel honored to have worked with you and incredibly thankful for all the encouragement and support received, often times far beyond the pure scientific sphere.

The uncountable hours spent in the lab and in the office would have felt overwhelming without the emotional and intellectual support of all the people in the ARPES group: Giorgio Levy, Sergey Zhdanovic, Art Mills, Michael Schneider, Eduardo da Silva Neto, Berend Zwartsenberg, Pascal Nigge, Alex Sheyerman, Amy Qu, Ryan Day, Elia Razzoli, Ketty Na, Sean Kung, Christopher Gutiérrez, Danilo Kuhn and Sydney Dufresne. A particular thank you to Matteo Michiardi and Fabio Boschini, who have played a big part in my research projects and encouraged me countless times. Each of you have made UBC a special place to grow both scientifically and personally.

Thank you to George Sawatzky and Robert Green for their precious involvement in the rare-earth project and to Philip Hofmann for offering his system in Aarhus to perform synchrotron measurements on these com-
pounds. Thank you to Tor Pedersen and Sergey Gorovikov for their support at the Canadian Light Source and to our collaborators Y. Yoshida, G. D. Gu, P. F. S. Rosa and Z. Fisk for providing the samples without which none of the projects here presented would have been possible.

A big thank you to all my committee members (supervisory and examining) for taking the time and effort to read and provide helpful feedbacks to improve my thesis.

Life is not just work, and the six years I spent in Vancouver have been enriched by new experiences and adventures with amazing people I feel incredibly lucky to call friends: Davide, José, Mirtha, Fernando, Aris and Ioanna, Hector and David, Daniel and Giulia, Tiffany and Edward in primis. Thank you to my “Verona-ties” Francesco and Alessandro, who always remind me how the world can feel small when the friendship is strong. And a deep thank you to Javiera for being there, showing me new horizons and making everything shine brighter when shared together. All the words in the world cannot express how profoundly thankful I feel for the infinite love and support I constantly receive from my parents, my brother and my sister: you all really are the pillars of my life. I do believe acknowledgments are better done in person, maybe in front of a nice meal and glass of good wine, so I will cut this short and do the rest in real life!

Marta Zonno
Vancouver, June 9, 2020
Dedication

To my brother and my sister
and to my parents
who have never stopped believing in me
and never will.

A mio fratello e mia sorella
e ai miei genitori
che non hanno mai smesso di credere in me
e mai lo faranno.
Chapter 1

Introduction

Many of our present-day technologies are based on materials such as silicon, aluminum, copper and diamond, whose macroscopic properties (electrical, mechanical and thermal) are fairly well described in terms of non-interacting electrons. The combination of an electronic structure governed by delocalized states, stemming primarily from $s$ and $p$ orbitals, and the Pauli exclusion principle leads to a ground state where the kinetic energy of the electrons dominates over the possible electron-electron interactions. The latter are thus often treated as afterthought in describing most familiar metals, band insulators and semiconductors. However, there is a wide class of materials for which the interaction among electrons is strong and plays a vital role in shaping their electronic, magnetic and sometimes even mechanical properties. These are the now-called strongly correlated electron systems, whose physics cannot be described in terms of non-interacting single-particle Hamiltonian. The resulting entanglement of all the significant degrees of freedom (orbital, spin, charge and lattice) gives arise to a plethora of intriguing exotic phenomena including Mott-Hubbard and charge-transfer insulators [1–4], High Temperature Superconductivity (HTSC) [5–8], mixed-valence and Kondo physics [9–11], heavy fermions [12–14] and various forms of charge and orbital ordering [15–19].
Figure 1.1: **Electron localization in the periodic table.** Illustration of the general evolution of the electron localization across the periodic table for the $d$- and $f$-compounds. Right inset: radial extend of the $3d$ and $4f$ wave functions of the valence electrons of the cations.

The investigation of this wide class of material dates back to the middle of the 20th-century, motivated at first by the discrepancy between the value of the electronic band gap as measured experimentally (usually few eV) and as predicated by band-theory (often much smaller or even null) for many Transition Metal Oxides (TMOs). This inconsistency was resolved by the inclusion of an on-site Coulomb repulsion energy $U$ in the so-called Hubbard model \[ \text{[2, 20]} \]. In fact, according to the conventional band-theory picture, a half-filled band would result into a metallic ground state; however, in the case of atomic-like electronic states, such as the $3d$- and $4f$-shell, the addition of an extra electron on the same site occurs at a cost of the large extra energy $U$, thus preventing hopping of the valence electron in the crystal in the form of fluctuations $d^n d^n \rightarrow d^{n-1} d^{n+1}$. The resulting charge localization drives the system into an insulating state (**Mott-Hubbard insulator**): the broad metallic band is split into an occupied Lower Hubbard Band (LHB) and an empty Upper Hubbard Band (UHB), the two separated by a gap determined by the size of $U$ (see Figure 1.2a, left panel). The presence of the large on-site Coulomb repulsion is then the keystone for strongly-correlated physics. In the context of the periodic table, strongly interacting electrons occur in well localized orbitals that can be arranged in
order of increasing localization as follow:

\[ 5d < 4d < 5f < 3d < 4f. \]  (1.1)

This trend is illustrated in Figure 1.1 and designates the compounds with partially filled 3d orbitals, as the family of cuprates HTSC, and the 4f rare-earth materials as prototypical examples of strongly-correlated electron systems. Although Equation 1.1 gives an indication on the strength of correlations, it is important to compare \( U \) with another relevant energy scale in the system, namely the bandwidth \( W \). This parameter is related to the near-neighbour hopping and represents the extent in energy of the valence band in the limit of non-interacting particles. The ratio \( U/W \) then encodes the interplay/competition between atomic-like and delocalized charge fluctuations and it determines the stability of the Mott-insulating phase.

While the Mott-Hubbard model marked a breakthrough for the inclusion of electron-electron interactions in the modeling of quantum materials, an additional step towards the understanding of correlated insulators was taken in the 1980s with the development of the Zaanen-Sawatzky-Allen theory. This laid the foundation for the definition of charge-transfer insulators [3]. In these systems, the insulating gap is not determined by \( U \), but rather by the charge-transfer energy \( \Delta \), which defines the energy cost for moving an electron between the anion and the cation within the same unit cell (see Figure 1.2a, middle panel). This picture describes the late 3d TMOs in which the lowest-energy excitations will occur between the occupied ligand (e.g. O or S) 2p band and the transition-metal (TM) 3d orbitals (e.g. Ni or Cu), in the form \( p^6d^n \rightarrow p^5d^{n+1} \).

By gradually reducing the charge-transfer energy \( \Delta \) up to the limit \( \sim \frac{W_{\text{lig}} + W_{\text{TM}}}{2} \) (where \( W_{\text{lig}} \) and \( W_{\text{TM}} \) are the bandwidths of the ligand and TM bands, respectively), the mixed-valent state emerges. Here, two different valence configurations of the TM (i.e. \( d^n \) and \( d^{n+1} \)) are simultaneously present in the system and jointly characterize the ground state, with LHB and UHB now separated by \( 2U \) (see Figure 1.2a, right panel). In this case, charge fluctuations can occur at very small energy scale involving both the TM


**Figure 1.2: Different types of correlated quantum states of matter.**

(a) Illustrative electron removal and addition spectra resulting from strong electron correlations in three different types of compounds: Mott-Hubbard insulator (left), charge-transfer insulator (middle) and mixed-valence system (right). A broad band is depicted in green, while the narrow correlated bands in orange (here associated to $p$-bands and $d$-bands, respectively, for illustrating purposes). Note that here the hybridization between the broad and narrow bands is not included. $U$ is the on-site Coulomb repulsion and $\Delta$ the charge-transfer energy. (b) Schematic of the lowest energy charge fluctuations for the three different classes of correlated compounds. Adapted from [4].

and the ligand states. Various rare-earth compounds exhibit mixed-valent behavior, where different valence configurations for the strongly correlated $4f$-shell are observed.
The classes of materials introduced thus far represent the starting point of the research presented in this thesis project on copper-oxide HTSC (known as cuprates) and La-substituted SmB$_6$. On one side, the Mott-insulating physics, driven by the strong correlations in the half-filled Cu 3$d$-states, defines the stochiometric cuprates, also known as parent compounds. Starting from this ground-state, many fascinating phases emerge upon hole- and electron-doping, such as superconductivity, pseudogap regime and charge-order, to name a few. Moving down in the periodic table to the rare-earth compounds, the strongly correlated 4$f$-shell comes into play and, among the various emerging phenomena, there is the Mixed-Valent (MV) state. SmB$_6$ is a prominent example where the description of the ground state gets particularly complicated by the physics of MV. Following, we will give a brief background on these compounds to set the stage for the specific investigations carried out in this thesis project.

1.1 Background: cuprate high-temperature superconductors

Superconductivity (SC) was first discovered in 1911 when co-workers in the group of Heike Kamerlingh Onnes observed an abrupt vanishing of the electrical resistivity of mercury when cooling the sample below 4.2 K [21]. Following this first experimental result, an intense theoretical and experimental effort focused in the developing of a theoretical description of SC and in the search of compounds exhibiting a higher transition temperature, $T_c$. However it was only in the mid 1950s that the first theory of superconductivity was developed by Bardeen, Cooper, and Schrieffer theory (BCS) [22, 23]. Twenty years later the maximum $T_c$ achieved was $\sim 23$ K in Nb$_3$Ge. A major breakthrough was achieved in 1986 when Bednorz and Müller discovered superconductivity near 40 K in the copper-oxide La$_{2-x}$Ba$_x$CuO$_4$ [5], marking the prelude of the field of HTSC. Since that first discovery, cuprates became subject of an intensive investigation. Soon it was realized that the observed high range of $T_c$ (as high as $\sim 138$ K in Hg$_{0.8}$Tl$_{0.2}$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ [24]) was one of many indicators of the emer-
Figure 1.3: Crystal structure of cuprates. (a) Crystal structure of the hole-doped Bi-based single-layer Bi$_2$Sr$_2$CuO$_{6+\delta}$ (Bi2201) and bi-layer Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi2212) cuprate. The lattice constants are approximately \( a = b = 3.86 \, \text{Å} \) and \( c = 24.7 \, \text{Å} \) (for Bi2201) and \( c = 30.7 \, \text{Å} \) (for Bi2212). (b) Crystal structure of the electron-doped Nd$_{2-x}$Ce$_2$CuO$_4$ (NCCO), with lattice constants of \( a = b = 3.9 \, \text{Å} \) and \( c = 12.1 \, \text{Å} \).
bilayer compounds, as \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_{8+\delta} \) (Bi2212); trilayer compounds, as \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta} \) (Bi2223) and beyond. Figure 1.3 shows the crystal structure for Bi-based hole-doped cuprates (as it evolves from one to two CuO\(_2\) layers) and for the electron-doped NCCO. Note that the anisotropy between the \( c \)-axis and the in-plane axis makes these systems quasi-2D, as confirmed by a recent Angle-Resolved Photoemission Spectroscopy (ARPES) experiment of monolayer Bi2212 [30]. Despite the difference in the crystal structure, all cuprates share the central role of the Cu-O block in determining the macroscopic electronic properties of the materials, including SC. In the parent compound, the Cu ions have a \( 3d^9 \) electronic configuration, corresponding to having the four lowest energy orbitals \( d_{xy}, d_{xz}, d_{yz} \) and \( d_{3z^2-r^2} \) fully occupied, with the only highest energy \( d_{x^2-y^2} \) being half-filled. Due to the vicinity in energy, the latter strongly hybridizes with the planar O \( 2p_x \) and \( 2p_y \) orbitals, leading to the formation of an antibonding band at the Fermi level. This same band is further split into a LHB and UHB by the Coulomb repulsion among electrons on the same Cu site, making the system an insulator.

Starting from this insulating state, novel phases of matter emerge as charge carriers are introduced into the CuO\(_2\) plane, either via chemical substitution of an element or change of oxygen content in the reservoir layers. In accordance with the charge-transfer insulator picture, the introduced holes preferentially reside in the ligand band with primarily oxygen character, while doped electrons locate on the Cu site. Figure 1.4 illustrates the simplified phase diagram for both electron- and hole-doped cuprates, here represented by NCCO and Bi2201, respectively. The two sides of the phase diagram show similarities and differences. First of all, in both cases a superconducting phase emerges at specific doping levels whose maximum \( T_c \) is reached at optimal-doping (OP) – lower and higher doping levels are referred to as underdoped (UD) and overdoped (OD), respectively. The SC phase in cuprates is characterized by an order parameter with \( d \)-wave symmetry: a node is observed along the \( (0, 0) \) – \( (\pi, \pi) \) direction (called \textit{nodal} direction), while the maximum amplitude occurs at the so-called \textit{antinode} corresponding to the Fermi surface crossing along the
Figure 1.4: Phase diagram of cuprates. Simplified phase diagram for electron- and hole-doped cuprates. An Antiferromagnetic (AFM) insulating state characterizes the parent compounds at zero doping. However, new phases develop upon electron or hole doping, such as SC, Charge-Order (CO) and the enigmatic Pseudogap (PG) characterized by the onset temperature $T^*$.\[\pi, 0\] − \((\pi, \pi)\) direction [31]. Over the years, extensive studies on various hole-doped cuprates disclosed fascinating phases as a function of doping and temperature, therefore extending the phase diagram beyond the dichotomy of antiferromagnetic (AFM) insulating regime and SC. States as spin-glass, Spin-Density Wave (SDW) and charge-order (CO) are now well established phenomena. If, on one hand, the richness of their phase diagram is what renders cuprates so attractive for exploring the interplay between various degrees of freedom in strongly correlated materials, on the other hand it makes the precise description of each separate phase challenging. The investigation of the CO phase is a clear example of this challenge. This electronic phase is defined by a self-organization of the valence electron density into periodic structures which break the native translational
symmetry of the lattice. Although CO has been reported as a ubiquitous property of cuprates experimentally observed in both hole- and electron-doped compounds [18,19], a comprehensive description of its microscopic origin and interplay with other phases has yet to be found. Another prominent example is the so-called pseudogap (PG) phenomenon observed in the UD regime. Spectroscopically, it manifests as a suppression of spectral weight in proximity of the Fermi level persisting for temperature above $T_c$ and eventually disappearing at the onset temperature $T^*$. Up to now, the intrinsic nature of the PG is still an open question, as well as its link (or lack thereof) with SC. In particular, it is still debated whether the PG is directly related to superconductivity and characterized by preformed Cooper pairs (therefore acting as a precursor of SC), or if it is a manifestation of a completely different competing order [32–35]. This open question also translates onto the expected structure of the phase diagram. While it is experimentally established that the onset temperature $T^*$ decreases as doping increases, its precise doping dependence in the OD regime, particularly in coincidence with the SC dome, is still subject of discussion. The scenario of a PG gradually merging the SC dome opposes to that of a $T^*$ line entering the SC dome at about optimal doping and defining a quantum critical point [32, 34].

Numerous theoretical models have been proposed to describe the PG in hole-doped cuprates, ranging from different type of density waves (being pair or charge) [36–38] to nematic order [39,40]. In electron-doped cuprates, the PG is believed to bear relation with the exceptionally robust AFM phase, that extends for a much wider doping range with respect to the $p$-type counterpart. The association of the PG with the buildup of AF correlations is based on various evidences, such as the development of long-range AFM order for a Néel temperature ($T_N$) about half of $T^*$, and a momentum dependence of the PG from photoemission experiments consistent with the picture of a 2D-AFM order characterized by a wave-vector $(\pi,\pi)$. That said, a direct analogy of the PG phenomenon between the two sides of the phase diagram is troublesome, mainly due to the large ambiguity in its definition for $p$-doped materials. Differences are observed in terms of
but not limited to) [33, 35, 41, 42]: (I) gap anisotropy, for electron-doped cuprates the PG is maximum at $(\pi/2, \pi/2)$ in contrast to the $(0, \pi)$ observed in hole-doped cuprates; (II) ground state of the UD regime where the PG is strongest, in the electron-doped it is dominated by the AFM order while SC plays a major role in the hole-doped case; (III) optical conductivity data, as no signature of the PG is reported in the $ab$-plane for hole-doped cuprates.

The study of the interplay between different phases of the cuprates phase diagram is a key aspect of this thesis project. In particular, in Chapter 3 we analyze the dynamical competition between pairing strength and phase coherence in the creation of the SC condensate, confirming that in the hole-doped single-layer Bi2201 the major contribution is given by the latter. Moreover, we explore the temperature evolution of the nodal quasiparticle spectral weight across different hole-doped cuprates (Bi2201 and Bi2212) and doping levels, revealing a universal $T$-dependence which is unrelated to both $T_c$ and $T^*$. Chapter 4 focuses on the relation between PG and AFM in electron-doped cuprates. By exploiting an ultrafast approach on NCCO, we track the temporal and temperature evolution of the PG spectral features directly in momentum-space, and demonstrate its explicit relation to the evolution of the spin-correlation length, even when only short-range AFM is present.

1.2 Background: samarium hexaboride

The concept of mixed-valence (MV) was introduced more than 50 years ago to describe the specific properties of the electronic state of a solid, in which a given element is present in the system in more than one oxidation state. After its discovery, this subject has attracted intense scientific interest in the past few decades in relation to valence fluctuations [9, 43–46]. MV occurs in numerous rare-earth compounds, driven by the strongly atomic-like and partially filled $4f$-shell (spatially located inside the $5d$ and $6s$ outer shells). Within the wide class of MV compounds, it is important to discriminate between inhomogeneously MV compounds and homogeneously MV compounds. In the former case, ions corresponding to different config-
urations occupy distinct crystallographic sites, and the MV state emerges at low temperature when the intersite Coulomb repulsion dominates the kinetic energy, thus suppressing the hopping of 4f electrons between the two species of ions having different valences. Rare-earth materials in this category include Sm$_3$X$_4$ (X=S, Se or Te) and Eu$_4$As$_3$. Contrarily, in the case of homogeneous MV, all the rare-earth ions occupy equivalent sites in the crystal structure, hence the MV state is primarily defined by a single-ion property where an exchange at the Fermi level between the atomic-like electrons and the conduction band arises via hybridization. Such scenario is expected to occur when the energies corresponding to the two different valence configurations are nearly degenerate. In the case of rare-earths, these are associated to different 4f-shell occupation numbers, $n$ and $(n-1)$: the ground state would then be a mixture of both 4f$^n$ and 4f$^{n-1}$d$^1$ configurations on each rare-earth ion. Stereotypical compounds exhibiting homogeneous MV state are TmSe, SmS, SmB$_6$ and YbB$_{12}$.

In this thesis we will focus on SmB$_6$ in particular, whose homogenous MV was disclosed in the second half of the 20$^{th}$ century, when spectroscopic studies reported the presence of two distinct valence configurations for the Sm ions: Sm$^{2+}$ (associated to 4f$^6$) and Sm$^{3+}$ (representing 4f$^5$5d$^1$) [47, 48]. Shortly after, additional peculiar properties were reported for SmB$_6$, such as a resistivity plateau and a linear specific heat developing at low temperatures [49, 50]. These features, commonly associated to gapless metallic states, were inconsistent with a description of SmB$_6$ based on the simplest hybridization picture, where an insulating state is driven by the gap opening via hybridization between the localized 4f states and the broad conduction 5d-band. A possible solution to this discrepancy was proposed ten years ago, when SmB$_6$ was indicated as the first possible realization of Topological Kondo Insulator (TKI) [51, 52]. Within this description, topologically protected surface states arise within the bulk band gap open through the hybridization of localized f electrons with the conduction electrons. These theoretical results triggered a renewed interest in SmB$_6$, with many experimental works trying to verify the TKI scenario. Although various transport and ARPES measurements claim to have successfully dis-
Figure 1.5: One-electron excitation spectrum of SmB$_6$. Calculated excitation spectrum for the mixed-valent SmB$_6$ in the atomic limit, including all the multiplets from the Coulomb interaction of the 4$f$-shell. Being a MV system, both Sm$^{2+}$ (4$f^6$) and Sm$^{3+}$ (4$f^5$) define the ground state generating four sets of features in the excitation spectrum, each corresponding to the electron removal ($f^5 \rightarrow f^4$ in blue and $f^6 \rightarrow f^5$ in red) and addition ($f^5 \rightarrow f^6$ in green and $f^6 \rightarrow f^7$ in purple) from one of the Sm configurations. The standard $^{2S+1}L_J$ notation is used to denote the contribution from different multiplets. Adapted from [4].

entangled the surface band dispersion from the bulk states, and to have unraveled the topological nature of the in-gap states [53–58], a clear answer has yet to emerge, with more spectroscopy studies indicating instead a bulk origin of the Fermi surface in SmB$_6$ [59–61]. Quantum oscillations experiments were also not conclusive, with two groups reporting de Haas van Alphen oscillations (dHvA) in the magnetization, yet giving opposite interpretations on whether the signal originates from a 2D or 3D Fermi surface [62, 63]. As a result, after years of intensive investigation, the ground state of SmB$_6$ still remains an open questions.

The difficulties in describing the physics in SmB$_6$ arise from the small energy scales involved. The hybridization between the partially filled strongly correlated 4$f$ states and the conduction electrons opens a gap of about $\sim$ 20 meV [56–58, 60, 64, 65] (note that this value is associated to the indirect bandgap, not excluding a direct gap as small as few meV). The Fermi level lies within this gap leading to a bulk insulating state and a mixture of the Sm$^{2+}$ (4$f^6$) and Sm$^{3+}$ (4$f^5$). At low temperature, the reported Sm valence
is $\sim 2.505$ [66-69], reflecting an almost equal presence of the two Sm configurations. Consequently, both of them need to be accounted for in the description of the electronic structure, as well as the 4f-shell strong multiplet effects. This gives rise to a particularly rich one-particle excitation spectrum for the 4f-shell in SmB$_6$, where the electron addition and removal components from both Sm configurations are present, as illustrated in Figure 1.5 for the atomic limit. In accordance to the schematic shown in Figure 1.2a (right panel), the LHB and UHB – here constituted of $f^5 \rightarrow f^4$ and $f^6 \rightarrow f^7$ features, respectively – are separated by an energy of the order of several eV corresponding to $2U$. Therefore, despite the overall extension of the excitations spectrum (as wide as $\sim 20$ eV), the low-energy scale is dominated by the one-electron removal from 4f$^6$-states reaching the low energy 4f$^5$ (Sm$^{2+}$ electron removal spectrum) and the one-electron addition to 4f$^3$ reaching the very low energy 4f$^6$-levels (Sm$^{3+}$ electron addition spectrum). The possible hole/particle excitations are narrowed down even further by the inclusion of the Coefficients of Fractional Parentage (CFPs), which describe the transition amplitudes between the many-body atomic configurations $l^{n-1}$ and $l^n$ via angular-momentum coupled electron addition (a comprehensive list of coefficients can be found in [70]). In the particular case of SmB$_6$, the spatially contracted 4f radial wavefunctions leads to very weak one-electron overlapping integrals complimented with the CFPs to reach the lowest energy states. Thus, in the first approximation, the relevant interactions are solely involving the Hund’s ground states of the two Sm electronic configurations, namely the $^7F_0$ singlet for Sm$^{2+}$ (4f$^6$) and the $^6H_{5/2}$ state for Sm$^{3+}$ (4f$^3$) (see the schematic of Figure 1.6 with the ground state and first excited states for the two configurations). The CFPs associated to these two ground states reveal a dramatic reduction in the direct f-f transition amplitudes between $f^5$ and $f^6$: the bandwidth of the f-shell gets reduced by almost 30 times with respect to the value predicted by Density Functional Theory (DFT) (which does not account for the multiplets and the associated CFPs) [4, 64, 65]. These observations suggest a scenario in which the direct f-f hopping can be at zeroth order neglected, leaving the mediated f-d hopping (which is significantly less affected by
the CFPs effect) as the primary particle/hole excitation channel. In light of the above discussion, it can be argued that SmB$_6$ differs from the conventional Kondo system, where the unoccupied and occupied $f$-states are within range of the Fermi level; instead, it may be thought of as a highly asymmetric Anderson-Hamiltonian impurity system, where the relevant low-energy particle/hole excitation involving the $f$-shell are made possible only by the hybridization between $f$- and $d$-states.

In order to get further insights on the physics of SmB$_6$, such as its MV character and the possible realization of TKI, we exploit chemical substitution to compare the low energy electronic states in SmB$_6$ with the analogous in LaB$_6$, a compound characterized by the same crystal structure but exhibiting a metallic ground state due to the lack of $4f$ electrons. Hereof, in Chapter 5 we report the study of the Sm$_x$La$_{(1-x)}$B$_6$ series, exploring the evolution of the electronic structure and the Sm valence by gradually

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**Figure 1.6: Energy level diagram of Sm$^{2+}$ and Sm$^{3+}$.** Ground state and first excited state energy diagram of the two Sm configurations. The ground state of Sm$^{2+}$ is a singlet state, while for Sm$^{3+}$ an additional splitting into a quartet and a doublet is driven by the cubic crystal field. The degeneracy of the states is indicated by the $n$ index. The charge density for 5 and 6 electrons are also shown. Adapted from [71].
changing the stoichiometry of the compounds.
Chapter 2

Experimental techniques

In this chapter we will briefly describe the experimental techniques employed during this research project, namely Angle-Resolved Photoemission Spectroscopy (ARPES), Time- and Angle-Resolved Photoemission Spectroscopy (TR-ARPES) and X-Ray Absorption Spectroscopy (XAS).

Since the mid ’90s, enduring technological advancements have fueled major improvements of both the momentum and energy resolutions, making ARPES the primary technique to study the electronic structure of strongly correlated materials. Based on the photoelectric effect, ARPES relies on the information carried by a photoelectron emitted from a crystal about its binding energy (related to the kinetic energy) and momentum (related to the emission angle) upon a monochromatic light excitation. By collecting and analyzing both, ARPES provides direct access to the material’s spectral function, which encodes information about the interactions between electrons and other particles.

Over the years, extensive efforts have been directed to include additional degrees of freedom, such as spin and time, to the conventional ARPES framework. In particular, the extension in the time-domain is achieved via pump-probe scheme in the so-called TR-ARPES. Here, an ultrashort low-energy laser pulse (pump) is used to excite the system and a second higher energy pulse (probe) to photoemit the electrons. The relaxation back to equilibrium can be tracked by changing the time delay between these
two pulses, thus obtaining insights on the related dynamics of the spectral function.

XAS is a core-level spectroscopy technique, in which monochromatic x-ray photons are employed to promote core electrons to the valence shell above the Fermi level. At some specific photon energies, the absorption probability suddenly increases as resonances corresponding to specific adsorption processes are reached. Although in a momentum-integrated fashion, XAS represents therefore a complimentary technique to ARPES to probe for example the Upper Hubbard Band.

2.1 Angle-resolved photoemission spectroscopy

Angle-resolved photoemission spectroscopy (ARPES) is one of the most powerful techniques to study the electronic structure of solids. It is a "photon-in" → "electron-out" technique based on the photoelectric effect, a phenomenon that was first experimentally observed in 1887 by H. Hertz and W. Hallwachs [73, 74], but only in 1905 Einstein was able to theoretically explain it [75]. Most of the information covered in this section follows from excellent review articles [76–78].

When monochromatic light of energy $h\nu$ illuminates the surface of a sample, photons are absorbed by the electrons in the materials and, if the energy is sufficiently high, a photoelectron can be emitted. From the energy conservation law, the kinetic energy of the emitted electron, $E_{kin}$, is related to the energy of the incoming photon $h\nu$ by the expression:

$$E_{kin} = h\nu - \Phi - |E_B|$$  \hspace{1cm} (2.1)

where $E_B$ is the binding energy of the emitted electron in the material and $\Phi$ is the work function of the material. The latter quantity, typically $\sim$4-5 eV, represents the energy barrier between the Fermi level ($E_F$) and the vacuum level ($E_{vac}$), i.e. the minimum energy required to remove one electron from the material, as illustrated in the schematic diagram of Figure 2.1. Different incident photon energies are commonly employed in ARPES experiments, ranging from laboratory-based ultraviolet sources – such as helium gas dis-
Figure 2.1: Energy scheme of the photoemission process. Schematics of the electron energy distribution as a function of the photoelectron kinetic energy as a result of an incoming photon of energy $h\nu$. $\Phi$ and $V_0$ are the material’s work function and inner potential, respectively. Adapted from [72].

Charge lamps (characterized by two emission lines, He I: 21.2eV and He II: 40.8eV) or lasers – to synchrotron facilities with tunable photon energies up to the x-ray regime. The relation of Equation 2.1 also dictates the high surface sensitivity of ARPES via definition of the electrons mean free path $\lambda$. This parameter represents the average length traveled by an electron inside a solid with a probability $1/e$ of not undergoing any scattering events; hence, $\lambda$ dictates the escape depth, i.e. the thickness of the sample which contributes to the primary signal. Interestingly, in spite of $\lambda$ being proportional to the dielectric function of the material [72], a "universal" curve is
found experimentally to describe the electron mean free path as a function of the kinetic energy (Figure 2.2). In the particular case of ARPES, where commonly used photon sources are in the ultraviolet range (10-100 eV), this implies that the resulting kinetic energies correspond to short mean free paths (very few topmost atomic layers of the surface), making ARPES one of the most powerful techniques for exploring the electronic properties at the surface of quantum materials. The main drawback of ARPES surface sensitivity is the requisite to perform the measurements in Ultra High Vacuum (UHV) – base pressure better than $10^{-10}$ torr – to ensure the sample remains clean on an atomic level throughout the experiment. This aspect of the ARPES technique also limits the investigation of those samples which can be appropriately prepared in-situ either by cleaving of bulk crystals, cleaning of the exposed surface via sputtering and annealing or by in-situ growth.

The key feature of ARPES is the possibility to analyze the emission angles of the photoelectrons in addition to their kinetic energy, allowing a full reconstruction of the electronic dispersion as a function of both energy and momentum. In this regard, a major advancement in the development of ARPES derived from the advent of two-dimensional detectors able to simultaneously analyze both the kinetic energy of the photoelectrons and the angles of emission. Such measurements are commonly achieved with hemispherical analyzers: the emitted electrons are collected through an entrance slit, subjected to an electric field in the lens column to match a preset pass energy and then dispersed in the hemisphere accordingly to their kinetic energy and emission angle, before reaching a phosphor screen and being subsequently detected by a camera. As in the case of Equation 2.1, conservation laws can be used to link the crystal momentum $\hbar \mathbf{k}$ characterizing the electron inside the solid with the momentum $\hbar \mathbf{K}$ of the photoelectron outside the material. However, since the translational symmetry is broken at the surface of the solid, only the parallel component of the momentum can be conserved:

$$k_x = K_x = \frac{1}{h} \sqrt{2mE_{\text{kin}}} \sin \theta \cos \varphi$$ (2.2)
Figure 2.2: Electron mean free path in solids. "Universal" curve for the electron escape depth as a function of the electron kinetic energy in various solids. Common energies involved in ARPES experiments (∼10-100 eV) correspond to few atomic layers, making it a high surface-sensitive technique. Adapted from [79].

\[ k_y = K_y = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}} \sin \theta \sin \varphi} \quad (2.3) \]

where \( \theta \) and \( \varphi \) are the polar and azimuthal angle, respectively, as defined in Figure 2.3. The determination of the perpendicular component of the momentum is not that straightforward and it requires the inclusion of the inner potential \( V_0 \), describing the bottom of the valence band. The third component of the momentum is then given by:

\[ k_z = \frac{1}{\hbar} \sqrt{2m(E_{\text{kin}} \cos^2 \varphi + V_0)} \quad . \quad (2.4) \]

Different strategies are used in order to determine \( V_0 \) [76, 80]; experimentally, the most commonly adopted one is by tuning the energy of the exciting photons and analyzing the resulting periodicity in \( k_z \). Note that the precise evaluation of \( k_z \) becomes relevant only in the investigation of three-
Figure 2.3: **Geometry of an ARPES experiment.** General geometry of an ARPES experiment where upon an incoming photon of energy $h\nu$ an electron is emitted at polar angle $\theta$ and azimuthal angle $\varphi$. Adapted from [76].

dimensional materials, while for (quasi-) two-dimensional compounds the electron dispersion is (mostly) fully confined in a plane and $k_z$ is irrelevant. In both cases, single crystals are needed to guarantee the translational symmetry required to measure electron momentum.

The creation and emission of a photoelectron is a more complex process than the one shown in Figure 2.1, where the electron is removed from its initial state in the material and directly collected onto the detector. Formally, it results easier to describe the photoemission process in terms of a three-steps model, in which each photoelectron undergoes three independent events:

1. Photoexcitation into a final bulk state due to the absorption of an incoming photon;

2. Transport to the surface, during which several inelastic scattering events might happen giving rise to the so-called *secondary electron signal* (a broad background with increasing intensity at low kinetic energies), to be distinguished from the *primary electrons*, which did not experience inelastic collisions and hence respond to the conservation
laws shown in Equation 2.1, Equation 2.2 and Equation 2.3;

3. Escape from the surface by overcoming the potential barrier and consequent collection into the detector.

In this framework, Fermi’s golden rule becomes instrumental for a formal description of the photoemission process. It describes the transition probability $w_{if}$ between an initial state, $\psi_i$, and an excited final state, $\psi_f$, upon absorption of a photon with energy $h\nu$:

$$w_{if} = \frac{2\pi}{h} \left| \langle \psi_f | H_{\text{int}} | \psi_i \rangle \right|^2 \delta(E_f - E_i - h\nu) ,$$

(2.5)

where $E_i$ and $E_f$ are the energies of the initial and final state, respectively. The term $H_{\text{int}}$ describes the light-matter interaction between an electron of mass $m$ and the electromagnetic field $A$ and, by using first order perturbation theory, it can be expressed by:

$$H_{\text{int}} = -\frac{e}{mc} (A \cdot p) .$$

(2.6)

So far the photoemission process has been addressed as a single-particle mechanism; however, in the realistic case of interacting systems, a N-body description must to be adopted. In this regard, a commonly used assumption is the *sudden approximation*, which considers the photoemission process instantaneous and therefore makes it possible to neglect any interactions between the photoelectrons and the core hole left behind in the photoemission process (*i.e.* the effective potential of the system changes discontinuously at the instant the photoelectron is instantaneously removed) \(^1\)

Note that such approximation may be inappropriate when probing the system with low photon energies since the resulting low kinetic energy of the photoelectrons may imply a longer time to escape in the vacuum than the system response time. In the following, the discussion to address in more

\(^1\)In particular, this assumption implies that the $(N - 1)$-particle wavefunction remains unchanged when the interaction $H_{\text{int}}$ is switched on and off, thus allowing the use of the instantaneous transition probabilities $w_{if}$ via Fermi’s golden rule [81].
details the analysis of the photoemission process will be restricted to the context of the three-step model and the sudden approximation.

Under these assumptions, both the $N$-particle initial state, $\psi_i^N$, and the excited final state, $\psi_f^N$, can be described in terms of single Slater-determinant product between the one-electron function $\Phi_k$ and a $(N - 1)$-particle term:

$$\psi_i^N = A \Phi_k^i \psi_{i-1}^N$$  \hspace{1em} (2.7)

$$\psi_f^N = A \Phi_k^f \psi_{f-1}^N$$  \hspace{1em} (2.8)

where $A$ is the antisymmetric operator ensuring the fulfillment of the Pauli’s principle. The matrix element of Equation 2.5 can then be written as:

$$\langle \psi_f^N | H_{int} | \psi_i^N \rangle = \langle \Phi_f^k | H_{int} | \Phi_i^k \rangle \langle \psi_{f-1}^N | \psi_{i-1}^N \rangle$$  \hspace{1em} (2.9)

where $M_{i,f}^k \equiv \langle \Phi_f^k | H_{int} | \Phi_i^k \rangle$ is the one-particle matrix element, while the second term represents the $(N - 1)$-particle overlap integral. By choosing the eigenstates of the $(N - 1)$-particle Hamiltonian (labelled by $m$) as convenient basis, we can sum over all the possible final states that can be involved in the excitation process to obtain:

$$W_{i,f} = \sum_{i,f} |M_{i,f}^k|^2 \sum_m |\langle \psi_{m-1}^N | \psi_{i-1}^N \rangle|^2 \delta(E_{kin} + E_{m-1}^N - E_{i-1}^N - h\nu) \hspace{1em} (2.10)$$

The summation over $m$ describes the probability of all possible electron-removal processes from an initial state $i$ and momentum $k$ to a $(N - 1)$-particle excited final state $m$, and it defines the spectral function (in this case for electron removal), $A^{-}(k,E)$. As can be seen from Equation 2.10 this quantity encodes fundamental information about the correlations present in the system. In fact, in the non-interacting picture $\psi_{i-1}^{N-1} = \psi_{m=1}^{N-1}$ for a particular $m = m^*$ and thus only the term corresponding to $m^*$ in the summation is not zero. However, in the case of strongly correlated materials, the photoelectron removal leads to a strong overlap of $\psi_{i-1}^{N-1}$ with multiple $\psi_{m}^{N-1}$, so $A^{-}(k,E)$ would deviate from a single series of delta functions.
and show instead additional peaks or tails corresponding to all the excited states \( m \) created in the process.

In mathematical terms, the most common approach to discuss the photoemission on solids is based on the Green’s function formalism, in which the time-ordered one-electron removal Green’s function (or propagator) describes the time evolution of a state where an electron with momentum \( k \) is removed from the system at time zero. By taking the Fourier transform, the real space propagator can be expressed in the energy-momentum representation:

\[
G^{-}(k, E) = \sum_{m} \frac{|\langle \psi_{m}^{N-1}|c_{k}|\psi_{i}^{N}\rangle|^2}{(E - E_{m}^{N-1} - E_{i}^{N} + i\eta)},
\]

(2.11)

where the operator \( c_{k} \) annihilates an electron with energy \( E \) and momentum \( k \) in the \( N \)-particle initial state \( \psi_{i}^{N} \) and \( \eta \) is a positive infinitesimal. In the limit \( \eta \to 0^{+} \), the identity \( (x + i\eta)^{-1} = \mathcal{P}(1/x) - i\pi\delta(x) \) is valid (where \( \mathcal{P} \) represents the principal value; furthermore, from here on we will take \( \hbar = 1 \)) and allows to rewrite the Green’s function as:

\[
G^{-}(k, E) = \sum_{m} (|\langle \psi_{m}^{N-1}|c_{k}|\psi_{i}^{N}\rangle|^2) \left( \mathcal{P}\left(\frac{1}{E - E_{m}^{N-1} - E_{i}^{N}}\right) - i\pi\delta(E - E_{m}^{N-1} - E_{i}^{N}) \right) - i\pi\delta(E - E_{m}^{N-1} - E_{i}^{N}) \)
\]

(2.12)

By comparing Equation 2.12 with Equation 2.10, a simple relation can be derived connecting the Green’s function to the one-electron spectral function:

\[
A^{-}(k, E) = -\frac{1}{\pi} \Im G^{-}(k, E).
\]

(2.13)

The main advantage of adopting the Green’s function formalism is the possibility to extend the photoemission description to the case of many-body interactions via inclusion of the complex electron self-energy \( \Sigma(k, \omega) = \Sigma^{'}(k, \omega) + i\Sigma^{''}(k, \omega) \). Its real and imaginary parts describe the renormalization of the energy and lifetime of an electron with bare-energy \( \epsilon_{k}^{b} \) and momentum \( k \) due to many-body interactions. The self-energy can be used to express both the one-electron Green’s function and spectral function as follow:

\[
G(k, \omega) = \frac{1}{\omega - \epsilon_{k}^{b} - \Sigma(k, \omega)}
\]

(2.14)
and

\[ A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma''(k, \omega)}{[\omega - \epsilon_k^b - \Sigma'(k, \omega)]^2 + [\Sigma''(k, \omega)]^2}. \]  

(2.15)

Following from Equation 2.10 and Equation 2.15, one can calculate the total photoemission intensity as a function of energy \( \omega \) and momentum \( k \):

\[ I(k, \omega) = I_0(k, \omega) f(\omega) A(k, \omega) \]

\[ = -\frac{1}{\pi} I_0(k, \omega) f(\omega) \frac{\Sigma''(k, \omega)}{[\omega - \epsilon_k^b - \Sigma'(k, \omega)]^2 + [\Sigma''(k, \omega)]^2}, \]  

(2.16)

where \( I_0(k, \omega) \) is proportional to the square of the dipole matrix element \( |M_{fi}|^2 = |\langle \Phi_f | H_{int} | \Phi_i \rangle|^2 \) and consequently depends on the momentum of the electron, the incident photon energy and polarization and the particular experimental geometry \([76, 80]\). Equation 2.16 also includes the Fermi-Dirac distribution term \( f(\omega) = \left[ \frac{e^{(\omega - \mu)/k_B T} + 1}{e^{(\omega - \mu)/k_B T} + 1} \right]^{-1} \) to properly describe the photoemission process as a probe of only the occupied energy states (electrons are removed from the system, \( \mu \) represents the Fermi energy). This term also explains why, in order to limit the broadening arising from \( k_B T \), most ARPES experiments are carried out at low temperature. Although effects due to resolution broadening in both energy and momentum, as well as possible background signal, may affect the photoemission intensity, Equation 2.16 shows the capability of ARPES to access the electron-removal spectral function and the encoded information about correlations via self-energy.

Experimentally, the aforementioned connection is achieved through the analysis of the spectral lineshape and two main strategies are often used, focusing either on the energy- or the momentum-dependence of the photoemission signal. The first approach consists in computing the photoemission intensity at a fixed moment \( k^* \) (where now \( k \) refers to the two-dimensional momentum conserved during the photoemission process) and thus analyzing the energy-dependence of the so-called Energy Distribution Curve (EDC). The second focuses instead on the momentum-dependence at a fixed binding energy \( \omega \) via the so-called Momentum Distribution Curve.
(MDC). Although the precise determination of $\Sigma(k,\omega)$, and consequently of $A(k,\omega)$, often turns out to be very challenging, the analysis of the spectral lineshape via EDC and MDC is a fundamental tool to this goal. In this regard, it is instructive to illustrate the simple interacting Fermi liquid case. Close to the Fermi level (i.e. $E_F - h\omega \gg |\Sigma''|$), the system can be modeled in terms of quasiparticles, describing electrons “dressed” with a collection of excited states moving coherently with them. Within this model, the quasiparticle spectral function can be divided into a coherent part and incoherent part ($A_{\text{incoh}}$), with only the former associated to the low energy excitations:

$$A^{FL}(k,\omega) = 2\pi Z_k \left( \frac{1}{\pi} \left( \frac{1}{\omega - \tilde{\epsilon}_k} + \frac{1}{\tau_k} \right)^2 \right) + A_{\text{incoh}}.$$  \hspace{1cm} (2.17)

Here, the term $Z_k = (1 - \frac{\partial \Sigma}{\partial \omega})^{-1}$ is a renormalization constant, also called coherent factor and it gives a measure of the quasiparticle strength (generally speaking, $Z_k$ equal to 1 corresponds to the non-interacting case, while $Z_k$ equal to 0 to the strongly correlated case where no coherent state can be excited). The other two terms involved in Equation 2.17, $\tau_k$ and $\tilde{\epsilon}_k$, are the quasiparticle lifetime and its renormalized energy, respectively. To first order, they are related to the real and imaginary part of the self energy by the following expressions: $\tilde{\epsilon}_k = Z_k (\epsilon^b_k + \Sigma')$ and $\tau_k = (-2\Sigma'')^{-1}$. Note that in the formalism of Equation 2.17, the self-energy and its derivatives are evaluated at $\omega = \tilde{\epsilon}_k$. EDC and MDC provide thus access to different aspects of the quasiparticle spectral function: while the former relates to the energy-dependence of $\Sigma(k,\omega)$, the latter assumes a Lorentzian lineshape (assuming that $\tilde{\epsilon}_k^b$ can be linearized about the MDC maximum) whose full width half maximum (FWHM) can be used to estimate the lifetime of the quasiparticle $\tau_k$. 

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2.2 Time- and Angle-resolved photoemission spectroscopy

ARPES provides the capability to directly probe the electronic structure of quantum materials by simultaneously resolving energy and momentum. However, being based on the photoelectron effect, its application is limited to the investigation of occupied electronic states in equilibrium conditions. In order to gain access to out-of-equilibrium phenomena and associated dynamical properties, a time resolved approach is needed. Non-equilibrium spectroscopies have attracted increasing interest in the context of the study of strongly correlated materials. They offer the unique opportunity to explore new phases of matter otherwise unattainable at equilibrium or to disentangle in the time domain energetically intertwined orders based on the distinctive timescale that describes the recovery of the equilibrium initial state. Figure 2.4 outlines the main relaxation processes occurring in a solid from a femto-second to micro-second timescale as a result of an optical excitation, where four regimes can be distinguished: carrier excitation, thermalization, carrier removal and thermal and structural effects [83]. In par-
Figure 2.5: Pump-Probe scheme for time-resolved ARPES. Illustration of the pump-probe approach adopted in a time-resolved ARPES experiment: pump and probe pulses, delayed by $\delta t$, are sent to the sample; at $t=0$ the infrared pump pulse hits the sample inducing a nonequilibrium state; the probe pulse ejects photoelectrons at a time $\delta t$ after the excitation, while the system is relaxing back to equilibrium.

In particular, in this thesis work we will focus on the fast dynamics, 0.1 ps - 10 ps (yellow shadow in Figure 2.4). The advent of ultrafast laser sources able to deliver ultrashort and coherent light pulses (of few to several hundreds of fs duration) triggered the development of time-resolved optical techniques based on the pump-probe scheme. The same approach is adopted to extend the conventional ARPES technique into the time domain, as shown in Figure 2.5. While in equilibrium ARPES only one ultraviolet light beam is employed, time-resolved ARPES (TR-ARPES) makes use of two ultrashort laser pulses of different frequency hitting the sample in close succession. The first pulse, called pump and typically in the infrared regime, excites the sample into a non-equilibrium state. Shortly after such excitation a second pulse, called probe and with sufficiently high photon energy, is sent to the sample to induce the photoemission process. By varying the time delay between the two pulses, snapshots of the electronic structure are collected as the system relaxes back to equilibrium, providing insights on the related electron dynamics and recovery mechanisms of the material under consideration.

At present, various TR-ARPES systems are available worldwide. The most common class of instruments relies on solid-state laser sources where the ultraviolet probe pulse is generated by sum-frequency generation in
nonlinear crystal [84–87]. This approach retains an upper limit on the maximum achievable probe energy of 6-7 eV, which provides remarkable momentum resolution but at the same time strongly constrains the accessible momentum-space via Equation 2.2 and Equation 2.3. Therefore, these systems are well suited for the investigation of those electronic states in the vicinity of the first Brillouin zone’s Γ point, such as the Dirac states in Topological Insulators or the nodal region in high-temperature cuprate superconductors. In order to overcome the low-photon energy limitation and get access to larger momenta, high-order harmonic generation (HHG) techniques have been developed by exploiting the nonlinear processes occurring when a strong laser pulse interacts with an atomic gas (e.g. Kr or Ar). Although the necessity of having large electric field to induce nonlinear processes in atomic gases negatively affects the energy resolution of the outcoming harmonics, recent developments of new HHG schemes yield to a resolution comparable to the standard 6 eV-setup but on a probe photon energy of the order of several tens of eV [88–91]. Finally, at the largest scale, TR-ARPES is recently being addressed in the context of newly built (or under construction) x-ray free electron laser (FEL) sources [92, 93]. The possibility of tunable photon energy, variable pulse duration and wide range of accessible momenta makes TR-ARPES experiments based on FELs sources an exciting prospect for future investigations of quantum materials.

2.2.1 TR-ARPES at UBC with 6.2-eV probe

Figure 2.6 shows the experimental apparatus employed for the TR-ARPES measurement presented in this thesis work. It is based on a commercially purchased Ti:sapphire laser consisting of the VitesseDuo oscillator (pumped by a 10W Nd:YVO₄ continuous-wave Coherent Verdi laser) and the regenerative amplifier RegA 9000 both by Coherent Inc. This combined system provides trains of light pulses in the near-infrared range (800 nm, corresponding to 1.55 eV) with a pulse duration of ~180 fs and at a repetition rate of 250 kHz. The output beam is split in two: the reflected portion is used as pump while the transmitted one is driven through a cascade of non-
linear processes to generate the fourth-harmonics probe at 200 nm, equivalent to 6.2 eV. In particular, the latter is achieved by three subsequent sum-frequency generations in phase-matched BBO ($\beta$-Barium Borate) crystals. Once undertaken the nonlinear generation, the probe is recombined to the pump beam in a collinear geometry (to guarantee spacial overlap) and focused on the sample in the UHV experimental chamber at a 45° angle of incidence. The spot size of the two beams have been estimated by using a beamprofiler to 250 $\mu$m and 180 $\mu$m for pump and probe, respectively. Finally, the time delay between the pump and the probe beam is controlled by a motorized translation stage placed in the pump path. Once the probe pulse hits the sample, the photoemitted electrons are collected and measured by means of their energy and momentum using an hemispherical analyzer conforming to the conventional ARPES technique.

The characterization of the overall temporal and energy resolution is imperative in any TR-ARPES experiment. One approach to estimate the system’s temporal resolution relies on tracking the photoemission inten-
sity as a function of the pump-probe delay for states well above the Fermi level (>2 eV) in polycrystalline gold. At this energies, the time resolution is expected to exceed the intrinsic electronic states lifetime so that in good approximation the temporal response of the photoemission signal is solely determined by that of the pump and probe themselves. The resulting temporal profile can be fit by a Gaussian whose FWHM returns a duration for the probe pulse of 250 fs (assuming a 180 fs pump pulse). As for the total energy resolution, an estimate can be achieved by measuring at low temperature the Fermi edge width of any samples with electronic bands crossing the Fermi level. In the case of TR-ARPES measurements on cuprate superconductors presented in this thesis, the equilibrium (i.e. acquired without the pump beam) band dispersion along the nodal direction can serve to this goal and sets the system’s energy resolution to 17 meV.

Beside the overall temporal and energy resolution, other aspects of the probe and pump pulses need to be examined in performing a TR-ARPES experiment. As the counting rate scales linearly with the incident photon flux, one might imagine that the statistics and the integration time could be drastically improved by simply increasing the intensity of the probe pulse. However, we must consider the space charge effect originating from repulsive Coulomb forces that photoelectrons exert on each other when they are emitted nearby in time and space. This effectively leads to a broadening and distortion of the ARPES spectrum, both in energy and momentum [94–97]. Although potentially relevant in any photoemission experiment, space charge becomes crucial in TR-ARPES measurements due to the combination of ultrashort laser pulses, small spotsize and typically low kinetic energy of the photoelectrons. In this work, space charge effects were minimized by decreasing the intensity of the probe beam until the related energy-resolution broadening effects at the Fermi level became comparable to the background resolution (17 meV). Note that in this setup the maximum pulse energies are typically < 50 nJ, thus excluding any field emission effects from a large (mm size) flat metal surface (comparable pulse energies are in fact used to induce field emission in nanometer tips) [98–100].
Lastly, the pump fluence represents another fundamental quantity in a TR-ARPES experiment as it directly relates to the initial density of excited carriers. By changing the pump fluence is thus possible to explore different excitation regimes of the system under study. Similarly to the probe pulse case, very high pump fluences may lead to distortions in the ARPES spectrum: as the excitation density increases, multi-photon photoemission from the pump pulses might take place creating additional photoelectrons which might even dominate the direct photoemission signal [94]. In our work, the value of the pump fluence was varied by directly adjusting the power of the pump beam using a variable filter placed along the beam path. For each selected pump fluence the absence of multi-photon effects was verified by the lack of photoemission signal with the only pump beam illuminating the sample. The inaccuracy in determining the average power of the pump beam (usually measured with a powermeter) and the spotsize on the sample, alongside with losses from the viewport, reflect in the uncertainty of the fluence values given for each TR-ARPES experiments presented in this thesis.

2.3 X-Ray Absorption Spectroscopy

X-ray spectroscopy techniques involve the production and monitoring of radiative transitions between ground and excited states. After the discovery of x-rays in 1895 by Rontgen [101], it took two decades before the first x-ray absorption spectrum was observed by De Broglie [102]. Since then, core-level x-ray spectroscopies have come a long way promoted by the remarkable advancements made in both the experimental and theoretical capabilities. As an example of groundbreaking theoretical progress, the application of Fourier analysis to the theory of x-ray absorption (XAS) made in 1971 by Sayers, Stern, and Lytle paved the way to a quantitatively estimation of structural parameters (such as bond distance and coordination number) from the experimental spectrum [103]. On the experimental side, the advent of broadband synchrotron radiation sources starting from the 1970s arguably represent the main advancement which fueled the develop of
x-ray spectroscopy techniques into reliable and routine experimental tools. The possibility to select a specific incoming photon energy and polarization, along with a high flux are just some of the significant benefits offered by modern synchrotron radiation facilities.

In a simple one-electron picture, XAS involves the interaction between an incoming photon and a core-level electron, as shown in Figure 2.7a. The absorption of the photon by the electron can either excite the latter to a bound unoccupied state or eject it into the continuum. A typical XAS experiment involves scanning the incoming photons energy while detecting the absorption of such photons: the resulting spectrum would then provide the x-ray absorption coefficient as a function of the incident x-ray energy (an example is displayed in Figure 2.7b). When such energy hits particular values, mainly determined by the atomic number of the absorbing atom, the absorption probability results strongly enhanced marking what is called an “edge”. Each edge represents a distinct core-level binding energy and by convention is labelled accordingly to the principal quantum number of the excited electron: K associated to \( n = 1 \), L to \( n = 2 \), M to \( n = 3 \).
and so on. The absorption below an edge is dominated by background processes which include elastic and inelastic scattering processes, lower energy edges absorption, etc. In the immediate vicinity of an edge, in the region often called the Near Edge X-ray Absorption Fine Structure (NEXAFS), the absorption is instead characterized by the presence of fine structure associated with resonant transition between core electrons and excited states of the material (Figure 2.7b). It is this fine structure that encodes information about the electron and magnetic structure of the absorbing atom. In the presence of a strong Coulomb interaction between the core-hole and the valence electron (as often the case in TMOs and rare earth compounds), the fine structure observed in NEXAFS (combined with the dipole selection rules discussed later in this section) provides direct information about the ground state occupation of the valence state [106]. The investigation of the part of the spectrum well above the edge is instead called Extended X-ray Absorption Fine Structure (EXAFS), where the excited core electron has sufficiently high energy to reach the continuum (Figure 2.7b). This region shows a gradual decrease in the absorption rate along with superimposed oscillating features reflecting the scattering processes undergone by the excited electrons with neighbouring atoms.

Any XAS experiments begin with the interaction between the incident photon and the bound core level electron. Although such interaction between x-rays and matter can be much more complicated, a single-particle picture can be used to provide a simplified approach which grasps the underlying physics and the fundamental derivation of the key dipole selection rules. As for the case of the ARPES technique presented in Section 2.1, the starting point for a formal description is the expression via Fermi’s golden rule of the transition rate of an initial state $\psi_i$ into a particular final state $\psi_f$ as a result of the absorption of a photon with energy $h\nu$, as in Equation 2.5. By applying a first order dipole approximation for the perturbing potential, the absorption rate can be written as:

$$R_{i\rightarrow f} \propto \sum_{i\rightarrow f} \frac{2\pi}{\hbar} \left| \langle \psi_f | \hat{\mathbf{p}} | \psi_i \rangle \right|^2 \delta(E_f - E_i - h\nu)$$  \hspace{1cm} (2.18)
where \( \hat{\epsilon} \) is the unit vector describing the polarization of the incident electromagnetic wave and \( \vec{p} \) the electron linear momentum operator. This probability is essentially what is being measured in XAS spectroscopy. By expanding the term \( \langle \psi_f | \hat{\epsilon} \cdot \vec{p} | \psi_i \rangle \) making use of the spherical harmonics and the Clebsch-Gordan coefficients, Equation 2.18 can be used to derive the dipole selection rules. These rules describe the restrictions in the transition process in terms of the quantum numbers and play a key role in the theory of core-level x-ray spectroscopy techniques. Equation 2.19 lists the more general selection rules for multi-electron atoms. In the presence of significant spin-orbit interactions, the restrictions on the total angular momentum \( J = L + S \) and its projection along the \( z \) axis, \( M_J \), have to be used rather than those for independent \( L \) and \( S \).

\[
\begin{align*}
\Delta L &= 0, \pm 1, \ (L = 0 \leftrightarrow L = 0) \\
\Delta l &= \pm 1 \\
\Delta S &= 0 \\
\Delta J &= 0, \pm 1 \\
\Delta M_J &= 0, \pm 1
\end{align*}
\] (2.19)

Note that the selection rules listed above are valid only within the electron dipole approximation, which holds only in the soft x-ray absorption process where the wavelengths are relatively long compared to the radial extent of the core level wave functions.

Different detection techniques can be employed in a XAS experiment. The simplest way to measure the absorption rate is by placing the sample between the source and the detector, in the transmission detection scheme (Figure 2.8a): the attenuation of the x-rays would be quantified by how much the signal drops on the detector. This process is described by Beer-Lambert law:

\[
I(\omega) = I_0(\omega) e^{\mu(\omega) D} \quad \Rightarrow \quad \mu(\omega) = -\frac{1}{D} \ln \left( \frac{I(\omega)}{I_0(\omega)} \right)
\] (2.20)

where \( I \) and \( I_0 \) are the transmitted and incident beam intensities respectively.
**Figure 2.8: Common detection approaches in XAS experiments.** (a) Illustration of the transmission technique, where the XAS is recorded by monitoring the fraction of photons passing through the sample. (b) Scheme of electron yield techniques (TEY or PEY), where the emitted electrons during the relaxation of the x-ray excited states are detected (either by direct collection of surface-emitted photoelectrons or by monitoring the replenishing current through the sample). (c) Depiction of the fluorescence yield technique (TFY, PFY and IPFY), where emitted fluorescence photons are detected. The blue shadow qualitatively represents the probing depth of each detection technique. From [105].

In many cases this transmission approach is not the most practical. First, for each sample it requires an energy-dependent optimization to match thickness and density. Second, if $\mu(\omega)D \gg 1$, the photons cannot penetrate through the sample in order to reach the detector, so no signal would be detected. Even in the case when the attenuation is not big enough to prevent any signal to be detected, it can still lead to artificial suppression of the absorption peaks and thus affect the analysis [105]. As an alterna-
tive approach, one can resort to yield techniques. After the absorption of an x-ray the system is left in an excited state which quickly decays by releasing energy in the form of Auger electrons or photons. In practice, it is often found that the number of transmitted photons (i.e. the absorption signal) can be mapped quite consistently into the number of these emitted Auger electrons or photons. When the emitted electrons are detected as a function of incident photon energy to reconstruct the XAS signal, the technique is known as Total Electron Yield (TEY) [see Figure 2.8a; if instead of detecting all the electrons, only the ones with certain energies are collected is called Partial Electron Yield (PEY)]. Note that, instead of directly detecting the electrons as they are emitted from the surface, a common procedure is to measure the magnitude of the positive current induced in the sample upon x-ray irradiation. In either case, a fundamental aspect of TEY/PEY is the small probing depth limited by the mean free path of the electrons that are freed in the absorption process (similar argument that applies for the surface-sensitivity of ARPES).

Total Fluorescence Yield (TFY) [or Partial Fluorescence Yield (PFY) if only a particular set of fluorescence transition is monitored] relies on the detection of the photons emitted in the relaxation process following the x-ray excitation (Figure 2.8c). The primary strength of this approach is the higher bulk sensitivity respect to electron yield techniques: the probing depth of TFY and PFY is dictated by the photons penetration depths which is of the order of \( \sim 100 \) nm for soft x-rays. This comes as a main advantage in the study of reactive materials where surface oxidation and contamination may affect the intrinsic signal probed by a surface-sensitive technique. Note that the fluorescence yield spectra are susceptible to some distortions such as saturation and self-absorption effects; these have then to be taken into account while analyzing the XAS signal [107–110].

Lastly, a new yield technique termed Inverse Partial Fluorescence Yield (IPFY) has been recently developed, in which fluorescence photons from a non-resonant lower energy edge are detected. As more incident photons are absorbed at the resonant edge, the non-resonant fluorescence background decreases giving an inverted signal directly proportional to the true
XAS spectrum [109, 110]. Although very recent and not always attainable (as it requires a lower energy edge available), when applied IPFY may provide the most reliable spectra among all the yield techniques. A combination of PFY and IPFY have been used to collect the XAS spectra presented in Chapter 5.
Chapter 3

Tracking the spectral function of Bi-based cuprates by TR-ARPES

Copper-oxide high-temperature superconductors are the prototypical example of 3$d$ strongly correlated systems and a multitude of competing ordering phenomena and phases characterize their phase diagram. Here, we employ TR-ARPES to directly access the temporal and temperature dynamics of the one-electron spectral function in hole-doped Bi-based cuprates. By optically perturbing the system, we report the ultrafast enhancement of the phase fluctuations in the single-layer $\text{Bi}_2\text{Sr}_2\text{CuO}_6+\delta$, while only mildly affecting the pairing strength, consistent to what was previously reported for the bi-layer compounds. Furthermore, this transient approach allows us to also address the temperature-dependent meltdown of the nodal quasiparticle peak with unprecedented sensitivity. The observed suppression of spectral weight is shown to be ubiquitous of the Bi-based cuprates family and proposed to stem from the temperature dependence of the imaginary part of the self-energy within the Fermi-liquid description.
3.1 Introduction

High-temperature superconductivity (HTSC) is one of the most fascinating phenomena and yet unsolved puzzle of the last 30 years in condensed matter. Among the different families of materials exhibiting HTSC, the Bi-based hole-doped cuprates are the most intensively studied [111, 112]. Over the years, extensive theoretical and experimental efforts (by means of different techniques ranging from optics, transport, photoemission spectroscopy and magnetic probes) gradually disclosed the richness of the cuprates’ phase diagram. Besides the Mott-insulating state characterizing the parent compounds and the superconducting dome, numerous intertwined phases such as charge-order, spin-density waves and pseudogap emerge upon doping, making the cuprates an exceptional platform to investigate the interplay and competition among different correlated states of matter. Along with this exciting opportunity comes the challenge to precisely describe each separate phase, with thermal excitations often obfuscating the appearance of different phases and potential thermodynamic phase transitions. In this context, the use of experimental tools capable to disentangle degrees of freedom associated to different competing orders become instrumental. Time- and angle-resolved photoemission spectroscopy (TR-ARPES) takes the capability of directly visualizing the electronic dispersion in momentum space typical of ARPES into the time domain, providing access to its dynamics and disclosing transient regimes otherwise unattainable for investigation within the equilibrium framework.

The interplay among different phenomena characterizing the SC phase transition in cuprates is a remarkable example where the possibility to disentangle in the time domain underlying mechanisms occurring on the same energy scale plays a crucial role in establishing the hierarchy in the formation of the condensate. In superconducting materials the transition temperature $T_c$ has been proposed to be controlled by two distinct phenomena, namely the creation of electron pairs (characterized by the pairing energy $E_p$) and the persistence of macroscopic phase coherence (whose energy scale $\hbar \Omega_0$ is related to the zero-temperature superfluid density) [113].
Figure 3.1: Electron pairing vs phase coherence and suppression of quasiparticle spectral weight in Bi2212. (a) Schematic phase diagram of cuprates illustrating the interplay between electron pairing (with onset $T_{\text{pair}}$) and the stability of phase coherence (with ordering temperature $T_\Theta$) in defining $T_c$. Adapted from [113]. (b) Cartoon of the possible suppression of SC driven by the loss of phase coherence: upon an optical excitation, while the gap size $\Delta$, which relates to the electronic temperature, gets only mildly increased (red sphere), the onset of phase fluctuations $T_\Theta$ gets reduced below the equilibrium $T_c$ (green sphere and dashed line), driving the system out of the SC state. Adapted from [114]. (c) Temperature dependence of the momentum-integrated spectra collected at the antinode (grey circle in the inset) for overdoped Bi2212 ($T_c \sim 84$K). (d) Temporal evolution of the amplitude of the quasiparticle peak $\Delta I_{\text{peak}}$ and FWHM (top panel) and the comparison with the penetration depth ratio $\lambda^2_{ab}(0)/\lambda^2_{ab}(T)$ – proportional to the superfluid density – (bottom panel), suggesting a direct relation between the suppression of quasiparticle spectral weight and superconductivity. Panels (c)-(d) adapted from [115].
While for conventional BCS superconductors the pairing energy is significantly smaller than the onset of phase fluctuations, hence unquestionably defining the SC phase transition, the low superfluid density within the Cu-O planes in cuprates leads the two phenomena to occur on the same energy scale (~ tens of meV in Bi-based compounds [113, 118]). The critical temperature $T_c$ may then be defined by the onset of phase fluctuations $T_\Theta$ rather than the temperature $T_{pair}$ below which the pairing mechanism becomes locally relevant (see schematic in Figure 3.1a) [113]. This proposal finds supports in various equilibrium measurements on UD cuprates reporting a non-zero pairing gap up to ~1.5$T_c$, while pair-breaking scattering processes emerge sharply at $T_c$ [119–122]. These findings suggest the possibility to induce a collapse of SC via manipulation of the density of phase fluctuations alone, independently of the number of across-gap excitations, as schematize in Figure 3.1b. The viability of this scenario has been validated in the UD bi-layer compound Bi2212 ($T_c \sim 82$ K) by a recent TR-ARPES experiment by Boschini et al. [114]. Upon an infrared ultrashort pulse excitation, while the amplitude of the SC gap is only slightly affected, the pair scattering rate $\Gamma_p$ (associated to the presence of phase fluctuations) exhibits a significant change and a faster dynamics with respect to that of charge excitations, designating the phase coherence as the primary mechanism controlling the formation of the macroscopic condensate (i.e. determining $T_c$). Furthermore, as an additional result of the ultrafast IR excitation, a clear suppression of the quasiparticle spectral weight has been observed, consistent to what was reported as a function of temperature in other ARPES studies on Bi2212 [114, 115, 123, 124]. Such a suppression of quasiparticle spectral weight, manifesting near the antinodal region ($\pi, 0$), as well as along the nodal direction where the SC gap is null, seems to exhibit an abrupt change around the superconducting phase transition temperature fading off for $T > T_c$, and thus suggesting a direct relation to the condensate density (see Figure 3.1c-d).

In order to further investigate the stability of the phase coherence in Bi-based cuprates as a function of the number of Cu-O planes, as well as the viability of the putative relation between the nodal quasiparticle spec-
tral weight and the superconducting state, we employed TR-ARPES on the single-layer Bi$_2$Sr$_2$CuO$_{6+\delta}$ (Bi2201). By adopting the same ultrafast approach proposed by Boschini et al. [114], we perturb the system with a IR ultrashort pulse and follow the relaxation dynamics of the spectral function. The comparison between our results and those reported for Bi2212 points towards the key role of phase coherence in the stability of the SC condensate in HTSC cuprates, and suggests the enhancing of phase fluctuations within the Cu-O plane as the major result triggered by the optical pumping. Moreover, by extending the equilibrium and ultrafast ARPES study to various compounds of both Bi2201 and Bi2212, we track the temperature evolution of the nodal quasiparticle spectral weight as a function of hole doping and materials, disclosing a universal dependence which links the suppression of the quasiparticle amplitude to the electronic temperature. The observed behaviour, which persists for temperatures much larger than T$_c$, rules out an explicit relation to the superconducting state.

Single-crystals of Bi2201 and Bi2212 were grown using the floating-zone method and hole-doped by oxygen annealing. All the samples were aligned along the $\Gamma$-Y direction and cleaved in situ. TR-ARPES measurements were performed at UBC using the 1.55 eV-pump and 6.2 eV-probe setup in Damascelli Laboratory (refer to [Section 2.2.1] for details). A variable filter was used to adjust the incident pump fluence in different datasets. Both the pump and the probe beams were s-polarized. Measurements were carried out at pressures lower than $<5\cdot10^{-11}$ torr and at a base temperature without the pump beam of 10 K. The angle and energy of the photoelectrons were resolved using a SPECS Phoibos 150 electron analyser. The energy and temporal resolutions of the system were estimated 17 meV and 250 fs, respectively. Complementary equilibrium ARPES measurements were carried out on Bi2212 at the Quantum Materials Spectroscopy Centre beamline at the Canadian Light Source in Saskatoon using a photon energy of $h\nu = 27$ eV at base pressure $<10^{-10}$ Torr with energy resolution better than 5.3 meV.
Figure 3.2: Static 6.2-eV ARPES of Bi2201. Equilibrium Fermi Surface mapping (FS, top) and ARPES spectrum along the nodal direction ((0,\(\pi\))-(\(\pi\),\(\pi\)), red cut in the FS) of Bi2201 for (a) an underdoped sample, \(T_c \sim 15\)K (UD15), (b) slightly overdoped, \(T_c \sim 30\)K (OD30) and (c) overdoped sample, \(T_c \sim 24\)K (OD24). The FS are obtained by an energy integration of 20meV and the solid green lines are tight-binding constant energy contours at \(\omega=0\) [125, 126]. (d) ARPES dispersion collected along Off-Node directions (blue cut in FS) defined by \(\varphi \approx 32^\circ\) (\(\varphi\) angle between (0,\(\pi\))-(\(\pi\),\(\pi\)) and the nodal direction) of OD24. (e) Schematic of the \(p\)-\(T\) diagram illustrating the position of the three explored dopings. All data acquired with 6.2-eV probe light at 10K base temperature.
3.2 TR-ARPES on Bi2201

Three different doping levels of the single-layer $\text{Bi}_2\text{Sr}_2\text{CuO}_6+\delta$ were studied in this investigation: underdoped sample with $T_c \sim 15\,\text{K}$ (Bi2201 UD15), slightly overdoped with $T_c \sim 30\,\text{K}$ (Bi2201 OD30) and overdoped with $T_c \sim 24\,\text{K}$ (Bi2201 OD24) – the schematics in Figure 3.2e shows the corresponding position in the $p$-$T$ diagram –. Figure 3.2a-c illustrate the equilibrium Fermi surfaces (FS) and the ARPES spectra along the nodal direction (red solid cut in the FS) for the three dopings acquired with 6.2-eV probe pulsed-light at 10 K. The solid green lines are the tight-binding constant energy contours at $\omega=0$ [125, 126] showing the evolution of the arc dispersion as a function of the doping level. The low photon energy of the probe pulse restricts the accessible $k$-space to the nodal direction and its vicinity, precluding the exploration of the antinodal region where the $d$-wave SC gap exhibits its maximum value. As a result, to capture non-zero contributions from the SC gap in the ARPES spectrum we instead focus on the momentum direction defined by $\varphi \simeq 32^\circ$ (Off-Node cut), $\varphi$ being the angle between $(0, \pi)$-$(\pi, \pi)$ and the nodal direction. By visual inspection of the Off-Node cut collected on OD24 and presented in Figure 3.2d, a modest bending of the electronic dispersion can be distinguished approaching the Fermi level as a manifestation of the (small) SC gap.

Given the high-quality of the observed spectral features, we first focus our experimental efforts on performing a comprehensive TR-ARPES study of Bi2201 OD24. The overall modification of the ARPES spectrum occurring upon the 1.55-eV pump excitation (mainly restricted to those states within range of the Fermi level) can be visualized by computing the dynamics of the phototemission intensity as a function of energy and momentum. Figure 3.3a shows the transient evolution of the photoemission intensity about the Fermi momentum $k_F$ as a function of binding energy and momentum direction (Node, upper panel and Off-Node, lower panel; directions as defined in Figure 3.2) acquired with a incident pump fluence of $(12 \pm 3)\,\mu\text{J/cm}^2$, hereon referred to as LF regime. We note that for both momentum directions the depletion (i.e. a suppression of spectral weight)
Figure 3.3: Energy-resolved TR-ARPES dynamics in Bi2201 OD24. (a) Temporal evolution of the photoemission intensity about the Fermi momentum \( k_F \) at different binding energies (5 meV integration window) along the nodal direction (top) and Off-nodal (bottom) of Bi2201 OD24. Data collected with an incident pump fluence of \((12 \pm 3) \mu J/cm^2\), referred to as Low Fluence (LF) regime. The solid lines are fits to an exponential function convoluted to a Gaussian accounting for the temporal resolution (for the \( \omega > 0 \) along the node, bi-exponential curves given by the sum of two exponential decays are used). (b) Dynamics of the nodal photoemission intensity in OD24 for incident pump fluence of \((42 \pm 6) \mu J/cm^2\) (Medium Fluence MF, top) and \((90 \pm 10) \mu J/cm^2\) (High Fluence HF, bottom). The solid lines are bi-exponential decay fits.
Figure 3.4: Energy-resolved decay times in Bi2201 OD24. (a) Relaxation decay times as a function of binding energies, describing the exponential decay of momentum-resolved photoemission intensity curves in the LF regime (as the ones presented in Figure 3.3a), along the nodal and off-nodal direction. Open red circles are decay times extracted with the same procedure for optimally-doped Bi2212 employing an incident pump fluence of $(15 \pm 4) \mu J/cm^2$. (b) Comparison of the decay times obtained in Bi2201 OD24 along the nodal direction for the three different fluences regimes explored in this work. The bottom inset shows the values characterizing the fast recovery component emerging at high fluences.

observed for $\omega < 0$ appears almost twice as strong as the population (i.e. increase of spectral weight) occurring at positive energies. The dynamics can be described by a single exponential decay convoluted by a Gaussian which accounts for the experimental temporal resolution and the intrinsic quasi-particle build-up time (solid lines in Figure 3.3a). In the case of the nodal low-energy population, a bi-exponential curve (given by the sum of two exponentials with different decay times) is instead used to fit the experimental data upon convolution to a Gaussian. The extracted decay times $\tau$ for the two momentum cuts are presented in Figure 3.4a, along with the values obtained along the node in optimally-doped Bi2212 ($T_c \sim 91$ K, OP91) with an incident pump fluence of $(15 \pm 4) \mu J/cm^2$. Despite the smaller SC gap characterizing Bi2201 and the consequent reduced scattering restrictions following phasespace considerations, the observed dynamics appear overall slower than in Bi2212 (especially clear for $\omega < 0$). In addition to the slow
few picoseconds recovery feature, proposed to be closely connected to SC, a sharp femtosecond relaxation dynamics has been reported in Bi2212 for pump fluences above the critical fluence \( F_c \), defined as the fluence at which the near-nodal gap is suppressed) \[127–130\]. In the case of Bi2201, the reported critical fluence \( F_c^{Bi2201} \sim 8 \mu J/cm^2 \) is comparable to the LF regime reported here, and indeed a faster dynamics can be seen starting to emerge in the population traces along the nodal direction (see Figure 3.3a). In order to verify this scenario, we performed additional TR-ARPES measurements on Bi2201 OD24 by increasing the incident pump fluence to \((42 \pm 6) \mu J/cm^2\), MF regime and \((90 \pm 10) \mu J/cm^2\), HF regime. The resulting nodal dynamics for selected binding energies are presented in Figure 3.3b and consistently exhibit two contributions to the relaxation recovery. While the decay time of the slow component decreases with increasing the incident pump fluence, the time constant of the fast component \( \tau_{fast} < 1.5ps \) does not exhibit a significant variation within the explored pump fluence range (see Figure 3.4b). This observation is in agreement with what was reported for optimally doped Bi2212 \[128\], although in the present case a much higher fluence \((\sim 10 F_c) \) has been employed.

By increasing the incident pump fluence, more energy gets transferred into the sample. In order to provide an estimate of the overall thermal effect induced by the presence of the pump beam on the sample before the temporal incidence with the probe (i.e. at negative delays) and on how the electronic bath responds to the optical excitation on a thermal level, we compute the evolution of the transient electronic temperature for each employed pump fluence. In virtue of the zero SC gap at the node, the analysis of the momentum-integrated energy distribution curves (EDCs) along the nodal direction can serve to this purpose as it maps into the Fermi-Dirac distribution, \[ \int I_{node}(\omega, k)dk \propto \int A_{node}(\omega, k)f(\omega)dk \propto f(\omega) \], as shown in Figure 3.5a. Photoexcited quasiparticles in cuprates, and in general in strongly correlated electron systems, release the energy deposited by the pump pulse through electron-electron and electron-boson scattering, thermalizing and reaching a state of quasi-equilibrium on an ultrafast time scale of about 100 fs \[131–136\]. Thus, the analysis of the nodal Fermi-
Figure 3.5: Transient electronic temperature $T_e$. (a) Momentum-integrated EDCs along the nodal direction before (-0.5 ps) and after (0.33 ps) the pump excitation, HF regime. The black lines are Fermi-Dirac distribution fits. (b) Transient electronic temperature $T_e(t)$ for LF. The solid line is a phenomenological exponential decay fit. (c) Same as in (b) but for MF and HF regimes. The temporal evolution can be described by double exponential-decay fits (solid lines), where a fast component (filled green and brown curves) grows on top of the same slow recovery which characterizes the LF dynamics (filled blue curve). Error bars in (b)-(c) reflect the systematic errors associated with the experiment and the number of averaging cycles acquired for each fluence.
edge width – approach already adopted in previous TR-ARPES studies on cuprates [124, 131] – allows for extracting an effective electronic temperature as a function of the pump-probe delay $t$. The resulting $T_e(t)$ for the three different fluences are displayed in Figure 3.5b-c, along with exponential-decay fits (solid lines) and show how, although only in the LF regime the base temperature can be safely placed below $T_c$ (dashed black line), the system does not relaxes back to equilibrium within the probed temporal window in any of the fluence regimes explored. Interestingly, the same long relaxation dynamics of $\sim 10$ ps (filled blue curve) well characterizes all the observed $T_e(t)$, on top of which a second fast dynamics emerges at high fluences on the timescale of 1 ps after the pump excitation (filled green curve, MF ; filled brown curve, HF). The knowledge of the temporal evolution of the effective electronic temperature upon the photo-excitation will be crucial in establishing the extension of pure thermal effects to the dynamics of the one-electron spectral function as discussed in the following section.

3.3 Tracking the ultrafast enhancement of phase fluctuations in Bi2201

As an extension into the time domain of the standard ARPES technique, TR-ARPES provides access to more information beyond the overall dynamics of the photoemission intensity as a function of energy and momentum. In particular, the dynamical response of the one-electron spectral function can be studied as a result of an ultrafast optical excitation, providing us with a tool to study the dynamical interplay between the electron pairing mechanism and the stability of phase coherence in the formation of the condensate in HTSC cuprates. As proposed by Norman et al. [137], these two phenomena may be accounted for in the approximated expression of the electron self-energy at the Fermi momentum ($k = k_F$) for a superconductor. It can be expressed as:

$$\Sigma(\omega) = -i\Gamma + \frac{\Delta^2}{(\omega + i\Gamma_p)}.$$  (3.1)
Here, $\Delta$ represents the amplitude of the SC gap which describes the across-gap excitations and whose value is momentum-dependent according to the established $d$-symmetry of the SC order parameter in cuprates. $\Gamma_s$ is the single-particle scattering rate while $\Gamma_p$ is the inverse pair lifetime proposed to reflect the presence of phase fluctuations and thus expected to vanish for $T \ll T_c$ [137,138]. TR-ARPES potentially provides access to the individual dynamics of these three parameters by tracking the temporal evolution of the spectral-function expressed by:

$$A(k,\omega) = -\frac{1}{\pi} \frac{\Sigma''(\omega)}{[\omega - \epsilon_k(\omega)]^2 + [\Sigma''(\omega)]^2}$$

(3.2)

where $\epsilon_k$ is the bare energy dispersion. Here we remark that while the presence of phase fluctuations has been shown to lead to a pair-breaking scattering rate as the one proposed in Equation 3.1 [138], a non-vanishing $\Gamma_p$ does not uniquely identify phase fluctuations as the driver for the observed spectral function phenomenology. Therefore, only in the UD and close to optimally-doped regime a direct correspondence $\Gamma_p$-phase fluctuations may be legitimate within the context of Emery and Kivelson’s phase diagram [113] (see Figure 3.1a), whereas the validity of such univocal relation remains questionable in the strongly OD regime.

Disentangling the contributions of $\Delta$, $\Gamma_s$ and $\Gamma_p$ to the ARPES spectrum can be challenging, especially in the presence of small SC gaps as in Bi2201 ($\Delta_{\text{max}} \sim 15\text{meV}$ at the antinode [111]). However, along the nodal direction the SC gap is null, making the second term in Equation 3.1 vanish, and thus allowing the investigation of the effect of $\Gamma_s$ alone. Moreover, the estimate of the overall thermal effect due to the pump beam on the sample presented in Figure 3.5 safely identifies the system in a SC state (before the pump excitation) only in the LF regime. We then start our analysis focusing on the temporal evolution of the nodal ARPES spectrum of Bi2201 OD24 in the LF regime. Figure 3.6a displays EDCs at $k = k_F$ acquired along the node for different pump-probe delays showing an evolution of the quasiparticle peak. In order to get quantitative information about the associated spectral function dynamics in terms of Equation 3.1 and Equation 3.2 we
compute the corresponding symmetrized EDCs (SEDCs) of the curves in Figure 3.6a. This commonly used procedure consists in adding to an EDC at \( k_F \) the symmetrized about \( E = E_F \) counterpart to rule out the contribution of the Fermi-Dirac distribution term \( f(\omega) \) to the ARPES spectra [139]. Note that this approach relies on the particle-hole symmetry property of the spectral function at \( k = k_F \), experimentally verified in the near-nodal region of Bi2212 [114, 140]. Assuming constant matrix elements in the explored momentum range, SEDC(\( \omega \)) \( \propto A(k_F, \omega) \). Figure 3.6b shows nodal SEDCs at different delays alongside fits to Equation 3.1 and Equation 3.2 obtained with \( \Delta = 0 \). The photoinduced modifications to the spectral function are accounted for by a change of the single-particle scattering rate \( \Gamma_s \). The full temporal evolution \( \Gamma_s(t) \) resulting from the fitting procedure is plotted in Figure 3.6c: starting from a value of (9.7 \( \pm \) 0.3) meV at negative delays, it exhibits an increase of almost 25\% upon the pump excitation. This range of values, as well as the characteristic several-ps long relaxation dynamics (exponential decay fit represented by the solid line in Figure 3.6c), are consistent with what is reported for optimally-doped and overdoped Bi2212 [114, 121].

Once we established the transient evolution of \( \Gamma_s \) along the nodal direction, we now move to the analysis of the spectral function along the Off-Node direction (\( \phi \approx 32^o \) as defined in Figure 3.2). In this case, the SC gap \( \Delta \) has a non-zero value and needs to be included in the fitting of SEDCs, as well as the possible spectral broadening induced by \( \Gamma_p \). In order to estimate the unperturbed value of \( \Delta \), we first fit the SEDC at negative delays (blue circles in Figure 3.7a) by assuming \( \Gamma_p = 0 \) (as expected in the case of fully coherent condensate). The best fit returns \( \Gamma_s^{eq} = (10.5 \pm 0.5) \) meV and \( \Delta^{eq} = (5 \pm 1) \) meV, which are in agreement with what is reported in previous equilibrium ARPES measurements [111, 121], further validating the base line of the fitting procedure. Next comes the analysis of the dynamics of the spectral function along the Off-Node cut as a function of the pump-probe delay when all the three parameters in Equation 3.1 possibly change. Having three unknown variables combined to the small value of \( \Delta^{eq} \) challenges the stability of the fitting procedure via Equation 3.1 and
Figure 3.6: Nodal single-particle scattering rate dynamics. (a) EDCs at the Fermi momentum $k = k_F$ for selected pump-probe delays, acquired along the nodal direction in Bi2201 OD24, LF regime. (b) Symmetrized EDCs (SEDCs) of the curves presented in (a). The solid black lines are fits obtained using Equation 3.1 and Equation 3.2 with $\Delta = 0$. (c) Temporal evolution of the single-particle scattering rate $\Gamma_s$ extracted by fitting SEDCs. The solid line represents a phenomenological exponential decay fit convoluted with a Gaussian. Error bars in (c) represent the confidence interval in the fit corresponding to $3\sigma$.

Equation 3.2, urging us in setting some constraints. To this purpose, we note that the equilibrium values of $\Gamma_s$ obtained along the nodal and off-nodal directions differ by less than 1 meV, a finding in agreement with the nearly momentum-independent behaviour reported by Kondo et al. [121] in the near-nodal region for Bi2212. This observation motivates our choice to lock the temporal evolution of $\Gamma_s$ along the Off-Nodal direction to the dynamics extracted at the node (solid line in Figure 3.6c), setting a tolerance of $\pm 1$ meV on the resulting fitting value. With this constraint in place, we fit the full temporal range of Off-Node SEDCs. Figure 3.7a presents SEDCs and corresponding fits for three selected pump-probe delays and, although the small gap size precludes even at negative delays the precise identification of a defined ”double-peak” feature typical of the SC state, we observe a modification of the spectra occurring mainly about $\omega = 0$. Such a modification encodes the temporal evolution of $\Gamma_s$, $\Delta$ and $\Gamma_p$ through Equation 3.1. In Figure 3.7b-d we present the resulting dynamics of these three parameters obtained by SEDCs fitting which reveals a transient modification of $\Gamma_p$ more than five times larger than what observed for the gap. Moreover,
Figure 3.7: Off-Node spectral function dynamics. (a) SEDCs at $k = k_F$ along the Off-Node direction ($\varphi \simeq 32^\circ$ as defined in Figure 3.2), LF regime. The solid black lines are fits obtained using Equation 3.1 and Equation 3.2. (b)-(d) Ultrafast dynamics of the single-particle scattering rate $\Gamma_s$ (b), the gap size $\Delta$ (c) and the pair scattering rate $\Gamma_p$ (d) obtained from the SEDCs fitting. The solid lines represents an exponential decay fit convoluted with a Gaussian. The dashed line in (b) is the temporal evolution of $\Gamma_s$ extracted along the nodal direction and used to constraint the fit of SEDCs shown in (a), as described in the main text. Inset in (d): Comparison between the $\Gamma_p$ dynamics obtained for Bi2201 OD24 ($F = (12 \pm 3) \mu J/cm^2$) and Bi2212 UD82 ($F = (30 \pm 4) \mu J/cm^2$, from [114]). Error bars in (b)-(d) represent the confidence interval in the fit corresponding to $3\sigma$. 
while both $\Gamma_\text{s}$ and $\Delta$ do not recover the equilibrium values within the temporal range explored, the dynamics of $\Gamma_p$ is completely decoupled exhibiting a relaxation time of $\approx 1$ ps, about ten times faster than what extracted for the former two parameters. In order to offer a more quantitative discussion of our results in terms of previous studies, the inset in Figure 3.7d offers a direct comparison between the temporal evolution of $\Gamma_p$ as extracted in this work for the single-layer Bi2201 OD24 to what reported for the bilayer Bi2212 UD82 [114]. Although the two datasets have been collected employing substantially different incident pump fluence – $(12 \pm 3) \mu J/cm^2$ and $(30 \pm 4) \mu J/cm^2$ for Bi2201 and Bi2212, respectively –, note that in both cases this value corresponds to $F \sim 2F^x_c$ ($x =$Bi2201, Bi2212) substantiating a direct comparison between the two results. A remarkable agreement is evidenced from the inset in Figure 3.7d not only in terms of the characteristic relaxation time on the 1 ps timescale but also of the absolute magnitude of the observed pump-induced increase. In fact, in both studies the transient pair-breaking scattering rate $\Gamma_p$ has its maximum at $\sim 15$ meV which corresponds to the energy scale at which phase fluctuations become relevant in Bi-based cuprates [113, 118]. This observation points towards the interpretation of the temporal evolution of $\Gamma_p$ in terms of an ultrafast enhancement of phase fluctuations upon IR excitation, as reported for the case of UD Bi2212 [114]. The analogy between the two studies also extends to the characteristic build-up time of the enhancement of $\Gamma_p$. The ultrafast response to the pump excitation is delayed with respect to that of $\Gamma_\text{s}$ and $\Delta$ with the maximum value reached about 600 fs, as shown by the normalized differential dynamics (defined as $|x(t) - x(0)|/\max|x(t)|$) in Figure 3.8a. This observation seems consistent with the proposal of a pump-induced non-thermal bosonic population as the key player in the increase of the phase fluctuations speculated for UD Bi2212 [114].

To conclude our discussion on the dynamics of $\Gamma_p$, we address the question on whether or not the observed ultrafast increase stems from a mere thermal effect induced by the presence of the pump on the sample. In fact, as shown in Figure 3.5b, the optical excitation generates a transient evolution of the electronic temperature casting doubt on what extend such
Figure 3.8: Disentangling $\Gamma_p$ and $T_e$ dynamics in Bi2201. (a) Normalized differential dynamics computed as $|x(t) - x(0)|/\max[x(t)]$ for $\Gamma_s$ (red line), $\Delta$ (ochre) and $\Gamma_p$ (blue) from data in Figure 3.7b-d. (b) Comparison between the $\Gamma_s$, $\Delta$ and $\Gamma_p$ normalized differential dynamics (left axis) and the temporal evolution of the electronic temperature extracted along the nodal direction (filled black circles, right axis; from data in Figure 3.5b).

A temperature change reflects onto the dynamics of the spectral function and consequently of the three parameters in Equation 3.1. To this goal, we plot in Figure 3.8b the normalized transient evolution of $\Gamma_s$, $\Delta$ and $\Gamma_p$ (left axis) alongside the electronic temperature as extracted along the nodal direction (filled black circles, right axis; refer to Figure 3.5b). By direct visual inspection is evident that both the single-particle scattering rate and the gap size exhibit a dynamics closely locked to the temporal evolution of the electronic temperature with a recovery time of $\sim 11$ ps. Thermally induced across-gap charge excitations solely determine both the pairing strength $\Delta$ and the increase of single-particle linewidth $\Gamma_s$ (in agreement with what is reported from equilibrium ARPES [115, 137]). Contrarily, the completely independent dynamics exhibited by $\Gamma_p$ with respect to $T_e$ testifies to the non-thermal origin of the observed transient enhancement of phase fluctuations.

All together the results reported here for Bi2201 OD24, along with the strong analogy to what was reported for Bi2212 UD82, suggest the loss
of phase coherence as the key mechanism in the ultrafast collapse of superconductivity (and the recovery thereof), even in the slightly overdoped regime and independently on the number of Cu-O layers within the unit cell. Future experiments will be instrumental to address whether such scenario holds in the very OD regime.

### 3.4 Nodal coherent-spectral-weight meltdown in Bi-based cuprates

While off-nodal quasiparticle spectral features observed below $T_c$ are strongly linked to the pairing strength and the Cooper pairs phase coherence, low-energy excitations along the nodal direction are usually regarded as minimally affected by SC. Therefore, while a meltdown of coherent spectral weight was reported by equilibrium ARPES studies at the antinode of the bi-layer Bi2212 and related to SC [115, 123], such an effect was not expected along the nodal direction where the SC gap is null. However, this nodal-antinodal dichotomy seems softened on the basis of a suppression of quasiparticle spectral weight along the node reported in a recent TR-ARPES study on optimally-doped Bi2212 and primarily observed in the SC state, thus suggesting a direct link between the nodal spectrum and SC itself [124]. As evinced from data reported in Figure 3.6a-b, a clear suppression of spectral weight is evident also in the present case of Bi2201 OD24: the ultrafast broadening of the quasiparticle peak alone (reflected in the increase of the broadening term $\Gamma_s$) does not compensate for the loss of Coherent Spectral Weight (CSW) in the vicinity of $E_F$. The SEDCs fitting procedure by Equation 3.1 and Equation 3.2 described in Section 3.3 provides us with access to the transient modification of the CSW amplitude in terms of an overall normalization constant in the fitting function. Note that, since each pump-probe delay is acquired in the same experimental configurations, this approach naturally sets the same background baseline for all SEDCs allowing for a direct measure of the relative variation of spectral weight, $\Delta$CSW, upon the optical pumping. Figure 3.9a-c present $\Delta$CSW(t) extracted via fitting of SEDCs along the nodal direction for the three dif-
Figure 3.9: Ultrafast suppression of coherent spectral weight in Bi2201 OD24. (a)-(c) Relative variation of the nodal quasiparticle coherent spectral weight, $\Delta$CSW, as a function of the pump-probe delay extracted by fitting SEDCs in Bi2201 OD24 for LF (a), MF (b) and HF (c) regime. The solid lines are phenomenological single (LF) or double (MF and HF) exponential decay fits convoluted to a Gaussian. Error bars reflect the systematic errors associated with the experiment and the number of averaging cycles acquired for each fluence. (d) Comparison between $\Delta$CSW extracted from SEDCs fitting (yellow circles), momentum-distribution curves (MDCs) fitting (orange line) and SEDCs integrated area (dashed light blue line); MF regime. A Lorentzian-like function is used to fit the MDCs at $E = -20\text{meV}$.

Different pump fluence regimes exploited in the investigation of Bi2201 OD24 (LF, MF and HF, respectively). The magnitude of the observed variation increases as the pump fluence increases going from $\sim 7\%$ for LF to as large as $20\%$ at HF. Interestingly, the temporal evolution can be phenomenologically described by a single (LF) or double (MF and HF) exponential decay reminiscent of the dynamics characterizing the transient electronic temperature shown in Figure 3.5, where a slow $10\,\text{ps}$-dynamics appears for all the three pump fluences, on top of which a fast feature develops for MF.
and HF. This observation suggests a close connection between the extracted suppression of CSW along the node and the transient electronic temperature. Before moving on to the investigation of such a relation, we test the reliability of our approach based on SEDCs fitting for determining $\Delta$CSW as a function of the pump-probe delay. Momentum Distribution Curves (MDCs) can be addressed as an alternative procedure in which the amplitude and broadening of the Lorentzian-like lineshape map into $\Delta$CSW($t$) and $\Gamma_s(t)$, respectively. Figure 3.9d compares the temporal dynamics of $\Delta$CSW as extracted from fitting of SEDCs (yellow circles) and MDCs (orange line), showing a solid agreement. To go beyond the specific model used to fit the data, we overimpose in Figure 3.9d also the total integrated area of SEDCs (dashed light blue line): the observed consistency across the three methods validates our experimental estimate of $\Delta$CSW.

In order to explicitly expose the relation between CSW and electronic temperature, we plot $\Delta$CSW directly as a function of the extracted $T_e$ in Figure 3.10b. Note that in order to account for the different base temperature observed for each pump fluence regime, the curves have been rescaled to match at $T_e \sim 30$K. Joint together, the results collected for the three different pump fluences show an almost-linear suppression of CSW as a function of the increasing electronic temperature for the entire range explored. Such significant linear suppression (up to $\sim 20\%$) appears unaffected by the SC phase transition and persists for $T_e \gg T_c$ (blue shadow in Figure 3.10b).

Note that, contrarily to what was previously reported for Bi2212 [124], this finding points towards a minimal (if not null) contribution of superconductivity itself to the here-reported nodal quasiparticle meltdown in Bi2201 OD24. For completeness, we present in Figure 3.10a also the temperature evolution of the single-particle scattering rate $\Gamma_s$ as extracted from fitting of nodal SEDCs for the different fluence regimes. The three curves are described by the same linear T-dependence increase, further supporting the major role played by thermally induced charge excitations in determining the ultrafast increase of $\Gamma_s$, as also reflected in the coupled $\Gamma_s$ and $T_e$ dynamics (see Figure 3.8b).
Figure 3.10: Nodal CSW and $\Gamma_s$ vs. temperature in Bi2201 OD24. (a) Temperature evolution of the single-particle scattering rate $\Gamma_s$ as obtained from nodal SEDCs fitting with different pump fluences. (b) Relative variation of the nodal coherent spectral weight $\Delta$CSW as a function of the electronic temperature $T_e$ for the three employed pump fluences. Curves have been rescaled to match at $T_e \sim 30$K to account for the different base temperature (i.e. at negative delays) observed in the three fluence regimes. The blue shadow area indicates $T_c$. Data points in (a)-(b) are displayed vs the electronic temperature derived by the phenomenological exponential decay fits shown in Figure 3.5b-d.

To establish the observed $\Delta$CSW behaviour as a general property of single-layer Bi-based cuprates, we extend our TR-ARPES study to different doping levels, namely Bi2201 UD15 and Bi2201 OD30, in the LF regime (for a general overview of the FS and ARPES dispersion of the three different Bi2201 compounds studied in this project, as well as the corresponding position in the $p$-$T$ diagram, see Figure 3.2). Following the same procedure outlined above, we extract the temporal evolution of the effective electronic temperature from momentum-integrated EDCs along the nodal direction (Figure 3.11a) and then relate it to the transient dynamics of $\Gamma_s$ and $\Delta$CSW as shown in Figure 3.11b-c, respectively. As expected from visual inspection of the nodal cuts presented in Figure 3.2, the single-particle broadening term is higher in the UD15 and OD30 samples with respect to what is detected for OD24; nevertheless, a similar slope describes the in-

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Figure 3.11: Doping dependence of the temperature evolution of CSW and $\Gamma_s$ in Bi2201. (a) Transient electronic temperature $T_e(t)$ extracted from momentum-integrated EDCs (as described in Section 3.2) for three doping levels of the single-layer Bi2201: UD15, OD30 and OD24, respectively. The solid lines are phenomenological exponential decay fits. Data acquired employing the low fluence for the pump beam ((12 ± 3) $\mu$J/cm$^2$). (b)-(c) Temperature evolution of $\Gamma_s$ (b) and $\Delta$CSW (c) obtained from nodal SEDCs fitting for Bi2201 UD15 (light blue data points), OD30 (orange) and OD24 (blue); LF regime. Shadowed areas in (c) indicate the SC critical temperature $T_c$ for the three dopings. Data points in (b)-(c) are displayed vs the electronic temperature derived by the phenomenological exponential decay fits shown in (a).
crement of $\Gamma_s$ as $T_c$ increases. Interestingly, despite being characterized by different single-particle broadening, the three dopings present a consistent $T$-dependence of the relative suppression of the nodal CSW, which does not exhibit any abrupt modifications across the corresponding $T_c$ (colored shadows in Figure 3.11c).

The findings presented thus far are in contrast to what was previously reported for bi-layer Bi2212 by ARPES and TR-ARPES studies [115, 123, 124] on at least two aspects: (i) no strong enhancement of the quasiparticle peak suppression is observed to occur below $T_c$, as a comparable effect is here detected in Bi2201 UD15 and Bi2201 OD30 despite the fact that in the former case the system is already out of the SC state before the optical pumping, while in the latter the condensate is fully coherent at negative pump-probe delays; (ii) no direct link is evinced between the $\Delta$CSW and the collapse of SC driven by the ultrafast enhancement of phase fluctuations, arguable in terms of the completely distinct dynamics of $\Gamma_p$ to that of $\Delta$CSW, which instead closely resembles the evolution of $T_e$. This discrepancy motivates additional investigations by employing the same TR-ARPES experimental approach described thus far but now applied on the bi-layer Bi2212. Moreover, conventional equilibrium temperature-dependent ARPES measurements are also imperative to address whether the observed effect is limited to the transient regime or consistent with a mere increase of the sample temperature. The next paragraphs will focus on these aspects.

First we discuss the modifications of the nodal CSW in the bi-layer Bi2212 induced by an ultrafast optical excitation equivalent to that employed for Bi2201. Figure 3.12a shows the extracted transient electronic temperature in optimally-doped Bi2212 OP91 ($T_c \sim 91$K) as a result of increasing pump fluences (in this specific dataset $(14 \pm 5) \mu$J/cm$^2$, $(23 \pm 7) \mu$J/cm$^2$ and $(62 \pm 10) \mu$J/cm$^2$, respectively). The corresponding $\Delta$CSW from nodal SEDCs are plotted as a function of $T_e$ in Figure 3.12b. Although in the present case the high $T_c$ precludes any conclusive claim on the influence of SC in the evolution of CSW, the observed suppression of spectral weight exhibits a dependence on the extracted electronic temperature which resembles that presented in Figure 3.10b and Figure 3.11c for Bi2201. This
Figure 3.12: Universal suppression of CSW in Bi-based cuprates. (a) Transient electronic temperature $T_e(t)$ extracted from momentum-integrated EDCs for Bi2212 OP91 ($T_c \sim 91$ K) in three different fluences regimes, namely $(14 \pm 5) \mu J/cm^2$, $(23 \pm 7) \mu J/cm^2$, $(62 \pm 10) \mu J/cm^2$, here labelled for LF, MF and HF, respectively. (b) Temperature evolution of $\Delta CSW$ for all three fluence regimes. Data points are plotted vs the electronic temperature determined by the phenomenological exponential decay fits shown in (a). (c) Comparison between $\Delta CSW(T)$ extracted for the single-layer Bi2201 (UD15, OD30 and OD24; full markers) and the bi-layer Bi2212 (OP91, OD80, OD60; open circles). All curves follow an almost-linear behaviour as a function of the electronic temperature. Shadowed areas mark the range of $T_c$ for the different compounds.

observation testifies the capability of our experimental approach in tracking the loss of quasiparticle spectral weight upon optical pumping in both Bi2201 and Bi2212.

A comprehensive picture of the nodal CSW meltdown in Bi-based cuprates is offered in Figure 3.12c. Here, computed $\Delta CSW(T_c)$ for different doping levels of single- (full markers) and bi-layer (open circles) compounds are combined and compared. Despite the large variation of $T_c$ across the
Figure 3.13: CSW from equilibrium temperature-dependent ARPES. (a) EDCs at the Fermi momentum $k = k_F$ (left) and corresponding SEDCs (right) as a function of sample temperature in optimally-doped Bi2212 OP91. Data acquired at the Canadian Light Source synchrotron facility with a photon energy of 27 eV. (b) Comparison between $\Delta CSW(T)$ as extracted from TR-ARPES (full markers) and equilibrium ARPES (open circles) measurements of Bi2212 OP91 (green) and Bi2212 OD60 (purple).

studied compounds (shadows in Figure 3.12c), a remarkable agreement is achieved between the tracked CSW vs. $T_e$ in Bi2201 and Bi2212 in terms of both functional form and magnitude, establishing the nearly linear temperature dependence of the nodal coherent spectral weight as a universal behaviour of Bi-based cuprates and uncorrelated to SC.

All the data presented thus far in this section (for both Bi2201 and Bi2212) have been acquired in an ultrafast fashion, where the effects induced by the pump excitation are tracked as a function of the pump-probe delay and subsequently discussed in terms of the evolution of the effective electronic temperature determined by the Fermi-edge width at each delay. Although this ultrafast approach ensures equivalent experimental conditions for each temperature (e.g. the same spot on the sample’s surface and momentum-space position), it might rise doubts on whether the observed behaviour is an exclusive property of the transient state. In this regard, we performed
conventional temperature-dependent ARPES studies on Bi2212 (OP91 and OD60) at the Canadian Light Source synchrotron facility. Figure 3.13a displays the temperature evolution of EDCs at $k = k_F$ (left) and corresponding SEDCs (right) acquired along the nodal direction of Bi2212 OP91 with a photon energy of 27 eV. Also in this case, the major effect of the temperature increase to up to $\sim 140$ K is the reduction of the quasiparticle amplitude rather than the broadening of the spectral features. To quantify this modification in the context of the data shown above, in Figure 3.13b we offer a direct comparison between $\Delta \text{CSW}(T)$ as obtained from equilibrium ARPES (open circles) and TR-ARPES (full markers) for Bi2212 OP91 and Bi2212 OD60. While equilibrium ARPES measurements cover a much wider temperature range, the curves obtained from the two experimental approaches are in good agreement and clearly exclude a vanishing of the CSW suppression within range of $T_c$, as instead previously reported at the antinode of Bi2212 [115, 123].

Here, it is important to remark that the observed behaviour of $\Delta \text{CSW}(T)$ is not caused by nonlinearity effects of the detector. Nonlinearity effects are common in electron spectrometers, especially when strong lineshapes occur along with a low level background, as often the case of low photon energy ARPES measurements on cuprates. It has been shown that this can result into an artificial enhancement of the quasiparticle peak, and post-acquisition procedures have been developed to correct the data for such effects [127, 141]. However, these procedures may mask a correct evaluation of small modifications in the quasiparticle peak of the order of few percentage units, like that reported in this section for $\Delta \text{CSW}(T)$ in Bi2201 and Bi2212. To address the possible contributions of the detector’s nonlinearity in the observed evolution of $\Delta \text{CSW}(T)$, we collected the TR-ARPES data shown in Figure 3.12a-b and the equilibrium data in Figure 3.13 in ”single pulse counting mode”, a detection regime of the electron analyzer not affected by nonlinearity effects. In spite of this, Figure 3.12c and Figure 3.13c show full consistency across all the performed measurements, therefore ruling out a suppression of spectral weight artificially induced by nonlinear effects in the detecting process.
As last note we recognize that, in virtue of the persistence of the hereby reported suppression of CSW for $T \gg T_c$ for both Bi2201 and Bi2212, it could be tempting to speculate an onset temperature associated to a different order than SC, such as the pseudogap. However, while the pseudogap characteristic temperature $T^*$ ranges well above 100 K for underdoped and optimally-doped compounds (and is thus beyond the probed temperature range of this work), no equilibrium pseudogap has been reported for the very overdoped Bi2212 OD60 compound [142–144]. In spite of this difference, a substantial modification of the nodal CSW appears in our TR-ARPES and equilibrium ARPES results on Bi2212 OD60, comparable in magnitude to that observed for the other compounds over the entire explored temperature range (including for $T_c < T < T^*$ for the Bi2212 OP91 sample, see Figure 3.13b). This observation excludes a direct connection to the physics of the pseudogap.

We propose that the observed CSW meltdown stems from the temperature evolution of the imaginary part of the electron self-energy included in the spectral function. Here, we limit the discussion to the spectral function at $k = k_F$. In fact, if we evaluate the spectral function always at the Fermi momentum (as is the case for all the experimental SEDCs reported thus far in this section), in first approximation the term $\epsilon_k^0 - \Sigma'(k, \omega)$ in the denominator of Equation 2.11 (which describes the renormalization of the electron dispersion) can be set to zero, to explore the effect of the imaginary part. This allows us to express the change in the spectral function solely in terms of $\Sigma''$, as follow:

$$A_{k_F}(\omega) = \frac{-1}{\pi} \frac{\Sigma''_{k_F}(\omega)}{\omega^2 + [\Sigma''_{k_F}(\omega)]^2}. \quad (3.3)$$

This approach suggests that the evolution of $\Delta\text{CSW}(T)$ may represent a metric tool to distinguish between the canonical Fermi-liquid (FL) and the marginal-Fermi-liquid (MFL) behaviour. The MFL model has been proposed as a phenomenological description of HTSC cuprates in particular to account for the observed strange metal behaviour, i.e. the linear electrical resistivity [145–147]. FL and MFL exhibit distinct temperature dependence.
Figure 3.14: Simulated $\Delta CSW(T)$ in a FL vs. MFL picture. (a) Imaginary part of the electron self-energy (top) and associated spectral function (bottom) for the Fermi-liquid (FL, black lines) and marginal-Fermi-liquid (MFL, red lines) models simulated via Equation 3.3 and Equation 3.3 at temperature equal to 10 K. (b) Comparison between the simulated suppression of $CSW$, as extracted from Equation 3.3 and Equation 3.4, and the experimentally observed $\Delta CSW(T)$ (filled and open circles for Bi2201 and Bi2212, respectively; data from Figure 3.12c). The best agreement is achieved within the FL picture (black line). In all simulations $\beta$ and $\lambda$ coefficients were set to 19.5 and 0.9, respectively, to match the relative variation of $\sim 22\%$ at 100 K exhibited by the experimental data.

\[
\begin{align*}
\Sigma''_{FL}(\omega, T) &= \beta [\omega^2 + (\pi k_B T^2)] \\
\Sigma''_{MFL}(\omega, T) &= \lambda \frac{\pi}{2} \max(|\omega|, T),
\end{align*}
\]  

where $\beta$ and $\lambda$ are coupling constants. Figure 3.14a shows $\Sigma''(\omega)$ (top) and the corresponding spectral function (bottom) simulated at 10 K using Equation 3.3 and Equation 3.4, for both FL and MFL. Following the same proce-
dure by varying the temperature parameter, the evolution of the coherent spectral weight can be computed as a function of $T$ for the two different models. Figure 3.14 displays the results of such computation overimposed to the experimental data already shown in Figure 3.12c. Here, the values of the two constants $\beta$ and $\lambda$ are set such that the magnitude of the simulated CSW suppression matches the $\sim 0.78\%$ at $100\,\text{K}$ observed experimentally. The best agreement is achieved by a FL description (black line), while the MFL (red line) seems to fail to reproduce the experimentally observed $T$-dependence. This finding is consistent with a recent ARPES study reporting true Fermi-liquid quasiparticles only along the nodal direction in overdoped $\text{La}_{1.77}\text{Sr}_{0.23}\text{CuO}_4$ cuprate, while proposing an angular breakdown of such FL behaviour moving towards the antinode [148].

### 3.5 Conclusions

To summarize, we have performed a comprehensive TR-ARPES study of both the single- and bi-layer hole-doped Bi-based cuprates. Firstly, by performing a detailed analysis of the dynamics of the spectral function in Bi2201-OD24 upon optical pumping, we have disentangled the temporal evolution of the pair scattering rate $\Gamma_p$ (related to the presence of phase fluctuations) from that of the gap amplitude $\Delta$. In addition, we have demonstrated that the ultrafast enhancement of phase fluctuations and subsequent fast relaxation (within $\sim 2\,\text{ps}$) do not map into the dynamics of the effective electronic temperature, and thus cannot be ascribed to a mere thermal effect. These results complement a similar TR-ARPES study on the bi-layer Bi2212 [114], thus establishing the persistence of macroscopic phase coherence as an essential ingredient in the formation of the SC condensate for underdoped and close to optimally-doped Bi-based cuprates, independently on the number of CuO$_2$ layers. Secondly, we have reported a comprehensive study of the nodal CSW meltdown as a function of the increasing temperature. By investigating various doping levels and compounds (Bi2201 and Bi2212 alike), we have revealed a universal temperature dependence unrelated from the characteristic critical temperatures of
the SC and PG, namely $T_c$ and $T^*$. Instead, the observed suppression of CSW can be simulated in terms of the quadratic temperature dependence of the imaginary part of the self-energy in the Fermi-liquid description. The results reported here suggest that the analysis of the temperature evolution of the CSW via TR-ARPES may be used as a sensitive investigation tool to explore as a function of momenta the potential Fermi-liquid to marginal-Fermi-liquid transition of the normal-state of Bi-based cuprates.
Chapter 4

Emergence of pseudogap from short-range spin-correlations in electron-doped cuprates

The strong electron Coulomb repulsion is considered the key ingredient to describe the emergence of exotic phases of quantum matter from high-temperature superconductivity to charge- and magnetic-order. However, a comprehensive understanding is often complicated by the appearance of a partial suppression of low-energy electronic states, known as the pseudogap. To elucidate the degrees of freedom associated with the pseudogap phenomenology in electron-doped cuprates, we apply TR-ARPES to unveil the temperature evolution of the low-energy density of states in the optimally-doped Nd$_{2-x}$Ce$_x$CuO$_4$, an emblematic system where the pseudogap intertwines with magnetic degrees of freedom. By photoexciting the electronic system across the onset temperature $T^*$, we report the direct relation between the momentum-resolved pseudogap spectral features and the spin-correlation length. This transient approach, corroborated by mean field model calculations, allows us to establish the pseudogap in electron-doped cuprates as a precursor to the incipient antiferromagnetic order even when long-range antiferromagnetic correlations are not established, as in the case of optimal doping.
4.1 Introduction

Exotic electronic phenomena are often masked by the interactions within and among various degrees of freedom [149–152]. A prominent example is the puzzling pseudogap (PG) phenomenon, a mysterious state of correlated matter by now notorious from systems as diverse as unconventional superconductors [153–155], dichalcogenides [156, 157], and ultracold atoms [158–160]. Generally speaking, the PG is associated with a partial suppression of the electronic spectral weight in the vicinity of the Fermi level ($\omega = 0$), and evidence for the PG has been widely reported [153–161]. This behavior may be anticipated in the presence of long-range (or mesoscopic) order, e.g. spin- or charge-order, which breaks the translational symmetry of the crystal: the loss of spectral weight in particular momentum-energy regions would be a simple consequence of the avoided crossings in the symmetry-reduced bandstructure [156, 157, 162, 163]. However, this argument may be unsatisfactory in the presence of strong electronic correlations and short-range orders with correlation length of few unit cells. Copper-oxide high-temperature superconductors are a clear example where the origin of the PG (which presents different phenomenology for hole and electron doping) and its relation with other phases are still debated, and a universal understanding has yet to emerge [41, 149, 153–155, 162–165].

In the specific case of electron-doped cuprates, the PG is believed to bear a relation to the robust antiferromagnetic (AF) order [41, 42, 166–173]. In fact, the family of electron-doped cuprates (much less studied than their hole-doped counterpart) is characterized by an AF phase extending over a wide doping range up to the SC dome, as illustrated in Figure 4.1a for the archetypal electron-doped cuprate Nd$_{2−x}$Ce$_x$CuO$_4$ (NCCO). However, scattering experiments on electron-doped cuprates have shown that the long-range AF order disappears when entering the narrow SC dome [169, 174], as evinced by the evolution of the instantaneous spin-correlation length ($\xi_{\text{spin}}$) presented in Figure 4.1b. Moreover, the commonly reported charge-order in cuprates does not exhibit a clear connection to the AF order [175, 176], although a coupling to dynamic magnetic correlations has been re-
Figure 4.1: Phase diagram and AF order of Nd$_{2-x}$Ce$_x$CuO$_4$. (a) Phase-diagram of the archetypal electron-doped cuprate Nd$_{2-x}$Ce$_x$CuO$_4$ showing the onset temperature of the pseudogap T* as an orange shadow [42, 166–168]. The doping measured in this study is highlighted by the yellow arrow. (b) Spin-correlation length $\xi_{\text{spin}}$ (here plotted in units of $a$, where $a$ is the lattice parameter) as a function of temperature detected by inelastic neutron scattering measurements [169]. Note that close to optimal doping, i.e. $x \geq 0.145$, $\xi_{\text{spin}}$ does not diverge a low T, indicating the lack of a long-range AF order.

Recently shown [177]. In electron-doped cuprates, a stable PG has been reported above the entire AF and SC domes by spectroscopy and transport probes, with its onset temperature indicated by T* (orange shadow in Figure 4.1a [41, 42, 166–168]). In the presence of long-range AF order, i.e. when the instantaneous spin-correlation length $\xi_{\text{spin}}$ diverges at low temperature and a Néel temperature is defined, T* has been proposed to be a temperature crossover for which the quasiparticle de Broglie wavelength ($\lambda_B \approx v_F / \pi T$, where $v_F$ is the Fermi velocity) becomes comparable to $\xi_{\text{spin}}$ [169, 178]. However, these considerations seem to fail at optimal doping where only short-range spin-fluctuations ($\xi_{\text{spin}} \approx 20 - 25 a$, where $a$ is the unit cell size) are detected by inelastic neutron scattering (Figure 4.1b) [169]. Indeed, for dopings where the long-range AF order disappears, i.e. when
the short-range $\xi_{spin}$ does not diverge at low temperature, an unambiguous identification of a temperature crossover with $\lambda_B$ is prevented. In addition, the underlying superconducting phase has been proposed to limit the development of $\xi_{spin}$ [169].

In order to tie together the momentum-resolved PG spectral features and short-range AF correlations in electron-doped cuprates, we performed a time- and angle-resolved photoemission (TR-ARPES) study of optimally doped NCCO ($T_c \approx 24$ K, yellow arrow in Figure 4.1a), which is characterized by $\xi_{spin} \approx 20a$ at low temperatures ($T \approx T_c$) [169]. TR-ARPES provides an alternative, more effective and controlled experimental approach to measure a detailed temperature-dependence than the standard equilibrium ARPES, which is often complicated by surface degradation as well as coarse and uncorrelated sampling. As in standard pump-probe spectroscopy, a near-infrared pump pulse is used to perturb the system, with its relaxation studied by varying the temporal delay of a subsequent UV probe pulse. After the initial fast relaxation within 100 fs [131–136], an effective electronic temperature $T_e$ may be defined at each point in time, allowing a temperature-dependent scan to be performed continuously and with remarkable accuracy [124]. Since the acquisition of TR-ARPES data is performed by cycling continuously the pump-probe delays, each time delay (and consequently each electronic temperature) is acquired in the same experimental conditions. By applying this transient approach, we demonstrate the direct relation between the subtle momentum-resolved spectroscopic features of the PG and short-range $\xi_{spin}(T_e)$, as extracted from inelastic neutron scattering [169]. In particular, we identify $T^*$ as the crossover temperature above which the spectral broadening due to the reduction of $\xi_{spin}$ exceeds the PG amplitude, establishing the PG as a precursor of the underlying AF order.

The optimally doped Nd$_{2-x}$Ce$_x$CuO$_4+\delta$ ($x \approx 0.15$) single crystals measured in this study were grown by the container-free traveling solvent floating zone technique and an additional post-growth annealing treatment was carried out to remove the oxygen surplus exhibited directly after growth. Such annealed crystals exhibit a transition temperature $T_c=23.5$ K with tran-
sition widths of 1 K [179, 180]. All the TR-ARPES experiments were performed using the 6.2-eV probe setup in Damascelli Laboratory at UBC exploiting the classic pump-probe scheme: the photon energy of the pump beam is 1.55 eV while the 6.2 eV probe is generated by fourth-harmonic generation of the fundamental wavelength (see Section 2.2.1 for details). The data presented here were acquired with two different incident pump fluences: 28±5 µJ/cm² hereon denoted as low fluence (LF) and 50±10 µJ/cm² denoted as high fluence (HF). The pump and probe beams were s-polarized. The samples were cleaved and measured at <5·10⁻¹¹ torr base pressure and 10 K temperature and the photoemitted electrons were detected by a Specs Phoibos 150 hemispherical analyzer. The overall energy and temporal resolutions were estimated at 17 meV and 250 fs, respectively.

4.2 Static 6.2-eV ARPES of Nd₂₋ₓCeₓCuO₄

The equilibrium Fermi Surface (FS) mapping of optimally-doped NCCO acquired with 6.2 eV probe pulsed-light is shown in Figure 4.2a. Note that despite the low photon energy of the probe beam, the experiment as designed allows for access to the intersection of the AF zone boundary (AFZB, red dashed line) and the tight-binding at ω=0, commonly referred to as the hot-spot (HS, purple dotted circles in Figure 4.2). This region in k-space coincides with the location where an AF-driven PG is expected to be particle-hole symmetric [41]. In a mean field description, the commensurate q=(π,π) folding of the FS originates from a strong quasi-2D AF order in the copper-oxygen plane [41]. The Green’s function can then be written as [163, 168, 178]:

\[ G^{-1}(k,\omega) = \omega - \epsilon_k + i\eta - \frac{\Delta_{PG}^2}{\omega - \epsilon_{k+q} + i\Gamma}, \]  

where \( \epsilon_k \) is the bare energy dispersion, \( \Delta_{PG} \) the AF-driven pseudogap spectroscopic amplitude determined by the local Coulomb interaction and spin susceptibility [178], η the single-particle scattering rate, and Γ a broadening term that leads to a filling of the pseudogap via the reduction of
Figure 4.2: Fermi surface of optimally-doped Nd$_{2-x}$Ce$_x$CuO$_4$. (a) Experimental FS of optimally-doped NCCO measured with 6.2-eV probe pulse, 10 K base temperature. The integration window in energy is 20 meV at the Fermi level. The solid blue line is a tight-binding constant energy contour at $\omega=0$ [181], the red dashed line the AF zone boundary (AFZB) and the purple dotted circle encloses the hot-spot (HS). The black dashed line represents the nodal direction, while the green and the black solid lines the two momentum directions mainly explored in this work, $\phi \approx 39^o$ and $\phi \approx 26.5^o$ respectively ($\phi$ angle between $(0,\pi)-(\pi,\pi)$ and the nodal direction). (b) Simulated Fermi surface using Equation 4.1, $\Delta_{PG} = \eta = \Gamma = 85$ meV.

Using Equation 4.1 we can calculate the spectral function $A(k, \omega) = -\frac{1}{\pi} \text{Im}[G(k, \omega)]$ [182] and compute the Fermi surface, as shown in Figure 4.2b. It agrees well with our experimental data and previous ARPES mapping studies [170, 171], clearly displaying a suppression of spectral weight at the HS (purple dotted circle). Here, we used $\Delta_{PG} = \eta = \Gamma = 85$ meV for simulation purposes, as evinced from our experimental data (see Figure 4.5 and Section 4.3) and in agreement with previous optical and ARPES studies [42, 166, 167, 170, 171, 183].

In order to verify the capability of our 6.2-eV ARPES setup to probe the pseudogap spectral features in NCCO, we plot in Figure 4.3 the equilibrium ARPES spectra acquired at 10 K along the nodal direction and at
Figure 4.3: 6.2-eV static ARPES spectra of optimally-doped NCCO. (a) ARPES dispersion along the nodal direction (left) and at the HS (right, as defined in Figure 4.2), measured with 6.2-eV probe photon energy, s-polarization, at the base temperature of 10 K. The black dashed line in the left panel is the tight-binding nodal dispersion from Ref.[181]. (b) Energy distribution curves (EDCs) at the Fermi momentum ($k_F$, arrows in panel (a)) along the two momentum directions.

the HS, together with the corresponding energy distribution curves (EDCs) at the Fermi momentum (arrows in panel (a)). The black dashed line in Figure 4.3a, left panel, displays the nodal dispersion as predicted by the tight-binding model from Ref.[181]. Note that no significant boson-mediated band-renormalization (i.e. kink) is observed along both the nodal direction and the HS. Electron-doped cuprates present broad spectral features in comparison to their hole-doped counterpart making a detailed lineshape analysis particularly challenging [167, 170, 171, 183]. However, by visual inspection of both ARPES spectra and EDCs, a clear suppression of the spectral weight is observed in the vicinity of the Fermi level only at the HS, as contrary to the nodal direction. In addition, to substantiate our work in the context of previous ARPES studies on the electron-doped
Figure 4.4: Pseudogap in static ARPES, comparison with previous studies. (a) Comparison of the momentum-integrated energy distribution curves (EDCs) ranging from the nodal direction (black) to the HS (ochre): left panel, data extracted from Matsui et al. [167]; right panel, 6.2-eV data of this work. (b) Fermi surface mapping with 6.2-eV. The four solid lines indicate the momentum cuts displayed in (a), right panel. (c) Direct comparison of the momentum-integrated EDCs at the HS for the two works. EDCs have been rescaled to match at $\omega \simeq -0.15$ eV.

NCCO, we provide a direct comparison between our equilibrium 6.2 eV ARPES mapping with that reported by Matsui et al. [167] for optimally-doped NCCO, acquired with 21 eV photons. This is done by computing momentum-integrated EDCs along different momentum cuts of the FS ranging from the nodal direction to the HS (see the FS shown in Figure 4.4b). As displayed in Figure 4.4a, the suppression of the spectral weight associated to the PG distinctly emerges approaching the HS (ochre curves) both in the ARPES spectra reported by Mastui et al. (left panel) and in the corresponding EDCs acquired with 6.2 eV light (right panel). A more unequivocal comparison of the observed PG spectral features is offered in Figure 4.4c.
in which momentum-integrated EDC at the HS acquired with 6.2 eV (dark green) is overimposed to that from Matsui’s work (orange) [167], showing a remarkable agreement (EDCs have been rescaled to match at $\omega \simeq -0.15$ eV) and thus validating our experimental approach. Note that the evolution of the EDCs as a function of the momentum cut displayed in Figure 4.4a reflects the dispersion of the pseudogap central energy along the FS. In particular, the PG center is expected to disperse from above to below the Fermi level moving from the nodal direction to the antinode [41]. This behaviour stems from the incipient 2D-(π,π) antiferromagnetic order included in Equation 4.1 as illustrated in Figure 4.5a only at the HS the pseudogap is centered at the Fermi level. This observation designates the HS as the primary choice for a momentum-resolved study in order to have direct access to the pseudogap spectral features and their evolution as a function of temperature.

To conclude the characterization of the 6.2-eV equilibrium ARPES mapping of NCCO, we present a novel scheme to visualize the energy dependence of the PG and its amplitude $\Delta_{PG}$. The symmetrization of the momentum-integrated EDC [i.e. Symmetrized Energy Distribution Curve (SEDC)] removes any dependence of the photoemission signal on the Fermi-Dirac distribution function [184], giving access to underlying modifications of the local density of states (DOS). Note that while the DOS is defined as the integral of $A(k,\omega)$ over the full Brillouin zone, in this work we focus on individual momentum cuts perpendicular to the FS, effectively analyzing a tomographic density of states [122]. Figure 4.4a shows how the extrinsic background level for $\omega < -0.05$ eV depends on the momentum direction and its intensity may be comparable to the one of the spectral features approaching the HS. The definition of a baseline may then be difficult, making the interpretation of SEDCs acquired along different momenta directions challenging. In this regard, here we define the quantity $R_{cut_{DOS}}(\omega)$ as:

$$R_{cut_{DOS}}(\omega) = \frac{SEDC_{cut_{NoPump}}(\omega)}{SEDC_{cut_{Pump}}(\omega)} \propto \frac{DOS_{cut_{NoPump}}(\omega)}{DOS_{cut_{Pump}}(\omega)}$$

(4.2)
Figure 4.5: Pseudogap dispersion and amplitude. (a) Momentum dispersion of the pseudogap as predicted by the simple $(\pi, \pi)$-folding model of Equation 4.1 ($\eta=\Gamma=10$ meV). $\varphi$ represents the angle between $(0, \pi)$-$(\pi, \pi)$ and the nodal direction as illustrated in Figure 4.3a. (b) $R_{\text{DOS}}(\omega)$ as defined in Equation 4.2 along the near-nodal direction (green markers) and at the HS (red markers) for the two pump fluences exploited in this work, LF (left) and HF (right). Data computed at the maximum effect of the pump excitation, i.e. $\sim 0.6$ ps. Blue dashed lines highlight the pseudogap amplitude.

where the label “Pump” refers to the time delay corresponding to the maximum effect of the pump excitation, i.e. $\sim 0.6$ ps. This function intrinsically mimics the energy dependence of the pseudogap along the specific momentum direction $k^{\text{cut}}$, independently of the underlying background characterizing different momenta along the FS. Figure 4.5b shows the computed $R_{\text{DOS}}(\omega)$ along the near-nodal direction (as defined in Figure 4.5a, second panel) and at the HS for the two pump fluence regimes used in
this work, LF and HF respectively. While we do not observe any relevant modifications of the $R_{\mathrm{DOS}}$ along the near-nodal direction (green markers), a clear PG feature appears at the HS (red markers) for both fluence regimes. From Figure 4.5b, we can estimate the pseudogap amplitude by assessing the extent of the spectral weight suppression from the gap center, i.e. the minimum in $R_{\mathrm{TDOS}}$ (blue dashed lines). The obtained value $\Delta_{\mathrm{PG}} \simeq 85 \text{meV}$ is consistent with what reported in previous optical and ARPES studies [42, 166, 167, 170, 171, 183]. The remarkable qualitative (Figure 4.4) and quantitative (Figure 4.5) agreement in the identification of the PG features between our work and previous spectroscopic studies on the electron-doped NCCO establishes a solid base for the definition of the pseudogap phenomenology and its characterization in our investigation.

### 4.3 Tracking the pseudogap spectral weight in an ultrafast fashion

Before moving to a detailed analysis of our data, we illustrate our experimental strategy for tracking the PG via TR-ARPES. Figure 4.6a compares simulated and experimental EDCs integrated along the momentum direction through HS for two (transient) electronic temperatures. The corresponding experimental SEDCs in Figure 4.6b, bottom panel, show the filling of the PG at high temperature, which can be well modeled by increasing the spin-fluctuation spectral broadening term $\Gamma$ from 85 meV (50 K, black curves) to 160 meV (130 K, red curves), while $\Delta_{\mathrm{PG}}=\eta=85 \text{meV}$ are fixed (Figure 4.6b, bottom panel). However, we recognize that any experimental estimate of the temperature dependence of the PG spectral weight by fitting of SEDCs may be affected by intrinsic and uncorrelated noise, as well as extrinsic electron background (arising from irregular cleaves, secondary electrons, and electrons scattered in the detection process). We overcome this limitation by computing the difference between the photoemission intensity for high temperature (130 K) and its counterpart for low temperature (50 K), as illustrated in Figure 4.6c. As discussed later in more detail in Equation 4.3, this quantity is proportional to the differential momentum-
Figure 4.6: Experimental strategy for tracking transient filling of the PG. (a) Momentum-integrated EDCs at the HS for 50 K (black) and 130 K (red). Top panel: EDCs simulated using Equation 4.1, and Γ=85 meV and 160 meV for low and high temperature conditions, respectively. Bottom panel: experimental background-subtracted EDCs in HF regime (dots, raw data; solid lines, smoothed data; the background is estimated from the integrated ARPES intensity in regions where no dispersive spectral features are detected). (b) Simulated (top) and experimental (bottom) symmetrized EDCs (SEDCs). For T_e=130 K the shortening of ξ_{spin} leads to a filling-up of the PG (red curves). (c) Simulated (top) and experimental (bottom) differential EDCs (dEDCs, as defined in Equation 4.3) demonstrating how a filling of the PG manifests as an increase of the photoemission intensity for ω ≃−50 meV (green arrows).

tegrated EDCs (dEDCs) and, by removing spurious contributions, highlights the temperature evolution of the PG spectral features and Fermi-Dirac distribution. While the latter would lead to a symmetrical suppression (increase) of the photoemission intensity for all ω < 0 (ω > 0), independently of the explored momentum region, it is evident that a filling of the PG may lead to an increase of the photoemission intensity at ω ≃−50 meV (green arrows in Figure 4.6c). Since thermal contributions are negligible at ω ≃ −50 meV within the range of electronic temperatures explored in this work (4k_B T~50 meV for T=150 K), this approach allows us to identify the increase of photoemission intensity for ω ≃−50 meV as the signature of the filling of the PG independently from the thermal broadening and
thereupon track its temperature evolution with high sensitivity. Note that a similar scheme has been recently used to track the electron-boson interaction in hole-doped cuprates via a transient analysis/modeling of the band renormalization (ie. kink) [185]. However, as shown in Figure 4.3a, in the specific case of NCCO only a very modest kink feature is observed (see also Ref. [183]), thus not affecting our analysis and conclusions.

Having defined the framework for our investigation, we now track the temperature-dependent modification of the low-energy DOS at the HS in optimally-doped NCCO by introducing thermal excitations via optical pumping. In order to establish a direct connection between the TR-ARPES phenomenology and the PG onset temperature $T^*$, we must convert the measured time dependence of our data to an effective temperature evolution [124]. This is done by fitting the Fermi edge width of the momentum-integrated EDCs along the near-nodal direction ($\phi \approx 38^\circ$, green solid line in Figure 4.2a), as depicted in Figure 4.7a for various pump-probe delays. Following this approach an effective electronic temperature $T_e$ can be determined as a function of time delay for both the pump fluences exploited in this work (Figure 4.7b, red and black circles for LF and HF, respectively). The transient $T_e$ can be phenomenologically fit by a double exponential function (solid lines in Figure 4.7b), reminiscent of the two-temperature-model framework [124, 131–134]. Note that the discrepancy between the values at negative pump-probe delays for the two fluences is the result of different overall thermal effects due to the pump beam. To further support our estimation of the transient electronic temperature, we performed a similar fitting procedure along the HS by centering the Fermi-Dirac fitting range to $\omega > 0$ for tracking the modification of the slope of the distribution. As shown in Figure 4.7c for the HF regime, the extracted $T_e$ (although naturally more scattered) appears in good agreement with the near-nodal counterpart. Another important aspect to consider while estimating the transient electronic temperature relies on the identification of possible non-thermal contributions to the electronic distribution, especially when pump and probe are overlapped in time. Figure 4.7d shows dEDCs for three different pump-probe delays in HF regime at the HS (we employ
Figure 4.7: Effective electronic temperature $T_e$. (a) Momentum-integrated EDCs along the near-nodal direction (green line in Figure 4.2a) for selected pump-probe delays. The solid black lines are Fermi-Dirac distribution fits. The inset displays three delays (-0.5 ps LF, +0.33 ps HF, +2 ps HF) in logarithmic scale. (b) Transient electronic temperature for both LF and HF. The solid lines are phenomenological double exponential-decay fits (decay times are: (0.6±0.1) ps and (7.5±1.3) ps for LF, (0.45±0.15) ps and (8.3±2) ps for HF). Error bars represent the confidence interval in the fitting procedure corresponding to ±3σ (σ is the standard deviation). (c) $T_e$ extracted along the near-nodal direction (green circles) and HS (red circles), HF regime. The black line is the phenomenological bi-exponential fit as in (b). (d) dEDCs at HS for different time delays $\tau$, HF regime. The black lines
are thermal fits given by the difference of two Fermi-Dirac distributions at different temperature (base temperature 60 K). A non-thermal tail is observed in the dEDC at $\tau = 0.08$ ps for $\omega > 50$ meV. In light of this, grey points and shadow in panels (b) - (c) indicate time delays for which a pure thermal-fitting is not accurate.

dEDCs for removing extrinsic electron background which may affect a correct estimate of thermal and non-thermal features). dEDCs have been fit by a thermal function given by the difference of two Fermi-Dirac distributions and while dEDCs at 0.3 ps and 0.8 ps resemble well a pure thermal electronic distribution, for $\tau = 0.08$ ps (when pump and probe pulsed are overlapped in time) non-thermal features appear on top of the thermal fit for $\omega > 50$ meV. Following these results, we identified the system well thermalized for pump-probe delays $\tau > 0.3$ ps, which timescale is comparable to the temporal resolution of our TR-ARPES system ($\simeq 0.25$ ps). Therefore, in Figure 4.7b-c we mark in gray the time delays exhibiting non-thermal features.

Figure 4.8a displays the transient enhancement of the photoemission intensity at the HS in a 20 meV energy window about $\omega = -50$ meV, $I_{\omega = -50}^{PG}$, given by the momentum-integrated EDC along $\varphi \simeq 26.5^o$ (momentum direction indicated by the black solid line in Figure 4.2a). This particular choice of energy window was motivated by the dEDCs at the HS (modeled and experimental) shown in Figure 4.6c and Figure 4.10b. The temporal response of $I_{\omega = -50}^{PG}$ exhibits different behavior depending on the pump fluence: while the enhancement of $I_{\omega = -50}^{PG}$ recovers exponentially within $\simeq 2$ ps for the LF regime, in the HF regime it saturates for approximately 2 ps and does not recover within the domain of pump-probe delay studied in this work. This saturation of $I_{\omega = -50}^{PG}$ in the HF regime suggests a full suppression of the PG. To further investigate the origin of the suppression of the PG spectral weight, we plot $I_{\omega = -50}^{PG}$ directly as a function of $T_e$ in Figure 4.8b (the non-thermal points – grey circles in Figure 4.7b-c and panel (a) – are omitted). The observed enhancement of photoemission intensity resembles the temperature dependence of the inverse of the spin-correlation length.
Figure 4.8: Pseudogap spectral weight vs. temperature in optimally-doped NCCO. (a) Temporal evolution of the photoemission intensity at the HS (see black line in Figure 4.2a) for $\omega=-50 \pm 10$ meV, $I_{PG}^{\omega=-50}$, for both the employed pump fluences LF and HF. The solid black line is a phenomenological single exponential-decay fit for the LF curve, while the HF curve saturates in the first 2 ps after the pump excitation. Error bars represent $\pm \sigma$. (b) Photoemission intensity at the HS, $\omega=-50 \pm 10$ meV, as a function of the electronic temperature $T_e$ (black and red circles for LF and HF, respectively; data points are plotted vs the electronic temperature determined from the phenomenological fits in Figure 4.7b). Non-thermal time delays – grey points and shadow in panels (a) – have been omitted. The green line and transparent shadow represent the inverse of the spin-correlation length $\xi^{-1}_{\text{spin}}$ from neutron scattering studies for optimal doping $T_c \approx 24$ K [169], appropriately scaled and offset. We identify $T^*$ as the temperature at which the PG is completely filled, in agreement with the observed saturation of $I_{PG}^{\omega=-50}$ for HF. Error bars as defined in (a) and Figure 4.7b for $I_{PG}^{\omega=-50}$ and $T_e$, respectively.

$\xi^{-1}_{\text{spin}}$ reported in Ref. [169] for optimally doped NCCO (superimposed in Figure 4.8b as a green line and shadow, with appropriate offset and scaling). However, for temperatures $T_e > 110$ K, $I_{PG}^{\omega=-50}(T_e)$ is found to saturate (red shadow in Figure 4.8b) marking a departure from $\xi^{-1}_{\text{spin}}$. Despite the novel dynamical approach employed here to perform a temperature dependent study at the HS, the observed onset of the saturation in Figure 4.8b is in good agreement with $T^*$ reported by other spectroscopy and transport
probes [42, 166-168]. Note that the unfolded deviation of $I^{{PG}}\omega_{=-50}(T_e > T^*)$ from $\sigma^1_{-\text{spin}}$ is not driven by a phase transition, but is rather a consequence of the PG filling, as discussed in the next Section 4.4.

Before moving to a comprehensive analysis and modeling of the photoinduced thermal modification of the PG for both LF and HF pump regimes, we substantiate the analysis of the momentum-integrated dEDCs at the HS as a procedure to extract valuable information regarding the transient evolution of the pseudogap. As shown in Figure 4.3, the spectral features of NCCO are inherently broad, precluding the sort of detailed analysis of the transient spectral function which has been achieved for hole-doped cuprates [114]. In this regard, an alternative approach involves the analysis of the temporal evolution of dEDCs, defined as the difference in the photoemission intensity after and before the pump perturbation, $I_{\text{Pump}} - I_{\text{NoPump}}$. If both the matrix-elements and the electronic distribution are momentum-independent, the photoemission intensity integrated along a well-defined momentum direction ($k_i \rightarrow k_f$) is proportional to the local DOS:

$$\int_{k_i \rightarrow k_f} I(\omega, k) d\mathbf{k} \propto \text{DOS}(\omega) \cdot f(\omega).$$

We can then express dEDC as:

$$\text{dEDC} \propto \int_{k_i \rightarrow k_f} I_{\text{Pump}}(k, \omega) d\mathbf{k} - \int_{k_i \rightarrow k_f} I_{\text{NoPump}}(k, \omega) d\mathbf{k} \approx \Delta\text{DOS} \cdot f + \text{DOS} \cdot \Delta f$$

where $\Delta\text{DOS}$ and $\Delta f$ are the relative variations of the DOS and the distribution function, respectively. In order to robustly identify and disentangle $\Delta\text{DOS}$ and $\Delta f$ at least two different momentum directions need to be examined. In this work the near-nodal direction and the HS were explored (see the green and black cut in Figure 4.2a, respectively), which showcase the two contributions to the dEDCs. In fact, along the near-nodal direction – where the PG is expected to be pushed well above the Fermi energy in the unoccupied states (see Figure 4.5a) – $\Delta f$ term of Equation 4.3 dominates and a mere thermal broadening is expected. Contrarily, at the HS the pseudogap is predicted to be particle-hole symmetric, thus facilitating the disclosure of the transient modification of the DOS (i.e. the $\Delta\text{DOS}$ term of Equation 4.3 gives a substantial contribution, especially for $\omega < 0$). The different contributions of $\Delta\text{DOS}$ and $\Delta f$ to the dEDCs are highlighted in Figure 4.3.
Figure 4.9: Energy- and momentum-resolved TR-ARPES dynamics. (a) Left panel: transient evolution of the momentum-integrated photoemission intensity at different binding energies (10 meV integration window) along the near-nodal direction, LF regime. Right panel: mapping of the transient photoemission intensity as a function of the electronic temperature $T_e$ reported in Figure 4.7b. (b) Same as in (a), but at the HS. The inset shows how the transient photoemission intensity at $\omega = +15$ meV along the near-nodal direction and at the HS are comparable. The green dashed line in the right panel is the inverse of $\bar{\xi}_{\text{spin}}$, appropriately scaled and offset, as discussed Figure 4.8b.

Figure 4.9 which displays the transient photoemission intensity as a function of the binding energy and the momentum direction (near node and HS) in the LF regime. Along the near-nodal direction the transient evolution of the photoemission intensity is approximately symmetric with respect to the Fermi level $\omega=0$ (Figure 4.9a, left panel), as we are mainly tracking the evolution of $\Delta f$ in Equation 4.3. In addition, the right panel of Figure 4.9a maps the change of the photoemission intensity at $\omega=\pm 15$ meV as a function of the electronic temperature, which displays a linear trend, as expected within this energy- and temperature-range. Both these observations confirm that along the near-nodal direction the dynamics of the ARPES signal is mainly driven by thermal effects. Otherwise, at the HS the transient photoemission intensity is strongly not symmetric with respect to $\omega=0$, as displayed in Figure 4.9b: while the excitation signal above the Fermi level is comparable to that from along near-nodal direction (see inset Figure 4.9b),
the signal for $\omega < 0$ displays a different behaviour, as the depletion (i.e. suppression of photoemission intensity) is less pronounced at the HS than its counterpart along the near-nodal direction. Moreover, an enhancement of the photoemission intensity is observed for $\omega \simeq -50$ meV (black curve), in agreement with the schematics of Figure 4.6. These results attest the significant contribution of $\Delta DOS$ to the dEDC signal at the HS, especially evident for $\omega \simeq -50$ meV where the thermal contribution is negligible (i.e. $f \simeq 1$ as $50$ meV$\simeq 4 k_B T$ for $T=150$ K). Indeed, for $\omega = -15$ meV, even if a contribution from $\Delta DOS$ is expected, the depletion at the HS (blue markers in Figure 4.9b, right panel) does not resemble the trend reported for $\omega = -50$ meV (black markers) as a consequence of the sizable thermal contribution. All together these observations validate our approach in tracking the transient photoemission intensity at the HS for $\omega \simeq -50$ meV as a direct signature of the evolution of the underlying PG.

4.4 Relation of the pseudogap to the spin-correlation length: theoretical model

In Figure 4.10 we present a comparison between experimental (panels a1-b1) and simulated dEDCs (panels a2-b2) as a function of the pump-probe delay ($\tau$) and binding energy ($\omega$). The TR-ARPES data reported here can be simulated remarkably well using the simple model of Equation 4.1 through a substantial increase of the broadening term $\Gamma$ alone, which phenomenologically describes the filling of the PG due to the reduction of the spin-correlation length [173, 186]. The qualitative and quantitative agreement between single experimental and simulated dEDCs along the near-nodal direction and HS for $\tau = +0.6$ ps (Figure 4.10b) attests the capability of this model in grasping the modifications of the DOS due to the PG filling. It is important to remark that a full closure of the gap fails to reproduce our TR-ARPES data. Figure 4.11a compares simulated dEDCs at the HS for a complete gap closure ($\Delta_{PG} \rightarrow 0$, black line) and gap filling ($\Gamma = 2.5 \cdot \Gamma_0$, red line), and only the latter reproduces well the experimental curves shown in Figure 4.10b1. This observation is in agreement with the SEDCs presented
Figure 4.10: Comparison of experimental and simulated TR-ARPES data. (a) Momentum-integrated dEDCs, experimental (a1) and simulated (a2), along the near-nodal direction (left panel, LF) and at the HS (middle and right panels for LF and HF, respectively). Simulated panels have been generated using the fit of the experimental transient $T_e$ shown in Figure 4.7b, and assuming $\Gamma(T_e) = C \cdot \xi_{spin}^{-1}(T_e)$, as in Ref. [178] ($C \approx 1.9 \, a_eV$, where $a$ is the unit cell size). (b), Experimental (b1) and simulated (b2) dEDCs along the near-nodal direction (green line, LF), and at the HS (black and red lines for LF and HF, respectively), at $\tau=+0.6$ ps.
Figure 4.11: Filling of the PG through a reduction of $\xi_{spin}$. (a) Simulated dEDCs at the HS assuming values $\Delta_{PG}=\eta=85\text{meV}$ and initial and final temperature 50 K and 130 K, respectively. dEDCs were simulated assuming $\Delta_{PG} \rightarrow 0$ (gap closure, black line) and $\Gamma = 2.5 \cdot \Gamma_0$ (gap filling, red line). (b) Simulated photoemission intensity at the HS, $\omega=-50\pm10\text{meV}$, as a function of the electronic temperature (black dashed line). The green line is the inverse of $\xi_{spin}$, obtained from Ref. [169] as discussed in Figure 4.8b.

in Figure 4.6b and scattering studies [169,174], which show that the spectral weight associated with magnetic excitations displays a much weaker temperature dependence than the one of the spin-correlation length. Finally, we plot in Figure 4.11b the simulated analog to Figure 4.8b, noting a remarkable correspondence between the two figures. In particular, assuming the direct relationship between the filling of the PG and $\xi_{spin}^{-1}$ (as predicted for 2D spin-fluctuations [178]), the simulated filling of the PG saturates for temperatures $T \simeq T^*$ when the broadening $\Gamma(T^*) \simeq 2\Delta_{PG} \simeq 170\text{meV}$. This empirical observation agrees with a recent theoretical study of the vanishing of the PG in the electron-doped cuprate Pr$_{1.3-x}$La$_{0.7}Ce_x$CuO$_4$ [187].

We conclude this section by providing more details on the different contributions of the various parameters in Equation 4.1 ($\Gamma$, $\eta$ and $\Delta_{PG}$) to the simulations shown in Figure 4.10 and Figure 4.11. Indeed, in our simulations only the spin-fluctuation-induced broadening term $\Gamma$ is assumed to
Figure 4.12: Contribution of $\Gamma$ and $\eta$ to the pseudogap modeling. (a) Temperature dependence of $\Gamma(T_e)$ used for simulations shown in Figure 4.10 and Figure 4.11. (b) Momentum distribution curves (MDCs) along the near-nodal direction ($\varphi \approx 38^\circ$) and near the HS ($\varphi \approx 31^\circ$) for two different transient electronic temperatures. The horizontal lines gives an estimate of the full-width-half-maximum (FWHM). (d) $\eta$-dependence of the simulated dEDCs at the HS.

display a temperature dependence, while the single-particle scattering rate $\eta$ and the gap amplitude $\Delta_{PG}$ remain unchanged. In particular, we have imposed $\Gamma(T_e) = C \cdot \xi^{-1}_{spin}(T_e)$ as shown in Figure 4.12a, where $\xi_{spin}$ is the spin-correlation length and $C$ a constant, in agreement with theoretical predictions by Vilk and Tremblay [178]. Neutron scattering experiments have reported a value of $\xi_{spin} \approx 20a$ (with $a$ lattice constant) for optimally-doped NCCO at low temperature (see Figure 4.1b) [169]. We set $\Gamma_0=85\text{ meV}$ as initial value of the broadening term, which qualitatively reproduces the low-temperature partial filling of the pseudogap at the HS due to the absence of a long-range AF order. TR-ARPES data are well reproduced by defining the constant $C \approx 1.9\text{ eV} \cdot \text{Å}$, as shown in Figure 4.10. In addition, in our simulations we set $\Delta_{PG}=\eta=85\text{ meV}$, both parameters independent on the temperature. The value of $\Delta_{PG}$ derives from previous spectroscopic studies [42, 166, 167, 170, 171, 183] and agrees well with our experimental results (see Figure 4.5). As for the single-particle scattering rate $\eta$, it can be estimated by fitting the momentum distribution curves (MDCs) FWHM (Figure 4.12b): $\eta = \frac{\text{FWHM}}{2} \cdot v_F$, where $v_F$ is the bare dispersion velocity from
the tight-binding model of Ref.[181]. In particular, we extracted a FWHM of $\sim 0.066 \, \text{Å}^{-1}$ and $\sim 0.076 \, \text{Å}^{-1}$ for the near-nodal and near-HS directions at low temperature, in agreement with MDCs FWHM reported from a recent high-resolution ARPES study of NCCO [183]. These values correspond to $\eta \sim 72 \, \text{meV}$ and $\eta \sim 85 \, \text{meV}$ for the near-nodal and near-HS directions, respectively. Note that for both momentum directions we do not observe any variation of $\eta$ larger than $\pm 5 \, \text{meV}$ within the range of transient temperature explored in this work. Following these observations, Figure 4.12c displays simulated dEDCs at the HS (50 K and 120 K initial and final temperature, respectively, $\Delta_{\text{PG}}=85 \, \text{meV}$, and $\Gamma$ tuned from 85 meV to 220 meV) as a function of different $\eta$ values, demonstrating how different values of $\eta$ (even well beyond the limits of our experimental estimate) alter only minimally the outcome of the simulations, thus not affecting our conclusions.

4.5 Conclusions

In conclusion, we have reported the direct relation between the partial suppression of the electronic spectral weight, a.k.a pseudogap, and short-range magnetic correlations in electron-doped cuprates. In particular, by performing a detailed ultrafast ARPES study at the hot-spot of the optimally-doped NCCO electron-doped cuprate, we have demonstrated that the temperature dependence of the low-energy DOS is closely related to the spin-correlation length $\xi_{\text{spin}}$. We identified two different temperature regimes for the PG, moving from low to high temperature: i) $T<T^*$, in which the PG begins to fill alongside with the reduction of $\xi_{\text{spin}}$; ii) $T>T^*$, where $\xi_{\text{spin}} \sim 10-15 \, \text{a}$ and the PG is completely filled-up. Our results show that the PG phenomenology in optimally-doped NCCO originates from short-range AF correlations, parametrized by $\xi_{\text{spin}}(T)$, and $T^*$ is a crossover temperature above which the spectral broadening driven by the reduction of $\xi_{\text{spin}}$ overcomes the PG amplitude $\Delta_{\text{PG}}$. This suggests that the frequently reported onset temperature $T^*$ does not represent a thermodynamic phase transition, i.e. a sharp quenching of a well-defined order parameter; rather, $T^*$ is associated with the weakening of the short-range AF correlations and
incipient \((\pi, \pi)\)-folding \([\text{173}, \text{186}]\). In addition, the observation of the filling – not closure – of the PG suggests that the energy scale associated with the PG survives to temperatures well above \(T^*\), possibly reminiscent of scattering results \([\text{169}, \text{174}]\) which show that the spectral weight associated with magnetic excitations remains finite up to much higher temperatures than the spin-correlation length itself. This phenomenology may bear a relation to the underlying Mott physics \([\text{178}]\), or to the recent proposal of a crossover of the SU(2) gauge theory for fluctuating spin-density-waves near optimal-doping \([\text{188}]\). Finally, we note that our transient momentum-resolved study demonstrates that even underlying orders with correlation lengths of about ten unit cells may play a significant role in shaping the Fermi surface topology and associated transport properties of complex materials \([\text{41, 42, 166, 167, 170–173, 183, 189, 190}]\).
Chapter 5

Exploring the mixed-valent state in Sm$_x$La$_{1-x}$B$_6$

Strong electron correlations originating from localized 4$f$-states are crucial in describing the electronic structure and associated properties of rare-earth compounds. An example of occurring phenomena in these materials is the emergence of the so-called mixed-valence, a state characterized by the existence of a given element in the system in more than one oxidation state. The precise determination of the value of the fractional valence, its role in shaping the electronic properties and the pursuit to tune it by means of external parameters such as temperature and pressure, have attracted a lot of attention from the scientific community in the last few decades. Here we report on the combined ARPES and XAS study of rare-earth Sm$_x$La$_{1-x}$B$_6$ series, employing chemical substitution as a tool to directly resolve the valence fluctuations of Sm ions as a function of correlations. By gradually varying the stochiometry, we track the evolution of the mixed-valent character in the series, and resolve the emergence of an impurity regime of intermediate-valent Sm ions for $x < 0.2$. 
5.1 Introduction

Rare-earth hexaborides have been studied for many years due to the wide range of exotic phenomena arising from the correlations among localized 4f electrons. These include (but are not limited to) heavy fermions, superconductivity, hidden order phases and mixed-valence (MV) \([191-194]\). In particular, the characteristic to exhibit a MV state is one of the most extensively studied \([9, 195, 196]\). In a homogenous MV system two valence configurations have nearly degenerate energies, so the ground state can be expressed as a linear superposition of the different configurations, each corresponding to a distinct oxidation state \([9, 43]\). In the specific case of rare-earth hexaborides, the two degenerate configurations correspond to different \(f\) occupation numbers, namely \(4f^n\) and \(4f^{n-1}\). Therefore, the interplay between correlated \(4f\)-states and band-like states, deriving from the \(5d6s\) shell and crossing the Fermi level, plays an important role in shaping the electronic structure of rare-earth hexaborides. This makes the investigation of fluctuations between different valence configurations crucial for the understanding of the low-energy physics of these compounds. It has been shown that external control parameters, such as temperature or pressure, may be used to tune the intermediate valence of the rare-earth ions and the associated properties of the hexaborides \([66-68, 197, 198]\). As an alternative approach, chemical substitution on the rare-earth element is a chemistry tool acting directly on the occupation of the \(4f\) states. This approach may allow the investigation of the modifications induced in the electronic structure as a function of electronic correlations, from the very dilute regime to the lattice limit. This approach becomes particularly intriguing in the context of an early theoretical work by Haldane \([199]\), which speculates on the potential occurrence of a MV state for a single impurity, thus raising the question on whether the MV concept can be extended to that limiting case and if it can be observed experimentally.

\(\text{SmB}_6\) represents a prototypical example of rare-earth MV compounds. Nearly fifty years after its characterization, its ground state still remains unsolved. The description in terms of Kondo insulator is challenged by
Figure 5.1: Crystal structure of Sm$_x$La$_{1-x}$B$_6$. (a) Crystal structure characterizing the Sm$_x$La$_{1-x}$B$_6$ series: rare-earth ions (La or Sm) and B-octahedra are located at the corners and at the center of the cubic lattice structure, respectively. (b) Corresponding bulk Brillouin zone (BZ) with high-symmetry points highlighted in red. (c) Schematic of the bandstructure of a mixed-valent rare-earth hexaborides: the localized $f$-state crosses the broad $d$ conduction band opening a gap via hybridization. The wavefunction character is indicated by the color scale. Inset: Zoom-in of the momentum region where the bands cross. Panels (c) adapted from [4].

the resistivity plateau at low temperature and the observation of quantum oscillations [49, 62, 63]. Furthermore, in-gap electronic states have been reported by ARPES, in relation to the recent proposal of the possible realization of TKI in SmB$_6$. In this scenario, the study of the intermediate valence state may be crucial for the understanding of the gap formation in this material. Here we report an Angle-Resolved Photoemission Spectroscopy (ARPES) and X-Ray Absorption Spectroscopy (XAS) study of the chemical-substitution-induced valence fluctuations in the Sm$_x$La$_{1-x}$B$_6$ series. All the compounds of the series share the same CsCl-type crystal structure with the rare-earth atoms at the cube corners and the B-octahedra at its body center (Figure 5.1a). The corresponding bulk Brillouin zone (BZ) is shown in Figure 5.1b, along with $\Gamma$, $X$ and $M$ high-symmetry points representing the center, face-center and edge-center of the cube, respectively. Despite the similarity in the crystal structure, the two ends of the series exhibit very different physics: LaB$_6$ ($x = 0$) is characterized by a metallic ground state, in contrast to the rich ground state driven by MV in SmB$_6$ ($x = 1$). Indeed,
Sm$^{2+}$ [Xe]$4f^6$ and Sm$^{3+}$ [Xe]$4f^{5}5d^{1}$ configurations are nearly degenerate and dominates the low-energy excitation spectrum of SmB$_6$ (see Section 1.2 and Figure 1.5). The reported value of the mean valency at low temperature is $\sim +2.505$, which increases to a plateau around $\sim +2.58$ above 100K [66, 200]. As shown in Figure 5.1c, a small gap opens at the Fermi level as a result of the hybridization between the localized $4f$-states and the broad $d$-band. A strong admixture characterizes then the wavefunction near the crossing points (i.e. where the small gap opens), while far away a defined character is retained (color scale in Figure 5.1c). In this work, by gradually varying the stochiometry in the Sm$_x$La$_{1-x}$B$_6$ series, we track the fluctuations of the mean valence of Sm ion, $v_{Sm}$, going from one end of the series to the other as $4f$ electrons are progressively introduced in the system. Our results reveal the persistence of the MV character in Sm$_x$La$_{1-x}$B$_6$ even in the very dilute regime, pointing towards the limit of mixed-valent impurity state.

The high-quality single crystals of Sm$_x$La$_{1-x}$B$_6$ studied in this investigation were grown using the aluminum flux method in a continuous Ar purged vertical high-temperature tube furnace [53]. Post-growth characterization by energy dispersive x-ray spectroscopy for the actual Sm concentration was carried out in Los Alamos National Laboratory. ARPES experiments were performed in Damascelli Laboratory at UBC using a photon energy of $h\nu = 21.2$eV, with a base pressure lower than $3 \cdot 10^{-11}$Torr and a base temperature of 10K. The electrons were collected using a SPECS Phoibos 150 hemisperical analyzer, with energy and momentum resolution of 25meV and 0.02 Å respectively. Additional ARPES measurements were carried out at the SGM3 endstation at the ASTRID2 synchrotron radiation facility [201], using a photon energy of $h\nu = 67$eV, with base temperature 35K and energy resolution 35meV. All samples were cleaved in-situ and measured along the (001) surface. XAS measurements were performed using the four-circle UHV diffractometer at the REIXS 10ID-2 beamline at the Canadian Light Source in Saskatoon [202], with base pressure and temperature of $5 \cdot 10^{-10}$Torr and 22K, respectively. DFT calculations for LaB$_6$ were performed with the WIEN2K software package [203].
5.2 LaB$_6$ and SmB$_6$: ARPES comparison

Before moving to a detailed analysis and discussion of the Sm$_x$La$_{1-x}$B$_6$ series, we provide a comprehensive ARPES comparison between the two ends of the series: LaB$_6$ and SmB$_6$. LaB$_6$ is the reference system for all rare-earth hexaborides compounds, with the absence of 4$f$ electrons and a metallic ground state. The fundamental B$_6$ block can be described in terms of a series of molecular orbitals (MOs) originating from the 2$s$ and 2$p$ B-atomic orbitals [204]. The trivalency of La ions leads to the partial occupation of one B$_6$ antibonding MOs (after entirely filling all the bonding MOs), which hybridizes – in a strongly momentum-dependent way – with the La-5$d$ band. Figure 5.2a illustrates the main features of the electronic structure of LaB$_6$ as obtained from DFT calculations: dispersing bands stemming primarily from B$p$-orbitals can be observed at higher binding energies, while the low energy electronic structure is dominated by large electron pockets centered at the X-high-symmetry points of the BZ and exhibiting a strong admixture of La5$d$ and B2$p$ character. For simplicity, we will denominate such electronic feature as “5$d$-pocket” or “X-pocket” throughout the rest of the chapter. Figure 5.2b presents the experimental ARPES spectra of LaB$_6$ acquired along two different crystallographic directions with 67 eV probe light, showing a good agreement with the DFT dispersion (white dots). In particular, we extract a Fermi velocity $v_F$ characterizing the half-filled X-pocket equal to $(5.4 \pm 0.2)$ eV $\cdot$ Å and $(6.5 \pm 0.2)$ eV $\cdot$ Å along X-Γ-X and M-X-M high-symmetry directions, respectively.

Moving right in the lanthanide series, the 4$f$ shell of the rare-earth element gets filled (4$f^n$, with $n$ varying from 1 for Ce$^{3+}$, to 14 for Lu$^{3+}$). Despite the variety of rich physics arising from the interaction of $f$-electrons, the electronic structure of all rare-earth hexaborides share the key-role played by the X-pocket, with primarily rare-earth 5$d$ and B2$p$ character, in dictating the low energy physics. In Figure 5.3 we compare the ARPES spectra of LaB$_6$ and SmB$_6$, as acquired along X-Γ-X (top) and M-X-M (bottom). Non-dispersing 4$f$-states are clearly visible in the SmB$_6$ spectrum (right side of panels a-b) at 15meV, 150meV and 1eV, consistent to what was reported
Figure 5.2: Electronic structure of LaB$_6$. (a) Electronic dispersion of LaB$_6$ obtained by DFT. The color scale shows the atomic character associated to each band. (b) ARPES spectra of LaB$_6$ along ΓX and XM high-symmetry directions, measured with $h\nu = 67$ eV and 35 K base temperature. The white dots represent the dispersion as obtained by DFT shown in (a). The green dashed line is the dispersion of the X-pocket for SmB$_6$ from slab-DFT calculations reported by Zhu et al. [60].

in previous ARPES studies [56-58, 64], and associated to the $^6$H and $^6$F Sm 4$f$-multiplets. As anticipated, both compounds exhibit bulk electron pockets centered at X, which dispersion is shown in Figure 5.3c-d. It is important to point out that, despite the hybridization between the X-pocket and the 4$f$-states in SmB$_6$ (red circles) leading to band-renormalization, the bare pocket dispersion can still be described by the same effective mass of LaB$_6$ (as also shown by the comparison of the DFT dispersion for LaB$_6$ (white dots) and SmB$_6$ (green dashed line) in Figure 5.2b). Moreover, the size of the X-pocket contours in SmB$_6$ is much smaller than in LaB$_6$. Note that this distinction does not originate from a difference in the crystal structure, as the lattice parameters differ by less than 1% ($a_{La} = 4.156$ Å$^{-1}$ and $a_{Sm} = 4.134$ Å$^{-1}$ [205]). This substantial variation indicates a change in the electronic occupation of the X-pocket, which arises from the charge compensation between $f$ and $d$ electrons in the presence of intermediate valence of the Sm ions in SmB$_6$. Indeed, if the system was entirely Sm$^{3+}$ ([Xe]$4f^55d^1$), the X-pocket would be exactly half-filled (as is the case for LaB$_6$), while it would be totally empty (i.e. above $E_F$), if only Sm$^{2+}$ ([Xe]$4f^6$) was present. In the case of a MV system as SmB$_6$, the Sm$^{2+}$/Sm$^{3+}$ ratio
Figure 5.3: ARPES dispersion of LaB$_6$ and SmB$_6$. (a) ARPES band mapping along X-Γ-X direction of LaB$_6$ (left) and SmB$_6$ (right), measured with 67 eV probe photon energy, at a base temperature of 35 K. (b) Same as panel (a), but along M-X-M direction. (c)-(d) Comparison of the X-pocket dispersion as extracted from the ARPES spectra of LaB$_6$ (black circles) and SmB$_6$ (red circles) along X-Γ-X and M-X-M directions, respectively.

determines the exact electronic occupation of the 5$d$ band at the X-point, $n_5^d$, as an intermediate value between 0 and 1 (where $n_5^d = 0, 0.5$ represent the two specific cases for all Sm$^{2+}$ and all Sm$^{3+}$, respectively). This close relation between $n_5^d$ and the fractional percentage of Sm$^{3+}$ will be fundamental to evaluate the possible fluctuations of the valence of the Sm ions in the Sm$_x$La$_{1-x}$B$_6$ series, as discussed in Section 5.3. Figure 5.4 shows the evolution of the ARPES iso-energy maps as a function of binding energy, highlighting the different size of the X-pocket ellipsoid contours in the two compounds. In addition, signatures of a (1 × 2) reconstruction are detected
Figure 5.4: ARPES iso-energy contours in LaB$_6$ and SmB$_6$. (a) ARPES iso-energy maps at various binding energies of LaB$_6$. (b) Same as in panel (a), but for SmB$_6$. Dashed green lines mark the crystallographic high-symmetry directions. All energy maps are taken at $h\nu = 21.2$ eV, base temperature 10 K. The integration window in energy is 20 meV.

at $\Gamma'$ in both cases, in accordance to what is reported in previous studies for SmB$_6$ [56, 57, 206, 207].

In order to substantiate a direct comparison between LaB$_6$ and SmB$_6$, we must discuss the $k_z$-dispersion of the electronic structure of the two compounds, given the three-dimensional (3D) nature of the crystal structure. In Figure 5.5a we present the photon energy dependence of the photoemission intensity along $X-\Gamma-X$ in LaB$_6$ and SmB$_6$. Note that the employed range of photon energy allows the mapping over a full $k_z$ period of the 3D BZ, as shown in Figure 5.5b. Given the cubic symmetry of both com-
Figure 5.5: Photon energy dependence of LaB$_6$ and SmB$_6$. (a) Photoemission intensity map at 500 meV (integration window 40 meV) along X-Γ-X as a function of the probe photon energy for LaB$_6$ (left) and SmB$_6$ (right). All data taken at a base temperature of 35 K. The green and blue solid lines mark the two photon energies employed in this work, $h\nu = 67$ eV and $h\nu = 21.2$ eV, respectively. We associated the bulk Γ high-symmetry point with 67 eV probe energy. (b) Illustration of the momentum cuts probed with different photon energies (inner potential of 14 eV). Note that the range of photon energy used in (a) covers a full Brillouin zone in $k_z$. Panel (b) adapted from Ref.[64].

pounds, the $k_z$-dispersion of bulk bands, such as the X-pocket here under consideration, is expected to resemble that along $k_x$ and $k_y$. Indeed, ellipsoidal contours associated to the X-pocket can be observed in Figure 5.5a and they exhibit an analogous photon energy dispersion in LaB$_6$ and SmB$_6$. Two different photon energies were employed for the ARPES measurements presented in this work: $h\nu = 21.2$ eV (blue cut) and $h\nu = 67$ eV (green cut), the latter identified as the photon energy corresponding to the bulk Γ high-symmetry point. Figure 5.6a illustrates how the photoemission intensity pattern across the X-point of SmB$_6$ varies by adopting 21.2 eV (left) and 67 eV (right) as probe photon energy light. As shown in Figure 5.6a, while at low photon energies the photoionization cross-section for Sm4$f$ is comparable to that of Sm5$d$ and B2$p$, for 67 eV (close to the 4$d$-4$f$ reso-
To conclude this section, we point out that the lack of a natural cleavage plane, along with the $k_z$ disorder likely characterizing the strong 3D dispersion in these Sm$_x$La$_{1-x}$B$_6$ compounds, leads to an extrinsic broadening of the spectral features. This precludes the sort of detailed lineshape analysis in terms of intrinsic scattering rates achieved in the previous chapters for high-temperature cuprate superconductors. Instead, here we focus our investigation on the overall evolution of the electronic structure as a function of $x$, with particular emphasis on the large electron pockets centered at X.

The resonance corresponds to a virtual transition $4d \rightarrow 4f$ followed by an Auger decay and a subsequent emission of a $4f$ photoelectron; this process would then have the same final state as the direct photoemission process (i.e. removal of one $4f$ electron).

Figure 5.6: Dispersion of SmB$_6$ probed with different photon energies. (a) $M$-X-$M$ ARPES spectrum of SmB$_6$ acquired with $h\nu = 21.2$ eV (left) and $h\nu = 67$ eV (right). The insets show EDCs extracted at $0.5\,\text{Å}^{-1}$ (white dashed lines), highlighting the enhancement of $4f$-states photoemission intensity observed with 67 eV. (b) Photoionization cross-section of the relevant orbitals defining the low-energy electronic states of LaB$_6$ and SmB$_6$. Data in panel (b) taken from [208].
5.3 Evolution of the mixed-valence character in the Sm$_x$La$_{1-x}$B$_6$ series

Once we established a solid base for a direct comparison between LaB$_6$ and SmB$_6$, we now present a detailed analysis of the Sm$_x$La$_{1-x}$B$_6$ series. Figure 5.7a illustrates the overall modification of the electronic structure upon Sm substitution. ARPES spectra were acquired with 21.2 eV along $\Gamma X$ direction (green solid line in inset of Figure 5.7c) for $x = (0, 0.2, 0.55, 0.7, 0.8, 1)$.

As $x$ increases, the non-dispersing Sm 4$f$-states emerge in the spectra and gain intensity, as highlighted in the EDCs displayed in Figure 5.7b. Clearly visible for all compounds, the B2$p$-character valence band (VB) centered at $\Gamma$ exhibits a gradual shift to deeper binding energies as a function of the Sm concentration $x$, with a maximum shift of $\sim 320$ meV across the series (see Figure 5.7d). This effect is related to the change in the attractive potential when trivalent ions, as La ions, are introduced in the 5$d$-band (i.e. by decreasing $x$). Note that the bottom of the large X-pocket is instead characterized by a much larger shift of the order of $\sim 0.9$ eV (the bottom of the band is observed at $\sim -2.5$ eV and $\sim -1.6$ eV for LaB$_6$ and SmB$_6$, respectively). This discrepancy may stem from the stronger effect that a change in the attractive interaction for the 5$d$-band would exert on the X-pocket, which partially retains 5$d$-character, with respect to the pure B2$p$-character VB.

As discussed in Section 5.2, the dispersion of the X-pocket in SmB$_6$ embodies information about the interplay between the rare-earth 5$d$- and 4$f$-electrons close to the Fermi level, stemming from the mixed-valent character of the Sm ions. This observation makes the investigation of the evolution of the bulk 5$d$ pockets centered at X instrumental to get insights on the possible fluctuations of the valence of the Sm ions in the Sm$_x$La$_{1-x}$B$_6$ series. Figure 5.8 offers an overview of the evolution of the X-pocket as probed by ARPES. By visual inspection, the size of the X-pocket progressively decreases as $x$ increases in the system (see ARPES maps in Figure 5.8b), as expected from the removal of the trivalent La ions, which contribute to the occupation of the 5$d$-band. However, we note that the observed behaviour...
Figure 5.7: ARPES spectra of $\text{Sm}_x\text{La}_{1-x} \text{B}_6$. (a) Evolution of ARPES spectrum along $X$-$\Gamma$-$X$ (green line in inset of panel (c)) in $\text{Sm}_x\text{La}_{1-x} \text{B}_6$ series. Data acquired for $x = (0, 0.2, 0.55, 0.7, 0.8, 1)$, with 21.2 eV photon energy at temperature 10 K. (b) Energy distribution curves (EDCs) extracted at $\Gamma$ (dashed white line in panel (a)) for the selected $x$ values. The two peaks close to $E_F$, and associated to Sm$^4f$ states, are visible, as well as the B2$p$ valence band (VB) at higher energy. (c) Binding energy of the B2$p$ VB centered at $\Gamma$ as a function of $x$. The overall shift is $\sim 320$ meV. Inset: Iso-energy map of LaB$_6$ at $E_F$ illustrating the momentum direction along which the ARPES spectra in panel (a) are acquired (green line).

departs from a constant-rate reduction, as the change in the ARPES dispersion is more pronounced for $x \leq 0.55$ than for higher Sm concentrations, as shown in Figure 5.8c. In order to quantify the observed variation and thus establish a direct relation between the ARPES dispersion and the fractional percentage of Sm$^{3+}$, we must convert the size of the $X$-pocket contours, as extracted from the ARPES data, to the electronic occupation $n_p^{5d}$. This is done via application of the Luttinger’s theorem. Here we stress that a direct comparison among different compounds in the series is made pos-
Figure 5.8: X-pocket dispersion in $\text{Sm}_x\text{La}_{1-x}\text{B}_6$. (a) ARPES spectra along $XM$ high-symmetry direction of the Brillouin zone (black dashed line in panel (b), left), for $x = (0, 0.2, 0.55, 0.7, 0.8, 1)$. (b) ARPES iso-energy contours close to $E_F$ for the same samples shown in (a). The integration window in energy is 15 meV. (c) Evolution of the X-pocket dispersion along $\Gamma X$ and $XM$ directions. All data acquired with $h\nu = 21.2$ eV at $T = 10\text{K}$.
sible by the fact that the bare $X$-pocket dispersion in $\text{Sm}_x\text{La}_{1-x}\text{B}_6$ can be described, in first approximation, by the same effective mass of $\text{LaB}_6$, with the only Fermi momentum $k_F^{5d}$ changing to accommodate for the different occupation (see Figure 5.3). This observation allows us to make use of the Fermi velocity as extracted for $\text{LaB}_6$ to estimate the value of $k_F^{5d}$ for samples with $x \neq 0$ in the series: that would be extrapolated in the limit of no hybridization between the $4f$ and $5d$ bands, where the Fermi surface defined by the crossing points in $k$-space would be consistent with the Luttinger’s theorem [209, 210].

Figure 5.9a displays the values of $n_{5d}^e(x)$ as extracted from ARPES spectra acquired with 21.2eV and 67eV. The total enclosed volume of the $X$-pocket was calculated by taking into account all the three $X$-point ellipsoids included in the 3D Brillouin zone (BZ). For $\text{LaB}_6$ (i.e. $x = 0$), the $X$-pockets cover $\sim 50\%$ of the bulk BZ (thus $n_{5d}^e = 0.5$), corresponding to having 1 electron in the $5d$ band and thus consistent with the picture of a metallic ground state. As $x$ increases, $n_{5d}^e(x)$ clearly deviates from the linear reduction expected in the case of a constant 1:1 ratio of $\text{Sm}^{2+}$ and $\text{Sm}^{3+}$, represented by the black dashed line in Figure 5.9a. In addition, the different slopes characterizing the evolution of $n_{5d}^e$ for $x \leq 0.2$ and $x \geq 0.55$ suggest the presence of two distinct regimes as a function of $x$, rather than a single monotonic increment or reduction of the $\text{Sm}^{2+}/\text{Sm}^{3+}$ ratio. In order to quantify this transition, we compute the fractional percentage of $\text{Sm}^{2+}$ and $\text{Sm}^{3+}$ (normalized over the total amount of Sm, i.e. $x$) from $n_{5d}^e(x)$ as follow:

$$\text{Fraction } \text{Sm}^{2+} (%) = \frac{1 - 2n_{5d}^e(x)}{x}$$
$$\text{Fraction } \text{Sm}^{3+} (%) = 1 + \frac{2n_{5d}^e(x) - 1}{x}.$$  (5.1)

The resulting values are plotted in Figure 5.9b. At $x = 1$, the fraction of both $\text{Sm}^{2+}$ and $\text{Sm}^{3+}$ is $\sim 50\%$, in accordance with the 1:1 ratio reported in the literature for $\text{SmB}_6$ at low temperature [66, 68, 200]. As $x$ decreases, the amount of $\text{Sm}^{2+}$ (top panel in Figure 5.9b) gradually increases upon reaching a maximum of $\sim 80\%$ at $x = 0.2$, followed by a reduction at even
Figure 5.9: Evolution of the Sm valence from the ARPES dispersion. (a) Electronic occupation number of the X-pocket, $n^{5d}_{e}(x)$, for different Sm$_{x}$La$_{1-x}$B$_{6}$ compounds. Data points were calculated using ARPES spectra acquired with 21.2eV and 67eV. Note the deviation from the case of constant 1:1 ratio of Sm$^{2+}$ and Sm$^{3+}$ (dashed black line), as in the case of pure SmB$_{6}$. (b) Calculated fractional percentage of Sm$^{2+}$ (top) and Sm$^{3+}$ (bottom) using Equation 5.1 for the various compounds measured by ARPES. (c) Mean valence of Sm ions, $v_{Sm}$, in the Sm$_{x}$La$_{1-x}$B$_{6}$ series as obtained from ARPES.

lower Sm concentrations. Note that the difficulties associated with probing minimal modifications of the X-pocket ARPES dispersion for concentrations $x \leq 0.1$, reflected in the large error bars in Figure 5.9b, preclude the exclusion of a saturation of the fractional percentage values rather than a decrease of Sm$^{2+}$ for very low $x$. Nevertheless, Figure 5.9a-b indicate a clear distinction between the low ($i.e. x \leq 0.2$) and high ($x \geq 0.55$) Sm concentration regimes, along with a substantial variation of the Sm$^{2+}$/Sm$^{3+}$ ratio as a function of $x$. These results naturally imply an evolution of the mean valence of Sm ions, $v_{Sm}$, in the Sm$_{x}$La$_{1-x}$B$_{6}$ series, as illustrated in Figure 5.9c.
In order to verify the two regimes scenario and get further insights on the low concentration regime, we performed a XAS study on the same Sm$_x$La$_{1-x}$B$_6$ series to complement the ARPES results illustrated above. In particular, in order to achieve a higher bulk sensitivity, and thus establish our results as an intrinsic bulk-property of the Sm$_x$La$_{1-x}$B$_6$ compounds, we exploit Partial Fluorescence Yield (PFY) and Inverse Partial Fluorescence Yield (IPFY), characterized by a probing depth of several tens of nm. This allows one to circumvent some of the challenges associated to a detailed ARPES study of Sm$_x$La$_{1-x}$B$_6$ samples, such as cleaving procedure and surface degradation. XAS has been shown to be a powerful technique to explore the physics of MV systems, such as SmB$_6$. The absorption spectrum can be described in first approximation by the sum of two independent components, in the present case corresponding to Sm$^{2+}$ and Sm$^{3+}$ ions. Here, by tuning the incident energy across the Sm $M_4$ and $M_5$ edges (i.e. exciting 3d core electrons into 4f orbitals), the XAS spectrum of Sm$_x$La$_{1-x}$B$_6$ can be mapped into a specific Sm$^{2+}$/Sm$^{3+}$ ratio, providing us with a tool to determine the specific valence of Sm ions as a function of $x$. Figure 5.10a presents the PFY spectrum of SmB$_6$ acquired by scanning the Sm resonances. Two different fluorescence lines are clearly distinguishable representing the direct and indirect Sm fluorescence peaks at higher and lower energy, respectively. The absorption profiles integrated around 850 eV (i.e. at the indirect Sm fluorescence peak, red dashed line in Figure 5.10a) are exploited in the present work to perform the detailed analysis. This choice was adopted to avoid additional distortions characterizing the spectra at the direct fluorescence peak energy due to selection rules [211]. Also note that since several natural mechanisms such as self-absorption effects often lead to distortions in the PFY spectra, a correction is needed to disentangle the intrinsic absorption signal [109, 212-214]. In Figure 5.10b we report the evolution of the XAS intensity at the Sm $M_5$ edge in the Sm$_x$La$_{1-x}$B$_6$ series. The experimental data is fit with a weighted sum (black lines) of the Sm$^{2+}$ (blue lines) and Sm$^{3+}$ (green lines) components. While for high $x$ (top part of Figure 5.10b) the Sm$^{3+}$ component dominates, its contribution dramatically reduces at $x = 0.2$. This observation is fully consistent with the re-
Figure 5.10: XAS study of the \( \text{Sm}_x\text{La}_{1-x}\text{B}_6 \) series. (a) PFY spectrum of \( \text{SmB}_6 \) acquired at the Sm \( M_4 \) and \( M_5 \) edges. (b) Evolution of the XAS intensity at the Sm \( M_5 \) edge for \( x = (0.07, 0.13, 0.2, 0.3, 0.7, 0.9, 0.975, 1) \) at the red dashed line in panel (a). The total spectral weight can be fit by a sum (black lines) of two independent components, associated to \( \text{Sm}^{2+} \) and \( \text{Sm}^{3+} \) ions (blues and green lines, respectively). (c) Mean valence of Sm ions, \( v_{\text{Sm}} \), calculated from the XAS spectra presented in (b). The raw values obtained by the fit are represented by the black open circles, while the orange diamonds are the values upon renormalization to account for the different cross-section of \( \text{Sm}^{2+} \) and \( \text{Sm}^{3+} \). Inset: Percentage variation of \( \text{Sm}^{2+} \) ions, \( \Delta \text{Sm}^{2+} \), with respect to the \( x = 1 \) case. All data taken at a base temperature of 20K.
ported evolution of the fractional percentages of Sm$^{2+}$ and Sm$^{3+}$ obtained from ARPES (Figure 5.9b). Moreover, a clear inversion in the progression of the XAS spectra occurs for $x \leq 0.2$, as the Sm$^{3+}$ component strengthens again. By exploiting the specific weights associated to the Sm$^{2+}$ and Sm$^{3+}$ components in each XAS spectrum, we compute $v_{Sm}$, in the Sm$_x$La$_{1-x}$B$_6$ series and plot it in Figure 5.10c. Note that in order to account for the difference in the relative cross-sections of the two Sm components at the energies the XAS measurements were performed, the weights obtained from the fits shown in Figure 5.9b were renormalized such that $v_{Sm}(x = 1) = 2.505$, as reported for SmB$_6$ at $T = 20$K [66, 68], base temperature for the XAS measurements. The black open circles in Figure 5.10c represent then the raw values, while the orange diamonds the actual valence upon normalization. $v_{Sm}$ as extracted via analysis of XAS spectra confirms the two regimes scenario already suggested by the ARPES results shown in Figure 5.9. For $x \leq 0.2$, the average Sm valence rapidly decreases as Sm is introduced in the system, before increasing again for higher $x$. A minimum value of $\sim 2.07$ is observed at $x = 0.2$, which corresponds to an increment of Sm$^{2+}$ ions in the system, $\Delta^{Sm^{2+}}$, as large as $\sim 45\%$ respect to the case of $x = 1$ (top inset of Figure 5.10c). Note that this percentage variation of Sm$^{2+}$ is much more substantial than what was reported for temperature ($\sim 8\%$) and pressure ($\sim 20\%$) dependent studies of SmB$_6$ [66, 197, 200].

5.4 Towards the limit of mixed-valent impurity regime

In Section 5.3 we showed that both ARPES and XAS measurements of Sm$_x$La$_{1-x}$B$_6$ display an evolution of $v_{Sm}$. Here, we start the discussion of the experimental data in terms of trivalent La ions substituting on the Sm site in SmB$_6$, known to have an equal fractional percentage of Sm$^{2+}$ and Sm$^{3+}$. In Figure 5.11 three ideal scenarios are presented for the La-substitution in SmB$_6$: Case 1 and Case 2 where only Sm$^{2+}$ and Sm$^{3+}$ are replaced first, respectively, and Case 3 representing the equal substitution of Sm ions corresponding to the two configurations. Recalling that only
La and Sm$^{3+}$ ions contribute to the occupation of the X-pockets, we can compute the expected evolution of $v_{Sm}$ as a function of $x$ by following the same procedure adopted for the experimental ARPES data (see Figure 5.9 and Equation 5.1). As illustrated by the comparison of Figure 5.11 with the experimental results of Section 5.3, Case 2 qualitatively captures the progression from an evenly Sm$^{2+}$/Sm$^{3+}$ regime into a predominant presence of Sm$^{2+}$ as $x$ decreases from 1. This result is consistent with the observation of the average Sm valence tending towards 2$^+$ upon trivalent ion
substitution (as La$^{3+}$ or Y$^{3+}$) reported in early studies exploiting XAS and the analysis of the variation of the cubic lattice parameter in the solid solutions [215, 216]. Furthermore, recent transport studies on La-substituted SmB$_6$ have reported the complete closure of the $d$-$f$ hybridization gap, and the consequent emergence of a metallic-like behaviour, for La concentrations higher than 25% ($x \leq 0.75$) [217, 218]. These observations corroborate the substantial increase of Sm$^{2+}$ in the system observed in this work as $x$ decreases from 1 (Figure 5.9b and inset in Figure 5.10c). Figure 5.11 represents ideal cases, where a fix equal amount of Sm$^{2+}$ and Sm$^{3+}$ (i.e. 50%) is assumed available in the starting system SmB$_6$. In practice, when trivalent La ions are introduced in the system (i.e. by decreasing $x$), two competing processes may occur to preserve the system’s charge neutrality: electrons can be accommodated in the 5$d$-band, thus shifting the bottom of the conduction band to deeper binding energy, or in the $f$-shell, thus facilitating the transformation of Sm$^{3+}$ into Sm$^{2+}$. Therefore, the delicate balance between these two processes to maintain charge neutrality is dictated by the total energy resulting from the increase in the attractive potential as more trivalent ions are added to the 5$d$-band and the conversion of Sm$^{3+}$ ions into Sm$^{2+}$ (recall that these two valence configurations are indeed nearly degenerate in SmB$_6$, making such transition available at a very low energy cost). Given the small energy scales involved, it is not possible a priori to designate either one as the dominating mechanism, but we are currently working on a theoretical description of how such delicate balance may occur.

Instead, here we offer a simplified phenomenological model to describe the observed transition of $v_{Sm}$ based on the two distinct regimes revealed experimentally in the Sm$_x$La$_{1-x}$B$_6$ series. For high $x$, we mimic the decrease of $v_{Sm}$ upon La-substitution by fitting the experimental data for $x \geq 0.2$ with a linear fit ($V_0(x)$, red line in Figure 5.12a). To provide a phenomenological description of the increase of $v_{Sm}$ observed for low $x$ (i.e. $x < 0.2$), we refer to an early work by Haldane examining the dilute limit of a single rare-earth impurity in a $d$-band metal [199]. The derivation is based on the addition to the Anderson-model Hamiltonian of a screening
Figure 5.12: Simplified model for the Sm valence in Sm$_x$La$_{1-x}$B$_6$. (a) Linear fit, $V_0(x)$, to $v_{Sm}$ for $x \geq 0.2$ capturing the decrease in the valence due to formation of Sm$^{2+}$ upon La-substitution. (b) Calculated probability for a Sm ions to have $N$ other Sm as nearest-neighbours from Equation 5.2 $P^0(x)$ (black line) is used to define the fraction of Sm ions which assumes the impurity valence $v_{imp} = 2.35$ at each $x$. (c) $v_{imp}$-dependence of $v_{\text{Model}}$ as defined by Equation 5.3. (d) Comparison between the model of Equation 5.3 (dashed blue line) and the experimental values of $v_{Sm}$ obtained from ARPES (light and dark green circles, acquired with 21eV and 67eV, respectively) and XAS (orange diamonds).

term, which describes the interaction between the impurity $f$-orbitals and the $d$-orbitals (expressed in terms of Wannier functions) on the same site. If this extra $f$-$d$ interaction is reasonably larger than the standard inter-site hybridization term, it stabilizes the $f$-electrons fluctuations, enabling the single impurity to be in a mixed-valent state. Although we recognize that the realization of such scenario would be very coincidental (for the energy of the $f$-states to be as such to return mixed-valence), the system described
in Haldane’s work retains a lot of similarity with Sm$_x$La$_{1-x}$B$_6$ for $x \ll 1$, where the Sm ions can be described as impurities in the $d$-band metal LaB$_6$. This observation stimulates us in considering the possibility of contributions to $v_{Sm}$ given by Sm ions acting as single impurities with a specific fixed fractional valence, $v_{imp}$. In this regard, we compute the probability for a Sm ion to have $N$ Sm in the nearest-neighbour sites, $P^N$ (with $N$ ranging from 0 to 6), as a function of $x$:

$$P^N(x) = x^N (1 - x)^{6-N} \binom{6}{N}.$$  \hspace{1cm} (5.2)

The calculated $P^N(x)$, $N = [0,6]$, are plotted in Figure 5.12b. The function $P^0(x)$ (black line) is used to define in first approximation the fraction of Sm ions which assumes the impurity valence $v_{imp} = 2.35$ (as extrapolated from the experimental results in Figure 5.9c and Figure 5.10c) at any given concentration $x$. Therefore, we can describe the evolution of the Sm valence in the Sm$_x$La$_{1-x}$B$_6$ series by:

$$v_{Model} = P^0(x) \cdot v_{imp} + (1 - P^0(x)) \cdot V_0(x).$$  \hspace{1cm} (5.3)

Note that $P^0(x)$ rapidly decays below 0.1 within $x = 0.3$, thus leading to negligible contributions to $v_{Sm}$ at high $x$. Figure 5.12d compares the simplified model of Equation 5.3 with the experimental values of the average Sm valence obtained from ARPES (light and dark green circles) and XAS (orange diamonds), showing a good agreement. In particular, the steep increase of $v_{Sm}$ observed for $x \leq 0.2$ is well described by the significant contribution given by the emerging impurity regime with fixed fractional valence. Furthermore, we note that a variation of $\pm 0.5$ in $v_{Sm}$, associated to the error in determining the extrapolated value, mainly reflects in a modification of the steepness of the upturn for $x < 0.2$, not significantly affecting the overall evolution of $v_{Model}$ and the distinctive crossover around $x = 0.2$ (Figure 5.12c).

In light of the fact that the phenomenological inclusion of an impurity regime with intermediate valence seems to grasp the evolution of the ex-
perimental data for low $x$, we conclude this section with a short discussion on the viability of having such a MV impurity regime in $\text{Sm}_x\text{La}_{1-x}\text{B}_6$. In this regard, we illustrate here the case of one Sm impurity hosted in the $d$-band metallic $\text{LaB}_6$, to verify whether or not an admixture of two different $f$-states is possible in the ground state wavefunction. According to the one-electron excitation spectrum presented in Figure 1.5, the high energy cost ($\sim 5 - 6\,\text{eV}$) associated to transitions of the form $f^6 \rightarrow f^7$ and $f^5 \rightarrow f^4$ allows to discard them in the following discussion of the lowest energy excitations, which are solely defined by the electron addition to $4f^5$ and removal from $4f^6$ states. In order to preserve the system’s charge neutrality, such excitations must involve adding/removing an electron from the $d$ conduction band. By considering only the lowest energy possible states and by replacing the multiplet quantum number with an effective spin $\pm 2$, we can write for the impurity $a$:

$$f_{a\uparrow}^5 \rightarrow f_{a\downarrow}^6 d_{k\downarrow} \rightarrow f_{a\downarrow}^5 d_{k\downarrow} d_{k\uparrow}^\dagger. \quad (5.4)$$

Visually, such transition resemble the Kondo-like interaction, where a conduction electron is scattered from $k$ to $k'$ along with a flip in the local spin. However, in the present case all the states involved (both the two $4f$ states and the $d_k$) are nearly degenerate at the Fermi energy. This aspect sets a crucial distinction from the conventional Kondo problem. Effectively, the $U$ included in the Anderson Hamiltonian-type way to describing the Kondo physics is nearly zero for the lowest energy $4f$ states and the $d_k$ involved in Equation 5.4. Therefore, the energy denominator in a perturbation-type treatment is $\approx 0$, making the Schrieffer–Wolff transformation – essential step in the description of the Kondo physics from the Anderson impurity model – not valid in this context. Despite this fundamental difference, Equation 5.4 shows the viability of having both $f^5$ and $f^6$ mixed into the ground state wavefunction accompanied by virtual fluctuations from $k$ to $k'$, spin-down to spin-up in the conduction electron sea. Although a highly

\footnote{In particular, $J = 0$ for the $4f^6$ state while $4f^5$ has $J = 5/2$, with the latter further split by the crystal field into a doublet and a quartet. Here we consider the doublet as the lowest energy state and associate an “effective spin” quantum number to such state.}
improbable scenario, requiring a critical balance of interactions such that the two \( f \)-states and the \( d_k \) are degenerate, that admixture could reflect into a mixed-valent character of the system even in the impurity limit.

5.5 Conclusions

To summarize, we studied the valence fluctuations in the \( \text{Sm}_x\text{La}_{1-x}\text{B}_6 \) series by gradually changing the stochiometry. Combining ARPES and XAS techniques, we tracked the evolution of the mean valence of the Sm ions, \( v_{\text{Sm}} \), revealing the persistence of the intermediate valence character even in the very dilute limit. In particular, our results disclose the presence of two distinct regimes for \( v_{\text{Sm}} \), moving from high to low Sm concentration \( x \): for \( 0.2 \leq x \leq 1 \), \( v_{\text{Sm}} \) linearly converges towards a predominant \( \text{Sm}^{2+} \) state, consistent with the substitution on the Sm site by a trivalent ion as \( \text{La}^{3+} \); contrary, for very low Sm concentrations, i.e. \( x < 0.2 \), \( v_{\text{Sm}} \) increases again, marking a substantial deviation from a monotonic evolution across the entire series. The formulation of a phenomenological model based on the inclusion of a Sm impurity regime, in which Sm ions exhibit a fixed fractional valence of \( v_{\text{imp}} = 2.35 \), succeeds in capturing the experimental results and the observed crossover at \( x \sim 0.2 \). Our study suggests the possible realization of a MV impurity state in \( \text{Sm}_x\text{La}_{1-x}\text{B}_6 \), a scenario speculated by Haldane few decades ago [199]. These results may pave the way for further theoretical and experimental considerations on the concept of MV and its influence on the macroscopic electronic and transport properties of rare-earth compounds in the impurity regime.
Chapter 6

Conclusions

This thesis brings together three projects, employing angle-resolved photoemission spectroscopy, both in its conventional and time-resolved fashion, to quantitatively investigate the interplay between different phenomena characterizing the physics of strongly correlated materials, in particular $3d$ and $4f$ systems.

Firstly, we extended the ability of ARPES to directly access the momentum and energy-dependent spectral function onto the time-domain, to study the dynamical interplay of competing phenomena characterizing the superconducting phase (SC) of hole-doped Bi-based cuprates. A scenario in which the macroscopic $T_c$ in the underdoped regime is primarily determined by the onset of phase coherence, rather the pairing strength $\Delta$, was proposed in the 1990s by Emery and Kivelson [113]. A recent time- and angle-resolved photoemission spectroscopy (TR-ARPES) study of the underdoped bi-layer $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212) confirmed such a scenario by reporting an ultrafast melting of superconductivity driven by the enhancement of phase fluctuations upon optical pumping, while leaving the pairing strength mainly unaffected [114]. Here, the same experimental approach was employed to extend such a study of the spectral function dynamics to the single-layer hole-doped $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$ (Bi2201). By perturbing with a 1.55 eV probe pulse the overdoped Bi2201 OD24 ($T_c \sim 24K$), we resolved an increase of the pair-breaking scattering rate associated to the
presence of phase fluctuations. This ultrafast response is comparable both in magnitude and in timescale to what was previously reported for Bi2212, and is completely decoupled from the dynamics of the pairing strength and the effective electronic temperature. These results testify to the importance of phase coherence in determining the macroscopic stability of the SC condensate in the underdoped and close to optimally-doped regimes of the Bi-based cuprates, independently of the number of CuO$_2$ planes within the unit cell. Whether or not this ultrafast experimental approach can be used to directly map the transition to a regime in which the formation of the SC condensate is instead solely ruled by the paring strength, as proposed for the very overdoped regime, has still to be assessed.

Next, we provided a comprehensive study of the temperature dependent suppression of the nodal coherent spectral weight in Bi-based cuprates. It has been proposed that such a quenching of the quasiparticle peak bears direct relation to the SC state and the superfluid density. Here, by combining data from different doping levels of both the single- and bi-layer compounds, we demonstrated that the nearly linear suppression of CSW is universal across the Bi-based cuprates’ family and it persists for $T \gg T_c$, therefore excluding an explicit link to SC. Instead, the observed nodal CSW meltdown can be described in terms of the quadratic temperature dependence of the imaginary part of the self-energy within a Fermi-liquid picture. In addition, these findings suggest that such a T-evolution of the CSW can be employed as a sensitive tool to explore the fragility of the Fermi-liquid behaviour as a function of momentum, while going from the nodal direction to the antinode. Given the low $T_c$, the single-layer Bi2201 represents an intriguing candidate to test such a momentum-dependent investigation of the normal-state self-energy in cuprates, with no complications arising from the SC gap.

The second project focused on the relation between pseudogap (PG) and antiferromagnetic (AF) correlations in electron-doped cuprates. In these materials, it is believed that the PG bears strong relation with the robust AF order, which extends for a wide doping range up to the SC dome. While this picture is well established in the underdoped regime, where a true
long-range AF order is present, close to optimal doping only short-range spin-fluctuations have been detected, arising the question on whether and how such short-range order relates to the spectroscopically observed PG. In this regard, we made use of the capability of TR-ARPES to perform an extremely detailed temperature-dependent analysis of the PG spectral features in optimally-doped Nd$_{2-x}$Ce$_x$CuO$_4$ (NCCO). We showed that such temperature evolution is closely linked to the spin-correlation length, $\xi_{\text{spin}}$, and that a complete filling of the PG is observed when the spectral broadening due to the reduction of $\xi_{\text{spin}}$ overcomes the paring amplitude $\Delta_{\text{PG}}$. These results demonstrate that the PG in electron-doped cuprates originates from short-range AF correlations and that the onset temperature $T^*$ represents a crossover temperature related to the reduction of $\xi_{\text{spin}}$, more so that a sharp phase transition. These findings also testify the importance of orders even with short-range correlation length in the shaping of the Fermi surface topology of correlated materials.

Lastly, the rare-earth haxaboride Sm$_x$La$_{1-x}$B$_6$ series was the subject of the third project. Among the multitude of novel phenomena driven by the highly correlated 4f electrons, the emergence of the mixed-valence (MV) state is a key element to account for in the description of the rich ground state of SmB$_6$. On the other hand, the lack of 4f electrons and the half-filled 5d-band make LaB$_6$ metallic. This provided us with the opportunity to investigate the evolution of the MV character as a function of 4f electrons gradually introduced in the system. By combining ARPES and x-ray absorption spectroscopy (XAS), we reported two distinct regimes characterizing the mean valence of the Sm ions across the series: while a linear transition from a predominant 2$^+$ to an even 2$^+$/3$^+$ state is observed for $x > 0.2$, an unexpected persistence of the MV emerges at low Sm concentration (i.e. $x < 0.2$). We showed that this behaviour can be described by the inclusion of a phenomenological impurity regime of Sm with intermediate valence. These results may stimulate further discussion on the concept of MV in the very dilute regime and the implications for the electronic properties of rare-earth hexaborides.


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Appendix A

Publications

During the course of my PhD I was involved in a number of research projects, some of which have resulted in peer reviewed publications. A list is provided here.

- Emergence of the pseudogap from short-range spin-correlations in electron doped cuprates
  
  
  *npj Quantum Materials 5, 6 (2020)

- Role of matrix elements in the time-resolved photoemission signal
  
  
• Room temperature strain-induced Landau levels in graphene on a wafer-scale platform


• Influence of Spin-Orbit Coupling in Iron-Based Superconductors


• Collapse of superconductivity in cuprates via ultrafast quenching of phase coherence


• Doping-dependent charge order correlations in electron-doped cuprates


Science Advances 2, 8 (2016)
• Evidence for superconductivity in Li-decorated monolayer graphene
  *PNAS* 112, 11795 (2015)

• Effect of Pt substitution on the electronic structure of AuTe2
  *Phys. Rev. B* 90, 144515 (2014)

• The Thinnest Carpet on the Smallest Staircase: The Growth of Graphene on Rh(533)
  B. Casarin, A. Cian, Z. Feng, E. Monachino, F. Randi, G. Zamborlini, M. Zonno, E. Minussi, P. Lacovig, S. Lizzit and A. Baraldi

• The momentum and photon energy dependence of the circular dichroic photoemission in the bulk Rashba semiconductors BiTeX (X=I, Br, Cl)