UNCONVENTIONAL PEIERLS PHYSICS IN UNDERDOPED BI2201

by

JONATHAN ADAM ROSEN

B.Sc., The University of California, Santa Cruz, 2006
M.Sc., The University of British Columbia, 2008

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES

(Physics)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

December, 2012

© Jonathan Adam Rosen, 2012
Abstract

The puzzling physics of the high-temperature superconducting cuprates has led to many important questions and investigations regarding the mechanism of high-$T_C$'s. This dissertation demonstrates that, through detailed experimental studies using angle-resolved photoemission (ARPES) and low-energy electron diffraction (LEED), a new type of periodic structural distortion exists in Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$ (La-Bi2201), leading to the existence of multiple periodic lattice distortions (PLD) in the underdoped material. Photon-energy dependent ARPES reveals photoelectron diffraction effects that exhibit all relevant length scales as oscillations in the ARPES matrix element, leading to the observation of all of the diffraction-replica (DR) bands associated with the multiple PLD's. Furthermore, a charge-density-wave (CDW) associated with the new PLD at the crystal surface with a temperature-dependent wavelength is observed. A Ginzburg-Landau mean field model is shown to exhibit the same temperature-dependence from a combination of Fermi surface nesting and lattice commensurability affected by the temperature-dependent harmonic content of the CDW. A detailed temperature-dependence of the antinodal pseudogap reveals two simultaneous energy and temperature scales: one associated with the CDW, and the other in agreement with the magneto-optical Kerr effect and magnetic neutron diffraction results in the literature. Detailed nodal ARPES lineshapes reveal a peak in the real-part of the self-energy that coincides with band-crossing positions and the nodal “kink” energies for all dopings, providing evidence that these disparate features can be collectively explained by band hybridization allowed in the fully incommensurate crystal, which does not preserve parity. This provides one route to explain these phenomena - as a product of nested van-Hove singularities along the nodal line in underdoped La-Bi2201, which result in a Peierls distortion similar to the dichalcogenide CDW superconductors.
Preface

Chap. 1 Introduces the experimental approach to angle-resolved photoemission and the electronic structure of the cuprate high-temperature superconductors, and Chap. 2 provides an introduction and theoretical background expanded from the literature, and applicable to angle-resolved photoemission, covering the first principles electromagnetic interaction and leading to a description of this single-particle spectroscopy technique as a way to observe the fully complex many-body states of the material. The work in Chap. 3 is applied towards reconciling contradictory claims of “arcs” and “pockets” in the underdoped Bi2201 Fermi surface. In particular, the work in Sec. 3.4 represents published work [1] in the form of a collaboration and co-equal authorship between P. D. C. King and myself to obtain a structural explanation for coexisting Fermi “arcs” and “pockets”, with collaboration on experimental work in ARPES and LEED with W. Meevasana, A. Tamai, E. Rozbicki, and our group members R. Comin, G. Levy, and D. Fournier, as well as K. M. Shen and N. J. C. Ingle, and done together with the senior co-authors A. Damascelli and F. Baumberger. Samples were provided by Y. Yoshida and H. Eisaki.

The rest of Chap. 3 and Chap. 4 demonstrates a novel approach to photon energy-dependent photoemission, as a way to overcome the ARPES matrix elements and confirm all the photoemission features predicted by the existence of multiple superstructures in Bi2201, and additionally for probing the photoelectron diffraction effects which arise from multiple real-space periodicities. This offers direct insight into the symmetry of the electronic wavefunctions in Bi2201. This chapter contains material for a manuscript in preparation for ARPES and LEED measurements and analysis that were carried out primarily by myself with assistance from D. Fournier, R. Comin, L. Petaccia, E. Rotenberg, and A. Damascelli, and with samples provided by Y. Yoshida and H. Eisaki.

The work in Chap. 5 describes a highly temperature-dependent modulation of the electronic states at the crystal surface in underdoped Bi2201, and provides evidence for a charge-density-wave instability in this material. Secs. 5.2 and 5.3 represent a collaboration on a submitted manuscript that is currently under review in Nat. Commun., of co-equal authorship between myself and group member R. Comin. ARPES and LEED measurements and analysis were carried out mainly by myself, and x-ray diffraction measurements and analysis by R. Comin, with support from group members G. Levy, D. Fournier, Z.-H. Zhu, B. Ludbrook, C. N Veenstra, D. Wong, P. Dosanjh. International support for ARPES measurements was provided by L. Petaccia, and for x-ray diffraction measurements, G. R. Blake, F. White, T. T. M. Palstra, A. Frañó Pereira, and Y. Lu. In addition, B. Keimer, G. Sawatzky, L. Petaccia, and A. Damascelli contributed senior co-authorship. Samples
were provided by Y. Yoshida and H. Eisaki.

Finally, Chap. 6 examines the “peak-dip-hump” lineshape phenomenology of the nodal angle-resolved photoemission spectrum from Bi2201, and draws connection to the charge-density-wave formation via the observed coincidence of the nodal “kink” and band-crossings originating in structural backfolding and a different perspective on electron-phonon coupling in these materials. This chapter contains material for a manuscript in preparation for ARPES measurements and analysis that were carried out primarily by myself with assistance from R. Comin, D. Fournier, L. Petaccia, and A. Damascelli, with samples provided by Y. Yoshida and H. Eisaki.
# Table of Contents

Abstract ............................................................................................................................... ii

Preface .................................................................................................................................. iii

Table of Contents .................................................................................................................. v

List of Figures ....................................................................................................................... viii

List of Abbreviations ........................................................................................................... x

Acknowledgements ............................................................................................................... xi

Dedication .............................................................................................................................. xii

1. Introduction ...................................................................................................................... 1
   1.1 Angle-Resolved Photoemission Measurements for the Study of High-Temperature
       Superconductors ............................................................................................................. 1
   1.2 The Electronic Structure of Cuprate High-T<sub>C</sub>’s .......................................................... 3
   1.3 Analysis Techniques in ARPES - EDC’s and MDC’s ......................................................... 5
   1.4 Scope of the Dissertation ................................................................................................. 7

2. Theoretical Background for Photoemission Applied to High-Temperature Superconductors 10
   2.1 Conductivity and Superconductivity ................................................................................ 10
   2.2 The Electron Gas ........................................................................................................... 11
   2.3 The First Principles Electromagnetic Interaction ............................................................ 12
   2.4 Simplifications of the Electromagnetic Interaction .......................................................... 14
   2.5 Green’s Functions .......................................................................................................... 17
      2.5.1 Single-Particle Green’s Function ............................................................................. 17
      2.5.2 Many-Particle Green’s Function ............................................................................. 20
      2.5.3 The Non-interacting Quasi-Particle in the Many-Particle Picture ............................. 22
   2.6 The Photoemission Intensity ........................................................................................... 23
   2.7 One- and Three-step Models of Photoemission .............................................................. 25
   2.8 Including Interactions in the Many-Body Spectral Function .......................................... 26
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3. Multiple Crystal Structure Modulations in Underdoped Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>30</td>
</tr>
<tr>
<td>3.1 Structural Considerations in the Cuprate High-T$_C$’s</td>
<td>30</td>
</tr>
<tr>
<td>3.2 A Puzzling Contradiction of Arcs and Pockets in the Cuprate Fermi Surface</td>
<td>33</td>
</tr>
<tr>
<td>3.3 LEED and Polarization and Doping Dependent ARPES on Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>36</td>
</tr>
<tr>
<td>3.4 Structural Origin of Apparent Fermi Surface Pockets in Angle-Resolved Photoemission of Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>37</td>
</tr>
<tr>
<td>3.5 Conclusive Evidence for Multiple Structure Modulations in Underdoped Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>47</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4. Photoelectron Diffraction Effects in Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>51</td>
</tr>
<tr>
<td>4.1 ARPES Matrix Element Effects</td>
<td>51</td>
</tr>
<tr>
<td>4.2 LEED and Photon-Energy Dependent ARPES in Underdoped Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>55</td>
</tr>
<tr>
<td>4.3 Evidence for Parity-Mixing of the Electronic Wavefunction in Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>66</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5. Temperature Dependence of Underdoped Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$ in the Pseudogap Phase</td>
<td>67</td>
</tr>
<tr>
<td>5.1 Introduction to the Pseudogap Phase</td>
<td>67</td>
</tr>
<tr>
<td>5.2 Temperature Dependent Density-Wave Periodicity Measured at the Surface by ARPES, LEED, and X-ray Diffraction</td>
<td>70</td>
</tr>
<tr>
<td>5.2.1 Possible Charge-Order in the Cuprates</td>
<td>70</td>
</tr>
<tr>
<td>5.2.2 Surface-Sensitive Probes: ARPES and LEED</td>
<td>72</td>
</tr>
<tr>
<td>5.2.3 Bulk-Sensitive Probes: XRD and REXS</td>
<td>73</td>
</tr>
<tr>
<td>5.2.4 Surface/Bulk Dichotomy and CDW Formation in Underdoped Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>75</td>
</tr>
<tr>
<td>5.2.5 Conclusions on Incipient CDW Order at the Surface</td>
<td>77</td>
</tr>
<tr>
<td>5.3 Ginzburg-Landau Mean Field Model for Density-Wave Order in Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>77</td>
</tr>
<tr>
<td>5.3.1 Introduction to Ginzburg-Landau Mean Field Theory</td>
<td>77</td>
</tr>
<tr>
<td>5.3.2 Mathematical Models for the Mean-Field Free Energy</td>
<td>78</td>
</tr>
<tr>
<td>5.3.3 Model Free Energy Results</td>
<td>81</td>
</tr>
<tr>
<td>5.3.4 Calculation of the Tight-Binding Susceptibility</td>
<td>82</td>
</tr>
<tr>
<td>5.3.5 Discussion of Mean Field Model and Tight-Binding Susceptibility Results</td>
<td>83</td>
</tr>
<tr>
<td>5.3.6 Finite-Size Effects and Flattening of the Free Energy Landscape</td>
<td>84</td>
</tr>
<tr>
<td>5.4 Temperature-Dependent ARPES in the Antinodal Region in Underdoped Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>86</td>
</tr>
<tr>
<td>5.5 Temperature Dependence of the Resistivity, Nodal MDC Widths, and Valence Band Energies</td>
<td>91</td>
</tr>
<tr>
<td>5.6 Conclusions</td>
<td>93</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6. The Peak-Dip-Hump Lineshape and Band-Crossing Hybridization in Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>96</td>
</tr>
<tr>
<td>6.1 Peak-Dip-Hump Lineshape in the Cuprates</td>
<td>96</td>
</tr>
<tr>
<td>6.2 The Nodal ARPES Spectra of Underdoped Bi$<em>2$Sr$</em>{2-x}$La$<em>x$CuO$</em>{6+\delta}$</td>
<td>98</td>
</tr>
<tr>
<td>6.2.1 MDC Analysis and the Self-Energy</td>
<td>98</td>
</tr>
</tbody>
</table>
# List of Figures

1.1 Hemispherical electron energy analyzer ........................................ 2  
1.2 Electron microscope ................................................................. 3  
1.3 Basic cuprate electronic structure .............................................. 5  
1.4 ARPES nodal cut ................................................................. 6  
1.5 MDCs and EDCs ................................................................. 8  

2.1 Orientation of the electromagnetic field ........................................ 15  

3.1 Sketch of the tetragonal Fermi surface ....................................... 31  
3.2 Fermi surface of the orthorhombic system .................................. 33  
3.3 Sketch of apparent Fermi pockets .............................................. 35  
3.4 ARPES Fermi surface of optimally doped Bi$_2$Sr$_{1.5}$La$_{0.5}$CuO$_{6+\delta}$ ....... 36  
3.5 Photon-polarization averaged ARPES Fermi surface for Bi$_2$Sr$_{1.5}$La$_{0.5}$CuO$_{6+\delta}$ ....... 38  
3.6 Polarization-dependence of the underdoped ARPES Fermi surface ........ 39  
3.7 S-polarization ARPES cuts for Bi$_2$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$ ............... 40  
3.8 P-polarization ARPES cuts for Bi$_2$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$ ............... 41  
3.9 LEED pattern for the underdoped x=0.8 sample ......................... 42  
3.10 Doping-dependent ARPES Fermi surface of La-Bi2201 ................. 43  
3.11 LEED pattern and ARPES Fermi surface of OP35K (Pb,La)-Bi2201 .......... 45  
3.12 Polarization-dependent ARPES on La-Bi2201 ............................ 46  
3.13 LEED of UD20K La-Bi2201 .................................................. 47  
3.14 Sketch of the Fermi surface for Fermi pocket and multiple superstructure pictures 48  
3.15 Photon-energy integrated ARPES nodal-direction cuts ............... 48  

4.1 Photoelectron interference effects .............................................. 53  
4.2 LEED image for underdoped Bi$_2$Sr$_{1.4}$La$_{0.6}$CuO$_{6+\delta}$ ............... 56  
4.3 Photon energy dependent ARPES Fermi map ................................ 57  
4.4 Photon-energy dependence of the ARPES Fermi map .................... 59  
4.5 Photon-energy dependence along high-symmetry Γ-Y direction .......... 60  
4.6 Photon-energy dependence parallel to Γ-Y in the 2$^{nd}$ Brillouin zone .... 62  
4.7 Image plot of the MDC’s for the 2$^{nd}$ Brillouin zone ................ 63  
4.8 Photon-energy integrated ARPES cut ........................................ 65  

viii
List of Abbreviations

(La-)Bi2201 \( \text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_6+\delta \)

ARPES Angle-Resolved Photoemission Spectroscopy

Bi2212 \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \)

CDW Charge Density Wave

DR Diffraction Replica

EDC Energy Distribution Curve (constant momentum)

LEED Low-Energy Electron Diffraction

MDC Momentum Distribution Curve (constant energy)

OP Optimally Doped

PDH Peak-Dip-Hump

PhD Photoelectron Diffraction

PLD Periodic Lattice Distortion

R(E/I)XS Resonant (Elastic/Inelastic) Soft- and Hard- X-ray Scattering

STM Scanning-Tunneling Microscopy/Spectroscopy

UD Underdoped

VHS van Hove Singularity

XRD X-Ray Diffraction
Acknowledgements

It is with special thanks that I would like to acknowledge the opportunities and assistance that have made this research possible. I am grateful for the guidance of my supervisor, Prof. Andrea Damascelli, and as well for assistance from the Quantum Materials research group members: David Fournier, Giorgio Levy, Thomas Roth, Jeff Mottershead, Suman Hussain, Ryan Wicks, Christian Veenstra, Jason Zhu, Bart Ludbrook, Riccardo Comin, and for additional technical assistance from Doug Wong and Pinder Dosanjh.

Thanks are given for samples provided by Y. Yoshida and H. Eisaki, and for collaborative assistance from L. Petaccia with the experimental work at the Elettra BadElPh beamline and endstation. Additional thanks go to E. Rotenberg and D. Fournier for assistance at the ALS Electronic Structure Factory beamline and endstation.
Dedication

I lovingly dedicate this thesis to the universe, and everything it contains.
1

Introduction

1.1 Angle-Resolved Photoemission Measurements for the Study of High-Temperature Superconductors

The measurement of the properties of photoelectrons is a technological feat, requiring the experimentalist to overcome many challenges. The most central and important of these challenges will be discussed in this section, regarding the experimental setup and apparatus used for the angle-resolved photoemission (ARPES) experimental technique.

Originally conceived in 1938 [2], the hemispherical energy analyzer is a fundamental component of the ARPES technique. It makes use of a vacuum region between two hemispherical plates, which are charged to form an electric field in the vacuum region. Photoelectrons enter the hemispherical vacuum region and their path can be controlled with the applied voltages. This device is illustrated in Fig. 1.1. The general calculation of the trajectories of charged particles can be calculated numerically, much of which is beyond the scope of this work. However, it is usually more useful to consider an electron path that transits the hemispherical vacuum region along its central path \( r = r_0 \). The relative trajectory of electrons to this path is given by,

\[
\begin{align*}
    x(\phi) &= x_0 \cos(\phi) + a_0 r_0 \sin(\phi) \\
    y(\phi) &= y_0 \cos(\phi) + b_0 r_0 \sin(\phi) + r_0 (1 - \cos(\phi)) \delta_0
\end{align*}
\]  

(1.1.1)

The \( x \)- and \( y \)-coordinates are defined corresponding to Fig. 1.1, and \( \phi \) corresponds to the angle of electron emission relative to normal emission. The parameters \( a_0 \) and \( b_0 \) are the ratios of the free electron momentum, \( a_0 = p_x/p_z \) and \( b_0 = p_y/p_z \), to the z-axis momentum, which is parallel to the normal incidence axis at the edge of the hemisphere. \( \delta_0 \) is the relative difference in the kinetic energy of the electron to the energy of the electron that transits the central (reference) path, \( \delta_0 = (E_K - E_K^{ref})/E_K^{ref} \). From equation (1.1.1), it is clear why the hemispherical analyzer is the instrument of choice for angle-resolved photoemission - the \( y \)-coordinate depends on the relative kinetic energy of the electrons, while the \( x \)-coordinate only depends on the initial velocity of the electrons along the \( x \)-axis. The result is that simultaneous spatial (angular) and energy resolution
Fig. 1.1: **Hemispherical electron energy analyzer**, which is used to resolve the energy of the photoelectrons.

is possible with a 2D detector that can measure both the x- and y-position of the electrons exiting the hemisphere.

The measurement of photoelectron kinetic energy is thus accomplished with the static electric fields in the hemisphere, which affect the electron trajectory in a way analogous to the way an optical lens bends a photon trajectory. Such a device is today understood in the sub-field of charged particle optics [3]. In the last 20 years these devices have been commonly utilized for ARPES [4, 5], currently including additional spin detection as well through the use of a detector outside the hemisphere that incorporates a magnetic field [6]. Another important feature of these devices is the electron optics that collect and focus electrons into the hemisphere from their origin at the photoemitting sample. An illustrative example of the optics stage is the two-element co-axial cylindrical electrostatic lens [3]. This device consists of two co-axial cylinders to which differential voltages are applied. The first order properties of such a lens can be studied numerically with the differential equations in (1.1.2).

\[
\begin{align*}
    x'' + \frac{1}{2} \frac{\phi'(z)}{\phi(z)} x' + \frac{1}{4} \frac{\phi''(z)}{\phi(z)} x &= 0 \\
    y'' + \frac{1}{2} \frac{\phi'(z)}{\phi(z)} y' + \frac{1}{4} \frac{\phi''(z)}{\phi(z)} y &= 0
\end{align*}
\]  

(1.1.2)

The coordinates in this expression correspond to the axes defined in Fig. 1.2. The function \( e\phi(z) \equiv E_K^{\text{ref}} - eU_0(z) \) describes the potential of the lens evaluated at its center \( (r = 0) \). These equations are coupled by the electron velocity along the optical axis, \( \{z(t), \phi(z(t)), \phi'(z(t)), \phi''(z(t))\} \), and so
are generally complicated to solve analytically. Numerical methods involving finite step analysis present a more straightforward method to calculate the electron trajectory.

Many devices have been created that utilize the dynamics of equation 1.1.2, and for other similar geometries, which generally fall under the category of electron microscopes [7, 8]. The basic elements of this device are illustrated in Fig. 1.2, with applied voltages noted that are typical of the angle-resolved electron lens setup. The electron lens used in conjunction with the hemispherical energy analyzer for ARPES will typically resemble a converging lens analogous to the optical case. This allows a photoelectron source located at the focal point of the lens to produce an angle-resolved collimated beam entering the hemisphere for energy analysis. Thus a 2D detector, such as a multi-channel plate [9], can be used to resolve the angle and energy of photoelectrons in a vacuum environment. For additional details regarding the experimental setup used for the measurements of this chapter, see reference [10].

1.2 The Electronic Structure of Cuprate High-\(T_C\)’s

The electronic structure of the CuO\(_2\)-plane, high-\(T_C\) superconductors has been extensively studied by electron-band theories such as the local-density approximation (LDA), as well as various \textit{ab initio} and strong-coupling theories. The starting point in the description of their electronic properties is the octahedral coordination of the Cu-atom and oxygen ligands. In this coordination, the 3d electrons of Cu are characterized by non-bonding \(d_{xy}\), \(d_{yz}\), and \(d_{zx}\) orbitals (\(t_{2g}\)), while the \(d_{x^2-y^2}\) and \(d_{z^2}\) orbitals (\(e_g\)) can form symmetry-adapted linear combinations (SLAC) with the ligand \(2p_{x/y}\) orbitals, leading to a single hole in the \(d_{x^2-y^2}\) orbitals as a result of crystal field splitting in the tetragonal symmetry and Jahn-Teller distortion that leaves the in-plane Cu-O bond distance.
smaller than the out-of-plane bond length to the apical oxygen. This leads to a dispersive bonding band crossing the Fermi level, which is composed of hybridized \( \text{Cu}3d_{x^2-y^2}-\text{O}2p_{x/y} \) states forming directly overlapping \( \sigma \)-bonds [11, 12, 13].

The cuprate high-\( T_C \)‘s are unusual in that the undoped parent compound is an insulator, despite the prediction of a metallic system from band-theory [13], and are thus Mott insulators. The presence of antiferromagnetic order in the half-filled parent insulator has led to the proposal of several strongly correlated ground states responsible for the insulating behavior. Among them is the Néel state [14] and the resonating-valence-bond state (RVB) [15].

Much of the experimentally observed phenomenology of the cuprates, including the zero-doping Mott-insulator state and characteristic crossover temperature \( T^* \) in the hole-doped, metallic phase, has been described in the framework of the strong coupling \( t-J \) model. The \( t-J \) model can be derived from the single-band Hubbard model, and describes a system of correlated, itinerant fermions which crossover into an antiferromagnetic insulating state for half-filling, due to a large superexchange constant of around 100-140meV, which is of the order of the conduction electron bandwidth. The resultant correlation effects are responsible for the insulating behavior at half-filling, and lead to the charge-transfer of the doped holes in to the oxygen p-states [16]. Furthermore, this model describes the correlation of doped holes into itinerant states that cannot be considered ordinary fermions, since they do not represent almost-filled band states, instead appearing as correlated many-body states not applicable to a single-particle description[17].

The lowest binding-energy ionization states of the \( \text{CuO}_2 \)-plane, quasi-2D cuprates can be described by a singlet antibonding combination of a \( \text{Cu} - 3d_{x^2-y^2} \) orbital, containing the intrinsic Cu-3d hole, and a coherent combination of the four neighboring \( \text{O}2p_x / \text{O}2p_y \) orbitals which can be thought of as containing the hole created in the photoemission process [18, 19]. This state is generally referred to as the Zhang-Rice singlet state. The singlet character of the first electron-removal states, at least in \( \text{CuO} \), has been experimentally verified using spin-resolved resonant photoemission [20]. However, an alternative mechanism for the dynamics of holes in the \( \text{CuO}_2 \) planes was proposed to arise when a photohole created by photoemission decays into spin and charge degrees of freedom, leading to the apparent dispersion in the photoemission experiment following a spinon dispersion. This decay of the quasiparticles is suppressed below the Néel temperature due to confinement [21, 22]. This type of spin-charge separation is predicted theoretically [23] in the context of the RVB state, which exhibits topological long-range order with soliton-like topological excitations.

Overall, there are many important questions regarding the cuprates still under debate, however it is widely regarded that the superconductivity is due to electrons in the \( \text{CuO}_2 \)-planes, with a superconducting gap that has \( d_{x^2-y^2} \)-symmetry [24]. Detailed LDA calculations have yielded valuable predictions for the detailed form of the electronic band structure in particular for the bilayer high-T\( _C \) cuprate \( \text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \) [25], which can be compared with theories of photoemission [26], and calculations of photoemission spectra for solids [27], and has led to detailed calculations of photoemission intensities in the cuprate high-T\( _C \)‘s [28].

One aspect of these calculations is their prediction of an additional Bi-O electron pocket near the antinode at \((\pi,0)\), which has never been seen experimentally, though it has been shown in LDA
Fig. 1.3: Basic cuprate electronic structure shown in (a) composed of the Cu3d_{x^2-y^2} and O2p_{x/y} orbitals. The resultant conduction band is sketched in (b) along the high symmetry directions of the Brillouin zone as shown with the band-structure predicted Fermi surface in (c).

calculations that hole-doping by excess oxygen lifts the Bi-O bands above the Fermi level [29]. Thus the starting point for understanding the electronic structure of the conduction band is its essentially two-dimensional character from Cu3d_{x^2-y^2} and O2p_{x} / O2p_{y} orbitals, as shown in Fig. 1.3(a), with a dispersion shown schematically in (b) (similar to [29]), and Fermi surface constant-energy contour shown in (c).

1.3 Analysis Techniques in ARPES - EDC’s and MDC’s

A representative ARPES image is shown in Fig. 1.4(a). This is an angle-resolved photoelectron emission image plot, which has been interpolated by the procedure outlined in Ref. [10] to render the intensity as a linear function of energy and momentum. The color scale in Fig. 1.4 is a linear gradient in R,G,B color space from blue to red, with an additional peak of white in the middle, which helps to clarify the details of the spectra by enhancing the visibility of the lower-half intensity (blue to white) and the upper-half intensity (from white to red). The usefulness of splitting the color scale this way is a result of the variation of the spectral intensity across orders of magnitude in the photoemission experiment. This can be a consequence matrix element effects or the spectral distribution, which is discussed in more detail in Chaps. 3 and 4.

The ARPES cut in Fig. 1.4(a) is for the high-T_C superconductor Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$ (Bi2201). This spectra was taken using the UBC ARPES system, with a photon energy of 21.22 eV from the He I emission line, produced in the laboratory from resonant excitation of neutral Helium atoms. The sample was aligned with the orientation shown in the inset. This is the “nodal” direction,
Fig. 1.4: ARPES nodal cut in (a) taken with 21eV photon-energy for underdoped Bi$_{2}$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$. The orientation of the cut is demonstrated in the inset by the green line in the 2$^{nd}$ Brillouin zone, and with polarization of the incident light indicated by the blue line. The highlighted curve in (b) shows the comparison of the corresponding portion of the LDA calculated conduction band.

referred to as such due to the angular nodes inherent in the d$_{x^2-y^2}$ superconducting gap, and can be compared to the LDA predicted band-structure highlighted in (b). Note that the inset also indicates the spectra in Fig. 1.4(a) is taken in the second Brillouin zone, since it is outside of the black square in the inset. The orientation of the blue marker refers to the photon polarization. For the spectra in Fig. 1.4(a), the photon polarization was set to be perpendicular to the plane of incidence, corresponding to s-polarization.

Taking a one-dimensional cut through the intensity spectra is often a useful way to analyze the data. The most common procedure involves taking a cut through the intensity at either fixed momentum or fixed energy. The first situation is referred to as an energy-direction curve (EDC). In the case where there are no strong matrix element effects, and the photoemission background is not strongly k-dependent, the EDC can be assumed to be given by the spectral function,

$$I_{EDC}(\omega) = A(k_0, \omega) \rightarrow \frac{1}{\pi} \frac{Z \Gamma(\omega)}{(\omega - \epsilon_{k_0})^2 + \Gamma(\omega)^2} + A_{inc}(k_0, \omega)$$

where we have assumed the intensity, $I_{EDC}$ is given by the spectral function in equation (2.8.18) evaluated at the fixed momentum $k_0$. The other common way to cut through the ARPES intensity
is to take a cut at fixed energy, which is referred to as a momentum-direction curve MDC. This corresponds to,

\[ I_{MDC}(k) = A(k, \omega_0) \rightarrow -\frac{1}{\pi} \frac{Z \Gamma(k)}{(\omega_0 - \epsilon_k)^2 + \Gamma(k)^2} + A_{inc}(k, \omega_0) \]  

(1.3.2)

where we have evaluated the spectral function at the fixed energy \( \omega_0 \).

Fig. 1.5(b) shows the EDC’s of the image plot in Fig. 1.4(a). The energy cuts shown are normalized to scale their intensity range to the interval from 0 to constant, and taken in equal intervals of the fixed momentum \( k_0 \), resulting in many curves of intensity versus energy. The curves have been equally spaced with a constant intensity offset interval so that they can be better seen, resulting in curves corresponding to lower (higher) values of the momentum in Fig. 1.4(a) towards the bottom (top) of Fig. 1.5(b). The evolution of the EDC lineshape near the \( k_F \) position, where the main band crosses the Fermi level, can be more clearly seen in the inset of Fig. 1.5(b), which displays the EDC’s corresponding to the region inside the marked rectangle. The near-\( k_F \) EDC’s are shown with no offset between the curves to better compare the evolution of the lineshape as a function of the fixed momentum \( k_0 \), which is possible because of the monotonic increase in spectral weight in the low binding-energy region as \( k \rightarrow k_F \) from below on the momentum axis.

In addition Fig. 1.5(a) shows the MDC, constant energy cuts. The curves have been normalized similarly to the MDC’s, and taken in equal intervals of the fixed energy \( \omega_0 \), with curves taken at lower (higher) binding energy at the top (bottom). The curves have been offset in multiples of a constant intensity offset to increase the visibility of the spectral features. In comparison to the EDC curves in Fig. 1.5(b), the MDC curves are seen to be without the complication of a Fermi-function cutoff, provided \( \omega \geq \sim (E_F + 2k_B T) \). The MDC has a well-defined peak as a function of momentum, which is much sharper than the broad EDC features, thus it is much easier to quantify the MDC peak position and peak width by applying a curve fitting routine. The MDC and EDC fitting-procedures will be demonstrated in detail in Chap. 6.

1.4 Scope of the Dissertation

The cuprate high-\( T_C \) superconductors are not metallic at half-filling, contrary to the predictions of band-theory, and instead are antiferromagnetic insulators at this filling, which is caused by many-body correlations that produce strong on-site repulsion between the electrons. However, the insulating phase disappears and a superconducting transition temperature appears upon partial chemical substitutions for sub-valent atoms, a process which is referred to as “hole-doping” and quantified by the parameter \( p \) given by the ratio of missing electrons to Cu atoms [30]. The appearance of an high-\( T_C \) superconductor arising from an insulating state after hole-doping conveys the extent of the rich physics of the electronic phase in the cuprates. The study of these materials has led to a distinction drawn between the underdoped phase, where increased hole-doping increases \( T_C \), and the overdoped phase, for which increased hole-doping decreases \( T_C \).

One key issue in the understanding of these materials involves the phenomena of the Fermi
Fig. 1.5: MDCs and EDCs in (a) and (b), respectively, for the spectra in Fig. 1.4(a). The curves have been spaced with constant offset for visibility. See text for discussion of the lineshapes.
surface. In the overdoped phase, general agreement is observed between the results of transport measurements and ARPES. The experimental results of both techniques are explained by a large, hole-like Fermi surface. However puzzling discrepancy exists for the underdoped cuprates, where transport measurements require Fermi surface reconstruction into small closed contours referred to as “Fermi pockets” (for more details on this discussion see Sec. 3.2). This is opposed to the phenomenology observed with ARPES in the underdoped cuprates, where a persistent d-wave “pseudogap” exists above $T_C$ and continuously evolves into the superconducting gap, leading to open segments of the Fermi surface, referred to as “arcs”. The discrepancy between the phenomena of “arcs” and “pockets” reveals a serious problem in the understanding of the cuprate Fermi surface, however subsequent claims of the coexistence of these two phenomena in underdoped Bi2201 raised new questions regarding the physical understanding of the cuprate high-$T_C$ superconductors, and inspired the undertaking of experimental work presented in this dissertation.

In order to gain a better understanding of the physics of the cuprates, this work utilizes the direct measurement of the photoelectron spectrum of the representative high-$T_C$ material Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$. Chap. 1 introduces the basic electronic structure of the cuprates, and the experimental methodology behind angle-resolved photoemission. Chap. 2 demonstrates the principles of photoemission with a theoretical background expanded from the literature, which is applicable to angle-resolved photoemission in Bi2201. In Chap. 3, the angle-resolved photoemission technique is applied in conjunction with low-energy electron diffraction to gain a better understanding of the Fermi surface topology in Bi2201, in order to reconcile reports of Fermi “arcs” and “pockets” coexisting in the underdoped Fermi surface, and fully establish a structural explanation for these features. Chap. 4 further demonstrates that the complex intensity variations observed by photoemission from Bi2201 are connected to “matrix-element effects” determined by the structural periodicities of multiple superstructures in a fully-incommensurate crystal. Chap. 5 demonstrates evidence for an incipient charge-density-wave instability in this material through a pronounced temperature-dependence of the lattice structure, and uncovers a remarkable surface/bulk dichotomy leading to a surface-enhanced charge-density wave. Chap. 6 additionally attributes the “peak-dip-hump lineshape” as a signature of charge-order, and provides connection to a new interpretation of the effects of electron-phonon coupling in Bi2201.
Theoretical Background for Photoemission Applied to High-Temperature Superconductors

2.1 Conductivity and Superconductivity

Early progress in condensed matter physics succeeded in an understanding of the basic resistive properties of conductors, which are materials that contain a Fermi surface defined by a constant energy contour representing the boundary of occupied and unoccupied states. Basic electrical conductivity can be expressed via the Drude formula,

\[ \sigma_0 = \frac{n_e e^2 \tau}{m_e} \]

Here, \( \sigma_0 \) is the DC conductivity and \( \sigma \) the AC conductivity, \( n_e \) is the number of conducting electrons, \( e \) is the electron charge, \( \tau \) the inverse mean electron scattering rate, and \( m_e \) the electron mass. However, deviation from this behavior was observed at low-temperatures for simple metals, leading to the discovery of the superconducting state by Heike Kamerlingh Onnes [31]. This is a state of matter characterized by zero electrical resistance below a critical temperature, denoted \( T_C \), which is characteristic of the material.

The subsequent realization of the important and novel electromagnetic properties of the state of matter produced [32] has driven research into superconductivity to advance significantly. Early on, metals such as Pb and Nb were observed to possess superconductivity at very low temperatures below 10K [30]. While such conventional superconductivity has been widely accepted as being fully explained by BCS theory [33], with the subsequent discovery of high-temperature superconductivity by Bednorz and Müller [34], the CuO\(_2\) superconductors have garnered much interest and currently hold the record for highest transition temperature.
A better understanding for the basic principles of photoemission experiments applied to the high-$T_C$ superconductors will be obtained by the detailed overview of the theoretical literature in the following sections of this chapter, beginning with an Fermi gas, and including the first principles of the electromagnetic interaction between incident light and the electrons, which is fully extended to a description of the single-particle spectroscopy technique as a way to observe the full many-body effects in the material.

2.2 The Electron Gas

Electron-hole excitations in a free electron gas can be understood to arise from the semiclassical free-fermion Hamiltonian, written as follows,

$$H = \sum_{k\sigma} \left( \frac{\hbar^2 k^2}{2m_e} - \mu \right) \hat{N}_{k\sigma}$$  \hspace{1cm} (2.2.1)

Where, for chemical potential $\mu$, reduced Planck constant $\hbar$, and electron momentum $k$, the state occupation number operator $\hat{N}_{k\sigma}$ is expressed in second-quantized notation as a normal-ordered product of the electron creation and annihilation operators,

$$\hat{N}_{k\sigma} \equiv c_{k\sigma}^\dagger c_{k\sigma}$$  \hspace{1cm} (2.2.2)

such that for the N electron gas,

$$\hat{N}_{k\sigma} |\Psi\rangle = c_{k\sigma}^\dagger c_{k\sigma} |n_{k_1\sigma_1}, n_{k_2\sigma_2}, ..., n_{k_N\sigma_N}\rangle = n_{k\sigma} |\Psi\rangle$$  \hspace{1cm} (2.2.3)

We can see from this Hamiltonian that the total energy of the system in state $|\Psi\rangle$ is,

$$\mathcal{E} = \sum_{k\sigma} \left( \frac{\hbar^2 k^2}{2m} - \mu \right) \langle \Psi | \hat{N}_{k\sigma} |\Psi\rangle$$  \hspace{1cm} (2.2.4)

In the ground state of the system at zero temperature, electrons will, by the Pauli exclusion principle, fill the states up from lowest energy toward higher energy without doubly occupying the same quantum state, up to a maximum energy defined from the chemical potential $\mu$ (the energy change of the system upon introduction of an additional particle). We can view an excitation from this ground state, with particle number conserved, as an electron removed from below the chemical potential to a state with energy above $\mu$. For the electron removed from state $k_1$ with energy $\epsilon_1$ into state $k_2$, the change in energy is $\epsilon_2 - \epsilon_1$.

The important concept behind this is the presence of a positive energy contribution for electron occupation above the chemical potential, and a negative energy contribution for an electron vacancy below the chemical potential. This can be further clarified with the definition of a new operator which takes into account the sign of the energy change above and below the chemical potential.
With this new operator, we can write the Hamiltonian as,

$$
H \rightarrow \sum_{|k| > k_F} \left( \frac{\hbar^2 k^2}{2m} - \mu \right) d_{k\sigma}^{\dagger} d_{k\sigma} - \sum_{|k| \leq k_F} \left( \frac{\hbar^2 k^2}{2m} - \mu \right) d_{k\sigma}^{\dagger} d_{k\sigma} 
$$

Thus the single-particle, noninteracting states of the Fermi gas are composed of electronic excitations above the Fermi level with positive energy, and what is understood to be “hole-like” excitations below with the negative energy spectrum. This is a direct affect of the chemical potential, which leads to the absence of an electron below $\mu$, or a “hole”, to be equivalent to the presence of an excitation with negative dispersion. The distribution of particles in these states is determined by the occupation probability of the Fermi-Dirac distribution, and the coexistence of particle and hole states is a concept of fundamental importance in the understanding of the electronic physics of the solid state material, and is directly relevant to the process of photoemission.

### 2.3 The First Principles Electromagnetic Interaction

To understand the interaction of the electrons in a solid with an externally applied incident electromagnetic field, we can begin from classical electrodynamics. From the Lagrangian mechanics for this system, we have

$$
\mathcal{L} = \mathcal{T} - \mathcal{U} 
$$

for which,

$$
F_j = \frac{d}{dt} \left( \frac{\partial \mathcal{T}}{\partial \dot{q}_j} \right) - \frac{\partial \mathcal{T}}{\partial q_j} 
$$

transforms the usual force equation for force $F_j$. Since the generalized forces must go to zero to satisfy the Lagrangian equations of motion, we have an additional equation,

$$
F_j = -\frac{d}{dt} \left( \frac{\partial \mathcal{U}}{\partial \dot{q}_j} \right) + \frac{\partial \mathcal{U}}{\partial q_j} 
$$

so that,

$$
\frac{d}{dt} \left( \frac{\partial (\mathcal{T} - \mathcal{U})}{\partial \dot{q}_j} \right) - \frac{\partial (\mathcal{T} - \mathcal{U})}{\partial q_j} = \frac{d}{dt} \left( \frac{\partial \mathcal{L}}{\partial \dot{q}_j} \right) - \frac{\partial \mathcal{L}}{\partial q_j} = 0 
$$

In the case of the electromagnetic force, the expression for which is,

$$
\vec{F} = e[\vec{E} + \frac{1}{c}(\vec{v} \times \vec{B})] 
$$
we can write this in terms of the vector potentials as,

\[ \vec{F} = e[-\vec{\nabla}\phi - \frac{1}{c} \frac{\partial}{\partial t} \vec{A} + \frac{1}{c} (\vec{v} \times \vec{\nabla} \times \vec{A})] \] (2.3.6)

Expanding the vector products results in,

\[ (\vec{v} \times \vec{\nabla} \times \vec{A})_i = \epsilon_{ijk} v_j (\vec{\nabla} \times \vec{A})_k \]

\[ = \epsilon_{ijk} \epsilon_{klm} v_j \partial_l A_m \]

\[ = (\delta_{il} \delta_{jm} - \delta_{im} \delta_{lj}) v_j \partial_l A_m \]

\[ = v_j \partial_l A_j - v_j \partial_j A_i \] (2.3.7)

Hence we have that,

\[ \vec{v} \times \vec{\nabla} \times \vec{A} = \vec{\nabla}(\vec{v} \cdot \vec{A}) - (\vec{v} \cdot \vec{\nabla})\vec{A} \] (2.3.8)

The total time derivative of the vector potential \( \vec{A} \) follows from the explicit dependence on time and spatial coordinates as,

\[ \frac{d\vec{A}}{dt} = \frac{\partial \vec{A}}{\partial t} + \vec{v} \cdot (\vec{\nabla} \vec{A}) \] (2.3.9)

so that we can rewrite the generalized force as,

\[ \vec{F} = e[-\vec{\nabla}\phi - \frac{1}{c} \frac{\partial}{\partial t} \vec{A} + \frac{1}{c} (\vec{v} \times \vec{\nabla} \times \vec{A})] \]

\[ = e[-\vec{\nabla}\phi - \frac{1}{c} \frac{\partial}{\partial t} \vec{A} + \frac{1}{c} \vec{\nabla}(\vec{v} \cdot \vec{A}) - (\vec{v} \cdot \vec{\nabla})\vec{A}] \]

\[ = e[-\vec{\nabla}(\phi - \frac{1}{c} (\vec{v} \cdot \vec{A})) - \frac{1}{c} \frac{d\vec{A}}{dt}] \]

\[ = e[-\vec{\nabla}(\phi - \frac{1}{c} (\vec{v} \cdot \vec{A})) + \frac{d}{dt} \frac{\partial}{\partial \vec{v}^i} (\phi - \frac{1}{c} (\vec{v} \cdot \vec{A}))] \] (2.3.10)

From the form of the equation which now matches the expression for a generalized force in the Lagrangian construction, we can read off the potential to be,

\[ U = -e\phi + \frac{e}{c} (\vec{v} \cdot \vec{A}) \] (2.3.11)

If we now transfer this result to the Hamiltonian formalism we obtain for the conjugate momentum,

\[ \vec{p} = \frac{\partial \mathcal{L}}{\partial \dot{\vec{x}}} = \frac{\partial \mathcal{L}}{\partial \dot{\vec{v}}} = \frac{\partial}{\partial \dot{\vec{v}}} (\mathcal{T} - \mathcal{U}) \]

\[ = \frac{\partial}{\partial \dot{\vec{v}}^i} (\frac{1}{2} m_e (\vec{v} \cdot \vec{v}) + e\phi - \frac{e}{c} (\vec{A} \cdot \vec{v})) \]

\[ = (m_e \vec{v} - \frac{e}{c} \vec{A}) \] (2.3.12)

13
The Hamiltonian is obtained via,
\[
H = \dot{\vec{x}} \cdot \vec{p} - \mathcal{L}
\]
\[
= (\vec{v} \cdot \vec{p}) - \left( \frac{1}{2} m_e (\vec{v} \cdot \vec{v}) + e \phi - \frac{e}{c} (\vec{A} \cdot \vec{v}) \right)
\]
\[
= (\vec{v} \cdot (m_e \vec{v} - \frac{e}{c} \vec{A})) - \left( \frac{1}{2} m_e (\vec{v} \cdot \vec{v}) + e \phi - \frac{e}{c} (\vec{A} \cdot \vec{v}) \right)
\]
\[
= \frac{1}{2} m_e (\vec{v} \cdot \vec{v}) - e \phi
\]

The quantum mechanical correspondence to this so far classical Hamiltonian can be simply obtained by expressing the coordinates in terms of the conjugate momenta as follows,
\[
H = \frac{(\vec{p} + \frac{e}{c} \vec{A})^2}{2 m_e} - e \phi
\]

### 2.4 Simplifications of the Electromagnetic Interaction

In treating the electromagnetic interaction with the charged electron, we can also simply note that the spin of the electron will experience a torque in an external magnetic field. This will add a term to the Hamiltonian we consider,
\[
H \rightarrow \frac{(\vec{p} + \frac{e}{c} \vec{A})^2}{2 m_e} - e \phi - \frac{e}{m_e c^2} \vec{S} \cdot \vec{B}
\]
\[
= \frac{1}{2 m_e} \left( p^2 + \frac{e}{c} (\vec{p} \cdot \vec{A} + \vec{A} \cdot \vec{p}) + \frac{e^2}{c^2} A^2 \right) - e \phi - \frac{e}{m_e c^2} \vec{S} \cdot \vec{B}
\]

Care must be taken in the order of the terms involving the dot product of the momentum operator and the vector potential, as in general \( \vec{p} \) does not commute with a function of \( \vec{r} \). We obtain simplification of this expression by taking a specific choice of geometry such that the electromagnetic wave described by \( \vec{A} \) is an incident plane wave with the following properties,
\[
\omega = ck
\]
\[
\vec{k} = k \hat{y}
\]
\[
\vec{E} = E \hat{z}
\]
\[
\vec{B} = B \hat{x}
\]

This configuration is illustrated in Fig. 2.1. We can make a convenient choice for the electromagnetic gauge such that the external contribution to the scalar field \( \phi \) is zero, and so the external electromagnetic perturbation can be fully described by the vector potential. The vector potential can be treated classically, in that the classical amplitudes of the complex vector \( \vec{A} \) are sufficient because we are not concerned with quantization of the electric and magnetic fields and we do not require a field with a definite number of photons. Therefore \( A_0 \) is a complex constant with argument depending on the choice of time origin.
Fig. 2.1: Orientation of the electromagnetic field with respect to the propagation wavevector for incident radiation on the sample surface.

\[
\vec{A} = A_0 \hat{z} e^{i(ky - \omega t)} + A_0^* \hat{z} e^{-i(ky - \omega t)}
\]
\[
\vec{E} = -\frac{\partial}{\partial t} \vec{A} = i\omega A_0 \hat{z} e^{i(ky - \omega t)} - i\omega A_0^* \hat{z} e^{-i(ky - \omega t)}
\]
\[
\vec{B} = \nabla \times \vec{A} = ikA_0 \hat{x} e^{i(ky - \omega t)} - ikA_0^* \hat{x} e^{-i(ky - \omega t)}
\]

(2.4.3)

We then define real field strength constants \( E \) and \( B \), and time origin such that \( A_0 \) is purely imaginary,

\[
\frac{E}{2} = i\omega A_0 \\
\frac{B}{2} = ikA_0 \\
\frac{E}{B} = \frac{\omega}{k} = c
\]

(2.4.4)

Then we write the fields as,

\[
\vec{E}(\vec{r}, t) = E \hat{z} \cos(\omega t - ky) \\
\vec{B}(\vec{r}, t) = B \hat{x} \cos(\omega t - ky)
\]

(2.4.5)

Since \( \vec{A} \) is a function only of the coordinate \( y \), yet is parallel to the \( \hat{z} \) direction, the term in our Hamiltonian \( p \cdot \vec{A} \) is just the product \( p_z A_z(y) \), and since the operator \( p_z \) commutes with \( A_z(y) \) the order is not important, so we can write,

\[
\mathcal{H} = \frac{p^2}{2m_e} - e\phi - \frac{e}{m_e c^2} \vec{p} \cdot \vec{A} - \frac{e}{m_e c^2} \vec{S} \cdot \vec{B} + \frac{e^2}{2m_e c^2} A^2
\]

(2.4.6)

In considering the relative importance of the terms in our Hamiltonian, one notes that for typical photon flux achievable in the laboratory setting, the intensity is low enough that terms of second order in the electric fields will be small, so we can neglect terms of order \( A^2 \) and higher. For the
term involving $\vec{S} \cdot \vec{B}$, we can estimate that the spin will be of order $\hbar$, so that,

$$\frac{\vec{S} \cdot \vec{B}}{\vec{p} \cdot \vec{A}} \sim \frac{\hbar k \mathcal{A}_0}{p \mathcal{A}_0} = \frac{\hbar k}{p}$$  \hspace{1cm} (2.4.7)

The de Broglie wavelength for the electron in an atom is on the order of a Bohr radius, $(a_0)=0.53\text{Å}$, while the incident electromagnetic plane wave has $k = 2\pi/\lambda_{\text{photon}}$ corresponding to the photon wavelength,

$$\lambda_{\text{photon}} = \frac{hc}{E} = \frac{1240 \text{eV} \cdot \text{nm}}{E}$$  \hspace{1cm} (2.4.8)

leading to the expression,

$$\frac{\vec{S} \cdot \vec{B}}{\vec{p} \cdot \vec{A}} \sim \frac{a_0}{\lambda_{\text{photon}}} = E \times (4.3 \times 10^{-5} \text{eV}^{-1}) << 1$$  \hspace{1cm} (2.4.9)

Given that the $\vec{S} \cdot \vec{B}$ term will be orders of magnitude smaller than the $\vec{p} \cdot \vec{A}$ term in the Hamiltonian, for photon energies smaller than several keV, we can drop the magnetic term in our discussion. Finally we separate the Hamiltonian into two terms, the first of which is $\mathcal{H}_0$, that accounts for the fully interacting ground state of the material, and in addition a small perturbation $\mathcal{H}_I$ from the electromagnetic field, to obtain,

$$\mathcal{H}_I = -\frac{e}{m_e c} \vec{p} \cdot \vec{A}$$  \hspace{1cm} (2.4.10)

The exponentials can be expanded as,

$$e^{iky} \simeq 1 + iky + \cdots$$  \hspace{1cm} (2.4.11)

again, however, the very long wavelength of the photon with respect the the electron wavelength means that the exponential is approximately constant over the microscopic dimensions of interest for electrons in solids, and we can take the first term only. We then obtain,

$$\mathcal{H}_I = -\frac{e}{m_e c} p_z (\mathcal{A}_0 e^{i(ky - \omega t)} + \mathcal{A}_0^* e^{-i(ky - \omega t)})$$  \hspace{1cm} (2.4.12)

In order to generalize this result to the case of polarization along an arbitrary direction, we can simply take the dot product of the momentum operator with a unit polarization vector,

$$\mathcal{H}_I = \mathcal{A}_0(t) \hat{\epsilon} \cdot \vec{p}$$  \hspace{1cm} (2.4.13)

Using this result, the matrix element of the interaction Hamiltonian becomes,
\[ \langle \phi_{f,k} | H_{\text{int}} | \phi_{i,k} \rangle = A_0(t) \hat{\epsilon} \cdot \langle \phi_{f,k} | \vec{p} \rangle | \phi_{i,k} \rangle \]  

(2.4.14)

If we make use of the full many-body Hamiltonian for the electronic system, which is composed of the kinetic energy and a potential that is solely a function of the particle coordinates, and consider a commutator with the position operator to obtain,

\[ [H_e, \vec{r}] = [\frac{\vec{p}^2}{2m_e}, \vec{r}] + [V(\vec{r}_1...\vec{r}_N), \vec{r}] = -\frac{ih}{m_e} \vec{p} + 0 \]  

(2.4.15)

We can replace the momentum operator in (2.4.14) with the result (2.4.15) to rewrite the matrix element of the interaction Hamiltonian as,

\[ A_0(t) \hat{\epsilon} \cdot \langle \phi_{f,k} | \frac{im_e}{\hbar} [H_e, \vec{r}] | \phi_{i,k} \rangle = \frac{im_e}{\hbar} A_0(t) \left( E_k^f - E_k^i \right) \hat{\epsilon} \cdot \langle \phi_{f,k} | \vec{r} \rangle | \phi_{i,k} \rangle \]  

(2.4.16)

Evidently the matrix element of the interaction Hamiltonian is proportional to the one-electron dipole matrix element.

2.5 Green’s Functions

2.5.1 Single-Particle Green’s Function

Beginning with the Schrödinger equation,

\[ i\hbar \frac{\partial}{\partial t} | \psi(t) \rangle = \mathcal{H} | \psi(t) \rangle \]  

(2.5.1)

and the existence of a basis of energy eigenstates to expand the wavefunction,

\[ \mathcal{H} | E \rangle = E | E \rangle \]
\[ | \psi(t) \rangle = \sum_E \langle E | \psi(t) \rangle | E \rangle \equiv \sum_E a_E(t) | E \rangle \]  

(2.5.2)

The energy eigenstates are assumed to be stationary in time for a Hamiltonian without explicit time dependence, other than the small time-dependent perturbation of the classical electromagnetic field to be considered. The Schrödinger equation can be rewritten and solved as,

\[ i\hbar \dot{a}_E = E a_E \Rightarrow a_E(t) = a_E(0)e^{-\frac{ith}{\hbar}} \]  

(2.5.3)

We can then write the wavefunction at any time in terms of the wavefunction at a chosen time origin,
\[
|\psi(t)\rangle = \sum_E \langle E | \psi(0) \rangle e^{-iEt/\hbar} |E\rangle \quad (2.5.4)
\]

or
\[
|\psi(t)\rangle = U(t) |\psi(0)\rangle \quad (2.5.5)
\]

Where we have defined the time-evolution operator in the energy-eigenstate basis as,
\[
U(t) \equiv \sum_E |E\rangle \langle E | e^{-iEt/\hbar} \quad (2.5.6)
\]

We can similarly construct the time-evolution operator in the spatial representation, where using the previous result and inserting a resolution of identity we obtain,
\[
\Psi(x, t) = \langle x | U(t) | \psi(0) \rangle = \int dx' \langle x | U(t) | x' \rangle \langle x' | \psi(0) \rangle \quad (2.5.7)
\]

If we now define the operator as,
\[
U(x, t; x', t') \equiv \theta(t - t') \langle x | U(t - t') | x' \rangle \quad (2.5.8)
\]

then,
\[
\Psi(x, t) = \int_{-\infty}^{\infty} dx' U(x, t; x', t') \Psi(x', t') \quad (2.5.9)
\]

If there is some observable quantity \(\alpha\), which is simultaneously diagonalizable with the energy, we can insert an additional identity to obtain,
\[
\Psi(x, t) = \sum_{\alpha} \int dx' \langle x | \alpha \rangle \langle \alpha | x' \rangle \Psi(x', 0) e^{-i\epsilon_{\alpha}t/\hbar} \quad (2.5.10)
\]

Finally, by taking the Fourier transform and inserting a small imaginary time argument for convergence, we obtain the space-energy propagator,
\[
U(x, x'; E) = \sum_{\alpha} \Psi_{\alpha}(x) \Psi^*_{\alpha}(x') e^{-i\epsilon_{\alpha}t/\hbar} \quad (2.5.11)
\]

This is the result for the propagator in a fully continuous spatial basis, however an analogous result can be demonstrated for a discrete propagator of the form,
\[
G(\omega) = (\omega \mathbb{1} - \mathcal{H})^{-1} \quad (2.5.12)
\]

Here, the Hamiltonian \(\mathcal{H}\) is a matrix of size \(n \times n\), where \(n\) is the dimension of the Hilbert space. A binomial expansion yields,
\[(\omega \mathbb{1} - \mathcal{H})^{-1} = \omega^{-1}(1 - \frac{\mathcal{H}}{\omega})^{-1} = \omega^{-1} \left[ 1 + \frac{\mathcal{H}}{\omega} + \frac{\mathcal{H}^2}{\omega^2} + \cdots \right] \quad (2.5.13)\]

Therefore, in the discrete basis \(|i\rangle\),

\[G_{ij}(\omega) = \omega^{-1} \left[ 1 + \frac{\mathcal{H}_{ij}}{\omega} + \frac{\mathcal{H}_{ik}\mathcal{H}_{kj}}{\omega^2} + \cdots \right] \quad (2.5.14)\]

Introducing the unitary operator \(\mathcal{U}\), which diagonalizes the Hamiltonian,

\[E_{kl} = \delta_{kl} \tilde{E}_k \]
\[\mathcal{H}_{ij} = \mathcal{U}_{ik} \mathcal{E}_{kl} \mathcal{U}_{lj}^\dagger = \mathcal{U}_{ik} \mathcal{U}_{kj}^* \tilde{E}_k = \mathcal{U}_{ik} \mathcal{U}_{kj}^* \tilde{E}_k \quad (2.5.15)\]

The product of the Hamiltonians collapses the product of the unitary matrices, so we obtain a similar result,

\[\mathcal{H}_{ik}\mathcal{H}_{kj} = \mathcal{U}_{il}\mathcal{E}_{kl} \mathcal{U}_{km}\mathcal{U}_{jm}^* \tilde{E}_m = \mathcal{U}_{il}\mathcal{U}_{jl}^* (\tilde{E}_l)^2 \quad (2.5.16)\]

This results in the propagator,

\[G_{ij}(\omega) = \omega^{-1} \left[ 1 + \frac{\mathcal{U}_{ik} \mathcal{U}_{jk}^* \tilde{E}_k}{\omega} + \cdots \right] = \sum_{k=1}^{n} \frac{\mathcal{U}_{ik} \mathcal{U}_{jk}^*}{\omega - \tilde{E}_k} \quad (2.5.17)\]

This can be converted to Dirac notation via,

\[\mathcal{U}_{i\alpha} = \langle i|\alpha \rangle \quad (2.5.18)\]

Finally we obtain for the matrix formulation of a discrete basis for an expression which is similar to the previous result (2.5.11) for the continuous basis propagator,
\[ G(\omega) = (\omega \mathbb{1} - \mathcal{H})^{-1} \]
\[ G_{ij}(\omega) = \sum_{k=1}^{n} \frac{\langle i|k \rangle \langle k|j \rangle}{\omega - E_{k}} \]  
\[ (2.5.19) \]

### 2.5.2 Many-Particle Green’s Function

For the case of many particles, the energy of the system of electrons arises from the kinetic and potential energies in the Hamiltonian, as well as the energy to add or remove an electron, which is defined as the chemical potential. We can therefore write the total energy operator and define total energy eigenstates as,

\[ K = \mathcal{H} - \mu N \]
\[ K|n\rangle = E_{n}|n\rangle \]  
\[ (2.5.20) \]

The time-evolution operator derived in the previous subsection can be generalized to the many-body case as a type of Green’s function. For a system of noninteracting electrons, we can expect that the total energy eigenstates propagate with exponential time-dependence and we can simply write down for both time and energy representation,

\[ G_{\text{ret}}^{(0)}(\alpha, t-t') = -i \theta(t-t')e^{-i\xi_{\alpha}(t-t')} \]
\[ G_{\text{ret}}^{(0)}(\alpha, \omega) = \frac{1}{\omega - \xi_{\alpha} + i\delta} \]
\[ \text{where the overall factor of } -i \text{ is for convenience and the designation as “retarded” meaning that it applies for all causally linked times where the step function is non-zero. Note that for simplicity we set } \hbar \rightarrow 1 \text{ for the remainder of this section. We will now define the Green’s function for the many-body system that includes interactions, and demonstrate that it produces the correct result in the non-interacting limit.} \]

\[ G_{\text{ret}}(\alpha, t-t') = -i \theta(t-t')e^{\beta \Omega} \sum_{n} \langle n|e^{-\beta K} \{ c_{\alpha}(t), c_{\alpha}^{\dagger}(t') \}|n\rangle \]
\[ (2.5.22) \]

For fermions the brackets \( \{ \hat{A}, \hat{B} \} \) denotes an anticommutator. \( \Omega \) is the Helmholtz free energy, so that the partition function is given by,

\[ Z = e^{-\beta \Omega} = Tr(e^{-\beta(H-\mu N)}) \]  
\[ (2.5.23) \]

The diagonal matrix element can be converted to an matrix including off-diagonal terms of a simpler operator by inserting the resolution of identity.
\begin{equation}
\langle n | e^{-\beta K} \{ c_\alpha(t), c_\alpha^\dagger(t') \} | n \rangle = e^{-\beta E_n} \langle n | \left( c_\alpha(t) c_\alpha^\dagger(t') + c_\alpha^\dagger(t') c_\alpha(t) \right) | n \rangle = e^{-\beta E_n} \sum_m \left[ \langle n | c_\alpha(t) | m \rangle \langle m | c_\alpha^\dagger(t') | n \rangle + \langle n | c_\alpha^\dagger(t') | m \rangle \langle m | c_\alpha(t) | n \rangle \right] \tag{2.5.24}
\end{equation}

In the Heisenberg representation we can expand the time dependent operators as,
\begin{equation}
\langle n | c_\alpha(t) | m \rangle = \langle n | e^{i K t} c_\alpha e^{-i K t} | m \rangle = e^{i (E_n - E_m) t} \langle n | c_\alpha | m \rangle \tag{2.5.25}
\end{equation}

and
\begin{equation}
\langle m | c_\alpha^\dagger(t') | n \rangle = \langle m | e^{-i K t} c_\alpha^\dagger e^{i K t} | n \rangle = e^{i (E_n - E_m) t} \langle m | c_\alpha^\dagger | n \rangle = e^{i (E_n - E_m) t} \langle n | c_\alpha | m \rangle^* \tag{2.5.26}
\end{equation}

We can therefore rewrite the Green’s function as,
\begin{equation}
G_{ret}(\alpha, t - t') = -i \theta(t - t') e^{\beta \Omega} \sum_{n,m} e^{-\beta E_n} \left( e^{i (E_n - E_m) t} \langle n | c_\alpha | m \rangle^2 + e^{-i (E_n - E_m) t} \langle m | c_\alpha^\dagger | n \rangle^2 \right) \tag{2.5.27}
\end{equation}

and interchanging the dummy label of the indices of the second term results in,
\begin{equation}
G_{ret}(\alpha, t - t') \rightarrow -i \theta(t - t') e^{\beta \Omega} \sum_{n,m} e^{i (E_n - E_m) t} \langle n | c_\alpha | m \rangle^2 \left( e^{-\beta E_n} + e^{-\beta E_m} \right) \tag{2.5.28}
\end{equation}

To obtain the frequency dependent version of this Green’s function, we take the Fourier transform,
\begin{equation}
G_{ret}(\alpha, \omega) = -ie^{\beta \Omega} \int_0^\infty dt e^{i(\omega + i\delta)t} \sum_{n,m} |\langle n | c_\alpha | m \rangle|^2 e^{i(E_n - E_m) t} \left( e^{-\beta E_n} + e^{-\beta E_m} \right) \tag{2.5.29}
\end{equation}

where the last term is the Cauchy principle part of the otherwise infinite integral. Therefore we obtain an additional delta-function term in the many-body Green’s function,
\begin{equation}
\lim_{\epsilon \to 0^+} \int_a^b \frac{f(x)}{x \pm i \epsilon} dx = \mp i \pi f(0) + P \left[ \int_a^b \frac{f(x)}{x} \right] \tag{2.5.30}
\end{equation}

Where the last term is the Cauchy principle part of the otherwise infinite integral. Therefore we obtain an additional delta-function term in the many-body Green’s function.
\[
G_{\text{ret}}(\alpha, \omega) = e^{\beta \Omega} \sum_{n,m} |\langle n|c_{\alpha}|m\rangle|^2 \left( e^{-\beta E_n} + e^{-\beta E_m} \right) \left( -i\pi \delta(\omega + E_n - E_m) + P \frac{1}{\omega + E_n - E_m + i\delta} \right)
\]

Now, introducing the spectral function, defined as
\[
A_{\alpha}(\omega) = -\frac{1}{\pi} \text{Im} \left[ G_{\text{ret}}(\alpha, \omega) \right],
\]
we have the many-body spectral function equal to,
\[
A_{\alpha}(\omega) = e^{\beta \Omega} \sum_{n,m} |\langle n|c_{\alpha}|m\rangle|^2 \left( e^{-\beta E_n} + e^{-\beta E_m} \right) \delta(\omega + E_n - E_m)
\]
which is understood to be valid only under \( \omega \) integration, as implied by the Dirac delta-function.

One notable property of this function is its finite convergence when integrated over all frequencies,
\[
\int_{-\infty}^{\infty} d\omega A_{\alpha}(\omega) = e^{\beta \Omega} \sum_{n,m} |\langle n|c_{\alpha}|m\rangle|^2 \left( e^{-\beta E_n} + e^{-\beta E_m} \right)
\]
\[
= e^{\beta \Omega} \sum_{n,m} e^{-\beta E_n} \left( \langle n|c_{\alpha}|m\rangle\langle m|c_{\alpha}^{\dagger}|n\rangle + \langle n|c_{\alpha}^{\dagger}|m\rangle\langle m|c_{\alpha}|n\rangle \right)
\]
\[
= e^{\beta \Omega} \sum_{n} e^{-\beta E_n} \langle n| \left( c_{\alpha}^{\dagger}c_{\alpha}^{\dagger} + c_{\alpha}^{\dagger}c_{\alpha} \right)|n\rangle
\]
\[
= e^{\beta \Omega} \sum_{n} e^{-\beta E_n} = 1
\]

2.5.3 The Non-interacting Quasi-Particle in the Many-Particle Picture

For a non-interacting free-particle, we can use,
\[
K_0 = H_0 - \mu N
\]
and,
\[
c_p(t) = e^{iK_0 t} c_p e^{-iK_0 t}
\]
We can use the Baker-Hausdorff formula to write,
\[
e^{A} C e^{-A} = C + [A, C] + \frac{1}{2!} [A, [A, C]] + \cdots
\]
Making the replacement in the above formula,
\[
A \to i \tau K_0 = i \tau \sum_p \xi_p c_p^{\dagger} c_p ; \quad \xi_p = (\epsilon_p - \mu)
\]
and by using the Fermionic anticommutation rules we obtain,

\[
[K_0, c_p] \to \sum_{p'} \xi_{p'} [c_{p'}^\dagger c_{p'}, c_p] \\
= \sum_{p'} \xi_{p'} \left( c_{p'}^\dagger c_{p'} c_p - c_p c_{p'}^\dagger c_{p'} \right) \\
= \sum_{p'} \xi_{p'} \left( c_{p'}^\dagger c_{p'} c_p - (\delta_{pp'} - c_{p'}^\dagger c_{p'} c_{p'}) \right) \\
= \sum_{p'} \xi_{p'} \left( c_{p'}^\dagger c_{p'} c_p - \delta_{pp'} c_{p'}^\dagger c_{p'} c_{p'} \right) \\
= -c_p \xi_p
\]

(2.5.38)

For the next higher order term in the series expansion we can write,

\[
[K_0, [K_0, c_p]] = -\xi_p [K_0, c_p] = \xi_p^2 c_p
\]

(2.5.39)

so that,

\[
e^{iK_0 t} c_p e^{-iK_0 t} = c_p \left( 1 - \left( it \xi_p \right) + \left( it \xi_p \right)^2 + \cdots \right) = c_p e^{-it \xi_p}
\]

(2.5.40)

Using the form of the retarded Green’s function that we had in the previous subsection, we can write for the free electron system,

\[
G_{\text{ret}}(p, t - t') \to -i \theta(t - t') e^{\beta \Omega} e^{-it(t-t')} \xi_p \sum_n e^{-\beta E_n} \langle n | c_p c_{p'}^\dagger + c_{p'}^\dagger c_p | n \rangle
= -i \theta(t - t') e^{-it(t-t')} \xi_p
\]

(2.5.41)

And in frequency representation,

\[
G_{\text{ret}}(p, \omega) = \frac{1}{\omega - \xi_p + i\delta}
\]

(2.5.42)

Under \( \omega \) integration, the spectral function for the non-interacting electron system becomes,

\[
A_0^0(\omega) = \delta(\omega - \xi_p)
\]

(2.5.43)

### 2.6 The Photoemission Intensity

A standard result of time-dependent perturbation theory is the “Fermi Golden Rule”, which describes the transition rate from a single initial state into a continuum of final states due to a frequency-dependent perturbation (in this case the electric field at frequency \( \omega \) as,

\[
\text{Rate} \propto \frac{2\pi}{\hbar} |\langle \Psi_f^N | H_{\text{int}} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - \hbar \omega)
\]

(2.6.1)
If we express the initial and final state wavefunctions as Slater determinants constructed from single-electron orbitals through the proper anti-symmetrization procedure we get,

\[ |\Psi_i^N\rangle = S|\phi_i^k\rangle|\Psi_i^{N-1}\rangle \tag{2.6.2} \]

where the operator \( S \) ensures proper antisymmetrization of the product wavefunction under interchange of coordinates for the single electron orbital \( \phi_i^k \) and the remnant \( N-1 \) wavefunctions. In the initial state \( \Psi_i^{N-1} \) is the relaxed \( N-1 \) system in the presence of the bound electron in the \( \phi_i^k \) orbital, while in the final state \( \Psi_f^{N-1} \) is the excited state of the \( N-1 \) system after photoemission of the electron into the unbound \( \phi_f^k \) orbital.

\[ \langle \Psi_f^N|\mathcal{H}_{int}|\Psi_i^N\rangle = \langle \phi_f^k|\mathcal{H}_{int}|\phi_i^k\rangle \langle \Psi_f^{N-1}|\Psi_i^{N-1}\rangle \tag{2.6.3} \]

For the overlap integral of the initial and final \((N-1)\) states, we note that the final state \( |\Psi_f^{N-1}\rangle \) is not an energy eigenstate of the \((N-1)\) system Hamiltonian, and if a particular final state is to be studied, we should expand in the basis of energy eigenstates. In the more general case that the total photoemission rate for all possible final states is to be considered, we can simply sum over all possible final states,

\[ |\Psi_f^{N-1}\rangle \rightarrow \sum_m |\Psi_m^{N-1}\rangle \tag{2.6.4} \]

In addition, the initial state of the system should be treated as a thermodynamic ensemble of both the energy and occupation quantum numbers of the \( N \) electron system,

\[ |\Psi_i^N\rangle \rightarrow \frac{1}{1 + e^{-\beta(\epsilon_k - \mu)}} e^{-\beta(\epsilon_k - \mu)} |\phi_i^k\rangle e^{\beta\Omega} \sum_n e^{-\beta E_n^N} c_k |\Psi_n^N\rangle \tag{2.6.5} \]

\[ \text{Rate} \propto \frac{2\pi}{\hbar} e^{\beta\Omega} \sum_{m,n} n_F(-E_B^k) |\langle \phi_m^k|\mathcal{H}_{int}|\phi_n^k\rangle|^2 e^{-\beta E_n^N} |\langle \Psi_m^{N-1}|c_k|\Psi_n^{N-1}\rangle|^2 \]

\[ \times \delta(E_{\text{fin}} + E_B^k + E_m^{N-1} - E_n^{N-1} - \hbar \omega) \tag{2.6.6} \]

This makes use of the replacements \( E_f^N = E_f^{N-1} + E_{\text{kin}} \), stating that the final state energy is the total of the bound \((N-1)\) system and the free photoelectron kinetic energy, \( E_{\text{kin}} \), as well as \( E_i^N = E_i^{N-1} - E_B^k \), so the initial state energy is equal to the bound \((N-1)\) system plus the binding energy of the photoelectron, \( E_B^k \). The Fermi function ensures that the photoemission process only probes the occupied states for which the binding energy, relative to the chemical potential, is defined as positive. Rewriting this, we obtain,
\[ n_F(-E_B^k) = n_F(E_{\text{kin}} - \hbar \omega + E_{m}^{N-1} - E_{i}^{N-1}) \]  \hspace{1cm} (2.6.7)

If we consider the initial state to be the highest occupied bound state, and the final state to be the lowest unoccupied vacuum state, then we can define the work function \( \phi_W \),

\[ E_{m}^{N-1} - E_{i}^{N-1} \geq \phi_W \]  \hspace{1cm} (2.6.8)

Here it is evident the photoemission rate will fall off rapidly for \( E_{\text{kin}} > \hbar \omega - \phi_W \), due to the presence of the Fermi function in equation (2.6.6). The matrix element involving \( c_k \) in equation (2.6.6) is similar in form to the spectral function (2.5.32), although the states involved in the summation are defined differently than the generic eigenstates of the many body system, and instead refer to the \( N \) and \( (N - 1) \) electron system. The presence of the single electron annihilation operator, \( c_k \), suggests that this can be related to a single-electron Green’s function [35] for these states, and therefore a single-electron spectral function.

In simplified notation, we can thus schematically write,

\[ \text{Rate} \propto |\langle \phi_k^f | H_{\text{int}} | \phi_i^j \rangle|^2 A_k(\omega)n_F(\omega) \]  \hspace{1cm} (2.6.9)

showing that the photoemission intensity is the product of the single electron matrix element, the many body spectral function, and a Fermi function cutoff at zero binding energy.

### 2.7 One- and Three-step Models of Photoemission

The three-step model of the photoemission process begins with the absorption of a photon, which is followed by a near instantaneous (\( \Delta t << t_{\text{adiabatic}} \)) emission of an electron. The following three-step photoemission process is described [36, 37, 38],

1. Optical excitation of the electron in the bulk of the material
2. Electron transport to the surface
3. Transmission of the electron through the surface into vacuum

The first step was discussed in detail in section 2.6, and contains all of the information regarding the many-body system and the relevant physics of interest. One additional component that should be included for completeness is an overall factor for the cross section of optical absorption. The second step involves non-equilibrium transport to the surface, which can be simply accounted for by a random probability of electron collisions with corresponding mean free path given by,

\[ \frac{\int_0^\infty xP(x)dx}{\int_0^\infty P(x)dx} = \frac{\int_0^\infty xe^{-\frac{x}{d}}dx}{\int_0^\infty e^{-\frac{x}{d}}dx} = d \]  \hspace{1cm} (2.7.1)

Finally, the transmission of the electron into the vacuum is modeled with a potential-barrier due to the nonzero gradient of the potential, \( \nabla V \), due to the surface.
The early theories of photoemission [26], and calculations of photoemission spectra for solids [27], have led to detailed calculations of photoemission intensities and lineshapes for CuO bands and surface states in the cuprate high-T_C’s [28]. The separate steps used for the three-step model are now understood to be better described simultaneously in one coherent step, and applied to accurately describe the photoemission intensity using complex \textit{ab initio} electronic structure calculations [35]. The variation of the near-E_F spectral weight with k_∥, photon-energy, and photon-polarization observed experimentally [39] can be understood by realistic calculations of the photoemission matrix element effects, which take into account the initial and final state wave functions and multiple scattering effects arising from a specific surface termination [40, 41].

2.8 Including Interactions in the Many-Body Spectral Function

In the previous derivations, an attempt has been made to describe many-body physics that utilizes the most general form of the relevant electronic propagator and related spectral function. Often in the process of quantitative evaluation of the properties of the Green’s function, it is more straightforward to begin with the simpler case of the free-electron, noninteracting system, and include the additional effects of the electron-electron Coulomb-interaction, the electron-phonon interaction, and quite generally any additional two-body interactions via perturbative expansion. Beginning with the noninteracting system,

\[ \mathcal{H} = \mathcal{H}_0 = \sum_k \xi_k c_k^\dagger c_k \]  

(2.8.1)

We have the free-electron propagator expressed as in equation (2.5.42),

\[ G_{\text{rel}}(p,\omega) = \frac{1}{\omega - \xi_p + i\delta} \]  

(2.8.2)

In analogy to equations (2.5.12) and (2.5.19), we can formally define the free-electron Green’s function as,

\[ G_0(E) = (E\mathbb{1} - \mathcal{H}_0)^{-1} \]  

(2.8.3)

The next step is to generalize to include the small interaction perturbation,

\[ \mathcal{H} = \mathcal{H}_0 + V \]  

(2.8.4)

We now define the propagator which included the effect of the interaction perturbation as,

\[ G(E) = (E\mathbb{1} - \mathcal{H}_0 - V)^{-1} \]  

(2.8.5)

We can then expand this to rewrite,
\[(E \mathbb{1} - H_0 - V)G(E) = \mathbb{1}\]

\[(E \mathbb{1} - H_0)G(E) = \mathbb{1} + VG(E)\]  

\[G_0^{-1}(E)G(E) = \mathbb{1} + VG(E)\]

\[\rightarrow G(E) = G_0(E) + G_0(E)VG(E)\]

(2.8.6)

One can iterate the expression (2.8.6) to obtain a solution expressed in a series expansion,

\[G = G_0 + G_0V(G_0 + G_0V(\cdots))\]

\[= G_0 + G_0VG_0 + G_0VG_0VG_0 + \cdots\]  

(2.8.7)

Solving equation (2.8.6) for the full propagator, we obtain,

\[G(E) = \frac{G_0(E)}{1 - G_0(E)V} = \frac{1}{G_0^{-1}(E) - V}\]  

(2.8.8)

This is known as the Dyson equation, and it serves as the fundamental link between the noninteracting system and the full propagator description of the interacting system. We can directly substitute the expression for the free-propagator (2.8.2) into (2.8.8). In the simplest cases we can make the assumption that \(V\), the part of the Hamiltonian which describes the microscopic two-body interactions, is small relative to the noninteracting terms in \(H_0\). In this case, a perturbative expansion involving a summation over irreducible diagrams can be used to describe the many-body interactions as the electron self-energy \(\Sigma\), although the full details of this calculation are lengthy, and can be found for instance in Ref. [42]. Following these results in the referenced literature it is demonstrated that with the assumption of small interactions, we can rewrite the propagator as,

\[G(k, \omega) = \frac{1}{\omega - \xi_k - \Sigma(k, \omega)} = \frac{1}{\omega - \xi_k - (\Sigma'(k, \omega) + i\Sigma''(k, \omega))}\]  

(2.8.9)

Here the self-energy is conveniently split up into its real part, \(\Sigma'(k, \omega)\), and its imaginary part \(\Sigma''(k, \omega)\). This can be rewritten as,

\[G(k, \omega) = \frac{1}{\omega - \xi_k - \Sigma'(k, \omega) - i\Sigma''(k, \omega)} \times \left(\frac{\omega - \xi_k - \Sigma'(k, \omega) + i\Sigma''(k, \omega)}{\omega - \xi_k - \Sigma'(k, \omega) + i\Sigma''(k, \omega)}\right)\]  

(2.8.10)

We can define the spectral function as previously in equation (2.5.32) to obtain,
\[ A(k, \omega) = -1/\pi \text{Im} [G_{\text{rel}}(k, \omega)] \]
\[ = -\frac{1}{\pi} \frac{\Sigma''(k, \omega)}{(\omega - \xi_k - \Sigma'(k, \omega))^2 + (\Sigma''(k, \omega))^2} \]  

(2.8.11)

For the study of the spectral function of high-temperature superconductors, it is useful to formulate these expressions into the description of a fully interacting metallic system described by Landau Fermi-liquid theory \[43, 44, 45, 46\]. This is achieved by adding a renormalization which accounts for the dressed interactions of the electrons in a quasiparticle description, and the principle result can be stated for the Fermi-liquid spectral function used to describe the normal state of metallic systems at low temperature. This can be done with the self-energy in equation (2.8.10), which is to be Taylor expanded to first order about the value \(\omega = \xi_k\) as,

\[ \Sigma'(k, \omega) \to \Sigma'_0 + \left( \frac{\partial \Sigma'(k, \omega)}{\partial \omega} \bigg|_{\omega=\xi_k} \right) (\omega - \xi_k) \]  

(2.8.12)

Replacement of the Taylor-expanded self energy into equation (2.8.10) results in,

\[ G(k, \omega) \to \frac{1}{(\omega - \xi_k)(1 - \frac{\partial \Sigma'(k, \omega)}{\partial \omega}) - \Sigma'(k, \xi_k) - i\Sigma''(k, \omega)} \]
\[ = \frac{Z_k}{(\omega - \epsilon_k) - i\Gamma(k, \omega)} \]  

(2.8.13)

with the following definitions,

\[ Z_k = \left( 1 - \frac{\partial \Sigma'(k, \omega)}{\partial \omega} \bigg|_{\omega=\xi_k} \right)^{-1} \]
\[ \epsilon_k = \xi_k + Z_k \Sigma'(k, \xi_k) \]
\[ \Gamma(k, \omega) = Z_k \Sigma''(k, \omega) \]  

(2.8.14)

Fermi-liquid theory is mostly concerned with the spectral function very close to the Fermi-surface. In the steps leading to equation (2.8.13), the Taylor-expansion is instead taken around \(\omega = 0\), and \(\Sigma'(k, 0) = 0\),

\[ \Sigma'(k, \omega) \approx \frac{\partial \Sigma'}{\partial \omega} \omega \]  

(2.8.15)

so that the bare-band \(\xi_k\) is renormalized according to,

\[ \epsilon_k = Z_k \xi_k \]  

(2.8.16)

The spectral function becomes,
\[ A_{FL}(k,\omega) = -\frac{1}{\pi} \frac{Z_k \Gamma(k,\omega)}{(\omega - \epsilon_k)^2 + \Gamma(k,\omega)^2} \] (2.8.17)

Due to the renormalized strength, \(Z_k\), of the pole at \(\omega = \epsilon_k\), an additional function must be added so that the spectral function sum rule derived in equation (2.5.33) is satisfied,

\[ A(k,\omega) \rightarrow -\frac{1}{\pi} \frac{Z_k \Gamma(k,\omega)}{(\omega - \epsilon_k)^2 + \Gamma(k,\omega)^2} + A_{inc} = A_{coh} + A_{inc} \] (2.8.18)

The term \(A_{inc}\) is referred to as the incoherent part of the spectral function, and is smooth and without poles, and hence unable to cancel the first term in the spectral function, the coherent part [47, 35].
Multiple Crystal Structure Modulations in Underdoped \( \text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_6+\delta \)

3.1 Structural Considerations in the Cuprate High-T\( \text{C} \)’s

There are more than 200 specific varieties of cuprate high-temperature superconductors accounting for the many modifications of the materials that are possible by substitution of elements within the same group of the periodic table, resulting in many structural varieties. Their common feature is a sandwich of insulating layers and the superconducting Cu-O planes, in the latter of which high-temperature superconductivity was shown to exist [48], even down to a single layer [49]. This implies that the electronic properties of these materials are extremely two-dimensional since the single layer has nearly the same superconducting properties as the bulk crystal.

The nominal symmetry of the Cu-O plane materials is tetragonal, meaning that the Cu-O plane is a two-dimensional square lattice in the a-b plane, which in real materials is between layers of various spacing along the c-axis in the bulk crystal. However, when one examines the details of the structure for the cuprates, the result is that they are all slightly different from each other and contain additional complexities.

For instance, \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_2 \) is observed to indeed be tetragonal at low-temperature, however at a higher temperature, an orthorhombic distortion along the Cu-O bond direction is observed to enhance superconductivity [50]. This structural transition has been connected to the proximity of the system to a Peierls instability from Fermi surface nesting [51], which however is suppressed by doping, leaving a strong electron-phonon coupling effect [52]. This results in the canting of the CuO\(_6\) octahedra along the (1 1 0) and (1 -1 0) axes, and the tetragonal phase seen at low temperature is actually a superposition of both canting types [53].

\( \text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta} \) is also notably different than tetragonal. Instead it has been shown to be orthorhombic along the Cu-O bond-direction, which is connected with the formation of Cu-O
chains in addition to the Cu-O planes [54]. The chains themselves have an ordering tendency that depends on oxygen doping. The Ortho-II phase occurs at higher oxygen doping, while the ortho-I phase, which doubles the a-axis lattice parameter, occurs at lower oxygen doping [55].

Bi$_{2+x}$Sr$_{2-x}$CaCu$_2$O$_{8+\delta}$ and Bi$_2$La$_x$Sr$_{2-x}$Cu$_2$O$_{6+\delta}$ are nearly tetragonal, but the crystallographic symmetry axes are not along the bond-direction. The Bi-cuprates differ from the other cuprates by having the the crystallographic axes along 45° to the Cu-O bond direction. They are slightly orthorhombic by having inequivalent a* and b* axes, by approximately 0.02 Å, and additionally they have an incommensurate superstructure in one direction [56, 57].

The 45°, $\sqrt{2} \times \sqrt{2}$ distortion requires two Cu-atoms per plane per unit cell for the irreducible representation of the space group $B_{bm}$ for the bilayer compound [58, 59], or $B_{2/b}$ for the single-layer compound [60].

The hole-doped Bi-cuprates are metallic systems with a doubly degenerate conduction band for the single-layer system mainly related to the Cu-O planes, with a bilayer-splitting in the bilayer compound arising from interaction between the planes [61, 62]. The resulting Fermi surface is hole-like with mainly Cu d$_{x^2-y^2}$ - O p$_{x,y}$ character, with large quasi-circular hole-pockets centered on the corners of the tetragonal Cu-O plane referenced Brillouin zone.

The electronic structure of the Bi-cuprates is strongly modified by reduced crystal symmetry corresponding to this orthorhombic distortion [63, 64, 65]. The effect of the orthorhombic distortion results in a new Brillouin zone that is smaller, and equivalently shows backfolding of the conduction band in the extended zone scheme. This is illustrated by the tetragonal Cu-O plane derived Fermi surface in Fig. 3.1(a) compared with the orthorhombic crystal derived Fermi surface in Fig. 3.1(b), showing the backfolding of the Fermi surface into the shadow-band centered on the Γ point and the new Brillouin zone as a dashed-line, all as a result of the real orthorhombic distortion in the crystal. In fact this is similar to the effect of antiferromagnetism, which has led to debate regarding a possible magnetic origin for the shadow-band [66, 67, 68, 69, 70].

In order to understand the origin of the shadow band, a detailed account of the crystal symmetry must be included to understand possible structural effects. As photoemission is a time-reversed
LEED state [38], the final state irreducible symmetry can be determined from a normal-emission plane-wave under the glide-plane symmetry operation [71, 72],

\[ O(\sigma_x|b/2) \psi_{\mathbf{k}_f}(\mathbf{r}) = \psi_{\mathbf{k}_f}(-x, y - b/2, z) = e^{i(k_f y(y-b/2)+k_f z)} \]
\[ = e^{-ik_f b/2} \psi_{\mathbf{k}_f}(\mathbf{r}) = e^{-i(k_y-G_y)b/2} \psi_{\mathbf{k}_f}(\mathbf{r}) \]
\[ = \delta e^{-in\pi} \psi_{\mathbf{k}_f}(\mathbf{r}) \]

(3.1.1)

The momentum \( k_y \) lies in the first Brillouin zone, and \( \mathbf{G} \) is a reciprocal lattice vector, and the glide operation is represented by \( \delta e^{-in\pi} \), for integer \( n \) value. The photoemission process must conserve momentum up to an integer multiple of the reciprocal lattice vector [35]. However, if we add the \( n \)th reciprocal lattice vector to the electron momentum, the result is the alternating sign, so that adding a reciprocal lattice vector along the glide-plane axis alternates the symmetry group. The first group, \( \Delta_1 \), occurs for even \( n \)-values and the second symmetry group, \( \Delta_2 \), occurs for odd \( n \)-values. This results in the need to account for both symmetry groups \( \Delta_1 \) and \( \Delta_2 \) in the primitive basis of the Bravais lattice, which effectively increases the size of the unit cell of the crystal. The subsequent electronic backfolding produces electronic states of opposite parity, since they are opposite-dispersing.

Under high-symmetry conditions the \( \mathbf{A} \cdot \mathbf{p} \) term alternates from \( \Delta_1 \) to \( \Delta_2 \) by alignment along either the reflection plane parallel to \( \Gamma-X \) or the glide plane parallel to \( \Gamma-Y \) (shown in Fig. 3.1), and accounting for the two inequivalent Cu atoms in the orthorhombic space group, the initial states can be put into the form of \( \Delta_1 \) and \( \Delta_2 \) [72]. This produces a sharp ARPES matrix-element effect along the \( \Gamma-Y \) direction, where the shadow-band and main-band intensity are switched by changing from s- to p-polarization [64].

The opposite parity of the main- and shadow-band observed in ARPES with linear polarization-dependence of the incident light, together with evidence for forbidden reflections along the \( \Gamma-Y \) direction in LEED, has signaled a reduced structural symmetry and the occurrence of a glide-plane along the \( y \)-axis in Pb-doped Bi2212 [64]. In addition it was shown that the ARPES shadow-band intensity does not depend on temperature, doping, or substitution of the Sr in the perovskite blocks, confirming that it is related to the Bi-O plane orthorhombic distortion [73]. Thus, consensus has now been reached that the shadow-band in Bi2212 is a purely a structural effect resulting in backfolding of the \((\pi, \pi)\) centered Fermi surface to the \( \Gamma \)-point, caused by the irreducible orthorhombic symmetry of the Bi-O plane.

However, the Bi-cuprates possess an additional characteristic superstructure along the \( b^* \) axis [74, 39, 75] with a periodicity incommensurate with the lattice but near \((1 \times 5)\) for the bilayer compound, and near \((1 \times 4)\) in the single layer compound, though with exact values that depends on the species and concentration of cation substitution [76]. The single-layer and bilayer crystals are thought to belong to the super-space group \( P_{111}^{B_{2h}} \) and \( N_{111}^{B_{6m}} \), respectively [58, 60], though there is still no general consensus.
Modification of the Fermi surface of the orthorhombic system in (a) by adding the effect of the long-wavelength supermodulation shown in (b).

The resulting reciprocal space periodicity can be expressed by the reciprocal lattice vector [58],

\[ \vec{G} = h \left( \frac{2\pi}{a^*} \right) \hat{x} + k \left( \frac{2\pi}{b^*} \right) \hat{y} + l \left( \frac{2\pi}{c} \right) \hat{z} + m\vec{q} \]  

(3.1.2)

The effect on the additional index, m, of the reciprocal lattice vector on the Fermi surface and band-structure is to displace the orthorhombic crystal derived band-structure in integer multiples of the superstructure vector, \( \vec{q} \) [75]. This is illustrated for the Cu-O derived Fermi surface with orthorhombic shadow-band backfolding in Fig. 3.2(a), where the additional translation by the supermodulation wavevector is sketched in Fig. 3.2(b), along with the effective reduced Brillouin zone shown by the dashed-line, which would be exact only in the case of a commensurate superstructure resulting in a true superlattice.

It is possible to use Pb-substitution to suppresses the supermodulation superstructure, though this can also lead to phase separation and weak but persistent supermodulation [77]. The (Pb,La) single-layer compound doping dependence was used to determine that the superstructure resulted from a mismatch between the Bi-O layers and the perovskite blocks, rather than from incorporating extra oxygen [78]. There have also been suggestions that local cation disorder affects the electronic properties of copper oxygen plane [79], and there is some speculation of the true effect of the superstructure as one including the direct modulation of the Cu-O planes, in addition to affecting the spatially removed Bi-O planes [80].

3.2 A Puzzling Contradiction of Arcs and Pockets in the Cuprate Fermi Surface

Early reports from photoemission measurements in Bi\(_2\)Sr\(_2\)Ca\(_{1-x}\)Dy\(_x\)Cu\(_2\)O\(_{8+\delta}\) showed that in under-doped samples, corresponding to higher Dy-content, there is a shift in the electron band-structure in energy, however in addition there is a suppression of the near-E\(_F\) spectral weight. This appears as a suppression of the antinodal region of the Fermi surface above the superconducting transition tem-
perature $T_C$, along the $\left(\pi, -\pi\right)-\left(\pi, \pi\right)$ or X-Y direction [81]. This was speculated to originate from the formation of small Fermi surface pockets in the underdoped samples, arising from a possible structural distortion or magnetic interactions.

A short time later, it was observed via ARPES studies of the spectral weight at the Fermi surface, that the gap responsible for the suppression of the Fermi surface above $T_C$, referred to as the pseudogap, has a specific onset temperature $T^* > T_C$ [82]. As the temperature is lowered from $T^*$ the pseudogap opens gradually along the Fermi surface, beginning at the antinodal region ($k_F$ near $(\pi, 0)$) and continuing towards the nodal region ($k_F$ along $(\pi, \pi)$). At $T_C$ the pseudogap evolves continuously into the superconducting gap, suggesting they could both originate from the formation of Cooper-pairs, where the higher $T^*$ associated with pairing and $T_C$ connected to the condensation of the pairs into a phase-coherent superfluid [83, 84].

Subsequent ARPES measurements on $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ demonstrated the extreme momentum-anisotropy of the photoemission spectral function between the persistent nodal quasiparticle and the broad features and persistent gap at the antinode [85]. This was suggested to be related to strongly momentum-dependent charge-ordering tendencies, such as the $4a_0 \times 4a_0$ electronic checkerboard seen in these materials via scanning-tunneling microscopy [86], as a general feature of the pseudogap state, possibly in competition with superconductivity. This has led to debate regarding whether the pseudogap is a precursor to superconductivity, or another order in competition with superconductivity [87, 88].

A puzzling picture began to emerge when small Fermi surface pockets in the high-$T_C$’s were indirectly observed in the form of quantum-oscillations of the electrical resistance [89] and magnetization [90] of YBa$_2$Cu$_3$O$_{6.5}$, and measurements showing a negative Hall coefficient in the pseudogap phase of underdoped YBa$_2$Cu$_3$O$_y$ and YBa$_2$Cu$_4$O$_8$ suggest the presence of electron-like pockets in the Fermi surface [91]. These measurement are consistent with the predictions of a mean field theory of the 1/8 magnetic antiphase stripe order, that for intermediate values of the stripe order parameter shows magnetotransport that is dominated by an electron pocket, with a particular size sensitive to the value of the density wave potential [92]. However, some theories predict that quantum-oscillations observed in the superconducting state originate in a quantum interference between the vortex lattice and nanoscale crystal modulations of the order parameter [93].

Shortly thereafter, the advancement of the ARPES experimental technique had allowed the possibility of in situ doping of the YBa$_2$Cu$_3$O$_y$ surface, and resulted in the observation of a continuous evolution from the overdoped, metallic regime with its complete Fermi surface to the disconnected arcs in the underdoped regime [94]. However, the Fermi pockets predicted from quantum oscillations were not seen, pointing towards a picture of disconnected Fermi arcs.

Attempts to reconcile the seemingly contradictory results of ARPES and quantum-oscillation experiments on the underdoped cuprates have considered the effect of slow antiferromagnetic fluctuations with a short correlation length detected by neutron-scattering experiments that could suppress the ARPES intensity for half the pocket which extends beyond the antiferromagnetic zone boundary, thus causing the pockets to appear as Fermi arcs [95]. In addition, calculations of the electronic structure of Ortho-II YBa$_2$Cu$_3$O$_y$ show two possible orbits, both of which require
Fig. 3.3: Location of Fermi pockets in the Brillouin zone proposed by reference [98] shown in (b) on top of the underlying orthorhombic+supermodulation Fermi surface shown in (a).

a small shift in the relative energies of the bands as necessary to have extremal areas compatible with those observed [96]. Similar calculations reveal that a correct interpretation of the quantum-oscillation results should account for electron correlation effects, and that a hole-like pocket in the Fermi surface is not necessarily incompatible with the negative Hall coefficient observed [97].

In 2009 a new set of ARPES experiments carried out on underdoped La$_x$Bi$_2$Sr$_{2-x}$CuO$_{6+\delta}$ presented evidence for an entirely different scenario [98]. The ARPES Fermi surface taken at 7 and 21 eV photon energy were composed of closed E$_F$ contours, forming hole-like Fermi pockets, which were smaller than anything previously observed by ARPES in the high-$T_{c}$'s. The pockets also showed a momentum position that placed them exactly adjacent to the orthorhombic zone boundary, such that the entire pocket was contained inside the $\sqrt{2} \times \sqrt{2}$ Brillouin zone. Since this type of pocket can not be produced by the orthorhombic structural distortion, it is incompatible with the backfolding that produces the shadow band. A hole-doping dependence showed that the pockets only appear in the underdoped region near 1/8 hole-doping.

Furthermore, the well known supermodulation in the single-layer material family Bi$_2$Sr$_2$CuO$_{6+\delta}$ is nearly a factor of two too large to produce the pocket that Meng et al. observed [75, 98]. Thus the coexistence of the original orthorhombic reconstructed and supermodulated Fermi surface band structure with the new anomalous Fermi pockets was claimed, as illustrated in Fig. 3.3. The Fermi arc feature was still observed on the original Fermi surface, pointing towards an unexpected direction, the coexistence of Fermi arcs and Fermi pockets in this underdoped High-$T_C$ superconductor.

However, given the extremely complex structural nature of these materials, in having both a $\sqrt{2} \times \sqrt{2}$ reconstruction in addition to a superstructure modulation, it was deemed worthwhile to investigate the connection between structural probes and the electronic Fermi surface seen in ARPES.
3.3 LEED and Polarization and Doping Dependent ARPES on Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$

To address this issue, we studied high-quality single crystals of Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$, with $x =$ 0.5, 0.6, and 0.8. Sr-site disorder has a significant effect of decreasing $T_C$ in the lanthanide-doped Bi-cuprates, thus the use of La as a chemical dopant, which has the smallest ionic radius mismatch and results in an optimal $T_C$ of about 33K ($x =$ 0.5) [79]. La donates additional electrons to the crystal, leading to reduced hole concentrations for the underdoped samples ($x =$ 0.6,0.8), with $T_C$ of 23K and 15K.

Samples were cleaved and ARPES measurements were carried out in ultra-high vacuum at pressures less than $5 \times 10^{-11}$torr, and at temperatures near 6K. Sample alignment was performed by Fermi surface mapping and adjusting the azimuthal angle of the sample holder (no Laue measurements were available for the samples studied in this chapter). ARPES was performed with photon source produced by a plasma discharge He-I emission line at 21.22 eV. The electron lens was set to a field of view of about 23° (wide-angle mode), corresponding to an angular resolution of about 0.02°, equivalent to about 0.01 Å$^{-1}$. Fermi surfaces were mapped with $\phi$-increments of 0.5°, corresponding to about 0.02 Å$^{-1}$ resolution.

The Fermi surface of the optimally doped $x =$ 0.5 sample is shown in Fig. 3.4(a). The features agree well with the superstructure-induced backfolding scenario, leading to many replicas of the main and shadow bands being visible. The replicas appeared shifted by a wavevector, $Q_{1}^{op} \sim 0.273 \text{Å}^{-1}$. The intensity distribution is increased for the main band in the second (or-
The polarization-averaged Fermi surface of the optimally doped $x=0.5$ sample is shown in Fig. 3.5(a). This data was taken over five polarizations between the angles defined by the diagonal lines of the dataset edges, and the polarization dependence was averaged. The sample orientation in this case leads to a geometry that does not allow for the high-symmetry crystal planes to be probed with a given polarization, and the resultant Fermi surface produced is similar to data taken with unpolarized light. This can be a useful way to avoid polarization-dependent matrix elements and to just focus on the bandstructure. A symmetrized version generated from this Fermi surface is shown in Fig. 3.5(b), which depicts the band structure. We note that by inspection all of the Fermi surface replicas due to the supermodulation in the optimally doped sample are shifted by a single wavevector, $Q_{OP}$.

The Fermi surface of the underdoped $\text{Bi}_2\text{Sr}_{1.2}\text{La}_{0.8}\text{CuO}_{6+\delta}$ sample, taken in $s$- and $p$-polarization is shown in Fig. 3.6(a,b). In comparison to the optimally doped sample, this shows additional features along the Γ-Y direction that are in between the bands seen for the optimally doped sample. These are the same apparent Fermi pockets from reference [98] for similar underdoped $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$ samples. Notably, the apparent pocket features are separated from each other by the same wavevector, $Q_1 \simeq 0.285\text{Å}^{-1}$, as the ordinary supermodulation replicas, and the separation between the apparent pocket bands and the supermodulation replicas is $Q_2 \simeq Q_1/2$.

Cuts taken through the first and second orthorhombic Brillouin zone along the Γ-Y direction for the underdoped $\text{Bi}_2\text{Sr}_{1.2}\text{La}_{0.8}\text{CuO}_{6+\delta}$ sample, in $s$-polarization, are shown in Fig. 3.7. The first Brillouin zone (a-c) shows decreased intensity compared to the second zone (d-f), and a switching of the dispersion direction simply due to the bandstructure. Only $Q_1$-replicas are prominent in the intensity, and a fairly strong dip feature near 60meV is visible in nearly all of the EDCs in (c,f).

ARPES cuts taken through the first and second orthorhombic Brillouin zone along the Γ-Y direction for the underdoped $\text{Bi}_2\text{Sr}_{1.2}\text{La}_{0.8}\text{CuO}_{6+\delta}$ sample, in $p$-polarization, are shown in Fig. 3.8. The first Brillouin zone (a-c) still shows decreased intensity compared to the second zone (d-f). Not only $Q_1$-replicas are prominent in the intensity, but a strong apparent pocket is located at the center of the image in (d), which is separated from the $Q_1$ superstructure by the wavevector $Q_2 \simeq Q_1/2$. The extra bands, compared to the $s$-polarization data, show up as extra peaks in the MDCs in (e), and as well all bands show a dip in the EDCs near 60meV binding energy in (c,f).

Finally, LEED data taken for the $x=0.8$ sample is shown in Fig. 3.9, where superstructure is observed to have periodicity of $Q_2 \simeq Q_1/2$, directly suggesting the presence of additional superstructure in the underdoped samples.

### 3.4 Structural Origin of Apparent Fermi Surface Pockets in Angle-Resolved Photoemission of $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$

To gain a better understanding of the origin of the apparent Fermi pockets described in reference [98] and the possibility of multiple superstructures as described in the previous section, we have
Fig. 3.5: Photon-polarization averaged Fermi surface in (a) taken for optimally doped B\textsubscript{2}Sr\textsubscript{1.5}La\textsubscript{0.5}CuO\textsubscript{6+δ}, in five polarizations between 0-90° of the dataset edge angle, thus off the high-symmetry direction to show band-structure. (b) Symmetrized Fermi surface generated from (a).
Fig. 3.6: Polarization-dependence of the Fermi surface of underdoped $\mathrm{Bi}_2\mathrm{Sr}_{1.2}\mathrm{La}_{0.8}\mathrm{CuO}_{6+\delta}$ in (a) $s$-polarization and (b) $p$-polarization, showing the strong dependence of the visible bands on the incident photon polarization. The visible bands are at noticeably different positions than in the case of the optimally doped sample (see text).
Fig. 3.7: S-polarization ARPES cuts for the (a) first and (d) second Brillouin zone for the underdoped Bi$_2$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$ sample. Corresponding MDCs are shown in (b,e) and EDCs in (c,f).
Fig. 3.8: **P-polarization ARPES cuts** for the (a) first and (d) second Brillouin zone for the underdoped Bi$_2$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$ sample. Corresponding MDCs are shown in (b,e) and EDCs in (c,f).
Fig. 3.9: LEED Pattern obtained at 10K for the underdoped x=0.8 sample. The superstructure peak-spacing indicates that there are multiple structure modulations that occur at the wavevector $Q_1$ and $Q_2 \approx Q_1/2$.

performed a detailed doping- and photon polarization-dependent study of the ARPES Fermi surface for Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$ (La-Bi2201). In addition, a complementary structural probe, LEED, has been utilized for the same samples, in order to directly compare the lattice superstructure observed with electron diffraction to the experimental ARPES Fermi surface. We combine an extensive k-space survey of the Fermi-surface topology of La-substituted Bi2201 with a detailed structural analysis, in order to separate generic electronic effects from the electronic diffraction replica (DR) superstructure periodicities of up to $14a_0$, which coexisting with the already well-established periodicity of $\approx 4.2a_0$. Such structural artifacts lead to imitations of closed Fermi-surface pockets in ARPES measurements. From their polarization dependence, we demonstrate that the front and back sides of the pockets derive from the main and shadow bands, respectively, and do not represent a single closed portion of Fermi surface intrinsic to the doped CuO2 plane as claimed previously [98].

We investigated optimally (OP) and underdoped (UD) La-Bi2201 with $x = 0.5$ (OP30K), $x = 0.75$ (UD20K), and $x = 0.8$ (UD14.5K) samples, resulting in multiple datasets showing agreement for the parameters determined. In addition, older data on optimally doped Bi$_{1.7}$Pb$_{0.35}$La$_{0.4}$Sr$_{1.6}$CuO$_{6+\delta}$ [(Pb,La)-Bi2201, OP35K] samples was analyzed for comparison. ARPES measurements on La-Bi2201 (corresponding to Figs. 3.10 and 3.12) were performed in the pseudogap phase at $\sim 17.5$ K and $\sim 33.5$ K for UD14.5K and OP30K La-Bi2201, respectively, with linearly polarized He-I$\alpha$ radiation ($h\nu=21.22$ eV) and a SPECS Phoibos 225 hemispherical analyzer. The additional data on (Pb,La)-Bi2201 (Fig. 3.11) was taken in the superconducting phase at 10 K with unpolarized light. The angular and energy resolutions for all measurements were set to $0.3^\circ$ and better than 20 meV, respectively. All low-energy electron diffraction (LEED) patterns
Fig. 3.10: ARPES Fermi surface of (a) UD14.5K and (b) OP30K La-Bi2201, measured with p-polarization. Extracted contours (blue circles) and a tight-binding model of the main (solid line), shadow (dashed line), and ±q₁ or ±2q₁ (green), ±q₂ (blue), and ±(q₁ + q₂) (red) Umklapp bands are overlaid on the data. LEED from (c) UD14.5K and (d) OP30K La-Bi2201. A magnified view of the blue region and a line cut along the Γ–Y direction (red line) are shown to the left of and below each pattern, respectively. Extracted peak positions (red dots) and those expected for superstructure peaks at \( k_0 \pm m_1 q_1 \pm m_2 q_2 \) (vertical gray lines) are in good agreement. The inset in (a) shows a simplified Fermi surface with only the main (MB) and shadow (SB) bands.

shown here were recorded at temperatures between \( \sim T_c \) and \( \sim 2T_c \) with an incident electron energy of 35 eV.

Fig. 3.10(a) shows the Fermi surface of UD14.5K La-Bi2201 as measured by ARPES. Fermi arcs are visible centered around the nodal directions, although their intensity is suppressed along Γ–Y due to matrix element effects which will be discussed shortly. Multiple copies of these arcs can be observed, separated by 0.28 Å⁻¹ along the Γ–Y direction, consistent with DR corresponding to the established dominant superstructure periodicity of this material. In addition, weak features with opposite dispersion to the Fermi arcs appear to form several small closed pockets along the nodal direction (white arrows in Fig. 3.10(a), labeled as p1p4). These features cannot be observed in optimally doped La-Bi2201, shown in Fig. 3.10(b), which is consistent with the findings of Meng et al [98].

In the following, we show that the closed pockets appear as a natural consequence of structural complications in La-Bi2201. Lines of periodic diffraction maxima, characteristic of superstructure modulation along the Γ–Y direction, are clearly discernible in the LEED pattern from OP30K La-Bi2201 (shown in Fig. 3.10(b)). From their spacing, the superstructure vector can be determined
as,
\[ \mathbf{q}_i = (q_i, q_i) \frac{\pi}{a} \]  
(3.4.1)

with \( q_1 = 0.235 \pm 0.015 \), in agreement with the DR in the ARPES and with earlier diffraction studies [99]. Intriguingly, LEED from UD14.5K La-Bi2201 (shown in Fig. 3.10(c)) shows not only a similar superstructure vector \( q_1 = 0.245 \pm 0.015 \) but exhibits yet further diffraction maxima revealing the coexistence of a second superstructure with \( q_2 = 0.130 \pm 0.015 \). In order to demonstrate how these superstructure periodicities lead to the impression of hole pockets in ARPES, we first fit a tight-binding model to the Fermi surface of the main band for each doping (solid black lines in Figs. 3.10(a) and (b)) and then translate this band by \((\pi, \pi)\) to describe the shadow band resulting from the orthorhombic distortion. Finally, we add Umklapp bands, that is, DR of the main and shadow bands, with the \( \mathbf{q}_i \) vectors determined independently from LEED. Without any further adjustment this simple model reproduces the entire measured Fermi surfaces for the UD14.5K and the OP30K samples over an extensive k-space range. In particular, it describes all apparent hole pockets in the underdoped sample and the absence of these pockets in optimally doped La-Bi2201. For example, the pockets p1 and p3 in UD14.5K La-Bi2201 are created by the \( \mathbf{q}_2 \) DR of the shadow band crossing the main band, while another pocket (p2) is formed by the \( -\mathbf{q}_1 \) DR of the main band overlapping the \( -\mathbf{q}_2 \) DR of the shadow band. All of these pockets are absent in OP30K La-Bi2201, which does not show the \( \mathbf{q}_2 \) periodicity in LEED. It is therefore evident that the seemingly closed portions of Fermi surface in underdoped La-Bi2201 are not intrinsic, and instead appear from the overlapping of DR resulting from multiple superstructure periodicities.

This is confirmed, for instance, by the appearance of these pockets, which is not directly tied to the hole concentration, or the presence of a pseudogap, but rather to the particular structural modulations. Indeed, we also observe multiple superstructures, with vectors of \( q_1 = 0.225 \pm 0.015 \) and \( q_2 = 0.072 \pm 0.015 \), in optimally doped (Pb,La)-Bi2201 (Fig. 3.11(a)). Although Pb doping tends to suppress superstructure-related features in ARPES from Bi-based cuprates, the measured Fermi surface (Fig. 3.11(b)) clearly shows the presence of Umklapps resulting from these superstructure vectors and their combinations, consistent with a tight-binding model using the \( \mathbf{q}_i \) vectors determined from LEED. Similar to the situation in underdoped La-Bi2201, the overlapping of several of these bands gives rise to features that appear as closed Fermi-surface pockets. However, as for UD14.5K La-Bi2201, this is entirely due to structural effects and should not be confused with either an intrinsic hole pocket or an incommensurate density-wave order.

The structural origin of the observed pockets can be further confirmed by polarization-dependent ARPES measurements, as shown in Fig. 3.12. The 3d_{x^2-y^2} symmetry of the hole in the Cu d shell is odd with respect to the \( \Gamma - Y \) direction. Consequently, for the experimental geometry employed here, with the incident light and detected electrons both within the horizontal plane, the main band can be observed when measuring with s-polarized light along the \( \Gamma - Y \) azimuth but is suppressed for p polarization. This is the reason why the intensity along the Fermi arc diminishes approaching the \( \Gamma - Y \) nodal line in Figs. 3.10(a) and (b). In contrast, the shadow band, which has the opposite parity of the main band [64], is visible in p-polarization but not in s-polarization. This switching
Fig. 3.11: LEED pattern and ARPES Fermi surface of OP35K (Pb,La)-Bi2201 in (a) and (b) respectively, showing the presence of two superstructure vectors, and the resulting apparent pockets in the Fermi surface. A tight-binding model, using superstructure vectors determined from the LEED analysis, is also shown in (b).

of intensities is clearly seen for OP30K La-Bi2201 in Fig. 3.12(a) (although the lack of complete suppression of the forbidden transitions is due to the finite degree of polarization (∼80% of the incident light in the experimental setup used here). For measurements in the 2nd Brillouin zone, along the cut shown in Fig. 3.12(d), the polarization is no longer strictly s or p since the sample is tilted off-vertical by ∼30°. Nevertheless, a strong relative intensity variation can still be observed between the main and shadow bands on switching from dominant p-polarization ($I_{MB}$ : $I_{SB}$ smaller) to s-polarization ($I_{MB}$ : $I_{SB}$ larger), as shown in Fig. 3.12(b).

The equivalent dispersion measured in UD14.5K La-Bi2201 is shown in Fig. 3.12(c). With p-polarization, two strong dispersions can be seen due to the main band and its $-\mathbf{q}_1$ DR, with two weaker neighboring bands which form the back side of the apparent Fermi-surface pockets (marked in the Fermi level momentum distribution curve by circles and crosses, respectively). This gives the appearance that the pocket on the Fermi surface is hole-like, as claimed in Ref. [98]. However, on switching to s-polarization, these “pocket-forming” bands are strongly suppressed relative to the main bands, as is the spectral intensity of the back side of all of the pocket features which can be seen in the ARPES Fermi surface (Fig. 3.12(d)). This switching of intensities due to different parities of the front and back sides of the Fermi-surface pockets is difficult to reconcile with intrinsic pockets of a reconstructed Fermi surface and confirms that these features are derived from the shadow band.

Given this, one must revise the conclusions of Ref. [98] regarding intrinsic hole pockets. Meng et al. [98] considered only Umklapp bands arising from a $q_1 \approx 0.24$ superstructure modulation and found that these DR could not explain their data. However, LEED from La-Bi2201 with very similar composition to the UD18K sample of Ref. [98] shows not only the $q_1 = 0.24$ superstructure but also a second superstructure with $q_2 = 0.12 - 0.015$ (see Fig.3.13(a)). In Fig.3.13(b), we show that the measured pockets, and indeed all features of the Fermi-surface topology extracted in Ref. [98], are accurately described by a tight-binding model of only the conventional main and shadow bands, provided DR are included corresponding to both of these superstructure vectors. Together with the polarization-dependent ARPES presented above, this shows unambiguously that the observations of Meng et al. [98] have a trivial interpretation and cannot be taken as evidence for elusive Fermi
Fig. 3.12: Polarization-dependent ARPES on La-Bi$_2$2201. (a) Dispersion along Γ – Y of OP30K. (b), (c) Dispersion close to the equivalent direction in the 2nd Brillouin zone [along dashed lines in (d)] of OP30K and UD14.5K La-Bi$_2$2201. (d) ARPES Fermi surface of UD14.5K La-Bi$_2$2201. All spectra were measured with either p- (top) or s-polarization (bottom).

We also note that a structural origin of the pockets explains several puzzling observations of Ref. [98]. First, the main band (Fermi arc) was observed to be longer than the back side of the claimed pocket (as also evident here in Figs. 3.10(a) and (b)). The lower intensity of the shadow band and its DRs, which appear to “close” the pockets, compared to the main band, naturally accounts for this seemingly contradictory coexistence of Fermi arcs and hole pockets. Second, the spectral weight of the back side of the pockets in Ref. [98] appears largest close to the nodal line. This is in contrast to theoretical expectations for an intrinsic pocket [100, 101] but consistent with a superstructure replica of the shadow band. Third, multiple hole pockets were observed in Ref. [98], attributed to a $q = 0.24$ superstructure replica of a single intrinsic pocket. However, the front- to back-side spectral weight ratio differs for these pockets. Again this suggests that the two sides of the pockets derive from different bands, namely, the main and shadow band, whose Umklapps display complex intensity variation due to matrix element effects. In addition, the superstructure vectors depend sensitively on doping as shown from the LEED analysis presented here, which provides a simple explanation for the unusual doping dependence of the hole pockets reported by Meng et al. [98].

We note that our findings do not exclude the presence of intrinsic Fermi-surface pockets in cuprates, where the back side of the pocket has negligible spectral weight in ARPES measurements [84]. However, we remark that, to date, clearly discernible hole pockets have been reported only from ARPES measurements in Bi-based and La-based cuprate systems [98, 102], which are both subject to structural distortions. No such observation has been made in compounds free of such distortions, for example, CCOC [85] and YBCO [94].
Fig. 3.13: LEED of UD20K La-Bi2201 in (a). (b) Red circles reproduce the Fermi-surface contours of UD18K La-Bi2201 from Ref. [98]. A tight-binding Fermi surface including Umklapp bands derived from our LEED analysis reproduces all features of the data from Meng et al. [98] including the apparent Fermi-surface pockets (labeled LP, HP, and LPS after Ref. [98]). The tight-binding bands are labeled by $(m_1, m_2)$, where $m_i$ is the order of the $(q_1, q_2)$ superstructure replica and prime denotes the shadow band.

3.5 Conclusive Evidence for Multiple Structure Modulations in Underdoped Bi$_2$Sr$_{2−x}$La$_x$CuO$_{6+δ}$

The doping-dependent ARPES and LEED measurements on La-Bi2201 demonstrated in Sec.3.4 establish the need to fully reconcile the Fermi “pocket” phenomenology as proposed in reference [98], and sketched in Fig. 3.14(a), with the additional superstructure defined by wavevector $Q_2$, which occurs in addition to the well-known $Q_1$ DR [1]. The multiple-superstructure model leads to the predicted Fermi surface sketched in Fig. 3.14(b), which was convincingly demonstrated by low-energy electron diffraction that shows the presence of additional superstructure peaks, only seen to occur in underdoped La-Bi2201, parallel to the well-known $Q_1$-superstructure. The heretofore lack of any direct observation of the $Q_2$-replica of the main band in the corresponding nodal ARPES data allows the question of whether the multiple-superstructure picture can fully explain the measured ARPES Fermi surface. This section demonstrates that photon-energy integrated ARPES data can be utilized to overcome the complex matrix element effects which partially suppress some of the multiple-superstructure DR, allowing the existence of all the Fermi surface features predicted by the two-superstructure model to be established.

ARPES measurements on underdoped ($T_C = 15K$, UD) and optimally doped samples ($T_C = 31K$, OP) at the Elettra BaDelPh beamline using a Specs PHOIBOS 150 electron analyzer set to angular acceptance of 24°, overall energy resolution of 10 meV, and angular resolution of 0.2°. The incident photon energy was varied from 19-31eV, in 2eV increments. In addition, this was done for incident light in both s- and p-polarization. Measurements were performed with the sample cooled to 10K and cleaved at low-temperature in vacuum at pressures below $8 \times 10^{-11}$ Torr. The samples were oriented with the orthorhombic b*-axis in the plane of detection, producing spectra close to the nodal line and parallel to both superstructure wavevectors, as depicted by shaded...
Fig. 3.14: Sketch of the Fermi surface in (a) described by Meng et al. [98]. The red traces show the main Fermi surface and its well-known superstructure replicas for the single layer Bi2201 (shown close to $1 \times 4$). The green curves show the Fermi pockets proposed to exist due to correlations. (b) The alternative model proposed by King et al. [1], which produces similar features due to an additional supermodulation in agreement with LEED patterns. The shaded region shows the momentum region measured in this paper.

Fig. 3.15: ARPES nodal-direction cuts taken at 19-31 eV photon energy and integrated over photon energy to overcome the effect of matrix-element suppression of the $Q_2$ features. (b-c) Photon polarization-dependence for underdoped samples reveals additional peaks highlighted in the MDC’s (a), which are only visible in p-polarization. These additional peaks are not detected in the same measurements performed on optimally doped samples (d-f). (g-j) EDC curves for both doping levels and polarizations corresponding to colored arrows in (b-c,e-f) show the relative strength in the quasiparticle peak depends strongly on the in-plane momentum.
The photon-energy-integrated ARPES spectra and momentum-direction curves (MDC’s) taken for the underdoped samples are shown in Fig. 3.15(a-c), where a remarkable polarization dependence gives rise to a switching of the visibility of particular bands. What is apparent is that in s-polarization there is no sign of the bands marked by colored arrows on the MDC’s in Fig. 3.15(a). In p-polarization, however, these additional peaks are detected at the positions corresponding to the peaks of the two-superstructure model, between the features detected in s-polarization. This includes a peak corresponding to the $Q_2$-replica of the main Fermi surface near 0.31 Å$^{-1}$. In addition there are no additional peaks beyond what is expected from this model.

The same ARPES measurements carried out for the optimally doped samples in Fig. 3.15(d-f) show very similar features in the false-color plot and MDC’s as the underdoped samples, owing to the presence of the ordinary $Q_1$-superstructure at both doping levels, and an estimated three degree offset from the nodal line determined by comparison to the experimental ARPES Fermi surface. The lack of these additional features for these spectra taken at both polarizations and over the entire range of photon energies 19-31eV shows a complete lack of the $Q_2$-superstructure features in the case of optimal doping.

The energy-direction curves shown in Fig. 3.15(g-j) corresponding to colored arrows in (b-c,e-f), show a quasiparticle peak only for bands that occur with enough intensity to resolve the spectral peak. For instance the main band of the underdoped sample near 0.45 Å$^{-1}$ in Fig. 3.15(a-c) appears with strong intensity in both polarizations, however in s-polarization the appearance of additional bands also increases the background resulting in a markedly different EDC lineshape. This reflects upon the fact that additional superstructure bands disperse in momentum and can contribute spectral weight as well at higher binding energies.

The $Q_2$-bands, which are visible for photon-energy integrated p-polarization spectra of the underdoped samples, are entirely consistent with the predictions of the two-superstructure model. The clearly visible separation of the peaks demonstrates the existence of spectral weight that is inconsistent with isolated pockets, which would not produce all of the spectral features, and conclusively results in the identification of these features as arising from multiple, coexisting superstructures only for the underdoped samples.

In addition, the integration of photon energies uncovers matrix elements effects which remain strongly dependent on the in-plane momentum, and with $Q_2$ superstructure often producing weaker intensity than $Q_1$, and explaining why these features were not originally observed. Yet the relative intensity of the bands along the nodal line is not always clearly related to the order of the diffraction replica as referenced from the main bands, particularly in the case of the underdoped samples with $Q_2$, for instance here in s-polarization the $Q_1$ replica is more intense than the main band itself. This shows that the structural effects are not weak diffraction, and instead are directly modifying the primitive spatial symmetry of the electronic environment.

The emerging physical picture shows a hierarchy of structural distortions - from tetragonal to orthorhombic, then $Q_1$ replicas, and now additional $Q_2$ replicas only in the case of underdoped samples of La-Bi2201, which can be understood roughly as the order of strength of the distortions.
from strongest to weakest, from the ratios of spectral intensity in ARPES. However, the presence of
so many structural complications, resulting in an extremely complicated electronic structure with
many bands closely spaced in momentum, in some way suggests that additional lattice instabilities
from electron-phonon coupling can be related in some way to these effects. A possible soft-phonon
coupled to a charge-density instability could be the driving force behind the structural distortion
at wavevector $Q_2$, similar to other possible charge-orderings observed in cuprates near 1/8 doping
[103]. However, the fact that the $Q_2$ modulation appears only for underdoping seems more likely
related the increased La content in the crystal, as this induces modulations in crystals where they
have been suppressed by Pb [78].
Photoelectron Diffraction Effects and Band-Crossing Hybridization in Bi$_{2}$Sr$_{2-\delta}$La$_{\delta}$CuO$_{6+\delta}$

4.1 ARPES Matrix Element Effects

The ARPES matrix element is the one-electron dipole matrix element given by (2.4.14) and (2.4.16),

$$M_{f,i}^{k} = A \hat{\epsilon} \cdot \langle \phi_{f,k} | \vec{p} | \phi_{i,k} \rangle \propto q \hat{\epsilon} \cdot \langle \phi_{f,k} | \vec{r} | \phi_{i,k} \rangle$$

and is responsible for the strong dependence of the ARPES photocurrent on the electron momentum and photon polarization (introduced in Sec. 1.3), and accounts for the photon-energy dependence of the photoionization cross-section [104].

Matrix element effects can have a pronounced influence on the photoemission intensity, which can be directly observed by the variation of the polarization and energy of the incident light. For instance they have been used to explain circular dichroism from oriented linear molecules [105], oscillations of the photoionization cross-section with final state energy in C$_{60}$ molecules [106], and linear and magnetic circular dichroism for samples with externally oriented magnetization [107].

The polarization dependence of the ARPES spectra along high symmetry directions of the crystal is governed by the symmetry operations allowed in the crystal across the plane being studied. If the photon momentum, photoelectron momentum, and surface normal lie in a mirror plane of the crystal, the final state will be even with respect to a mirror operation far away from the sample [35], and it is also even in the crystal since it can be identified as a time-reversed (equiv. momentum-reversed) electron-diffraction state [38].

Simultaneous energy and parity eigenstates will exist if the Hamiltonian commutes with the parity operator,

$$[\mathcal{H}, \hat{\Pi}] = 0$$

(4.1.2)
where $\hat{\Pi}$ is the parity operator, which is both hermitian and unitary, and corresponds to the operation $\vec{x} \to -\vec{x}$, $\vec{p} \to -\vec{p}$. Eigenstates of the parity operator obey the relation,

$$\hat{\Pi}\ket{\pi} = \pm\ket{\pi} \tag{4.1.3}$$

The positive value corresponds to the state being even under parity operation, while the minus sign corresponds to states that are odd under parity operation. Since the parity operator commutes with any even function of $\vec{p}$ or $\vec{x}$, it commutes with the Hamiltonian, thus leading generally to energy eigenstates that are also eigenstates of parity [108].

The initial-state wave function has a well-defined parity, and the parity of the dipole operator is completely determined by the polarization vector: it is even for p polarization and odd for s polarization [35]. In order to be nonzero the overall product of the terms in the matrix element must be even. Since the final state is even, this implies that both the dipole interaction operator and the initial state have to be simultaneously even or odd, otherwise the matrix element can be strictly zero in the high-symmetry mirror plane [109].

Detailed ARPES work on the magnetization averaged Ni(111) single-crystal [110] shows strong variation in the intensity with the external experimental parameters such as incident photon energy and polarization, both linear and circular, and the orientation of the crystal with respect to its high-symmetry directions (mirror planes). Altogether these results show that in order to disentangle the effects of initial state symmetry and matrix element effects, a detailed description of the experimental geometry should be included in photoemission calculations from first-principles electronic structure, in order to make comparison between theory and experiment. This has produced good agreement in the case of ARPES band mapping of bulk Cu [111, 112], with its fully three dimensional electronic structure and the resultant $k_\perp$ dependence of the matrix element.

The results of ARPES experiments are expected in some cases to show photoelectron-intensity angular-distributions that follow the momentum structure of the final states in addition to the initial states. This has also been measured in Co and Ni films and the 3d bands of bulk Cu [113], which demonstrates the additional importance of the effects of the final state momentum and energy structure in the experimentally observed ARPES Fermi surface.

Photon energy dependent ARPES has been used for several cuprates to distinguish whether certain features in the dispersion arise from the energy and momentum dependence of the spectral function, or instead are the result of matrix element effects [114]. In the near-$E_F$ states of Sr$_2$CuO$_2$Cl$_2$, the so-called “Zhang-Rice singlet” (ZRS)[18], oscillations in the photoemission intensity with variation of the incident photon-energy are observed. This is connected to interference effects between the final states from the periodic structure of the crystal along the c-axis. In ARPES on this material, the intensity of the ZRS contains oscillations as function of $k_\perp(h\nu)$ for a given $k_\parallel$, with period $\Delta k_\perp = 2\pi/c_{\text{CuO}_2}$, the distance between the CuO$_2$ planes along the c-axis. The inverse length-scale corresponding to the separation of the CuO$_2$ planes is explained to give rise the the oscillations from its agreement with the corresponding periodicity of intensity oscillations versus $k_\perp$ [115].
Fig. 4.1: Photoelectron interference effects originating from the c-axis periodic arrangement of the CuO$_2$-plane photoemitters, for the Bi2201 structure shown in (a). (b) The final states for given energy where the wavelength of the photoelectron is an integer multiple of the inter-plane spacing, and (c) where the wavelength is a half integer of the spacing, leading to constructive and destructive interference, respectively.

The energy-dependence of the photoemission matrix element that arises from structural ordering is understood in the context of photoelectron diffraction (PhD) [116]. This process describes the interference effects produced by spatially separated photoelectron emitters and the interference caused by scattering of photoelectrons from nearby atoms. These effects are characterized by the forward scattering processes that dominate above about 500eV, while at lower photon energies, backscattering and multiple scattering become important due in part to kinematics and to large atomic scattering cross-sections. These interference effects are driven not just by the path differences from spatially removed scatterers, but also by the intrinsic, energy-dependent phase-shifts brought on by the scattering process itself, and PhD final state effects can produce variations in the ARPES matrix element on the order of 10 percent [117]. In this way, the photon-energy dependence of the ARPES matrix element near $E_F$ in the cuprates can contribute valuable information regarding the local structure of the CuO$_2$-planes.

To illustrate the principles behind this effect, Fig. 4.1(a) shows the b*-c plane projection of the Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+y}$ structure, highlighting the position of the CuO$_2$-planes, which are separated by half of the c-axis lattice constant ($c/2$). The wavefronts drawn in (b) show a situation of constructive interference between the photoelectrons originating from CuO$_2$ planes, due to the electron wavelength being an integer multiple of the inter-plane distance leading to the overlapping maxima and minima along the c-axis direction. The opposite situation is illustrated in (c), where a change in the electron wavelength results in destructive interference between the photoelectron wavefronts originating on the planes, which occurs for wavelengths that are half-integer multiples.
of the inter-plane distance.

The interference effects illustrated in Fig. 4.1 occur due to the well defined periodicity of the photoelectron emission centers in the lattice, which can create interference effects in photon-energy dependence of the ARPES intensity. This creates a type of matrix element effect that is entirely due to the coherent sum of final states from the different emission centers. In order to demonstrate this, the relevant matrix element that must be found is,

$$\hat{\epsilon} \cdot \langle \phi_{k,f} | \vec{k} | \phi_{k,i} \rangle$$  \hspace{1cm} (4.1.4)

The final state is constructed as a superposition of plane-wave final states originating on the separated CuO$_2$ planes,

$$|\phi_{k,f}\rangle = \sum_{j} e^{i\vec{k} \cdot \vec{r}_j} = 2 e^{i\vec{k} \cdot \vec{r}} (\cos(k_{\perp}c/2) + \cos(k_{\perp}c) + \cos(3k_{\perp}c/2) + ...)$$  \hspace{1cm} (4.1.5)

Thus, the overlap of final states between neighboring planes will create a fundamental $\Delta k = 2\pi/(c/2)$ periodicity, as well as higher harmonics which will affect the waveform and may enter a more realistic calculation of the final state as a summation with more complicated coefficients for the higher harmonics. However, this does not change the fundamental periodicity, which is seen to be a significant contribution to the ARPES matrix element effects via the structural periodicity. Furthermore, for photoemitters with periodic arrangements perpendicular to the c-axis, the multiple scattering described in the PhD process at soft x-ray to ultraviolet photo-energies can contribute photoelectron interference from path lengths and scattering phase shifts from periodic arrangements perpendicular to the sample surface.

Photon-energy dependence of the EDC lineshape in Sr$_2$CuO$_2$Cl$_2$ has been shown to affect the apparent dispersion of the Cu-O states determined from the peak in the spectral function [118]. In addition, the relative weights of the coherent and incoherent parts of the spectral function can be examined according to a procedure proposed from theoretical studies that involve the exact diagonalization of the reduced Hubbard model [119], whereby the valence-band tail (Lorentzian) is subtracted from the spectra, and a Gaussian is fit to the remaining spectra to define the coherent part. The incoherent part includes the remaining weight after subtraction of the Gaussian. This procedure was performed on Sr$_2$CuO$_2$Cl$_2$, resulting in a ratio of coherent to incoherent spectral weight that varies from 0.6 [$(\pi/2,\pi/2)$] and 0.5 [$(0.7\pi,0)$] for 16 eV photon energy and 2.4 [$(\pi/2,\pi/2)$] and 3.8 [$(0.7\pi,0)$] for 22 eV photon energy [115]. Such a strong effect is not expected to result from a photoelectron matrix element, as the ratio of intensities of the form (2.6.9) given by,

$$\frac{I_{\text{coherent}}}{I_{\text{incoherent}}} = \frac{|\langle \phi_f^k | \mathcal{H}_{\text{int}} | \phi_i^k \rangle|^2 A_{\text{coherent}}(k,\omega)n_F(\omega)}{|\langle \phi_f^k | \mathcal{H}_{\text{int}} | \phi_i^k \rangle|^2 A_{\text{incoherent}}(k,\omega)n_F(\omega)} = \frac{A_{\text{coherent}}(k,\omega)}{A_{\text{incoherent}}(k,\omega)}$$  \hspace{1cm} (4.1.6)

which is independent of the matrix element effect, though this is neglecting final state effects.
Possible explanations for the observation of such dramatic photon energy dependence of the apparent spectral function includes extrinsic final-state effects such as the aforementioned c-axis diffraction or inelastic collisions [120], as well as the possibility of significant final state dispersion. Another possibility is the presence of additional, different, electronic states contributing to the intensity in the incoherent region. An alternative explanation for the complex photon-energy dependence of the matrix elements in Sr$_2$CuO$_2$Cl$_2$ is that it can arise from resonant photo-injection into a surface state, and produce a Fano resonance between the surface channel and the continuum of vacuum plane wave final states [121], however this would require a suitable surface state to exist.

Similar photon-energy dependence has been reported for the EDC lineshape in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [122], and in Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$, suggesting that the ratio of coherent to incoherent weight is photon-energy dependent in this material as well [123]. In addition, LEED I-V curves show significant dispersion and momentum structure in the Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ final states [65].

4.2 LEED and Photon-Energy Dependent ARPES in Underdoped Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$

This section describes the results obtained for ARPES measurement carried out at the Advanced Light Source (ALS) beamline 7.0 : Electronic Structure Factory (ESF), which utilizes an ultra-high vacuum chamber (~ 10$^{-11}$Torr) with motorized 6-axis sample manipulator and helium-flow cryostat in conjunction with monochromatic synchrotron radiation source for photons with energy from 80-1200 eV and flux ~ 10$^{12}$ photons/second, resolving power E/\(\Delta E\) ~8000, and spot size ~ 50\(\mu\)m. ARPES data was collected with a Scienta R4000 analyzer with photon polarization in the plane of detection (p-polarization) and photon incidence at 45° to the sample normal, with the \(\Gamma\)-Y plane oriented in the plane of detection. Measurements were carried out on two underdoped samples of Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$ with \(x=(0.6,0.8)\) with \(T_C = (23\text{K},15\text{K})\), respectively, at temperatures close to 10K.

However, to begin, a LEED image taken with the UBC ARPES system at the relatively large incidence angle of approximately 23° from the sample surface normal helps elucidate the basic structural situation, which is shown in Fig.4.2(a) for the moderately underdoped Bi$_2$Sr$_{1.4}$La$_{0.6}$CuO$_{6+\delta}$. Despite the hemispherical geometry of the LEED screen, the image in (a) possesses a distortion which makes the determination of the spacing of scattering peaks more difficult, though a quadratic distortion correction, analogous the corrections that render raw ARPES data into functions of in-plane momentum and binding-energy, can be applied to remedy this problem, the result of which is shown in Fig. 4.2(b). The momentum scale can thus be determined by the spacing perpendicular to the superstructure peak lines, along the orthorhombic a*-axis or vertical direction in (b), which defines the momentum spacing of 2\(\pi/a^*\) =1.151\(\AA^{-1}\). The resultant cut in (c) demonstrates peak separations in agreement with \(Q_1 =0.280\pm0.015\AA^{-1}\) and \(Q_2 =0.135\pm0.015\AA^{-1}\). The relative peak heights do not distinguish between the basic structure and the \(Q_1\) and \(Q_2\) superstructure peaks, which demonstrates that the structure of the cleaved surface is fully incommensurate, evidencing the complex structural situation in the material to be studied by ARPES.
Fig. 4.2: **Raw LEED image** for underdoped Bi$_{2-y}$Sr$_y$La$_x$CuO$_{6+\delta}$ in (a), with (b) quadratic distortion correction. The LEED cut in (c) with position indicated by the arrow in (b) demonstrates a truly incommensurate structure.
**Fig. 4.3:** Photon energy dependent ARPES Fermi map for the underdoped $\text{Bi}_{2}\text{Sr}_{2-\text{x}}\text{La}_{\text{x}}\text{CuO}_{6+\delta}$ sample in (a,d). (b,e) Corresponding $\Gamma$-Y and (c,f) $\Gamma$-X MDCs are shown at the positions indicated by arrows.
The ARPES Fermi surface mapped with photon energy of 95 and 130 eV for Bi$_2$Sr$_{1.4}$La$_{0.6}$CuO$_{6+\delta}$, with $T_C = 23$K, is shown in Fig. 4.3(a,d). The photon-energy dependence of the ARPES matrix element shows variation nearly everywhere as a function of photoelectron momentum. MDC cuts parallel to the $\Gamma$-X and $\Gamma$-Y directions in Fig. 4.3(b-c,e-f) demonstrate the significant photon-energy dependence of relative intensities among the superstructure replicas. The ARPES Fermi surface mapped with photon energy of 80-130 eV for Bi$_2$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$, with $T_C = 15$K, is shown in Fig. 4.4. The distribution of intensity along the nodal line in p-polarization shows that the even-parity shadow band and the odd-parity main band (+respective replicas) are both suppressed, and only the $Q_2$-replicas of the shadow band has appreciable intensity on this line throughout the range of photon energies 80-130eV.

An interesting resonance at 80eV shows increased intensity at the $\Gamma$-point relative to the other bands, somewhat similar to the effect of photoelectron diffraction, where the free-electron generated by x-ray photoemission is directly diffracted by elastic scattering from a lattice with well-defined periodicity. The photon energy of 80eV corresponds to a wavelength of the photoelectron $2\pi/k_\perp = \sim 1.38\text{Å}$, which is plausible for the onset of photoelectron diffraction since it is shorter than the minimum bond length in the material of around 2Å [59]. However, there is also a general suppression of the other bands at this energy, suggesting the effect may be just due to the suppression of intensity at this photon-energy.

An additional resonance at 100eV contributes sharp features in the Fermi surface that are not visible at the other photon energies, as can be seen in the MDCs in Fig. 4.4(c). The average over photon energies demonstrates a general trend of the suppression of the intensity along the $\Gamma$-Y direction with $k_\parallel$ from the $\Gamma$-point to the $k_F$ of the shadow band near 0.70 Å$^{-1}$.

The ARPES cut along the high symmetry $\Gamma$-Y direction, taken over the range of photon energies from 80-130 eV for Bi$_2$Sr$_{1.4}$La$_{0.6}$CuO$_{6+\delta}$, with $T_C = 23$K, is shown as an integrated cut in Fig. 4.5(b) with corresponding MDCs at several selected binding energies in (a). Nearly all the visible bands are $Q_2$ replicas of the orthorhombicity-produced shadow band, in that their $k_F$ positions lie between the expected position of the shadow band and its $Q_1$ replicas as determined by ARPES on this material at other polarizations and photon-energies.

The predominant feature of the photon energy dependence of the near-$E_F$ MDCs in Fig. 4.5(b) is weak oscillations that are apparent in the band-selected MDC peak height curves (PhD curves) shown in (c). These are obtained from the MDC peak heights, which have a constant baseline subtracted and are normalized to the integrated intensity above $E_F$. The above-$E_F$ intensity is a measure of inelastic electrons produced with a cross-section that is proportional to the incident photon-flux, arising from higher-order light in the incident photon beam. This allows an accurate comparison of ARPES spectra that is independent of the incident flux. It is evident that these curves appear as oscillations with approximately 20eV periodicity.

As in the case of Sr$_2$CuO$_2$Cl$_2$, these oscillations can be compared to the $k_\perp$ periodicity and the corresponding wavelength associated with such periodicity. Using the the kinematic constraint on the total momentum,

$$|k| = \frac{1}{h}\sqrt{2m_eE_K} \quad (4.2.1)$$
Fig. 4.4: Photon-energy dependence of the ARPES Fermi map for the underdoped Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$ sample in (b). (a) The averaged Fermi map over all photon-energies shows sharp features corresponding to peaks in the (c) Γ-Y MDCs.
Fig. 4.5: Photon-energy dependence along high-symmetry Γ-Y. (a) MDCs from $E_F$ to $E_B=30$ meV in 10 meV steps. (b) ARPES Γ-Y cut. (c) PhD curves for bands indicated in (b). (d) Photon-energy dependence of the Γ-Y MDCs.
for free-electron mass $m_e$ and kinetic energy $E_K$, we can separate the momentum into the in-plane and out-of-plane components to obtain,

$$k_\perp = \sqrt{|k|^2 - (k_\parallel)^2}$$

$$= \sqrt{\frac{2m_e E_K}{\hbar^2} - (k_\parallel)^2} \quad (4.2.2)$$

the expression for $k_\perp$ in terms of the kinetic and binding energy and the material work-function, $\hbar \nu = E_K + E_B + \phi_W$. The resultant periodicity corresponds to a length scale of $\sim 12.7\text{Å}$, which agrees well with the distance between CuO$_2$-planes, $c/2=12.29\text{Å}$.

Another photon-energy dependence for the ARPES cut taken parallel to the Γ-Y direction, however in the second Brillouin zone and thus off the high-symmetry plane, is shown integrated in photon-energies from 95-130eV in Fig. 4.6(b), and the corresponding near-E$_F$ MDCs of the integrated cut are shown in (a). More bands are visible compared to the data taken in high-symmetry plane in Fig.4.5. Interestingly the most visible bands in the 2nd Brillouin zone are Q$_1$-replicas of the odd-parity, $X$-centered main-band. This contrasts the situation in the 1st Brillouin zone, where the high-symmetry cut shows mainly the Q$_1$ + Q$_2$-replicas of the even-parity shadow-band. This shows the existence of an effect where the intensity switches from Q$_2$-replica shadow-bands to Q$_1$-replica main-bands when in-plane momentum of the electron picks up the reciprocal lattice vector $2\pi/a^*$. In addition, a dramatic photon-energy dependence of the MDC peak intensity contributes a band-switching effect between the main-band and its Q$_1$-replica in the photon-energy range studied, which can be clearly seen in the photon-energy dependence of the 2nd Brillouin zone Γ-Y $E_F$ MDCs in Fig. 4.6(d). An image plot of these MDCs is shown in Fig. 4.7(a), which highlights the dramatic change in the relative intensity of the bands.

If the material probed by photoemission exhibits a spatial periodicity, then this will produce PhD effects via the ARPES final state, and therefore govern the separation of maxima and minima in the ARPES matrix element. For normal emission of the photoelectron, the intensity maxima are spaced such that the change in perpendicular momentum, $\Delta k_\perp$, due to the change in photon-energy, corresponds to the wavevector of the periodicity ($\Delta k_\perp = 2\pi/\lambda$). This is determined by setting $k_\perp$ in Eq. 4.2.2 to the desired periodicity - which defines an electron kinetic energy as a function of $k_\parallel$,

$$E_K = \left(\frac{\hbar^2}{2m_e}\right)\sqrt{(\Delta k_\perp)^2 + (k_\parallel)^2} \quad (4.2.3)$$

This defines a path in photon-energy ($\hbar \nu = E_K - \phi_W$) and $k_\parallel$ which can be predicted for a corresponding fixed periodicity assigned to $\Delta k_\perp$. All the relevant structural wavevectors can be compared to the energy and momentum dependence of the experimental ARPES intensity contours by these relations.

An example is shown for the photon energy-dependent $E_F$ MDC’s in Fig. 4.7(a). Due to the multiple crystal modulations, Q$_1$ and Q$_2$ in underdoped Bi2201, there are many DR’s at discrete values of $k_\parallel$ at the Fermi surface. If we neglect all other processes which can distribute the intensity
Fig. 4.6: Photon-energy dependence parallel to Γ-Y in the 2nd Brillouin zone. (a) MDCs from $E_F$ to $E_B=30\text{meV}$ in 10 meV steps. (b) ARPES Γ-Y direction cut. (c) PhD curves for bands indicated in (b). (d) Photon-energy dependence of the Γ-Y direction MDCs.
Fig. 4.7: **Image plot of the MDCs** in (a) from 4.6(d) for the 2nd Brillouin zone Γ-Y direction ARPES image. (b) Contours for real space periodicities corresponding to $\Delta k_\perp = 2\pi/b*$ (purple), $2\pi/(c/2)$ (orange), $Q_1$ (green), and $Q_2$ (blue). (c) Overlapping structural contours from removed intensity maxima describe constructive interference in the ARPES matrix element in the presence of multiple coexisting periodic length scales, which explain the main band intensity distribution as corresponding to the effect of simultaneous c-axis and $Q_1$ periodicities.

amongst the various DR bands and only consider the contribution from PhD, then we expect the intensity to be distributed such that when a constant $\Delta k_\perp$ contour in $E_K$ and $k_\parallel$ crosses the discrete $k_\parallel$ position of an occupied band, we expect a local maxima in the intensity at this crossing, both as a function of photon-energy and momentum. However, since the data shown in Fig. 4.7(a) only covers a finite range of photon-energy and momentum, we do not know where to place these contours. To overcome this difficulty, we can assume that the local intensity maxima over the region measured corresponds to a point on the contour of the global constant $\Delta k_\perp$ intensity maxima contour as previously described.

This is demonstrated by the contours of constant $k_\perp$ periodicity shown in Fig.4.7(b), which coincide at the maximum intensity value of the 2nd-order $Q_1$-replicas of the main band nearest the X-point. By considering this point as a maximum, the subsequent maxima generated by real-space periodicities corresponding to $Q_1$, $Q_2$, the CuO$_2$-plane separation, and the b* axis are shown for comparison. The comparison of the experimental intensity distribution of the ARPES matrix-element maxima of the main band and first-order $Q_1$-replica demonstrate agreement with the periodicity generated by the $Q_2$ wavevector, while the main band matrix-element maximum agrees with the periodicity of the $Q_1$ wavevector.

The general picture includes multiple coexisting structural and superstructural periodicities in underdoped Bi2201. This leads to the description of multiple $k_\perp$ periodicities. If we consider a disconnected maxima at another band to correspond to the global constant $\Delta k_\perp$ contour for a different periodicity, then we obtain a description where these contours should be translated to subsequent maxima so the crossings of the contours thus generated reveal the interference effects of the multiple structural periodicities in the ARPES matrix-element, as shown in Fig.4.7(c). This
demonstrates good agreement for the experimental intensity distribution of the maxima in the main band, which thus results from the multiple constructive interference effect of both the c-axis CuO$_2$-plane separation and the Q$_1$ supermodulation.

A similar photon-energy dependence was done at lower energies at the BadElPh beamline of the Elettra synchrotron, using a SPECS Phoibos 150 electron analyzer [124]. Agreement was observed between the ARPES cuts taken from 17-31 eV and the results taken at higher photon-energies for Bi$_2$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$. The low-energy cuts were measured for both s- and p-polarized incident light, along the high-symmetry Γ-Y direction. The photon-energy integrated Γ-Y cut is shown in Fig. 4.8(a,d), together with photon-energy dependence of the MDCs in (b,e), and band-selected MDC peak height curves in (c,f). In s-polarization, the intensity of the main band and its Q$_1$-replicas are enhanced at 25eV photon-energy, while shadow band Q$_1$-replicas near the Γ-point show a clear antiphase relation with the main band features. This antiphase relationship between the main and shadow bands leads to suppression of shadow band features near 25 eV, and enhancement of shadow band features at 19 eV, where the main band Q$_1$-replicas are suppressed. The energy separation of the maxima in the PhD curves in Fig. 4.8(c) is roughly 5 eV, which gives the length scale of 22.9 Å, which matches the wavelength of the Q$_1$ modulation. The main band itself, however, is not suppressed at 19eV, though it is strongly suppressed at 21eV in what appears to be a sharp resonance that could be related to a coherent absorption process specific to this excitation energy (which coincides with the common 21.22 eV HeIα gas emission line used in many ARPES systems.)

An additional behavior is seen in the same PhD in p-polarization shown in Fig. 4.8(f). The antiphase relation between main and shadow band features appears to remain for the Q$_1$-replicas, however it is not seen for all the same bands as in s-polarization, instead revealing an effect where the antiphase relation itself is modulated by 180° as $k_\parallel \rightarrow k_\parallel + Q_1$. The antiphase relation also seems to show a slight offset of around 2eV. Such a spacing in the perpendicular momentum component cannot be explained by the difference in $k_\parallel$ for the closely spaced features, and would point to length scales of roughly 50 Å (though this is at the limit of the energy interval studied). The only comparable structural length scale is the Q$_2$ modulation with wavelength 44.6 Å, corresponding to an energy shift of about 2.5 eV, which is in agreement with the observed offset.

Another interesting aspect of the p-polarization PhD in Fig. 4.8(f) is the intensity modulation of the Q$_2$-replicas of the main and shadow band, which do not show an antiphase relation - in contrast they are exactly in-phase. Furthermore, the Q$_2$-replicas show the same 25 to 19 eV peak-to-peak intensity modulation as the Q$_1$-replicas in s-polarization, which was seen to coincide with the Q$_1$ modulation wavelength. This points to a picture where the Q$_1$-replicas (Q$_2$-replicas) show scattering from the Q$_2$-periodicity (Q$_1$-periodicity), highlighting the important multiple scattering effects inherent to the local symmetry of the electrons being probed.
Fig. 4.8: Photon-energy integrated ARPES cut along the high-symmetry Γ-Y direction in (a) s- and (d) p-polarization, with corresponding MDCs in (b,e) and PhD curves in (c,f).
4.3 Evidence for Parity-Mixing of the Electronic Wavefunction in Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$

In the attempt to unravel the details of the conduction electrons in Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$ (La-Bi$_2$2201), we have measured the ARPES matrix element photon-energy dependence. The underdoped Fermi surfaces in Fig. 4.3 and Fig. 4.4 directly demonstrate the effects of the complex crystal structure on the measured electronic structure, producing many overlapping bands. In addition, the relative intensity of the bands is seen to be strongly dependent on the photon-energy, showing that the matrix element effects are quite complicated.

In order to improve our understanding of these effects, photoelectron diffraction (PhD) curves in the 1st and 2nd BZ, shown in Fig. 4.5 and Fig. 4.6 reveal that multiple scattering effects impart c-axis, as well as in-plane periodicities, to the PhD of the ARPES matrix element. This can be understood as a coherent interference between the plane-wave final states for the photoemitted electrons in the presence of the lattice. Comparison of the photon-energy dependence of the MDCs along the Γ-Y direction in the 2nd Brillouin zone in Fig. 4.7 demonstrates strong PhD effects that can be explained by accounting for interference between multiple structural length scales - $Q_1$, $Q_2$, and $c/2$.

In addition, the low-energy PhD curves in Fig. 4.8 reveal an antiphase relationship, which is itself consistent with the $\pi$-phase shift inherent in parity difference between the two bands, however the modulation of the antiphase relationship as a function of $k_\parallel$ indicates that the relative parity of the two overlapping bands is changing, something that could possibly occur if the glide-plane symmetry was strongly perturbed. The fact that the modulation of the antiphase relationship appears with periodicity $Q_1$ suggests that this modulation is responsible for the mixture of opposite parity states as the result of overlap between relatively strong high-order main and shadow bands.

The polarization-dependence of the ARPES matrix element is also seen in Fig. 4.8, which shows the appearance of additional bands corresponding to the $Q_2$ modulation for p-polarization, as discussed in Chap. 3. However, the fact that this is not simply a parity-switching of the dispersion features is contrary to what is reported in Bi$_{2-y}$Pb$_y$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Pb-Bi$_2$2212), where there are no incommensurate modulations [64], further suggesting that there is parity-mixing of the electronic states in the incommensurate crystal.

The truly incommensurate structure means that the local symmetry of the CuO$_2$-plane in underdoped Bi$_2$2201 cannot be assigned to a specific space-group symmetry [125], but instead must necessarily be represented by a superspace group, which describes the incommensurate crystal as the intersection of a 4-dimensional “supercrystal” with the 3-dimensional space [126]. This leads to the possibility that such a complex structure might permit hybridization between the overlapping bands. In the present case for underdoped Bi$_2$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$, the $Q_1$-replicas ($Q_2$-replicas) show scattering from the $Q_2$-periodicity ($Q_1$-periodicity), highlighting the important multiple scattering effects inherent to the local symmetry of the electrons being probed. These final-state effects are also intimately related to the symmetry of bound-state wavefunctions, since the two must maintain orthogonality in a proper energy-basis.
Temperature Dependence of Underdoped $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$ in the Pseudogap Phase

5.1 Introduction to the Pseudogap Phase

The pseudogap state is an electronic phase found in the underdoped cuprates, characterized by a partial gap in the Fermi surface. All cuprate high-temperature superconductors have shown direct evidence of a temperature-dependent pseudogap, which has been detected in ARPES, tunneling spectroscopy, nuclear magnetic resonance, resistivity, specific heat, Raman scattering, and magnetic neutron scattering [34].

DC resistivity measurements for optimally-doped cuprates show that the normal state resistivity exhibits linear temperature-dependence from 10-1000K, extrapolating to zero resistivity at zero Kelvin - all of which is anomalous when compared to good metals, which show a resistivity that is linear only over a limited range of temperatures, extrapolates to the temperature axis at a fraction of the Debye-temperature, and saturates at high temperature [127, 128]. Notable theories aiming to describe high-temperature superconductivity also predict $\rho \propto T$ behavior, such as quantum percolation theory [129, 130], resonating valence-bond (RVB) theory [131], and the marginal Fermi liquid hypothesis [132].

However, in underdoped materials, the presence of the pseudogap leads to deviations from this simple linear behavior. The experimental observation of a reduced resistivity in $\text{YBa}_2\text{Cu}_4\text{O}_8$ below the same $T^*$ as seen by NMR, was thus connected to the crossover temperature of the spin-lattice relaxation rate coinciding with reduced scattering by spin fluctuations due to the opening of a spin-excitation gap [133]. Similar evidence of a $T^*$ pseudogap has been observed in many cuprates, suggesting a nearly universal phenomenon of a crossover from high-temperature linear temperature-dependence of the resistivity to a low temperature "superlinear" resistivity, onset below $T^*$, and related to the reduced scattering due to the formation of partial excitation-gap "pseudogap" [34].
There are several notable features of the pseudogap such as a $d_{x^2-y^2}$-symmetry, thus $\propto \cos(2\phi)$, varying with the azimuthal angle $\phi$ around the Fermi surface. This is the same symmetry as the superconducting gap, however it is experimentally observed to persist into the normal state above $T_C$, thus leading to the continuous evolution from pseudogap to superconducting gap. The doping dependence of the pseudogap $T^*$ follows a linear trend that decreases with increased hole-doping, becoming tangent to or intersecting the superconducting dome [83]. The temperature scale $T^*$ implies an electronic phase in the high-$T_C$'s characterized by a gap that opens continuously as the temperature is decreased.

ARPES measurement in the pseudogap phase are characterized by the continuous suppression of antinodal spectral weight at the Fermi surface at temperatures below $T^*$ (discussed in section 3.2). Debate has centered on whether the pseudogap is a precursor to superconductivity, or due to spin, charge, or other orderings in addition to superconductivity. Notably, there has been evidence from scanning-tunneling microscopy (STM) for static checkerboard charge-ordering in the pseudogap phase of $\text{Bi}_{2-y}\text{Pb}_y\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, particularly near $p=1/8$ [134, 135], and charge-stripe order has also been seen by neutron diffraction in the nickelates [136, 137, 138], and has been reported in the cuprate $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ at a doping of $p=1/8$ [139]. This is a particularly interesting doping level, as it coincides with a deviation of the doping-dependence of $T_C$ from the Presland parabolic superconducting dome, resulting in the suppression of $T_C$, and has been experimentally measured in many cuprates at $p=1/8$, including $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, $\text{HgBa}_2\text{Cu}_2\text{O}_{4+\delta}$, $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$, and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [140, 141, 142, 143].

ARPES measurement in deeply underdoped $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{CuO}_{8+\delta}$ show a dichotomy between the antinodal gap, which appears at $T^*$ and follows the doping dependence of the $T^*$ energy-scale, and a near-nodal gap, which has a different doping dependence that does not grow with underdoping, and only appears below $T_C$ [144, 145]. ARPES measurements of the spectral gap as a function of the angle around the Fermi surface for the single-layer Bi2201 shows a near-nodal superconducting gap and a much larger antinodal gap that is dominated by the pseudogap, suggesting the two gaps are not related [146]. Sensitive quasiparticle interference measurements with STM show a nodal Bogoliubov gap only in the superconducting state, which contrasts an antinodal pseudogap that involves translational symmetry breaking [147]. In addition, ARPES measurements on $\text{Bi}_{2-y}\text{Pb}_y\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$ have compared the spectral-weight gap at the antinodal region of the Fermi surface in the pseudogap phase, and a coherent peak formed in the superconducting phase, which increases from the node with monotonic $d_{x^2-y^2}$ symmetry, but is suppressed where the antinodal gap is maximum, suggesting that the pseudogap is in competition with superconductivity [148].

Such a two-gap state has also been shown theoretically to arise from coexisting spin-, charge-, and pair-correlations that form stripes, which allows extended quasiparticles along the nodal direction, while states along the antinodal direction are localized on the order of the stripe spacing, suggesting a dichotomy between the localized (delocalized) states near the antinode (node) [149]. However, it was recently argued from detailed doping and temperature dependence of ARPES antinodal EDCs for $\text{Bi}_{2-y}\text{Pb}_y\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$, that a separate pseudogap and second gap contribute to the antinodal Fermi surface - the second gap is onset at a temperature, $T_P$, that scales
with the associated depletion of spectral weight universally for all doping levels [150]. As a result, the second gap was associated with high-temperature preformed-pairing coexisting with pseudogap order, however this assumes the pseudogap opens linearly with temperature. Furthermore, the effect of $T_P$ is not observed for significantly underdoped samples, suggesting that there is no antinodal preformed pairs in addition to the pseudogap for these samples (though $T_P$ was observed just off the antinodal direction).

Recent ARPES measurements on Bi$_{1.5}$Pb$_{0.55}$Sr$_{1.6}$La$_{0.4}$CuO$_{6+\delta}$ have shown an antinodal band back-bending that occurs at a momentum well separated from $k_F$, which has been interpreted as a signature of non-particle-hole symmetry [151]. It was also shown that there is temperature-dependence of the energy position of this back-bending momentum position, which was onset near $T^*$, and thus attributed to the pseudogap. The observation of two energy scales in the EDCs was claimed to show that superconductivity and the pseudogap coexist at the antinode. Finally, agreement between the temperature dependence of the back-bending momentum position and polar Kerr rotation observed in optical experiments led to the connection between the pseudogap and a broken symmetry state (possibly translational or rotational symmetry, however the exact broken symmetry could not be resolved).

The early theoretical predictions of a crossover, between a Cooper paired state and a Bose-Einstein condensate (BEC) state as the pairing coherence lengths are reduced, noted that the high-$T_C$’s were in an intermediate regime of the coherence length suggesting a nontrivial interplay between the pair amplitude and phase coherence [152]. The experimentally observed universal scaling of $T_C$ with the ratio of the carrier density to effective mass [153], has been confirmed by similar theories which attribute the pseudogap to noninteracting electron-pairs [154]. Additionally, it was proposed that the pseudogap state in the cuprates is similar to granular metallic films, where phase coherence is not fully established between the Cooper pairs, despite the presence of a significant number of pairs in the material [155].

Early theories of the pseudogap predicted an important role of spin-correlations from the proximity to the Mott insulator phase, leading for example to the predicted $\pi$-flux phase [156, 157], together with proposed spin-charge separation in the RVB state [15, 23], with possibility of separate transition temperatures for the RVB and BEC states [158], showing the evolution of the RVB state from the doped Mott insulator [159]. A model has been proposed that describes the formation of local spin-charge separated stripes leads to a spin-gap below $T^*$ [160].

In addition, there has been the theoretical prediction that a disorder-rounded transition to a state with $d_{x^2-y^2}$-order, or "d-density wave" (DDW), could be responsible for the pseudogap [161]. In the large-N limit of the $t$-$J$ model, it has been shown that short-range fluctuations of d-density charge order (d-CDW), even without long-range order, can produce $(\pi, \pi)$-scattering which leads to Fermi arcs and a pseudogap, which is diminished as temperature is increased [162, 163].

The contradiction between the Fermi-arcs seen in ARPES and Fermi-pockets from transport, has inspired many proposals attempting to explain the hidden order in the pseudogap phase, which has been comprehensively reviewed by Norman [164]. Recently is was hypothesized that at low hole-doping, that isolated hole-doped sites interact, leading to a splitting of energy levels at the
Fermi surface which is consistent with the pseudogap [165]. However, despite the impressive work that has been done, there is still no consensus on an explanation of the pseudogap state, on both the theoretical and experimental sides.

5.2 Temperature Dependent Density-Wave Periodicity Measured at the Surface by ARPES, LEED, and X-ray Diffraction

5.2.1 Possible Charge-Order in the Cuprates

The underdoped cuprates, with their pseudogap phenomenology [34, 166, 83] and marked departure from Fermi liquid behavior [167], have led to proposals of a wide variety of possible phases ranging from conventional charge and magnetic order to nematic and unconventional density wave instabilities [168, 169, 170, 171, 172, 173, 174, 175, 176, 85, 177, 178, 89, 179, 180, 134, 181, 182, 183, 184, 135, 151, 185]. Despite the extensive theoretical and experimental effort, the generic phase behavior of the underdoped cuprates is still a matter of heated debate, primarily because of the lack of an order parameter that could be universally associated with the underdoped regime of the high-$T_c$ cuprates (HTSCs). For instance, early on evidence was obtained for long-range spin and charge order in the form of uniaxial stripes [169]. However, this phenomenology was only detected in three compounds [169, 186, 187, 188] belonging to the La$_{2-x-y}$(Sr,Ba)$_x$(Nd,Eu)$_y$CuO$_4$ family (Eu-LSCO, Nd-LSCO, LBCO), and was associated with the family-specific reduction of superconducting $T_c$ near 12% doping, the so-called ‘1/8-anomaly’.

More recently, high-field quantum oscillations [89], Hall resistance [91], thermoelectric transport [189], and nuclear-magnetic resonance [190] results on underdoped YBa$_2$Cu$_3$O$_{6+x}$ (YBCO) were interpreted as a signature of a magnetic-field induced reconstruction of the normal-state Fermi surface, suggesting that stripe order and/or a charge-density-wave (CDW) phase might be more general features of HTSCs’ underdoped regime. Interest in this direction has been burgeoning with the latest resonant x-ray scattering (REXS) and x-ray diffraction (XRD) results [191, 192, 193], which provide direct – i.e. structural – evidence for a long-range incommensurate CDW in YBCO around 10-12% hole doping, which shows a suppression for $T < T_c$ and an enhancement with increasing magnetic field. Although this phenomenon bears some differences with respect to charge stripes, a common intriguing aspect is that they both are electronically-driven forms of ordering and appear to compete with superconductivity.

If a CDW phase in underdoped cuprates is universal, it should be observable in compounds with similar doping levels regardless of their structural details. In addition, it is of fundamental importance to connect structural observations (XRD, REXS) to those of electronic probes, such as angle-resolved photoemission (ARPES) and scanning tunneling (STM) spectroscopy. However, for YBCO this might be prevented altogether by the polar instability and self-doping of the (001) surface; in fact, ARPES studies have not detected a Fermi surface reconstruction [167, 94] consistent with either quantum oscillation [89] or x-ray diffraction experiments [191, 192, 193]. To broaden the search and attempt this connection, the most interesting family is the one of Bi-cuprates.
which, owing to their extreme two-dimensionality and natural cleavage planes, have been extensively studied by single-particle spectroscopies [75, 194]. ARPES and STM have provided rich insight into the electronic properties of the CuO$_2$ plane, including signatures of broken symmetries [173, 176, 86, 85, 178, 184, 185, 151] and hints of a ‘pseudogap phase-transition’ [151], although the identification of a bona-fide order parameter has remained elusive. More specifically, in regard to a potentially underlying CDW instability, pristine Bi-cuprates have been shown to exhibit multiple superstructures. While some of these modulations originate from the structural mismatch between BiO and CuO$_2$ lattice planes and hence are non-electronic in origin [75, 76, 195, 64, 1], others have been recognized by STM to evolve strongly with doping and magnetic field [174, 175, 134, 135]; however, their relationship to the ‘structural’ superstructures and the Fermi surface has remained unclear. Our experimental results will provide new and surprising insight in this direction.

Here we study the structural and electronic properties of Bi$_2$Sr$_{2-\delta}$La$_\delta$CuO$_{6+\delta}$ (Bi2201), whose crystal structure exhibits a stacking of well-spaced, single CuO$_2$ layers in the unit cell and a highly-ordered superstructure [1], by means of surface-sensitive photoemission spectroscopy (ARPES) and low-energy electron diffraction (LEED) probes, as well as bulk-sensitive resonant (REXS) and non-resonant (RXD) x-ray diffraction. We focus on the temperature dependence of the electronic structure from under ($p \approx 0.11$, $T_c = 15$ K, UD15K) to nearly optimal doping ($p \approx 0.15$, $T_c = 30$ K, OP30K). We discover a temperature dependent evolution of the CuO$_2$ plane band dispersion and apparent Fermi surface pockets, which is directly associated with the evolution of the incommensurate superstructure. Surprisingly, this effect is limited to the surface (ARPES-LEED), with no corresponding temperature evolution in the bulk (XRD-REXS). The quasilinear, continuous variation of the surface modulation wavelength $2\pi/Q_2$ from $\sim 66$ to 43 Å, below a characteristic $T_{Q_2} \approx 130$ K, provides evidence for a surface-enhanced CDW instability, driven by the interplay of nodal and antinodal Fermi surface nesting.

An important aspect to consider for the study of Bi-cuprates is that these materials are not structurally tetragonal, but instead orthorhombic, with 2 inequivalent Cu atoms per CuO$_2$ plane [75, 76, 195, 64, 1]. This leads to a 45$^\circ$ degree rotated and $\sqrt{2} \times \sqrt{2}$ larger unit cell, as compared to the tetragonal one, with lattice parameters $a^* \cong b^* \cong \sqrt{2} \times 3.86$ Å, where 3.86 Å is the planar Cu-O-Cu distance (note that throughout the paper we refer to the orthorhombic unit cell, with momentum axes expressed in units of $2\pi/a^*$ and $2\pi/b^*$). The orthorhombicity and consequent band backfolding have been shown to be responsible for the observation of the so-called “shadow bands” [64], a replica of the hole-like CuO$_2$ Fermi surface centered at the Γ point, thus settling a longstanding debate on their possible antiferromagnetic origin [66]. In addition, the presence of incommensurate superstructure modulations, arising from a slight lattice mismatch between the BiO layers and the CuO$_2$ perovskite blocks [78], further adds to the complexity of the Fermi surface. As for single-layer Bi2201 specifically, while a single $Q_1$ superstructure vector is known to give rise to additional folded replicas along the orthorhombic $b^*$ axis at optimal doping (OP) [75], two distinct structural modulations with $Q_1$ and $Q_2$ wavevectors arise with underdoping (UD). If these complications are not fully taken into account in analyzing ARPES data, the resulting highly complex Fermi surface appears to be composed of a small set of closed pockets [1].
**Fig. 5.1:** Temperature dependence of the nodal electronic structure of UD15K Bi2201. (a,b) Sketch of one quadrant of the tetragonal Brillouin zone for $T = 100$ and 10 K, respectively. (c,e,f) The region measured by ARPES with various photon energies and temperatures; [(e) and (f) present a comparison for 19 and 8 eV photons]. Momentum distribution curves (MDCs) at $E_F$ for 10 and 100 K are directly compared in (d). The momentum axes are expressed in units of $2\pi/a^*$ and $2\pi/b^*$, where $a^* \approx b^* \approx \sqrt{2} \times 3.86\,\text{Å}$ refer to the orthorhombic unit cell of Bi2201 (3.86 Å is the in-plane Cu-O-Cu distance).

### 5.2.2 Surface-Sensitive Probes: ARPES and LEED

ARPES data from UD15K Bi2201, taken along the nodal direction, is presented in Fig. 5.1. As demonstrated in previous work [1], and here sketched in Fig. 5.1(a,b) for a simpler identification of the various bands, the high crystallinity of these samples allows resolving the Fermi surface of Bi-cuprates to an unprecedented level of detail: the main (M) CuO$_2$-plane band (black solid line), its $Q_1$ and $Q_2$ superstructure replicas stemming from the BiO-layer-induced incommensurate superstructure (red and blue solid lines), and all the corresponding backfolded bands due to the orthorhombicity of the crystal (dashed lines). Furthermore, as shown in Fig. 5.1(c) for UD15K at $T = 100$ K, and emphasized in the highlighted nodal strip in Fig. 5.1(a), by taking advantage of the polarization-dependent selection rules [1] one can selectively suppress the redundant backfolded bands to highlight more cleanly the behavior of main (M) and $Q_1$-$Q_2$ bands. The ability to simultaneously detect all superstructure replicas allows us to uncover – in the temperature dependence – a new and unprecedented aspect of the data: while the position of the main CuO$_2$ band is completely temperature independent, between 100 and 10 K there is a significant shift in momentum of only (and all) the $Q_2$-related bands [see Fig. 5.1(e) and (f), and Fig. 5.1(d) for the direct comparison between 10-100 K momentum distribution curves (MDCs) at $E_F$]. This is summarized in the 10 K Fermi surface sketch of Fig. 5.1(b), which illustrates that a critical consequence of this effect is a seeming volume change of all ostensible Fermi surface pockets defined by the various backfolded bands, despite the fact that the actual number of carriers is not changing at all.

The ARPES results are complemented by a detailed analysis of the superstructure diffraction
Fig. 5.2: Temperature dependence of the superstructure modulations of UD15K Bi2201. (a) Typical LEED pattern measured at $T = 6$ K. The rectangular box in (a) highlights the region shown in detail for $T = 150$ K and $T = 6$ K in (b) and (c), respectively. In (b,c) symbols represent the data from a vertical cut along the center of the box in (a), while blue and red curves are a Voigt fit of the $Q_1$ and $Q_2$ superstructure peaks. (d) Length of the $Q_1$ and $Q_2$ superstructure vectors in Å$^{-1}$ versus temperature, as inferred from LEED and ARPES-MDC analysis at 21 eV photon energy (and in agreement with ARPES from 7 to 41 eV). Note that, for the almost temperature independent $Q_1$, half of the actual value is plotted for a more direct comparison with $Q_2$ and only the LEED data are shown (the ARPES data are equivalent and thus omitted).

vectors from LEED. On UD15K at 6 K, rather than individual Bragg peaks [Fig. 5.2(a)], the experiment gives lines of $Q_1$ and $Q_2$ fractional spots along the orthorhombic $b^*$ axis. From the fit of the LEED data [Fig. 5.2(c)], we obtain the values $Q_{1K}^6 = 0.285\pm0.015\text{Å}^{-1}$ and $Q_{2K}^6 = 0.142\pm0.015\text{Å}^{-1}$. Also LEED, on this highly-resolved superstructure, reveals a remarkable temperature dependence [Fig. 5.2(b) and (c)]. Consistent between LEED and ARPES-MDC analysis [Fig. 5.2(d)], while $Q_1$ is virtually temperature independent from 5 to 300 K, $Q_2$ increases with respect to its high-temperature value $Q_{2300K}^3 = 0.095\pm0.015\text{Å}^{-1}$ below a $T_{Q_2} \simeq 130$ K. The evolution of $Q_2$ – as seen by both electronic and structural probes – implies an inter-unit-cell structural and/or electronic modulation, with a wavelength $2\pi/Q_2$ evolving from 66 to 44 Å (i.e. from 12 to $8\times b^*$) upon cooling from 130 down to 5 K.

5.2.3 Bulk-Sensitive Probes: XRD and REXS

The surface sensitivity of ARPES and LEED calls for an investigation of the same phenomenology by means of light scattering spectroscopies, which are known to probe materials deeper in the bulk. In the following discussion, we will refer to reciprocal space coordinates as $H^*$, $K^*$, $L$ (representing the reciprocal axes of respectively $a^*$, $b^*$, $c$), and reciprocal lattice units will be used. At all photon energies it is possible to clearly identify the near period-4 $Q_1$ modulation. REXS maps taken on UD15K Bi2201 at the Cu, La, and O soft x-ray edges all exhibit a clear enhancement at this wavevector. This confirms that the corresponding modulation is present throughout the unit cell, and therefore also in the CuO$_2$ plane, explaining the strong folded replicas observed in ARPES. However, modulations with longer periods are not detected. These can be probed by XRD maps measured at 17 keV photon energy, thus revealing a much larger portion of reciprocal space, as
Fig. 5.3: X-ray measurements of the superstructure modulations in UD15K Bi2201. (a) 3D view of the basal planar sections of XRD maps at $E_{ph} \sim 17$ keV (only positive axes are shown). (b) Stack of constant-H$^*$ slices, showing the appearance of period-8 diffraction rods for H$^*$ = 1, 2. (c) Zoomed view of corresponding region of interest in (b) for the H$^*$ = 2 slice. (d) Schematic cartoon explaining the multiple features that are visible in (c); Bragg peaks (blue circles) correspond to integer K$^*$, L orders, Q$_1$ (black crosses) are the 1/4-order peaks, while Q$_2$ (red ellipses) are the 1/8-order peaks. (e) RSXS map acquired on Cu K edge ($E_{ph} \sim 8.9$ keV) at 6 K, representing a K$^*$-L plane at H$^*$ = 1. (f) Same as (e), but acquired at 120 K.

shown in Fig. 5.3(a-c) for T=300 K. The H$^*$-K$^*$ section in Fig. 5.3(a), which can be compared to the LEED map in Fig. 5.2(a), also features a multitude of superstructural satellite peaks along K$^*$ (the Bragg peaks being the most intense ones). Fig. 5.3(b) displays a stack of K$^*$-L sections, taken at H$^*$ = 0, 1, 2 going from bottom to top. Diffraction slices at H$^*$ = 1 and 2 reveal the presence of new features exhibiting a peculiar elongation along L and with K$^*$ = $(2n+1)/8$, thus incompatible with a period-4 superstructural peak or any of its harmonics (no similar features are found for H$^*$ = 0, thus explaining the lack of period-8 rods in soft x-ray REXS). Different orders of this period-8 modulation can be seen when zooming in to the H$^*$ = 2 slice in Fig. 5.3(c), with their assignment given more schematically in Fig. 5.3(d). These are located at positions $Q^{ij}_2 = n \mathbf{G} \mp i Q_1 \pm j Q_2$, where G is a reciprocal lattice vector, Q$_1$ = 1/4 $\hat{a}$K$^*$, and Q$_2$ = 1/8 $\hat{b}$K$^*$ (corresponding to the ARPES and LEED low-temperature $Q^{2K}_2$ value). Notably, the same features can be seen in resonant scattering at Cu and Bi deeper edges (i.e., in the hard x-ray regime). Fig. 5.3(e,f) show corresponding K$^*$-L sections (H$^*$ = 1), taken at the Cu-K edge at low (6 K) and high (120 K) temperature, respectively. Similar results were obtained at the Bi-L$_3$ edge and off-resonance.

The intensity of the Q$^{ij}_2$ rods is approximately 1 order of magnitude smaller than the most intense Q$_1$ peak, within the same K$^*$-L sections. Considering the large probing depth of hard x-rays, this intensity ratio is too large to identify these as crystal truncation rods, or ascribe them to surface modulations. These period-8 spots therefore originate from an additional supermodulation which must be present in the bulk of the material, and characterized by poor c-axis coherence, as the elongated structure suggests. On the other hand, these features exhibit long-range order in the a*-b* plane, as evidenced by their well-defined shape in H$^*$-K$^*$ sections, with correlation lengths $\xi > 100 \times b^*$.

To summarize the findings from XRD and REXS on UD15K, no significant temperature de-
dependence is observed between 300 and 6 K in all scans (more temperature points were taken both in XRD and REXS), neither in the peak positions nor in the relative intensities. Altogether, these results suggest a scenario contemplating the presence of an additional bulk supermodulation with a well-defined periodicity along $b^*$ ($\sim 8$ lattice periods), stable over a broad range of temperatures, and characterized by large correlation lengths within the (001) planes but poor coherence perpendicular to them.

5.2.4 Surface/Bulk Dichotomy and CDW Formation in Underdoped Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$

The combination of surface (ARPES, LEED) and bulk (XRD, REXS) sensitive probes has enabled us to establish that $Q_1$ and $Q_2$ superstructure modulations are present both in the bulk and at the surface of underdoped Bi2201, close to 1/8 doping. In addition, we have uncovered an unprecedented bulk-surface dichotomy in the temperature dependence of the superstructure modulations and corresponding electronic structure. While no dependence is observed for the $Q_1$ and $Q_2$ superstructure in the bulk and also for $Q_1$ at the surface, we detected a pronounced temperature evolution associated with the surface $Q_2^{\text{surf}}$. The dependence of the $Q_1/Q_2^{\text{surf}}$ ratio versus temperature is summarized in Fig. 5.4 and allows some important phenomenological observations: (i) The temperature dependence of $Q_2^{\text{surf}}$ below $T_{Q_2}$ shows commensurability with the static $Q_1$ modulation, as evidenced by the $Q_1/Q_2^{\text{surf}}$ ratio varying from 3 to 2 over a range of 130 K. (ii) The evolution of $Q_1/Q_2^{\text{surf}}$, and similarly $\Delta k_F$, exhibits transient lock-in behavior when the wavelength of the $Q_2^{\text{surf}}$ modulation is commensurate with the orthorhombic lattice: $2\pi/Q_2^{\text{surf}} = n \times b^*$, with $n$ ranging from 12 to 8. A similar type of behavior has been observed for charge-stripe order in La$_2$NiO$_{4+\delta}$ from neutron scattering [196]. (iii) In analogy to what was reported for manganites [197], the continuous evolution of incommensurate wavevectors over a wide temperature range hints at competing instabilities, which can lead to a soft electronic phase. (iv) Finally, the fact that at low-temperature (LT) also $Q_2^{\text{surf,LT}} \simeq Q_2^{\text{bulk}}$ indicates a direct connection between the bulk and surface modulations.

As shown by the comparison of LEED and theoretical ($V_B = 0$, see below) results for the evolution of $Q_1/Q_2^{\text{surf}}$ in Fig. 5.4, this behavior is well captured by a phenomenological Ginzburg-Landau description based on the minimization of the surface free energy, and is thus consistent with an incipient CDW instability at the surface (the agreement can be further improved to reproduce also the orthorhombic structure commensurability effects, e.g. $n \times b^*$ steps in Fig. 5.4, via the inclusion of corresponding lattice potentials; see Sec. 5.3 for a complete treatment). As for the specific high- and low-temperature values observed for the surface CDW modulation on UD15K, $Q_2^{\text{surf,HT}} \simeq 0.095 \text{ Å}^{-1}$ and $Q_2^{\text{surf,LT}} \simeq 0.142 \text{ Å}^{-1}$, these are associated with competing Fermi surface nesting instabilities of the $Q_1$-modulated orthorhombic crystal structure. The electronic susceptibility has been calculated for various doping levels starting from an electronic structure comprised of main, shadow, and $Q_1$-folded bands and is shown for $p = 0.12$ and 0.14 in the right-hand side panel of Fig. 5.4. Two peaks occur in the susceptibility at $q = 0.095$ and 0.140 Å$^{-1}$ for $p = 0.12$, closely matching the
**Fig. 5.4:** LEED $Q_2$ mean-field theory for UD15K Bi2201. Temperature evolution of the $Q_1/Q_2$ ratio, as inferred from the LEED data in Fig. 5.2, compared to the evolution of the mean-field predicted wavevector that minimizes the free energy (see Sec. 5.3 for details); dashed lines indicate when the modulation associated with $Q_2$ becomes commensurate with the underlying orthorhombic lattice $Q_2 = (2\pi/b^*)/n$, for various values of $n$. The colored curves demonstrate the effect of increasing $V_B$, showing the bulk structure can pin the CDW to suppress the temperature dependence of $Q_2$. The susceptibility demonstrates the doping dependent electronic instability towards the low- and high-temperature $Q_2$ value.

UD15K results, and allow associating $Q_2^{\text{surf,HT}} \approx Q_1/3$ and $Q_2^{\text{surf,LT}} \approx Q_1/2$ with *nodal* and *antinodal* Fermi-surface *nesting*, respectively. These nesting instabilities are very sensitive to the hole doping, especially for the steeper nodal dispersion; as shown in Fig. 5.4, for $p = 0.14$ the nodal peak is already mostly suppressed while the antinodal one splits and broadens, and both peaks vanish at optimal doping.

This is qualitatively consistent with the doping trend we have observed experimentally: while the $Q_1$ modulation survives all the way to optimal doping ($Q_1 \approx 0.280$ and 0.273Å$^{-1}$ for UD23K and OP30K, respectively), the $Q_2$ modulation is substantially weakened and temperature independent on UD23K ($Q_2 \approx 0.135\text{Å}^{-1}$), and can no longer be detected in either LEED or ARPES on OP30K.

Most importantly, this identifies the temperature dependent $Q_2$ surface CDW as a phenomenon limited to the underdoped regime, near 1/8 doping.

Finally, in the Ginzburg-Landau description we can also include the effect of the bulk potential $V_B$ associated with the ‘static’ $Q_2^{\text{bulk}}$ modulation as determined by x-ray diffraction ($V_B = |V_{Q_2}|$, with $V_{Q_2}$ as defined in Sec. 5.3). As shown by the simulated colored traces in Fig. 5.4, incorporating this potential causes the CDW to lock in to the bulk structural modulation wavevector $Q_2^{\text{bulk}} = Q_1/2$, thus suppressing the temperature-dependence. The two regimes $V_B = 0$ and $V_B \gg 0$ represent the temperature-dependent-surface and temperature-independent-bulk limiting cases, providing agreement with the results of ARPES-LEED on the surface and XRD-REXS for the bulk. Intermediate values of $V_B$ describe the subsurface region, which shows a CDW with reduced dependence on temperature, and instability towards first-order lock-in transitions to the $Q_2^{\text{bulk}}$ wavevector (Fig. 5.4).
5.2.5 Conclusions on Incipient CDW Order at the Surface

The temperature dependent evolution of the CuO$_2$ plane band dispersion and $Q_2$ superstructure on the highly-ordered Bi2201 surface can be understood to arise from the competition between nodal and antinodal Fermi surface nesting instabilities, which give rise to a dynamic, continuously evolving wavevector. This also indicates that such a remarkable electron-lattice coupling is directly related to the ordinary, static $Q_1$ superstructure - as a necessary precursor to Fermi surface nesting at the low- and high-temperature $Q_2^\text{surf}$, and giving rise to commensurability effects. Since the nodal nesting-response is very sensitive to the hole-doping, this also explains why the surface temperature-dependence disappears towards optimal doping. This establishes the importance of surface-enhanced CDW nesting instabilities in underdoped Bi-cuprates, and reveals a so-far undetected bulk-surface dichotomy. The latter is responsible for many important implications, such as the temperature-dependent volume change of all apparent Fermi surface pockets in ARPES, and could play a hidden role in other temperature-dependent studies.

5.3 Ginzburg-Landau Mean Field Model for Density-Wave Order in Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$

5.3.1 Introduction to Ginzburg-Landau Mean Field Theory

Mean-field theory has been well utilized since the work of Landau, and has since been expanded and applied to describe many thermal and statistical systems, which typically possess phase transitions and ordering behavior. In particular, Ginzburg-Landau mean-field theory is used to explain the onset of a charge-density-wave (CDW) below a critical temperature, with a wavevector and amplitude given by the microscopic details of the problem [198, 199, 200, 201]. More recently, Ginzburg-Landau theory was also shown to be effective at describing a soft electronic phase [197], in which an additional interplay with magnetic order leads to charge-ordering with doping- and temperature-dependent wavelength.

To relate to the temperature-dependence of $Q_2$ in our measurements of underdoped Bi2201, we have constructed a similar mean-field free-energy functional $F[\psi]$ [198, 199, 200, 201] and solved this model based on numerical minimization of $F$ with respect to its order parameter $\psi$. The main result of this study is to connect the $Q_2$ temperature-dependence observed with LEED to the temperature-dependent harmonic content of the CDW. In addition, the calculation of the Fermi surface nesting susceptibility function provides information regarding the low and high-temperature endpoints of the observed temperature-dependence. Note that, in relation to $T^*$ and the pseudogap in the underdoped cuprates, our model does not incorporate any additional order parameter besides the CDW and a static $Q_1$ modulation.
5.3.2 Mathematical Models for the Mean-Field Free Energy

The order parameter of the model is the charge-density, which is Fourier transformed according to:

\[ n(x) = \sum_q n_q e^{iqx}, \]  

(5.3.1)

so that the problem can be reformulated in momentum coordinates. Only the even-order terms in the free-energy are considered (due to symmetry between positive and negative CDW amplitude as described in Ref. [200]), of the form:

\[ F_2 = \sum_q f_q |n_q|^2 \]

\[ f_q = A_q \left( \frac{q}{Q_0} - \frac{Q_0}{q} \right)^2 + B \]

(5.3.2)

\[ F_4 = C \int n(x)^4 dx. \]

The second-order \( F_2 \) term is a summation of \( f_q \), which contains a combination of a gradient-term (\( \propto q^2 \)) preventing short wavelength oscillations, and a Coulomb term which screens long wavelength oscillations (\( \propto 1/q^2 \)), so that \( f_q \) is minimized by \( q = Q_0 \), a temperature-independent wavevector set by the microscopic details. The factors \( A_q \) and \( C \) are also temperature-independent and positive, and \( B \) is linearly dependent on temperature and changes sign at the CDW critical temperature: \( B \to \tilde{B} (T - T_{CDW}) \) [201]. Fig. 5.5 shows the shape of the \( f_q \) potential, which implies that for \( T < T_{CDW} \) the system can lower its free-energy by having nonzero CDW amplitude for wavevectors in the range corresponding to the shaded region (i.e. when \( f_q \) is negative, which requires that \( B/A_q < 0 \)).

Recall that the summation over wavevectors in \( F_2 \) is due to the Fourier-transform of the charge-density in Eq. 5.3.1. However, if the charge-density is a periodic function \( (q = 2\pi/\lambda) \), it can be represented as a Fourier-series:

\[ n(x) = \sum_{j=-\infty}^{\infty} n_j e^{i(jq)x}, \]

(5.3.3)

which naturally leads to the notion of harmonics, which have shorter wavelengths corresponding to integer multiples of the wavevector, \( j \neq q \). This allows us to mathematically treat a single, general waveform for the charge-density as a superposition of these harmonics. The free-energy \( F_2 \) in Eq. 5.3.2 therefore involves the summation of \( f_q \) evaluated for the harmonics. This gives terms in the free-energy \( \propto f_{jq} \), which are minimized by wavevector \( q_0 \) satisfying \( j \neq q_0 = Q_0 \). Thus the \( f_{jq} \) term is negative for wavevectors between the two values \( q_j^\pm \) given by:

\[ \frac{q_j}{Q_0} = \frac{1}{j} \sqrt{1 - 2\beta \pm 2\sqrt{\beta^2 - \beta}} ; \beta \equiv B/4A_q. \]

(5.3.4)

In the quadratic term \( F_2 \), the wavevectors \( q_j^- \to q_j^+ \) (for \( j \)th harmonic) set the range for energetically
favorable CDW amplitude, as a function of the temperature ($T \propto \beta$ in Eq. 5.3.4).

The fourth order term $F_4$ prevents divergence of the amplitude of $n(x)$. Together with the lack of a third-order term in the free-energy [200], this leads to a situation where only odd harmonics of the charge-density-wave occur in the wavevector expansion of the free-energy; for the other terms, the phase factors of the momentum representation of $n(x)^4$ terms do not cancel, and the integral in Eq. 5.3.2 is oscillatory and averages to zero. These considerations allow us to rewrite (5.3.1) as:

$$n(x) \to \sum_m n_m e^{imqx}; \quad m = \pm 1, \pm 3, \pm 5, ...$$  \hspace{1cm} (5.3.5)

Furthermore, since we expect the charge-density $n(x)$ to be a real function, this gives the requirement that $n_q = n_{-q}$. When we compute $F_4$ in momentum-space, we obtain the following integral:

$$C \int dx \sum_{m_1...m_4} n_{m_1} n_{m_2} n_{m_3} n_{m_4} e^{iqx(m_1+m_2+m_3+m_4)}. \hspace{1cm} (5.3.6)$$

This results in the condition that $m_1 + m_2 + m_3 + m_4 = 0$, however since $n_q = n_{-q}$, we are free to switch the sign of any $m_i$, so that we may instead write $m_1 + m_2 + m_3 - m_4 = 0$, and all other combinations of signs, which we can satisfy for certain combinations of positive and odd $m_i$. This yields:

$$F_4 \to C \sum_{m_1...m_4} n_{m_1} n_{m_2} n_{m_3} n_{m_4} \cong C(\sum_i n_i)^4,$$ \hspace{1cm} (5.3.7)

(i odd and positive)

leading to the free-energy functional that is sufficient to describe the experimental wavevector from

---

**Fig. 5.5:** $f_q$ profiles for several values of $B/A_q = -2, 0, 2$ (blue, green, and red curves, respectively). The shaded region shows the range of wavevectors, $q^- \rightarrow q^+$ for the 1st harmonic, for which the system can lower its energy by having a nonzero CDW amplitude.
LEED on underdoped Bi2201, by identifying the wavevector $Q_0 \rightarrow Q_1$:

$$F = \left( A_1 \left( \frac{q}{Q_1} - \frac{Q_1}{q} \right)^2 + B \right) |n_1|^2$$

$$+ \left( A_3 \left( \frac{3q}{Q_1} - \frac{Q_1}{3q} \right)^2 + B \right) |n_3|^2$$

$$+ C(n_1 + n_3)^4.$$  \hspace{1cm} (5.3.8)

Note that the right-hand side in Eq. 5.3.7 is written as approximate because it includes cross-terms which do not satisfy the constraint that the subindex sum is zero, and which will cancel in the integral Eq. 5.3.6. Here we consider only the first and third harmonics, then we just have one extra term of this kind, $4Cn_3^3n_1$. In Eq. 5.3.8 we keep the full term corresponding to the approximation in Eq. 5.3.7. This is due to the short correlation lengths observed for the temperature-dependent wavevector in ARPES and LEED, which are connected to finite-size effects resulting in a flattening of the free-energy near the minimum (see Sec. 5.3.6).

In order to compare with the experimental finding of commensurability effects in the LEED wavevector temperature-dependence, the model of Eq. 5.3.8 is supplemented by potentials which can account for the attractive forces experienced when the lattice is commensurate with the CDW (integer multiple of the wavelength), as well as the repulsive forces for intermediate wavelengths (incommensurate, non-integer). Commensurability with the bulk $Q_2$ modulation, as found by x-ray diffraction, arises naturally by considering an additional, periodic potential:

$$F_{Q_2} = \int V(x) n(x) \, dx$$

$$= \int V_{Q_2} e^{iQ_2 x} n(x) \, dx \simeq \frac{V_{Q_2} n_1}{\epsilon + |q - Q_2^{\text{bulk}}|}.$$  \hspace{1cm} (5.3.9)

Where the additional $\epsilon$ term is needed to turn the singularity at $q = Q_2^{\text{bulk}}$ into a finite peak, for numerical convergence, and only includes the first harmonic, $n_1$, as there is no need to consider higher harmonics matching $Q_2^{\text{bulk}}$, which would lead to a first harmonic with unnecessarily long wavelength ($q << Q_2^{\text{bulk}}$). For negative $V_{Q_2}$ the system is attracted to the $Q_2^{\text{bulk}}$ wavevector, which is favored when $V_{Q_2}$ is larger in magnitude than the energy cost from the other terms in the free-energy.

The effect of the $Q_2^{\text{bulk}}$ potential, $V_{Q_2}$, is shown in Fig. 5.6, for various strengths of the potential. This potential causes the CDW to lock in to the bulk structural modulation wavevector ($q = Q_2^{\text{bulk}}$), and acts to suppress the temperature-dependence. The limiting cases $V_{Q_2} = 0$ and $V_{Q_2} >> 0$ represent the surface (LEED/ARPES) and bulk (REXS/XRD) temperature-dependence, respectively. Intermediate values of $V_{Q_2}$ describe the region just below the surface, which shows a CDW with reduced dependence on temperature, and instability towards first-order lock-in transitions to the $q = Q_2^{\text{bulk}}$ wavevector. An additional potential can be added to account for the tendency of the
Fig. 5.6: The effect of the $V_{Q_2}$ potential for the structural bulk $Q_2$ wavevector, showing suppression of the temperature-dependence of the CDW wavevector. Here $(V_L, V_{Q_1})=(0, -0.15)$, and the red, magenta, orange, cyan, green, blue, purple, and black curves correspond to $V_{Q_2}/A_1=0$, -0.2, -0.5, -1, -1.5, -2, -2.5, and -3 respectively. The jump in the wavevector for nonzero $V_{Q_2}$ shows the pinning of the CDW to the bulk $Q_2$ structure near $Q_1/2$, with complete suppression of the temperature-dependence beyond $V_{Q_2}/A_1=-3$.

CDW to be commensurate with the orthorhombic lattice periodicity [201]:

$$F_L = V_L \left(n_1^2 + n_3^2 + \cdots \right) \cos\left(\frac{2\pi G}{q}\right),$$  \hspace{1cm} (5.3.10)

where $G$ is a reciprocal lattice vector, such that with the inclusion of $F_L$ in the free-energy, the system is weakly attracted to wavevectors for which $q = G/j$, for integer $j$, provided that $V_L$ is negative. These wavevectors correspond to a CDW wavelength that is an integer multiple of the lattice constant, $\lambda_{CDW} = j \times b^*$. A similar potential can be included for the static $Q_1$ modulation observed in Bi2201, which is identical except for the replacement $G \rightarrow Q_1$:

$$F_{Q_1} = V_{Q_1} \left(n_1^2 + n_3^2 + \cdots \right) \cos\left(\frac{2\pi Q_1}{q}\right).$$  \hspace{1cm} (5.3.11)

Recall that the wavevector from the experiment shows commensurability with both the lattice and $Q_1$. The endpoints of the temperature-dependence occur at $q = Q_1/2$ and $q = Q_1/3$, and this commensurability to $Q_1$ is already present in the free-energy of Eq. 5.3.8. However, the additional commensurability potential in Eq. 5.3.11 accounts for a weak repulsion on intermediate wavevectors (incommensurate with $Q_1$).

5.3.3 Model Free Energy Results

Fig. 5.7 shows the CDW wavevector obtained by numerical minimization of the free-energy for the first and third harmonic only, in the temperature region $0 < T < T_{CDW}$. The parameter values $A_1 = 162$ and $A_3 = 2.05 \times A_1$ were chosen to have $T_{CDW} \geq 300K$, following the fact that we observe $Q_2$ with LEED up to room temperature, and to scale the temperature of the model to that of the...
Fig. 5.7: CDW wavevector obtained by numerical minimization of the free-energy for the first and third harmonic only. The blue curve is for \((V_L, V_{Q_1}) = (0, 0)\), and the red curve has \((V_L, V_{Q_1}) = (-4, -0.15)\). \((A_1 = 162, A_3 = 2.05 \times A_1, C = 200, Q_0 = 1)\)

ARPES/LEED experiments (see Sec. 5.3.6). The potential \(V_B\) is zero to model the surface of the crystal, and the results for both \((V_L, V_{Q_1}) = (0, 0)\) and \((V_L, V_{Q_1}) = (-4, -0.15)\) are shown in Fig. 5.7. The \(V_{Q_1}\) potential has a moderate flattening effect on the shape of the temperature-dependence of the CDW wavevector between \(Q_{1}/2\) and \(Q_{1}/3\), and improves the agreement with the experiment. Additional inclusion of the lattice commensurability potential, \(V_L\), creates inflection points in agreement with the LEED temperature-dependence. Altogether this indicates that, for Bi2201, there is a tendency of the CDW towards commensurability with both the periodic lattice distortion, \(Q_1\), and the orthorhombic lattice.

5.3.4 Calculation of the Tight-Binding Susceptibility

In addition the electronic susceptibility, or Lindhard function,

\[
\chi_0 = \sum_k \frac{n_F(\epsilon_{k+q}) - n_F(\epsilon_k)}{\epsilon_k - \epsilon_{k+q}},
\]

has been calculated for various doping concentrations, particularly \(p=0.12\) and \(p=0.14\), from the tight-binding Fermi surface with hopping parameters extracted from the experimental ARPES Fermi surface [1] to accurately reproduce nesting for this material. The tight-binding model used for the calculation is depicted in Fig. 5.8(a) for \(p=0.12\), and includes the main band and shadow band, plus their \(Q_1\) replicas. The calculation is performed as described in Ref. [202], and the result is shown in Fig. 5.8(b). Two important nesting susceptibility peaks occur at \(q=0.095\) and \(q=0.14\), which closely match the low and high-temperature values of the \(Q_2\)-wavevector measured in the experiment. The effect of doping was incorporated by a shift of the chemical potential in the tight-binding model, thus changing the size of the Fermi surface, and resulting in the suppression of the \(Q_{1}/3\)-peak and a gradual splitting of the \(Q_{1}/2\)-peak (see again Fig. 5.8(b)). This suggests that the \(Q_{1}/3\) instability only exists in a narrow range of dopings, and the \(Q_{1}/2\) peak in a comparatively

82
Fig. 5.8: **Tight-binding fit** of the experimental Fermi surface (a) for underdoped Bi2201, (x=0.8, p=0.12). The main band and its $Q_1$ replicas are shown in red, while those for the shadow band are shown in blue. Nesting-susceptibility calculated from the tight-binding Fermi surface (b) is shown at two doping levels. There are two peaks near $q=0.95$ and $q=0.14$, corresponding to nodal and antinodal nesting, (c,d) respectively. The weaker nodal peak disappears with increased hole-doping, while the antinodal peak splits into two smaller peaks.

larger range of dopings, near $p=1/8$. In particular, we report that the $Q_1/3$-peak arises from nodal nesting between the main (shadow) band and the $Q_1$ replica of the shadow (main) band as shown in Fig. 5.8(c), while the $Q_1/2$-peak comes from antinodal nesting between the main (shadow) band and its own $Q_1$ replica, Fig. 5.8(d).

### 5.3.5 Discussion of Mean Field Model and Tight-Binding Susceptibility Results

There are several important features of the mean-field model described here, in relation to the non-trivial temperature-dependence of the CDW wavevector, which arise due to interaction between the two lowest harmonics. The interplay of the CDW harmonics is connected with the influence of the structural $Q_1$ modulation on the third CDW harmonic, $3 \times Q_2^{\text{surf,HT}} = Q_1$ at higher temperatures. Flattening the free-energy near the stable minimum results in enhanced interaction between harmonics of the surface CDW state, which is marked by a large temperature-dependence of the CDW wavevector, whose slope increases at low-temperatures. The reduction in the $3^{rd}$ harmonic content at low-temperatures leads to a dramatic steepening of the charge-driven temperature-dependence of $Q_2^{\text{surf,LT}}$ at low-temperature, when it is near $Q_2^{\text{bulk}} = Q_1/2$. This suggests that the surface experiences finite-size effects that result in a flattening of the energy-landscape, indicating electronic phase competition (see Sec. 5.3.6 for details). Comparison to the measured wavevector from ARPES
Incorporating the effect of a periodic bulk potential, with wavelength $Q_2^{\text{bulk}} = Q_1/2$ as determined by x-ray diffraction in underdoped Bi2201, results in suppression of the temperature-dependence. This suppression is related to the $Q_2^{\text{bulk}}$ modulation, which pins the CDW wavevector to the structural modulation in the underlying bulk, resulting in temperature-dependence of the CDW wavevector occurring only near the surface, and thus leading to a static bulk structure and charge-density wave, while the surface can evolve energetically. A nesting-driven, electronic response peak at the Fermi energy is apparently connected to the bulk supermodulation and the surface CDW at low-temperature ($Q_2^{\text{bulk}} = Q_2^{\text{surf} \cdot \text{LT}} = Q_1/2$), and at high-temperature ($Q_2^{\text{surf} \cdot \text{HT}} = Q_1/3$). This leads to the possibility that there are a number of instabilities driven by nodal and antinodal Fermi surface nesting, related to the bulk orthorhombic distortion and $Q_1$ modulation, and the resulting CDW wavevector is dynamically chosen by the temperature-dependence of the surface CDW harmonic content and commensurability, which only occurs with the susceptibility peaks near the doping level of $p=1/8$. As a final remark, we note that the apparently weaker $Q_1/3$ peak in the (nodal) nesting susceptibility does not necessarily correlate to the strength of the instability, as has been noted in the chalcogenide CDW superconductors [203].

5.3.6 Finite-Size Effects and Flattening of the Free Energy Landscape

As mentioned in Sec. 5.3.2, the approximation in Eq. 5.3.7 involves an additional term in the free-energy, $4Cn_3^3n_1$, which is forbidden by the integration in Eq. 5.3.6. Re-including only the lowest order term that is excluded, can be understood to originate from finite-size effects connected to the short coherence-lengths seen in ARPES and LEED for the surface. The LEED spots have a half-width at half-maximum corresponding to a coherence-length of $\sim 15\text{Å}$, so that the electronic coherence-length is smaller than the $Q_2$ wavelength ($\sim 45\text{Å}$ at low-temperature). The short LEED coherence-length could be caused by the formation of domains with random local deviation in the $Q_2$ value, for instance due to impurities. The finite domain variations in the integral (5.3.6) will reintroduce these forbidden terms, in particular the lowest order ones, that contain the longest wavelength oscillation in the integrand of Eq. 5.3.6. This suggests that an impurity driven “finite-size” interaction between the CDW harmonics can play a role in the soft-wavevector phase. This is also consistent with the bulk/surface dichotomy that is observed, as the coherence lengths for $Q_2$ from bulk x-ray measurements are an order of magnitude larger ($\sim 500\text{Å}$) than those seen with surface-sensitive probes ($\sim 50\text{Å}$).

Fig. 5.9(a-c) shows that a well-shaped minimum of the free-energy occurs at a particular wavevector, $q$, and charge-density amplitudes, $n_1$ and $n_3$. In Fig. 5.9(a-b,d) the effect of the approximation in (5.3.7) is shown to cause a flattening of the free-energy along the line $n_1 = -n_3$. Fig. 5.9(d) shows the sharp temperature-dependence that develops due to this flattening of the free-energy. This results in a low-temperature instability, illustrated in Fig. 5.10(a), which highlights the range of temperatures and wavevectors for which the $f_q$ potentials are negative. There is a tendency to
increase either $n_1$ or $n_3$, in the corresponding shaded region for each wavevector, in order to lower the energy of the system. In the range of temperatures for which the two potentials cannot be simultaneously negative for any wavevector, the system will have a temperature dependent CDW wavevector resulting from the balance of the $n_1$ and $n_3$ terms. The amplitudes of these terms will be opposite in sign in order to minimize the $F_4 = C(n_1 + n_3)^4$ energy cost, while trying to increase (decrease) the component which has a negative (positive) potential at a given wavevector. Just below $T_{CDW}$ the system can reduce its energy by choosing the $Q_0$ ($Q_0/3$) wavevector in the case of $A_1 > A_3$ ($A_3 > A_1$).

There is a region in Fig. 5.10(a), where both $f_q$ potentials are negative, below a temperature $T' = 4A_1\beta'_1$. In this region both $n_1$ and $n_3$ will increase to lower the free-energy, but they are also free to take opposite sign in order to cancel the fourth order term energy cost. For any wavevector in the overlap region, the free-energy can go arbitrarily negative by continuing to increase the charge-density while maintaining equal but opposite values for the first and third harmonic, leading to divergent behavior. Including higher order harmonics does not remedy the situation as long as the system is free to set these components to zero in the event they have a positive $f_q$ value in this region. This creates an unphysical divergence in the CDW amplitude for $q = Q'$ below $T'$, which also results in a low-temperature instability that attracts the CDW wavevector to $Q'$ even above $T'$.
Fig. 5.10: Model curves (a) showing the wavevector where the $f_q$ potential crosses zero for the first and third harmonic ($A_3 = 2.05 \times A_1$), in blue and red respectively. The shaded regions in (a) show the range of wavevectors for which the respective potential is negative. The black dot is the temperature and wavevector at which both potentials become negative at $(Q', T')$. The value of $A_1$ is set by the relations shown in (b-c) for the experimental results in Fig. 5.7, to yield the temperature axis of the experiment.

Thus the experimental temperature range is scaled to the physical range $T' < T < T_{CDW}$. This can be done with $T' = A_1 + 4 \beta_1' + T_{CDW}$, for $\beta_1'$ given in Fig. 5.10(c). To explain the high-temperature behavior, $A_3 > A_1$ gives $q = Q_0/3$ just below $T_{CDW}$, and the low-temperature behavior is obtained by choosing $A_3/A_1$ to set $Q'$, and choosing $A_1$ such that $T' < 0$ and thus outside the physical range considered. $T_{CDW} = 300K$ is chosen to represent the experimental observation of LEED diffraction peaks up to room temperature, though making this temperature higher does not have any significant impact on the temperature-dependence, and only gives a temperature-independent wavevector that persists at higher-temperatures. This effectively defines the temperature coefficient:

$$\tilde{B} = \frac{4A_1 \beta_1' (A_3/A_1)}{300}. \quad (5.3.13)$$

Such choice provides excellent agreement with experimental data for the parameters indicated in Fig. 5.7, which suggests that an impurity-driven enhancement of the CDW harmonic interaction could effectively indicate a flat or competing free-energy landscape playing a role in the surface CDW wavevector temperature-dependence.

5.4 Temperature-Dependent ARPES in the Antinodal Region in Underdoped Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$

Given the distinct fingerprints of a well-defined spatial ordering and an underlying broken-symmetry phase associated with a CDW described in the previous sections of this chapter, one notes that this is observed to occur only in the underdoped phase. In the attempt to connect these effects to the opening of the antinodal pseudogap characteristic of the underdoped cuprates, a temperature-dependent measurement of the antinodal energy distribution curves has been performed for UD15K.
Fig. 5.11: **Temperature dependence of the antinodal electronic structure of UD15K Bi2201.**

(a) Symmetrized ARPES spectra from the antinodal Fermi wavevector, normalized to the integrated area between 150 and 350 meV; (b) corresponding difference spectra defined as \( \Delta A^T(\omega) = A^T(k_{AN}^F, \omega) - A^{200K}(k_{AN}^F, \omega) \). Note that while the \( \Delta A^T(\omega) \) data have been smoothed for a clearer visual comparison in (b), the quantitative fit and analysis were performed directly on the raw data. (c) Demonstration of the two component fit, \( A_1^T \) and \( A_2^T \), performed on the \( \Delta A^T(\omega) \) curves (the two energy scales are indicated by the vertical dashed lines): (c1) fit superimposed to the data for \( T = 6 \) and 150 K; (c2) \( A_1^T \) and \( A_2^T \) contributions to the 6 K fit; (c3) comparison of the fit results for 6, 80, and 150 K. The inset of (c3) is a blow up of the data, which emphasizes the low-energy lineshape evolution with its onset around 130 K, as shown in (e). (d) Temperature dependence of the second derivative of \( \Delta A^T \) evaluated at \( \omega = 17 \) meV (the energy dependence is shown in the inset), together with (e) corresponding evolution of \( A_1^T \) and \( A_2^T \) fit components: \( A_1^T \) and \( A_2^T \) exhibit distinct and independent temperature evolutions.

Bi2201, with onset of the pseudogap at the temperature scale \( T^* \approx 190 \) K as determined by resistivity (shown in Sec. 5.5).

In order to quantify the redistribution of spectral weight at \( E_F \), we assume particle-hole symmetry and use the symmetrization procedure in the literature [148, 150] to remove the effect of the Fermi function and instead focus on the spectral function, shown in Fig. 5.11(a). This includes an additional step regarding the temperature dependence of these spectra, where the spectral function taken at \( T>T^* \) is subtracted from the data taken for \( T<T^* \), in order to remove the normal state spectral function and focus on the pseudogap itself, which produces the curves shown in Fig. 5.11(b). In the difference spectra between symmetrized antinodal energy distribution curves, we demonstrate the fitting method used to extract quantitative details of the temperature-dependent gap. This requires a new method for quantification of the spectral features, for which we demonstrate the significance of our method with a statistical measure of comparison between a more basic single energy-scale model and the two energy-scale model, which is based on a rigorous likelihood ratio analysis [204, 205, 206, 207, 208].
In Fig. 5.11, the symmetrized ARPES spectra from the antinodal $k_F$ and the difference $\Delta A_T^T(\omega) = A_T^T(k_{F}^{AN},\omega) - A_{200K}^T(k_{F}^{AN},\omega)$ are plotted as a function of temperature in panels (a) and (b). The opening of the pseudogap can be directly seen in the raw data, though the $\Delta A_T^T(\omega)$ plot more clearly unveils the underlying energy scales. The close inspection of the $\Delta A_T^T(\omega)$ spectra reveals the presence of two energy scales: the first one is the positive hump structure developing upon cooling at $\sim 55$ meV binding energy; a more subtle one, at $\sim 17$ meV, is evidenced by the change in the slope of the spectra leading-edge upon approaching the Fermi level, which becomes obvious only in the low temperature regime as shown in the inset of Fig. 5.11(c3). For the analysis of the spectra lineshape and the quantitative estimate of the temperature dependence of the two energy scales, we have developed a fitting method shown in Fig. 5.11(c), and the complete temperature dependence of low ($A_T^1$) and high-energy ($A_T^2$) features is summarized in Fig. 5.11(e). The second derivative of the two-component fit function described below (Eq. 5.4.1) is shown in Fig. 5.11(d), which emphasizes how the slope of spectra leading-edge exhibits the same temperature dependence as the $A_T^1$ term in Fig. 5.11(e).

The choice of fitting with Hermite functions is due to this being a complete and orthogonal system, with the realization that this is a natural basis for expanding the symmetrized lineshape. Several reasons for this are: (1) The even parity of the symmetrized lineshape requires that odd parity terms in the series expansion are identically zero; (2) because the spectral functions at high and low temperature are normalized at high binding energies between 150-350 meV, the subtracted spectral function that is being fit is required to go to zero at high binding energy, as do the

---

**Fig. 5.12: Example fitting at 6 K and 150 K.** Fits for the one-function model at 6 K (a) and 150 K (b) showing that antinodal symmetrized EDC spectra are well represented at high temperature but not at low temperature, where deviations from the model are clearly visible. The two-function model at 6 K (c) and 150 K (d) for comparison, where it shows good agreement with the symmetrized spectra at all temperatures.
normalizable functions in the Hermite basis; (3) the number of zero crossings for the difference spectra is two, limiting the meaningful Hermite basis subset for this fit to the first two even terms in the series. Thus the Hermite basis implies a highly efficient and compact set of only two functions for fitting the spectra.

Fitting is performed by minimization of a $\chi^2$-test statistic for the model in question, generated as a sum of squares of deviation from the model, and minimized by recursive sampling to optimize the model parameters. Fluctuations in the intensity are assumed to be normally distributed about their central value, with the size of fluctuations estimated from the variance of the intensity about a line in the flat region of the spectra at high binding energies between 200-300 meV. Error bars for the best-fit model parameters are determined from the second derivative of the $\chi^2$-statistic with respect to each model parameter, with all others held fixed, and evaluated at the best fit value of the parameters.

The form of the fit function is shown below, together with a one-function model used for comparison. The two-function and one-function models are written as:

$$\Delta A_{1,2}^T(\omega) = -A_{1,2}^T e^{-\frac{\omega^2}{2\sigma_1^2}} - A_{2}^T \left(1 - \frac{\omega^2}{\sigma_2^2}\right) e^{-\frac{\omega^2}{2\sigma_2^2}}, \quad (5.4.1)$$

$$\Delta A_2^T(\omega) = -A_2^T \left(1 - \frac{\omega^2}{\sigma_2^2}\right) e^{-\frac{\omega^2}{2\sigma_2^2}}, \quad (5.4.2)$$

The parameters $\sigma_1$ and $\sigma_2$ in the two-function model are optimized for the lowest temperature spectra in a fully unconstrained fit, but subsequently fixed to $\sigma_1 = 10$ meV and $\sigma_2 = 32$ meV to simplify the fit procedure for minimization in the amplitude parameters $A_{1,2}^T$ only. Therefore these two energy scales are a temperature-independent feature of the model function. The one-function model only contains a single energy scale $\sigma_2 = 32$ meV, which is similarly fixed to the value giving the best overall agreement to the data. The shoulder feature defining the low energy scale is related by definition to the maximum in the second derivative of the $A_1^T$ term, which occurs at $\sqrt{3}\sigma_1 = 17$ meV; similarly, the energy position of the hump in the $A_2^T$ term is $\sqrt{3}\sigma_2 = 55$ meV.

In our main text it is shown that the temperature dependence of the low-energy feature is quantified by the amplitude, $A_1^T$, of the first even term, a Gaussian centered at $E_F$. We motivate the necessity of this term in the overall accuracy of the fit by constructing a $\chi^2$-test statistic for the fit performed with and without this term in the model. In Fig. 5.12 we show the results of both models at 6 K and 150 K, where it is qualitatively clear that the single-function model does not fit the data well at low temperatures, in which case the two-function model instead provides a vastly improved fit of the spectra.

To quantify the improvement in the accuracy of the fit with the two-function model, the $\chi^2$-test statistic for fitting with the two models is shown as a function of temperature in Fig. 5.13(a). While both models give equivalent goodness-of-fit at higher temperatures, above 130 K, below this temperature the single-function model is seen to give a worse fit while the two-function model shows a slightly improved fit statistic compared to its high temperature value. Fig. 5.13(b) highlights that, with the assumption that the $\chi^2$-test statistic follows a $\chi^2$-distribution with degrees of freedom
Fig. 5.13: **Statistical comparison of one and two-function models.** (a) The $\chi^2$-statistic for the one and two-function models shows agreement above 130 K, but below this temperature the two-function model gives much better agreement with the data. (b) The $\chi^2$-statistic in (a) follows a $\chi^2$-distribution, showing that both models agree with the spectra at high temperatures, but at low temperatures below 130 K the probability of obtaining such a large $\chi^2$ – if the one-function model were correct – is reduced drastically. (c) The probability of the obtained likelihood ratio demonstrates that two energy scales are required to fit the spectra below 100 K, above the 95% significance level, shown as a dashed line in (c), with 50% probability at 130 K.

Equal to the number of unsymmetrized data points minus the number of model parameters, the probability of observing a test statistic of the size calculated or larger is approximately between 0.4-0.5 for the two-function model, in agreement with the one-function model above 130 K. Below 130 K it is seen that the probability of observing this test statistic for the one-function model decreases rapidly to below 0.1 at the lowest temperature. This is a consequence of the increase in the test statistic for the one-function model below 130 K, which is indicative of a poor fit to the lineshape for the one-function model below $T_{CDW}$.

While a more complicated function such as a high-order polynomial fit could reproduce the spectra with arbitrary accuracy, the efficiency and simplicity of the one versus two-function models compared in this supplement demonstrate the underlying occurrence of two energy scales in the EDC lineshape. It is interesting to note that these two functions are of the same polynomial order as a Gaussian and its second derivative for the $A_1^T$ and $A_2^T$ terms respectively. This suggests a connection between the two components – the low-energy lineshape exhibiting $T_{CDW}$ temperature dependence is related to a rescaled second integral of the pseudogap spectra function’s characteristic lineshape. This may be a necessary consequence of the redistribution of spectral weight from near $E_F$ to the larger energy scale connected to $T^*$. 

In order to have a quantitative comparison of the goodness-of-fit for the two models, a likelihood ratio is constructed as the difference between the test statistic for the one-function model and the two-function model at all temperatures. Because the one-function model is a subspace of the more general two-function model, we assume that the likelihood ratio is distributed according to a distribution with one degree of freedom for the single additional parameter of the Gaussian amplitude. The probability that the single-function model is an accurate model is presented in Fig. 5.13(c), which shows the probability is 0.5 or greater above 130 K, but drops rapidly to between 0 and 0.05 below 100 K. We use this criterion to distinguish the two temperature regimes above
and below 130 K - as necessarily described by a one or two energy scales, respectively.

This procedure demonstrates the high statistical significance of an appearance of a second energy scale at low temperatures, which is significant below 100 K at the 95 percent level, and 50 percent level at 130 K. This is strong evidence for the separation of the antinodal pseudogap into a superposition of two distinct features, whose sum follows the previously reported temperature dependence in the spectral weight at the Fermi-level [150], but with a low-energy component that follows the temperature dependence of the nodal \( Q_2 \) wavevector. We consider this result to be a convincing evidence for a direct connection between nodal \( \Delta k_f \) and \( A_T^{1} \) below \( T_{CDW} \), with implied connection between the antinodal electronic structure and the finite-\( Q \) order in underdoped Bi2201.

### 5.5 Temperature Dependence of the Resistivity, Nodal MDC Widths, and Valence Band Energies

Several supplemental datasets can be compared to the detailed \( Q_2 \) temperature-dependent phenomenon. The in-plane resistivity was measured for underdoped, post-annealed \( \text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta} \) samples, as shown in Fig. 5.14(a). A clear pseudogap deviation of the linear resistance is observed, which depends on the doping level. The derivative of the resistivity with temperature in (b) shows the \( T^* \) onset temperature is about 200K for the \( x=0.8 \) sample, and as well there is a quasi-inflection point defined by the dip position in the resistivity derivative. If the dip extended all the way to zero, this would define the position of an upturn in the resistivity. However it does not extend to zero, which is the result of a linear background superimposed on the upturn behavior. A temperature scale \( T_{\text{inflection}} \) can be defined from the dip position.

This is compared with the temperature-dependence of the ARPES nodal MDC widths in Fig. 5.14(c), which are obtained from a Lorentzian-model chi-square minimization fitting routine. An interesting effect occurs, where the main band \( E_F \)-MDC has a monotonically decreasing peak width as the temperature is reduced, while the highly-backfolded (orthorhombic+\( Q_1 + Q_2 \)) band adjacent to the main band has an upturn in the MDC width. The agreement between the temperature scales, \( T_{\text{inflection}} \), for the resistivity and MDC width upturn at low temperature suggest that structural effects can drive the resistivity upturn, in addition to pseudogapping of the Fermi surface.

The temperature dependence of the LEED widths can also be quantified in an analogous way for the underdoped sample, as shown in Fig. 5.15. Again an upturn in the \( Q_2 \)-peak width at low temperature suggests that the \( Q_2 \) superstructure could be intrinsically disordered, in the form of inhomogeneity or patchiness, which causes the diffraction peaks to broaden.

Finally, the temperature dependence of ARPES over a large binding-energy window was performed for the underdoped sample, in the antinodal orientation used for the antinodal-gap supplement of the previous section, shown in Fig. 5.16(a). There is a temperature dependent shift of the valence bands seen in (b), which saturates below \( \sim 110K \). This is in agreement with the in-plane thermal expansion saturation that is reported in the literature [209]. This demonstrates that the temperature dependence of \( Q_2 \) is distinct from the thermal expansion behavior. It in fact appears
Fig. 5.14: Temperature and doping-dependence of the in-plane resistivity and ARPES MDC widths for underdoped Bi$_{2}$Sr$_{2-x}$La$_{x}$CuO$_{6+\delta}$ (x=0.6,0.8). (a) The a-b plane resistivity for two underdoped samples demonstrates a deviation from high-temperature linear behavior, which is characteristic of a pseudogap. The most underdoped sample shows an additional increase in the resistance at low temperature, which gives an inflection point at $T_{\text{inflection}}$ indicated in the (b) temperature-derivative of the resistivity. (c) The ARPES MDC widths show different behaviors below $T_{\text{inflection}}$, where the main-band width at $E_{F}$ decreases, while the higher order ($Q_{1} + Q_{2}$)-replica of the shadow band shows a broadening that is consistent with producing the low-temperature upturn in resistivity for the x=0.8 sample in (a).
Fig. 5.15: Temperature-dependence of LEED peak widths from (a) LEED measurements performed for the x=0.8 sample between 6-200 Kelvin, with (b) prominent peak widths from the region indicated by the box in (a), obtained from Voigt-peak-fitting analogous to the procedure for the MDC widths. The results show there is a different behavior for $Q_1$ and $Q_2$ peaks, where the former have decreasing widths, while the latter broaden at low temperature similar to the high-order replica band $E_F$ MDCs, suggesting the possibility of phase-separation.

that the saturation in thermal expansion coincides with the onset of $Q_2$ temperature dependence, suggesting that it is energetically more favorable for the lattice to pursue internal distortions than overall contraction in this temperature range.

5.6 Conclusions

The importance of these results lies in the ability to improve our understanding of the coexistence of density wave order with the pseudogap and superconductivity in the underdoped cuprates. Given the complex nature of this region of the phase diagram, there are many unanswered questions regarding the microscopic origin of these effects and the relationship between these separate phenomena. Nevertheless the clear signature of density wave order with a strong impact on the surface electronic structure and crystal structure reveals that additional complexity arises on the surface where the effects of the structure are reduced, and this may affect the results of the other temperature-dependent and surface-sensitive experimental probes that are used to gain insight into these materials.

The unusual behavior seen in the temperature dependence of ARPES and LEED, which involves commensurability between the $Q_1$ and $Q_2$ wavevectors at the high and low temperature limits, also appears related to the nodal and antinodal Fermi surface nesting instabilities observed in the calculation of the Lindhard function. Together with the predicted temperature dependence of the harmonic content of the CDW, or equivalently the waveform predicted by Ginzburg-Landau theory, the resulting picture is one where the harmonic content itself results in commensurability effects
Fig. 5.16: **Temperature-dependence of the valence bands** for the underdoped, x=0.8 sample, shown as (a) angle integrated EDCs for the antinodal ARPES cut at 10K (blue) and 200K (red). These bands are a mixture of Cu3d and O2p states which have very little dispersion and appear as three broad peaks with widths on the order of the level spacing ∼1-2eV. (b) Linear fit of the leading edge position indicated by the arrow in (a) shows a continuous temperature dependence down to about 100K, and a saturation below this temperature.
that tip the balance between two Fermi surface nesting instabilities. This has a dramatic effect on the periodicity of the $Q_2$ crystal modulation and the wavevector of electronic order for the density wave.

The question of the nature of the pseudogap phase may be somehow linked to the current observation of temperature dependent density-wave order shown in this chapter. Some key observations suggest that they may be two different things, such as the difference of about 70 K between the transport-derived pseudogap temperature and the onset of density wave order, and the appearance of two energy-scales at the antinode with these different temperature scales and different temperature evolution. Nevertheless, the presence of density wave order near 1/8 doping can be recognized as an important aspect of the underdoped region, and appears to be associated with electronic Fermi surface nesting instabilities.

Finally, it was shown that there is a resistivity upturn at low temperatures for the underdoped sample. The inflection point representing the onset of the upturn occurs at the same temperature as the observed upturn in the MDC with for the $Q_2$-related electronic band replicas. In the simplest view, the resistivity is related to the momentum width of the quasiparticle spectral function if the scattering process associated with both distributions is related. A possible explanation for this effect is that it is due to variation of the $Q_2$ modulation itself, and the possibility of the ARPES experiment probing a distribution of $Q_2$ values with variation microscopically in the sample. The LEED diffraction peak widths, however, do not show the same temperature-dependence as the ARPES MDC widths, and instead show that $Q_1$ peak widths monotonically increase with temperature, while the $Q_2$ peak widths decrease. The opposite temperature dependent behavior of the two diffraction peak widths seems to suggest that the $Q_2$ ordering becomes more irregular at low temperature, which could ultimately result from a similar variation of $Q_2$ that increases at low temperature, perhaps due to the formation of microscopic domains with locally fixed $Q_2$ values.
The Peak-Dip-Hump Lineshape and Band-Crossing Hybridization in Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$

6.1 Peak-Dip-Hump Lineshape in the Cuprates

In order to better understand the ARPES lineshape, we begin with the general ARPES spectral function, (2.8.11),

$$A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma''(k, \omega)}{(\omega - \xi_k - \Sigma'(k, \omega))^2 + (\Sigma''(k, \omega))^2}$$  \hspace{1cm} (6.1.1)

In systems with electron-phonon coupling, the spectral function has an imaginary self-energy contribution which can be assumed independent of momentum. At zero temperature this can be written as,

$$|\Sigma_I(\omega)| = \pi \hbar \int_0^{\mid\omega\mid} \alpha^2 F(\omega') d\omega'$$  \hspace{1cm} (6.1.2)

where $\alpha^2 F(\omega)$, called the Eliashberg coupling function, is the phonon density of states weighted by the electron-phonon coupling [210]. In the Debye model, which approximates acoustic phonons with linear dispersion, this is given by,

$$\alpha^2 F(\omega') = \lambda (\omega/\omega_D)^2$$  \hspace{1cm} (6.1.3)

where $\omega_D$ is the Debye energy and $\lambda$ is the dimensionless mass enhancement parameter [211]. This leads to the following expressions for the self-energy,

$$|\Sigma''(\omega)| = \hbar \lambda \pi |\omega|^3/(3\omega_D^3), \ |\omega| < |\omega_D|$$

$$|\Sigma''(\omega)| = \hbar \lambda \pi \omega_D/3, \ |\omega| > |\omega_D|$$

$$\Sigma'(\omega) = - (\hbar \lambda \omega_D/3) \times [(\omega/\omega_D)^3 \ln(|\omega_D^2 - \omega^2|/\omega^2)$$
$$+ \ln(|\omega_D + \omega|/|\omega_D - \omega| + \omega/\omega_D)]$$  \hspace{1cm} (6.1.4)
Fig. 6.1: Debye model spectral function depicting the peak-dip-hump lineshape for various values of the binding energy.

The form of the EDC lineshape for the resulting spectral function is shown in Fig. 6.1 for the parameters $\lambda = 0.65$ and $\omega_D = 65\text{meV}$. This lineshape is characterized by a sharp quasiparticle peak followed by a dip in the spectral intensity and then a broad hump feature at higher binding energy, which is referred to as the peak-dip-hump lineshape (PDH). This lineshape closely matches ARPES experiments on the Be(0001) surface state, and is fully explained by a surface state enhancement of electron-phonon coupling around 5 times the bulk value [212]. Similar mass-enhancement for the low-energy quasiparticles that has been ascribed to electron-vibration coupling that has been reported for the Mo (110) surface state, as well as surface adsorbates and high-symmetry C$_{60}$ molecules [213, 214, 215]. In addition, the PDH has been observed in bilayer Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ at $(\pi,0)$, and was proposed to have the same energy scale as the $(\pi, \pi)$ magnetic resonance observed in neutron scattering [216, 217, 218].

Later ARPES measurements in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, that scanned from the nodal region to the antinodal region of the Fermi surface, show that there is a continuous evolution of the spectral dip at the antinode to the nodal kink. In the bilayer material, this feature only appears below $T_C$, and coincides with a drop in the MDC widths for $|\omega| \leq \omega_{\text{kink}}$, and a single energy scale is defined by the dip that is constant throughout the Brillouin zone [219]. However, later studies have shown a doping dependence of the energy scale of the antinodal dip, which coincides with that of the nodal kink only for optimal doping, and for which there is significant doping dependence of the antinodal dip energy scale. Meanwhile, the nodal kink energy remains constant with doping [220, 221]. ARPES on Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4}$ (n=1-3) show the nodal kink is always present. In
addition, the antinodal spectral dip disappears above $T_C$ for $n=2$ to $3$ but a small kink remains for antinodal spectra taken on the single-layer compound above $T_C$ [222].

The nodal kink has been ascribed to the mass enhancement effect of electron-phonon coupling [223, 224], and has been observed to occur at an energy that is nearly independent of doping or temperature, and is a feature present in a wide variety of cuprates. These materials as well share a universal nodal Fermi velocity [225]. ARPES on several doping levels of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ has shown a doping-dependent dispersion only for $\omega \geq \sim 50$ meV, as well as a temperature-dependent amplitude for a peak in the real part of the self-energy, at the energy of the nodal kink. The self-energy peak was observed only for under- and optimally-doped samples, but not in the case of overdoped [226].

ARPES photon-energy dependence in $\text{Pb}_y\text{Bi}_{2-y}\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (a material with suppression of the supermodulation) shows EDCs that vary greatly in the ratio of intensities in the peak and hump structures, indicating that self-energy effects cannot explain the PDH lineshape, and leading to identification of the hump structure as the bonding band of the bi-layer split conduction band [227]. However, more recently it was claimed that the PDH lineshape is observed in the single layer material $\text{Bi}_2\text{Sr}_{1.6}\text{La}_{0.4}\text{CuO}_{6+\delta}$, which is connected to the unusually small energy scale of 19meV, and again discussed in relation to spin excitations [228]. A PDH is observed in the underdoped single-layer material $\text{Bi}_2\text{Sr}_{1.25}\text{La}_{0.75}\text{CuO}_{6+\delta}$ for nodal $k_F$ EDCs in the normal state above $T_C$. The real part of the self-energy shows a strong kink coinciding with the energy dip-position near $\sim 60$meV [229].

The appearance of a strong PDH feature in ARPES on $\text{Bi}_2\text{Sr}_{1.2}\text{La}_{0.8}\text{CuO}_{6+\delta}$ is examined in this chapter in order to draw a comparison between the previous reports regarding the nodal “kink” mass-enhancement and the additional presence of multiple superstructure modulations. Conclusion will be reached on the origin of PDH in this material, providing suggestion for the further improvement of our understanding of electron-phonon coupling in the cuprates with regards to the effect on the phenomenology of the nodal spectral function.

### 6.2 The Nodal ARPES Spectra of Underdoped $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$

#### 6.2.1 MDC Analysis and the Self-Energy

The MDCs for underdoped $\text{Bi}_2\text{Sr}_{1.2}\text{La}_{0.8}\text{CuO}_{6+\delta}$ previously shown in Chap. 1, in Fig. 1.5(a), can be further analyzed to extract the details of the self-energy. This is accomplished by a chi-square fit with a Lorentzian function, as shown here in Fig. 6.2. The colored curves are the result of the Lorentzian MDC fit for various fixed binding energies. The lighter colored points in each color shows the experimental MDC spectra. The Lorentzian fit curves are a good approximation to the ARPES intensity over the range of momenta considered, with some exceptions due to the existence of weak-intensity features present in the spectra, for instance near 0.64 Å$^{-1}$ at $E_F$, where a peak roughly one order-of-magnitude smaller than the main band can be observed. These additional features
will be discussed in the conclusion of this chapter, however we are currently only concerned with the behavior of the intensity in a range of momenta near the vicinity the high-intensity, main band MDC peak. The MDC spectra in Fig. 6.2 do show some additional asymmetry in comparison to the Lorentzian fit, however this does not appreciably shift the peak position determined.

The result of the peak position of the MDC peak fitting for all binding energies is shown in Fig. 6.3. The momentum position of the peak for the fit of the MDC taken at $\omega$ is $k_{\text{max}}(\omega)$, and is shown by the points, and the error bars show the chi-square derived standard model deviation for the MDC fit. The error bars quantify the accuracy of the determined peak position with random noise in the spectra, which causes a random deviation of the determined model parameter, though they do not take into account the systematic error associated with the approximation of choosing a simple Lorentzion curve. It is seen in Fig. 6.3 that the uncertainty in the peak position increases with binding energy, due to the broadened spectrum having a less well-defined peak and therefore a relatively larger uncertainty in the peak position.

The resulting peak positions in Fig. 6.3 are shown in Fig. 6.4 together with the colored image of the ARPES intensity from Fig. 1.4. Fig. 6.4 provides a quantitative aspect to the colored ARPES image, in order to establish a connection between the visual aspect of the image and the MDC peak positions determined from fitting. In addition Fig. 6.4 shows a set of points $\omega_{\text{linear}}(k)$ which have been established as a linear approximation to the actual band structure $\xi_k$. This represents a crude approximation to the bare band structure of the noninteracting system, reduced to this simple form only to highlight the essential features, and given as,

$$\xi_k = v_F^0(k - k_F) \quad (6.2.1)$$
Fig. 6.3: MDC fit peak position determined by the chi-square minimum for a simple Lorentzian lineshape, with relative uncertainty error bars given by the local curvature of the chi-square distribution at each energy. Note that the error bar is larger than the random deviation of the peak positions, as it accounts for the probability variance of the best-fit model parameters in the fitting routine.
Fig. 6.4: Comparison with ARPES intensity plot along the Γ-Y direction for the fit-result MDC peak positions (green) and reference linear bare-band construction (black), for the corresponding data shown in Fig. 1.5(a).
The momentum at which $\xi_k = E - E_F = 0$ is $k_F$, which is also true for the MDC peak positions at $k_{\text{max}}(\omega)$, as a consequence of Luttinger counting. This fixes the intercept of the linear $\xi_k$ with the peak positions $k_{\text{max}}(\omega)$ at the point $k_{\text{max}}(\omega = 0) \equiv k_F$. A second $\omega(k)$ point is all that is needed in order to obtain $v_F^0$ in equation (6.2.1) to fully specify the bare-band linear approximation. However, this is not possible without additional information, and in general $v_F^0$ is not exactly known. In this section we will simply take an arbitrary bare-band $v_F^0$ defined by a second $\omega(k)$ point located at $k_{\text{max}}(\omega_{\text{max}})$ [223], corresponding to the highest binding energy point in Fig. 6.3. Therefore in general we may consider a correction to all parameters $v_F^0 \rightarrow v_F^0 \times \text{(constant)}$, though we will obtain results which depend on the ratio of velocities which are independent of the bare-band velocity correction. The value of $v_F^0$ determined from the maximum binding-energy MDC peak position is $\hbar v_F^0 = 3.59$ eV Å.

The MDC cut through the ARPES intensity is equivalent to the spectral function evaluated at $\omega = \text{constant}$, as long as matrix element effects are small and the cut is taken just at, or below, the Fermi level - where the intensity is not suppressed by the Fermi-function. This has the general form of equation (2.8.11),

$$A_{\text{MDC}}(k) = -\frac{1}{\pi} \frac{\Sigma''(k, \omega_0)}{(\omega_0 - \xi_k - \Sigma'(k, \omega_0))^2 + (\Sigma''(k, \omega_0))^2}$$ (6.2.2)

The real-part of the self-energy in equation (6.2.2) is evaluated at the energy $\omega_0$ of the cut through the ARPES intensity, and at this point defines an energy difference between the location of the peak in the spectral function and the bare-band energy, though this is only true at the momentum-value of the peak. At other momenta for the same $\omega_0$, the function $\xi_k + \Sigma'(k, \omega_0)$ is assumed to behave as a linear function of $k$, at least in the vicinity of the MDC peak. Given the linear assumption of the bare-band dispersion, the simplest description invokes an often used approximation, that the real-part of the self-energy is independent of explicit momentum dependence,

$$\Sigma'(k, \omega) \rightarrow \Sigma'(\omega)$$ (6.2.3)

This assumption requires the real-part of the self-energy to be momentum-independent explicitly, though it will still contain the implicit momentum dependence given by the dispersion of the pole in the experimental spectral function $k_{\text{max}}(\omega_{\text{max}})$. The reason for this is shown in Fig. 6.5, where the experimentally determined $k_{\text{max}}(\omega)$ is compared with the assumed linear $\xi_k$. Under this assumption, at each point $\omega = \omega_0$, there is a corresponding experimental $k_{\text{max}}(\omega_0)$, where the difference, $\omega_0 - \xi(k_{\text{max}}(\omega_0))$, is the real-part of the self-energy. This can be seen by evaluating the bare-band dispersion at the momentum value which corresponds to the MDC peak at $\omega$,

$$\xi_k \rightarrow \xi_{k_{\text{max}}(\omega)}$$ (6.2.4)

Using this replacement, the pole of the spectral function of equation (6.2.2) becomes,
The real-part of the self-energy, which is parameterized as a function of energy via the bare-dispersion as shown, is defined by the energy difference between the experimental $k_{\text{max}}(\omega)$ (green) and the bare-band (black).

$$\omega - \xi_{k_{\text{max}}(\omega)} - \Sigma'(\omega) = \omega - v_0^F(k_{\text{max}}(\omega) - k_F) - \Sigma'(\omega) = 0$$

$$\Rightarrow \Sigma'(\omega) = \omega - v_0^F(k_{\text{max}}(\omega) - k_F)$$

(6.2.5)

This defines the real-part of self-energy in terms of the experimentally determined $k_{\text{max}}(\omega)$, and the approximated $v_0^F$. This has been calculated for the band dispersions shown in Fig. 6.5, and the result is shown in Fig. 6.6. The slope at low binding energy is found by linear regression in the range of $\Sigma'$ in Fig. 6.6 from 0-50 meV, and is found to be 1.23 in dimensionless units. At binding-energies higher than about 60 meV, the form of $\Sigma'$ in Fig. 6.6 is seen to depart rapidly from the linear behavior at low binding-energy. A peak also occurs at the 60 meV position, indicating the experimental dispersion begins to bend back towards the bare-band dispersion until $\sim$150 meV, when the slope of $\Sigma'$ becomes close to zero. From 150-250 meV the experimental dispersion is parallel to the approximate linear bare-band, and then at higher binding energies it again bends back towards the bare-band, and the slope of $\Sigma'$ is near -.36 from around 250-350 meV. It should be noted that the values of these slopes depends on the choice of the bare-band slope, and correction to the bare-band velocity is equivalent to adding a global constant to the slope of $\Sigma'$.

The definition of the coherence factor $Z$ in equation (2.8.14) has an equivalent definition in terms of the “coupling constant” $\lambda$. 

Fig. 6.5: The real-part of the self-energy, which is parameterized as a function of energy via the bare-dispersion as shown, is defined by the energy difference between the experimental $k_{\text{max}}(\omega)$ (green) and the bare-band (black).
**Fig. 6.6:** Experimentally determined real-part of the self-energy from the MDC fitting procedure outlined in the text. The slope values indicated represent the effective coupling constant, $\lambda$, which are known only up to a global constant due to the unknown “true” bare-band velocity.

\[-\lambda \equiv \frac{\partial \Sigma'(\omega)}{\partial \omega} = 1 - v_0^F \frac{\partial k_{\text{max}}(\omega)}{\partial \omega} \]

\[\Rightarrow Z = \frac{1}{1 + \lambda} = \left( v_0^F \frac{\partial k_{\text{max}}(\omega)}{\partial \omega} \right)^{-1} \tag{6.2.6} \]

Recalling the result of Fermi-liquid theory for the renormalized band dispersion near $E_F$ in equation (2.8.16), the coherence factor $Z$ can be put in the form of the ratio of the local derivative of the experimental dispersion to that of the bare-band,

\[Z(\omega) \sim \frac{1}{v_0^F} \frac{\partial \omega}{\partial k_{\text{max}}} = \frac{\epsilon_k}{\xi_k} \tag{6.2.7} \]

This relies on the assumption that the bare-band is linear. If the bare-band in equation (6.2.5) is replaced with a more complicated function of $k_{\text{max}}(\omega)$, the coherence factor derived from the derivative of the real-part of the self-energy in equation (6.2.6) will not be merely proportional to the experimental dispersion, but rather a more complicated function of $k_{\text{max}}(\omega)$.

The coherence factor defined by equation (6.2.6), and calculated using the band dispersions shown in Fig. 6.5, is shown in Fig. 6.7. This has been calculated by taking the numerical derivative of the experimental band dispersion, which requires some smoothing due to random errors in the peak position from fitting MDC’s for $k_{\text{max}}(\omega)$. The coherence factor plotted in Fig. 6.7 is seen to drop quickly from its value at the Fermi-level to a minimum at $Z = 0.48$. This corresponds to the slope of $\Sigma'$ of 1.23, so that,
Fig. 6.7: **Coherence factor** as defined by the numerical derivative of the MDC band-dispersion measured by ARPES. The value is defined up to an unknown multiplier, however the ratio of the coherence factor above and below the “kink” gives a mass renormalization factor of 2.2.

The fact that it appears as a minimum in Fig. 6.7 is the result of smoothing in the numerical derivative routine, as the real-part of the self-energy can be seen to be nearly linear throughout the range 0-50 meV in Fig. 6.6. At higher binding energy, the coherence factor is about 1 for the range 150-250 meV. The value of the coherence factor determined here is proportional to a correction to the bare-band velocity, and therefore is only defined up to a global scaling factor. It is important to keep in mind that the coherence factor shown here is generalized and shown as a function of binding energy, which contains some artifacts due to the fact that it is a derivative, especially near the kink energy, where it is peaked. This behavior seen for the renormalization constant obtained under the Fermi-liquid description appears strange, though it will be shown in Sec. 6.3 that this is likely related to the backfolded features present in the electronic dispersion, and possibly accompanies an electronic gap near the kink energy.

The imaginary part of the spectral function can be determined from the width of the MDC Lorentzian peak, which under the assumption of momentum independence is proportional to the lifetime,

\[
\Sigma''(k, \omega) \to \Sigma''(\omega) \approx -|v_F^0| \Delta_{HWHM}(\omega) \tag{6.2.9}
\]

The MDC width is found by the least-squares-fit Lorentzian MDC widths, which are inserted into equation (6.2.9), and the result is shown in Fig. 6.8, together with the chi-square determined model parameter standard deviations shown as error bars. A correction to the bare-band velocity will
Fig. 6.8: **Imaginary-part of the self-energy** calculated from the best-fit MDC Lorentzian width and the bare-band velocity. A change in the evolution with binding energy from quadratic to linear occurs near 100 meV.

Contribute a global scaling factor to $\Sigma''$, inverse to the correction for the coherence factor. A fit of the imaginary part is shown in Fig. 6.9, where for the energy range from 0-100 meV the behavior of $\Sigma''$ is very nearly quadratic in energy, and can be described by,

$$
\Sigma''(\omega) \simeq 7.3 \omega^2 + 0.33 \omega + 0.06 
$$

(6.2.10)

This can also be analyzed in accordance with the Fermi-liquid model, where the lifetime is given as,

$$
\Gamma = \sqrt{(\alpha \omega)^2 + (\beta k_B T)^2} 
$$

(6.2.11)

with the result $\alpha = 2.1$ and $(\beta k_B T) = 3.8$ meV, corresponding to $(\beta T) = 44.1$K. For this data which was taken at 6 K, this gives $\beta = 7.35$. However, at higher binding-energies from 100-350 meV, $\Sigma''$ becomes nearly linear and can be described by,

$$
\Sigma''(\omega) \simeq 0.75 \omega + 0.08 
$$

(6.2.12)

6.2.2 EDC Analysis and the Peak-Dip-Hump Dispersion

In this section we can consider the alternative method which involves quantifying the information present in the EDC lineshape, given by equation (1.3.1) such that it can be fit with a suitable
Fig. 6.9: **Model fitting** of the experimentally measured imaginary-part of the self-energy for linear (orange) model above the kink and a quadratic (blue) model at low binding-energy. In addition, the Fermi-liquid model prediction (purple) shows good agreement at low binding energy using the coefficients given in the text.

function. By choice, here a 2-peak fit is used motivated by the PDH shape of the EDCs. The fit is a chi-square minimization best-fit model parameter determination which uses a model with the functional form of a two Lorentzian-peaks times a Fermi function, plus a linear background.

Examples of the EDC fitting for the data from underdoped Bi$_2$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$ in Fig. 1.4 are shown in Fig. 6.10. These are analogous to the MDC fits shown in Fig. 6.2, though utilizing the two-peak fit in order to quantify both the quasiparticle peak (“peak”) near $E_F$, and the broadly-peaked background (“hump”). The results in Fig. 6.10 are shown as best-fit curves, which are seen to be in reasonably good agreement with the same-colored data points in the momentum range from 0.68-0.72 Å$^{-1}$. This suggests that the peak positions determined from the fitting procedure should accurately describe the dispersion of the EDC maximum.

The best-fit peak positions from the fitting results demonstrated in Fig. 6.10 are shown in Fig. 6.11. The points at low binding-energy correspond to the first peak position, and the second peak positions appear at higher binding-energy. The results from the MDC peak positions from Fig. 6.3 are shown as well for comparison. In the region of momentum greater than 0.73 Å$^{-1}$ the two peaks collapse to the same position with similar widths, so only one set of positions is plotted. In this region a single peak fit is sufficient for good agreement the lineshape, likely due to the effect of the kink in the dispersion which leads to a larger band velocity around these energies.

The results of the EDC and MDC fitting peak positions is summarized in Fig. 6.12, together with the colored ARPES image. The regions of agreement and disagreement between the two fitting methods can be readily seen, and raises questions over what is causing the discrepancies. The low
binding-energy (first peak) EDC peak position appears to bend downward as the band approaches the Fermi-level, suggesting that there is residual spectral weight across a large region of momentum as the band crosses the Fermi energy. In addition, the high binding-energy (second peak) EDC peak position shows a persistent intensity and anomalous dispersion away from the main band, followed by a downturn near the MDC peak-positions.

The results demonstrated in Fig. 6.11 can be studied by detailed comparison to the MDC fitting of Fig. 6.2, both at low and high binding-energy. The comparison at low binding-energy is shown in Fig. 6.13(a), where the EDC quasiparticle peak position is seen to have a significant departure from that of the MDC fit-determined position.

In Fig. 6.13(b), the EDC dispersion is compared to a Bogoliubov quasiparticle dispersion for fixed gap size $\Delta$:

$$E_k = \sqrt{\epsilon_k^2 + \Delta^2}$$  \hspace{1cm} (6.2.13)

Good agreement between the near-$E_F$ EDC dispersion and the gapped quasiparticle dispersion is obtained with a gap size of 5 meV. While this is indicative of some kind of gapped quasiparticle at $E_F$, the gap size is on the order of the experimental resolution, so a more accurate determination is needed. While this result is in agreement with the experimental observation of a near-nodal gap from previous ARPES measurements [88], in the present case it truly appears at the node, and is more likely related to the finite energy and momentum resolution of the experimental intensity distribution [230].
Fig. 6.11: **EDC best-fit peak positions** determined by the fitting procedure described. The near-$E_F$ peak is shown (blue), together with the higher binding-energy broad peak position (red), as well as the MDC peak positions (green) for comparison. Error bars represent the statistical uncertainty in the best-fit position obtained from the second-derivative of the chi-square distribution.
Fig. 6.12: **EDC and MDC peak positions** in (orange) and (green), respectively, determined as best-fit model parameters and shown on the ARPES intensity map for comparison.
6.2.3 Summary of ARPES Nodal Analysis

The results of the ARPES nodal analysis for underdoped Bi$_2$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$ demonstrate that many quantities of interest can be probed from a snapshot of the complex physics of the single-particle spectrum. One way of quantifying this spectrum is via the MDC peak positions, $k_{\text{max}}(\omega)$. This has been determined from a fitting procedure that obtains the best-estimate Lorentzian model parameters by chi-square minimization, with corresponding statistically determined random errors determined by the local second derivative at the chi-square minimum. The resulting dispersion shown in Fig. 6.3 produces an accurate representation of the spectral peak that occurs at the pole of the coherent single-particle propagator.

Nonlinear dispersion of the MDC peak positions is clearly seen, and demonstrated as well in the real-part of the self-energy shown in Fig. 6.6. A mass-renormalization is seen at low binding-energy, which is possibly due to a quasiparticles dressed by an electron-boson interaction. The mass-renormalization continues up to around 60±5meV, and a region of back-bending is seen over a short range near this energy, producing a peak in the real-part of the self-energy.

The imaginary-part of the self-energy can also be experimentally determined from the fitting-determined MDC widths, under the assumption of momentum-independence, by multiplying by the Fermi velocity. The result shown in Fig. 6.8 can be compared to simple linear and quadratic fits, as well as the form predicted by a Fermi-liquid model, which is shown in Fig. 6.9. A crossover occurs in the energy dependence, from quadratic to linear behavior, around 100meV, that cannot be explained by the Fermi-liquid model prediction. However, this is likely due the effect of the pseudogap on the frequency-dependence of the scattering rate, as it has been shown that the optical...
conductivity has frequency-dependent lifetime that matches the behavior of the imaginary-part of the self-energy shown here [34].

Alternatively, a similar fitting procedure can be performed to obtain the EDC positions, which clearly show two peaks in Fig. 6.10. One peak appears sharp with higher intensity near $E_F$, and the second peak is broad and weaker in intensity at higher binding-energy. The dispersion of the low binding-energy EDC peak position (“peak”) follows the MDC positions except near $E_F$, where EDC dispersion exhibits a down-turn caused by finite-resolution effects, shown in Fig. 6.13. In addition, the higher binding-energy EDC peak position (“hump”) shows sign of anomalous dispersion until it becomes close to the MDC peak positions, where it rapidly turns around and shows agreement with the MDC results.

The region of anomalous dispersion of the “hump” from 0.7-0.73 Å$^{-1}$ is characterized by dispersion very similar to that of the MDC positions, however demonstrating opposite parity. This is shown in Fig. 6.14(a). The close agreement between the momentum-reflected MDC positions and the anomalous dispersion of the EDC second peak is highly suggestive of a back-folding scenario with greatly reduced intensity. This is also consistent with anomalous spectral weight found equally spaced from the back-folded band, however shifted by about half of the ordinary supermodulation, corresponding to the low-temperature $Q_2$-wavevector discussed in Chaps. 3-5. This leads to a more complete identification of the full band structure contribution, which includes band-crossings along the nodal direction, that appear to coincide with the back-bending regions of the real-part of the self-energy as shown in Fig. 6.14(b).

### 6.3 ARPES Evidence for Nodal “kink” Originating from Structural Back-Folding

The photon-energy dependence of the EDC lineshapes for the strong features seen in the s-polarization ARPES high-symmetry $\Gamma - Y$ nodal cut is shown in Fig. 6.15 for the energy range from 19-31 eV. Dramatic changes can be seen in the relative intensity of the peak and hump feature for the lineshapes of the selected bands. In particular, the antiphase PhD effect described for the two bands crossing in the center near 0.16Å$^{-1}$ leads to an switching from the $Q_1$-replica main (shadow) band PDH lineshape and shadow (main) band hump-only lineshape at 25eV (19eV). The apparent photon-energy dependence of the PDH EDC lineshape is caused by the PhD effects from the crystal structure together with the identification of the peak and hump as coming from separate features due to structural backfolding of the CuO$_2$ bands. Therefore the PDH lineshape can be entirely attributed to the effects of the $Q_1$ superstructure, which lead to the band-crossings between main and shadow band replicas.

ARPES high-symmetry $\Gamma - Y$ nodal cuts through the main band of the optimally doped (x=0.5, $T_C$ =30K) sample, taken at 19 and 25 eV photon-energy, are shown in Fig. 6.16(a,b), with markers for the best-fit MDC peak positions. Markers showing the one-peak MDC fit done at 25eV for the main band is compared with the two-peak MDC fit done at 19eV in Fig. 6.16(b).

Fig.6.16(c) shows the MDC peak positions and the chi-square determined error bars for the
Anomalous spectral weight in (a) the ARPES nodal cut can be explained if the hump dispersion (red arrow) is the result of back-folding of the bandstructure (black curve). This is also consistent with anomalous spectral weight (blue arrows), shifted by a momentum value that is half of the ordinary supermodulation, $Q_{SM}/2$. The resulting bandstructure contains band-crossings along the nodal direction, which coincide with (b) anomalous back-bending in the real-part of the self-energy ($E_1$-$E_2, E_3$-$E_4$).
Fig. 6.15: **Photon-energy dependence of the EDCs** for underdoped Bi$_2$Sr$_{1.2}$La$_{0.8}$CuO$_{6+\delta}$ taken in s-polarization from 19-31 eV photon-energy.
peak position for the ARPES cuts in (a,b), showing agreement for the main band positions, and revealing the bandcrossing that occurs near 60 meV between the main band and the Q1-replica of the shadow band. Just as in the case of the analysis done for the underdoped sample in chapter 1, there is a peak in the real self-energy shown by the comparison of markers and lines in Fig. 6.16(a). This reveals an energy scale coinciding with the “kink” energy and the peak in the real part of the self-energy as well for the optimally doped sample.

EDCs for the optimally doped sample dataset in Fig. 6.16(a,b) are shown in Fig. 6.17(a-d) at the main band and Q1-replica shadow band nodal \( k_F \) positions, as well as MDCs shown in (e,f). Despite the asymmetry of the intensity resulting from a matrix element that strongly favors the main band at 25eV, the shadow band replica EDCs are in agreement with the data taken at 19eV where the shadow band replica has more intensity, albeit with a much weaker quasiparticle peak just appearing as a shoulder at \( E_F \) at 25eV, which is seen to disperse towards the bandcrossing. This demonstrates how the strong variation in intensity due to matrix element effects with the overlapping bands will significantly alter the EDC lineshape, and accounts for the photon-energy dependence effects seen in the EDCs.

6.4 Possible Band-Crossing Hybridization in \( \text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta} \)

The “peak-dip-hump” lineshape shown in Fig. 6.15 is observed to change with photon-energy and polarization, and coincides with the overlapping of oppositely dispersing DR bands. From this observation it can be clearly stated that the PDH lineshape in \( \text{Bi}_2\text{Sr}_{1.2}\text{La}_{0.8}\text{CuO}_{6+\delta} \) is mainly the result of the back-folding due to the incommensurate structure producing overlapping band dispersions. However, the nodal cut for the optimally doped sample, shown at two photon-energies in Fig. 6.16, demonstrates a striking universal coincidence of the “kink” energy position and band-crossing, showing that this effect is independent of doping and likely related the ordinary incommensurate structure modulation Q1 in addition to Q2 if present.

The total picture of a coinciding real-part of the self-energy peak, the bandcrossing position, and the nodal “kink” mass-enhancement points to band hybridization effects between the overlapping bands, which produces a van Hove singularity (VHS) about 60meV below the Fermi surface - illustrated in Fig. 6.18(a). This could arise due to the primitive crystal symmetry operations, such as in the case of a glide-plane symmetry along the orthorhombic \( b^* \) axis, which gives rise to an effective bonding-antibonding representation of the main and shadow Cu-O \( d_{x^2-y^2} \) bands [72]. This suggests that this effect could be related to a finite hybridization of the parity-mixed main and shadow band replicas. Such parity-mixing is a direct consequence of the incommensurate structure, which produces overlapping main and shadow bands for 1st- (2nd-) and higher-order bands for opposite (parallel) dispersion, indicative of the parity-mixing discussed in Sec. 4.3.

The coincidence of the seemingly disparate phenomenologies of i) the energy of the peak in the nodal self-energy, ii) the electron binding-energy range of the nodal mass-enhancement (“kink”), and iii) the nodal PDH lineshape - are completely explained by the orthorhombic and supermodulation backfolding - which leads to a backfolding-originated PDH lineshape, and subsequent opening
Fig. 6.16: ARPES spectral function for optimally doped Bi$_2$Sr$_{1.5}$La$_{0.5}$CuO$_{6+\delta}$ ($T_C=30$K) sample at (a) 25eV and (b) 19eV photon-energy, together with one-peak MDC-fit result (green), two-peak MDC-fit result (orange, purple), and lines (black) that are a linear fit to the dispersion above and below the “kink” energy. (c) MDC peak positions and chi-square deviations show good agreement for the coincidence of the kink energy and the bandcrossing.
Fig. 6.17: **Photon-energy dependence of EDCs** for (a,c) 25eV and (b,d) 19eV, and corresponding MDCs shown in (e,f), respectively.
Fig. 6.18: Possible hybridization at the (a) band-crossings is evidenced by the coincidence of the “kink” with the crossing position, and the appearance of back-bending in the real-part of the self-energy. The (b) resulting bandstructure is oscillatory and contains nested VHS’s along the nodal line.
of a hybridization gap between the backfolded features as a result of a fundamental change in the primitive symmetry of the CuO$_2$ plane electronic structure in the fully incommensurate material.

The resultant band-structure is illustrated in Fig. 6.18(b), and compared to the ARPES spectra in Fig. 4.8(a). Interestingly this shows the PDH lineshape could still point towards electron-phonon coupling, but with a different interpretation - the hybridization gap will produce a VHS at the energy of the kink, which has been connected to a bond-stretching optical phonon in the apical oxygens [223]. This demonstrates a highly correlated system where renormalization of the nodal $k_F$ is coupled to the low-energy mass-enhancement in a way that accounts for the supermodulation wavevector, lattice parameter, and phonon energy scale, suggesting the effects of the basic symmetry of the lattice and the lattice dynamics are connected via the conduction electrons. Such a strongly coupled system could exhibit soft-phase behavior as the lattice and electrons are intimately related.

In the current picture, the doping dependence shows the band-crossing occurs just off of the nodal direction for the optimally doped sample, but due to the hole-doping level-shift, the band-crossings occur along the nodal line in the underdoped samples. In both cases the “kink” coincides with the bandcrossing, as does the real-part of the self-energy back-bending. An important difference between the underdoped and optimally doped samples is the presence of the Q$_2$ modulation, which may be caused by the appearance of the bandcrossing along the nodal line. If a hybridization gap developed this would lead to the formation of nested VHS along the nodal direction. In fact, it was suggested early on that the nesting of VHS’s near $E_F$ could drive CDW formation [231], and some VHS pairing effects have been discussed in relation to superconductivity in the cuprates [232]. This type of oscillating band structure is predicted for CDW materials, such as the chalcogenide “sphaghetti-bands” [233], and is similar to the theoretical predictions for the dispersion of ordered stripe phases [234]. This is a type of electronic phase-separation scenario, in which the electronic spectrum becomes discretized as the stripes become smaller, leading to quantum size-effects (QSE) that can open a gap [235].

In the present case, this is taken as strong evidence a Peierls-distortion CDW [203, 233] and/or charge/spin stripe correlations resulting directly from the presence of the incommensurate crystal symmetry and band-crossings along the lower-dimensional nodal line. This will produce both the doping- and temperature-dependent effect that is observed with single-particle spectroscopies, and also strongly momentum- and energy-dependent, as band-mixing will take place at positions corresponding the the band-crossing with the backfolding DR’s. Interestingly this leaves open the question of the separate Q$_1$ and Q$_2$ modulation scales, which may have different origin due to their differing doping dependence and photoemission intensity in the results of Chap. 3. One possibility is that Q$_1$ is mostly a structural effect, but Q$_2$ is a more complicated CDW superstructural order in the presence of VHS formation.

6.5 Conclusions

An important re-definition of the PDH lineshape has been reached in this chapter, which accompanies an explanation that appears to modify the long-held belief that it is a signature of electron-
boson coupling. Instead it appears in Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$ to primarily result from a superstructure bandcrossing, defining the peak as the coherent quasiparticle spectral function from one band, and the hump as the incoherent quasiparticle from another band. Thus the peak in the EDC lineshape is formed by the coherent part of the spectral function at low binding energies, and the incoherent part of the spectral function at binding energies above the kink energy forms the hump feature, though these two features result from separate bands as shown by the dispersion obtained from fitting to the Fermi-liquid spectral function.

A traditional analysis using the properties of the self-energy and renormalization effects obtained by comparison to the Fermi-liquid theory demonstrates renormalization of the quasiparticle dispersion, resulting in a strong kink feature. In addition, the coincidental appearance of the kink and the band crossing at the same energy and momentum, independent of doping level, suggests that there may be more of a relationship between the kink and the bandcrossing than has been recognized previously. The possibility that the oppositely dispersing bands comprising the bandcrossing can interact in the fully incommensurate crystal adds another point of complexity to the picture of the resultant electronic structure, as this would now show a tendency to open a hybridization gap at the bandcrossing position. The lack of well-defined parity of the superstructure replicas in the fully incommensurate crystal, as compared to the purely orthorhombic crystal in which parity is well defined for the states, offers one way to explain how the bandcrossing could show a hybridization gap. Accounting for the relatively short lifetime of the quasiparticle and the finite experimental resolution, the appearance of a small gap at the bandcrossing would appear very similar to the dip feature in the PDH lineshape of the EDC’s.

These results provide a way to explain many of the disparate phenomena that have been observed in underdoped Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$, including the nodal kink, nodal bandcrossing, backbending in the real-part of the self-energy at the kink position, the presence of multiple supermodulations both Q$_1$ and Q$_2$, and the temperature dependence of Q$_2$ at the surface. These findings suggest that these effects are all directly related to the electronic and structural distortions analogous to a Peierl’s transition, that is essentially rooted in the effects of strong-electron phonon coupling, despite the fact that this picture requires a fundamental redefinition of the PDH lineshape as caused by overlapping dispersions of the backfolded bands.
Conclusion

The results of this writing advance a new approach to understanding the physics of the cuprate high-
$T_C$ superconductors. This is partially accomplished by clearing up the misconception of previous
claims for pockets in the Fermi surface of Bi$_2$Sr$_{2-x}$La$_x$CuO$_{6+\delta}$, which have been shown conclusively
to arise from an additional crystal modulation that has been detected by doping-, temperature-
, polarization-, and photon energy-dependent ARPES, together with doping- and temperature-
dependent LEED measurements in this work. A static bulk modulation with wavevector periodicity
Q$_2$ is observed, and a significant temperature dependence of Q$_2$ is found at the surface. This
can be understood to arise in part from Fermi surface nesting, calculated from the tight-binding
parameterization of the experimentally measured ARPES Fermi surface, which produces a doping-
dependent peak in the susceptibility at the Q$_1$/3 value. In addition, a stronger nesting peak is
found at Q$_1$/2, which is less doping-dependent. This nesting could be partially responsible for a
Peierls CDW along the nodal direction. Ginzburg-Landau mean-field theory demonstrates that the
temperature dependence of the surface modulation can occur from a higher thermal population of
the third CDW harmonic, which is commensurate with the strong Q$_1$ modulation. In addition,
the broadening of the nodal MDC widths for higher-order replica bands at low temperatures, and
similar effects for the LEED Q$_2$-peak width, may suggest an inherently disordered nature of the
corresponding structural effects, which could be caused by a macroscopic phase segregation of
domains with slightly different modulation periodicities, particularly at the surface.

The analysis of the antinodal gap allows comparison of these effects to the existing pseudogap
phenomenology. The observation of two energy-scales in the antinodal gap for UD15K, which
demonstrate two distinct temperature evolutions, shows the coexistence of a large 55meV gap that
follows the classic T$^*$ pseudogap, and a smaller $\sim$15meV gap that follows the surface Q$_2$
temperature evolution. This shows a coexistence of the pseudogap and the surface dynamics. ARPES results
provide evidence for a distinct antinodal pseudogap coinciding with the temperature-dependence
of magnetic order observed from neutron diffraction [180], and the nodal k$_F$ and antinodal gap
temperature-dependence reported here suggests there is also charge-ordering, at least on the surface,
in the pseudogap phase.

In the Bi-cuprates, there has been the long-known Q$_1$ supermodulation of the crystal structure
that arises as a result of the misfit of the perovskite blocks [78]. However, what is evident here is that this modulation can have a profound effect on the electronic structure. This is evidenced by the role of the incommensurate structure leading to a back-folding scenario, where overlapping band-dispersions are the main effect responsible for producing the PDH lineshape. This is further demonstrated by an anomalous back-bending region of the real-part of the self-energy for the nodal dispersion near the band-crossing position, which is observed even when one band is almost fully suppressed by the polarization-dependence of the ARPES matrix element. This implies that the back-bending is intrinsic to the spectral function and not produced by matrix element effects. The “kink” energy scale is consistent with van Hove singularity (VHS) formation at the band-crossing positions independently of doping, and coincides with back-bending in the real-part of the self-energy.

While the formation of the VHS can arise from a CDW or charge/spin-stripe order, it is argued that the incommensurate structure plays an important role in mixing the even- and odd-parity states, producing nontrivial coupling at the level crossing. The resulting picture has nested VHS’s along the nodal direction, suggesting that the lower-dimensional nodal nesting of the VHS plays a role in the coincident formation of the Q2 modulation in the underdoped samples. The interrelated aspects of a system with nodal-line nested VHS’s near EF, together with strong mass-renormalization, and Fermi surface nesting instabilities points towards a Peierls distortion instability in the underdoped nodal Fermi surface of Bi2Sr2−xLaxCuO6+δ. This is a fundamental revision of the physics of the cuprates, in the sense that it explains many disparate observations such as the “kink” and the 1/8-anomaly, which arise from band-crossing level-splitting due to the incommensurate symmetry. At and below a critical doping near p=0.125, the band-crossing migrates to the nodal direction, producing a series of nested VHS’s, which could produce a number of unusual effects in many measurements. The presence of the VHS’s near the Fermi surface also suggests that there is a possible relationship with the superconducting TC of Bi2201, such that at OP the VHS is at the chemical potential and therefore unstable to superconductivity, and for UD the VHS occurs near the energy of phonons associated with Q2 formation, thus providing a natural explanation for the doping-dependent variation in TC caused by the tuning of the VHS energy and thus the respective electronic instabilities of the electron-electron interaction and the electron-phonon interaction in the material.
Bibliography


[77] Olaf Lübben, Lenart Dudy, Alica Krapf, Christoph Janowitz, and Recardo Manzke. Structural behavior of pb$_y$bi$_{1.95-y}$sr$_{1.49}$la$_{0.4}$cu$_{1.15}$o$_{6+\delta}$ for 0 < y < 0.53. Phys. Rev. B, 81:174112, 2010.


[126] P. M. de Wolff, T. Janssen, and A. Janner. The superspace groups for incommensurate crystal

[127] M. Gurvitch and A. T. Fiory. Resistivity of La_{1.825}Sr_{0.175}CuO_{4} and YBa_{2}Cu_{3}O_{7} to 1100 k:


[130] J. C. Phillips. Reconciliation of normal-state and superconductive specific-heat, optical,


[133] B. Bucher, P. Steiner, J. Karpinski, E. Kaldis, and P. Wachter. Influence of the spin gap on

[134] W. D. Wise, M. C. Boyer, Kamalesh Chatterjee, Takeshi Kondo, T. Takeuchi, H. Ikuta, Yayu
Wang, and E. W. Hudson. Charge-density-wave origin of cuprate checkerboard visualized by

[135] Colin V. Parker, Pegor Aynajian, Eduardo H. da Silva Neto, Aakash Pushp, Shimpei Ono,
Jinsheng Wen, Zhijun Xu, Genda Gu, and Ali Yazdani. Fluctuating stripes at the onset of
the pseudogap in the high-Tc superconductor Bi_{2}Sr_{2}CaCu_{3}O_{8+x}. *Nature*, 468:677–680, 2010.


ordering in La_{2−x}Sr_{x}NiO_{4.00} with x =0.135 and 0.20. *Phys. Rev. B*, 51:12742–12746, 1995.


