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DOPING THE COPPER-OXYGEN PLANES WITH ELECTRONS: THE VIEW WITH PHOTOEMISSION*

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DOPING THE COPPER-OXYGEN PLANES WITH ELECTRONS: THE VIEW WITH PHOTOEMISSION

A DISSERTATION SUBMITTED TO THE DEPARTMENT OF PHYSICS AND THE COMMITTEE ON GRADUATE STUDIES OF STANFORD UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

> Norman Peter Armitage October 2001

I certify that I have read this dissertation and that in my opinion it is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

> Zhixun Shen (Principal Advisor)

I certify that I have read this dissertation and that in my opinion it is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

Robert B. Laughlin

I certify that I have read this dissertation and that in my opinion it is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

Martin Greven

Approved for the University Committee on Graduate Studies: To my first teachers, my parents.

.

'... I like arguments,' said the Rocket.

'I hope not,' said the Frog complacently. 'Arguments are extremely vulgar, for everybody in good society holds exactly the same opinions. Good-bye a second time; I see my daughters in the distance;' and the little Frog swam away.

'You are a very irritating person,' said the Rocket, 'and very ill-bred. I hate people who talk about themselves, as you do, when one wants to talk about oneself, as I do. It is what I call selfishness, and selfishness is a most detestable thing especially to any one of my temperament, for I am well known for my sympathetic nature. In fact, you should take example by me, you could not possibly have a better model...'

'There is no good talking to him,' said a Dragon-fly, who was sitting on the top of a large brown bulrush; 'no good at all, for he has gone away.'

'Well, that is his loss, not mine,' answered the Rocket. 'I am not going to stop talking to him merely because he pays no attention. I like hearing myself talk. It is one of my greatest pleasures. I often have long conversations all by myself, and I am so clever that sometimes I don't understand a single word of what I am saying.'

- Oscar Wilde in The Remarkable Rocket

Abstract

The undoped parent compounds of high-temperature cuprate superconductors are known to be antiferromagnetic Mott insulators. As the CuO₂ planes are doped with charge carriers, the antiferromagnetic phase subsides and superconductivity emerges. The symmetry, or the lack thereof, between doping with electrons (n-type) or holes (p-type) has important theoretical implications as most models implicitly assume symmetry. However, most of what we know about these superconductors comes from experiments performed on p-type materials. The much fewer number of measurements from n-type compounds suggest that there may be both commonalities and differences between the two sides of the phase diagram. This issue of electron/hole symmetry has not been seriously discussed, perhaps, because the experimental database of n-type results is very limited.

This thesis presents a high-resolution angle-resolved photoemission spectroscopic (ARPES) study of the *n*-type cuprate superconductor $Nd_{2-x}Ce_xCuO_{4\pm\delta}$. The evolution of spectral features is tracked through the full doping range, from the half-filled Mott-insulator to the optimally doped superconductor, concentrating on measurements from the highest- T_c samples.

For the x = 0.15 samples, a comparison of leading edge midpoints between the superconducting and normal states reveals a small, but finite shift of 1.5-2 meV near

the $(\pi, 0)$ position, but no observable shift along the zone diagonal near $(\pi/2, \pi/2)$. This is interpreted as evidence for an anisotropic superconducting gap in the electron doped materials, which is consistent with the presence of *d*-wave superconducting order.

In the normal-state electronic structure, it is found that there are regions along the Fermi surface where the near- E_F intensity is suppressed and the spectral features are broad in a manner reminiscent of the high-energy "pseudogap" in the underdoped p-type cuprates. However, instead of occurring near $(\pi, 0)$, as in the p-type materials, this pseudogap falls near the intersection of the underlying Fermi surface with the antiferromagnetic Brillouin zone boundary. The fact that the high-energy pseudogap and the superconducting gap have different momentum space symmetries, points to a non-pairing origin of the pseudogap in the extreme underdoped regime of the p-type materials.

In the undoped compound Nd_2CuO_4 , for the first time the charge transfer band is revealed. As electrons are doped to the system, spectral weight forms near- E_F with a concomitant decrease in the intensity of the charge transfer band. The momentum dependence of this near- E_F spectral weight is shown and it is demonstrated at least phenomenologically how the large Fermi surface of the x = 0.15 material forms. These findings shed light on the nature of the Mott gap, its doping dependence, as well as the anomalous transport properties of the electron-doped cuprates.

Acknowledgments

It has been an amazing six years here at Stanford. At graduation my grandfather, in his characteristic understated manner, asked me, "You've had a good experience here at Stanford haven't you?" I answered him quickly and the response surprised me. "It's been the highlight of my life", I had replied. I was right. It had been, but I hadn't realized it until then.

Paradoxically, getting my Phd. has been both the hardest thing I've ever done and the easiest thing I've ever done. It's been the hardest for obvious reasons. The concentration, effort, and dedication to the final goal has been something that few people ever get a chance to experience. And it's been the easiest in that for the first time in my life I was doing something every day that felt natural. Reading, writing, learning was something that 'school' had always interfered with before and now, for the first time in my life, it was my job.

First and foremost, I'd like to thank my advisor Z.-X. Shen for his principal role and his advice, limitless energy, and enthusiasm. Truly, he has created an environment where the students feel that they are at the center of the intellectual world when it comes to these physical problems. Not many students are afforded the opportunities for travel and discussion that I have received and I thank him for that. I will be proud to be known as his intellectual progeny.

I've been fortunate to work with a great collection of people in the Shen group. Changyoung Kim and I had more than one heated argument over physics in the last *n*-years...I've never learned so much. Donghui Lu and I worked closely together for a year and a half successfully bringing the new beamline 5-4 online. These two gentlemen have taught me everything I know about actually doing photoemission experiments. Andrea Damascelli came along a little later in my grad career and interactions with him got me ready for the physics world beyond the protective enclave of Stanford. I always appreciated his need to understand basic but neglected things, him instilling in me the "Groningen" way, and of course his sense of humor. Stuart Friedman "big-brothered" me through my early days in the group and was an early source of information and inspiration. Pasha, Donglai, and Filip were chronologically a year behind me, but we were all very much contemporaries and progressed together. Kyle tolerated being the low man on the totem pole admirably. It has been great seeing him go from a newbie who was always peppering us with questions to someone I could learn from. I'd also like to thank Zahid and Alessandra for "helpful discussion" too many to list. Marilyn Gordon and, before her, Gloria Barnes always came to my administrative rescue.

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I can't say enough about all my dear friends that I've met through the Stanford cycling team. I only wished we'd had more time to spend doing fun stuff. Thanks. My family has always been supportive and tolerated my many foibles and idiosyncrasies. Seldom are children fortunate enough to be raised by two more different people than my parents. I think it shows in the interests and outlooks of my brothers and myself how they have completed us. They always believed in me and maintained I could be the best at what ever I wanted, even when there wasn't any tangible evidence that this was true. Thanks Mom and Dad. I wouldn't have made it without you and to you I dedicate my thesis.

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Stanford, California October 17, 2001 N. Peter Armitage

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Chapter 1

Introduction

Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics...Perhaps it will be wise to approach the subject cautiously.

- David Goodstein, in the Introduction to States of Matter

1.1 Finding the High- T_c 's

Superconductivity is a remarkable phenomenon in which at a certain temperature metals can enter a state that conducts electricity with absolutely zero resistance and carries infinitely persistent electrical currents. Superconductivity results not just from the suppression of single particle scattering effects, but instead is a macroscopic manifestation of phase coherent quantum mechanics, as evidenced by the Meissner effect, i.e. the complete expulsion of magnetic field from a superconductor's interior.

The effect was first discovered in mercury by H.K. Onnes's group shortly after



Figure 1.1: Periodic table showing superconducting elements, both at ambient pressure and under high pressure [5].

their successful liquification of helium in 1911 [1]. Although phenomenological models of superfluidity and superconductivity were advanced by London, Landau and others [2, 3], a complete description of the phenomenon had to wait until the seminal achievement of Bardeen, Cooper, and Schrieffer with their BCS model [4]. They proposed that a phonon mediated electron-electron interaction caused normally repulsive electrons with opposite momenta to attract each other, such that they formed bound "Cooper" pairs. This bound $\vec{k} = 0$ state is a boson and many such bosons, acting in concert in a single $\vec{k} = 0$ state, can exhibit macroscopic quantum phenomena. Bardeen, Cooper, and Schrieffer were able to demonstrate how such a state supports persistent currents, the origin of the Meissner effect, and that the effect has an onset at a well defined transition temperature T_c .

Since the early days of the field, the search for new superconductors and higher T_c 's has been ongoing. Many elemental materials have been shown to be superconducting. In fact, approximately half the elements on the periodic table are known superconductors (Fig. 1.1); some of them are only at ultra-low temperatures and/or

exceedingly high pressures. The maximum elemental T_c at ambient pressure is 9.25K in niobium. Compounds based on superconducting elements showed greater promise for raising T_c and advances were made that pushed up transition temperatures by a factor of 2. Although the BCS theory remained (and remains) a poor predictor of transition temperatures or even the existence of superconductivity [6] various empirical rules were found by materials scientists. Famously Bernd Matthias elucidated the now so-called *Matthias* rules

- 1: High-symmetry crystals are best
- **2:** High near- E_F density of states is favorable.
- **3:** Stay away from oxygen.
- 4: Stay away from magnetism.
- 5: Stay away from insulators.
- 6: Stay away from theorists. This addendum to the original 5 is blamed on S. Girvin [7]. It wasn't one of Matthias's original rules, but it is good advice and not just in making superconductors.

The above proved to be an excellent guide for almost for 75 years of superconductivity research, with maximum T_c 's steadily rising in a series of niobium based intermetallics (Fig. 1.2) culminating in the discovery of 23K superconductivity in Nb_3Ge in 1976.

Theoretically, a weak coupling analysis of the BCS equation by Cohen and Anderson [8] argued that the maximum T_c was constrained within an electron-phonon mechanism by competing effects and that very high electron-phonon coupling typically leads to structural transitions that kill superconductivity. Specifically they argued starting from an equation of the form

$$T_{c} = \frac{\omega_{0}}{1.45} \left[\frac{-1.04(1+\lambda)}{\lambda - \mu^{*}(1+0.62\lambda)} \right]$$
(1.1)

Naively, one would believe that increasing ω_0 (the Debye energy) would lead to higher T_c 's, however increases made here are compensated by effects elsewhere. A simple relation for the effective pseudopotential $\mu^* = \mu/[1 + \mu ln(E_F/\omega_0)]$ gives that the effects of ionic screening enter here and becomes less effective as the Debye lattice vibration frequency scale increases. For similar reasons the effective electronphonon coupling parameter $\lambda = \kappa/(M_{ionic}\omega_0)$ decreases as ω_0 increases where M_{ionic} is the ionic mass. One could increase κ , but this is a parameter governed by such particularities as Fermi surface shape and large κ values (due to nesting effects for instance) typically lead to structural instabilities. Cohen and Anderson, argued that for these reasons, T_c 's were limited to $\sim 10K$. Although their's was only a weak coupling analysis these rough considerations seem borne out by the experimental fact that many materials had been found within a factor of 2 of 10K, but none much higher.

All this changed in 1986. Bednorz and Müller, were looking for superconductivity in a class of cuprate perovskites with a structural transition in which the CuO₆ octahedra vertically distort (Jahn-Taylor distortion). Since this phase transition was driven by a large electron-phonon coupling, it was hoped that these insulators, made metallic by doping, could become superconductors. They discovered 30K superconductivity in $La_{2-x}Ba_xCuO_{4\pm\delta}$ [9]. This sparked a flurry of activity, and superconducting T_c 's of 90K or higher soon followed, by Chu and others [10].



Figure 1.2: The history of maximum T_c in the field of superconductivity

At the time of this writing over 15 years have passed since the discovery of superconductivity in this material class and still a general understanding, or indeed much of any consensus at all on the underlying physics, has not been reached. Despite being one of the most deeply and widely researched issues in physics of all times, a coherent understanding still eludes the community. It is considered by most that the anomalous properties of the metallic normal state and the close proximity to an antiferromagnetic phase hold the key to the high transition temperatures. The more that is learned about these materials in both their normal and superconducting states, the more complex and interesting they have been revealed to be.

1.2 Overview of the high-temperature superconductors

1.2.1 Major experimental results

The high-temperature cuprate superconductors are based on a certain class of ceramic materials. All share the common feature of square planar copper-oxygen layers separated by "block" charge reservoir layers. These block layers serve to donate charge carriers to the CuO₂ planes. Shown in Fig. 1.3 is the crystal structure for the canonical single layer parent material La₂CuO₄ (LCO) and Nd₂CuO₄ (NCO). These undoped materials are antiferromagnetic insulators. With the substitution of Sr for La in La₂CuO₄, holes are introduced into the CuO₂ planes. The Néel temperature precipitously drops and the material at some finite doping becomes a superconductor.

As shown in Fig. 1.5, approximately the same behavior exists upon doping the CuO_2 planes with electrons. The similarities and differences observed upon doping with the two signs of charge carriers will be discussed in more detail below.

The high- T_c phase diagram is characterized by the obvious existence of two distinct phases. At "half-filling" (one charge carrier per site) the antiferromagnetic state is described by the basic Heisenberg Hamiltonian

$$H = \sum_{i\delta} \mathbf{S}_i \cdot \mathbf{J} \cdot \mathbf{S}_{i+\delta} \tag{1.2}$$

where the sum over i is a sum over Cu spins and **J** is the exchange coupling. Note that in addition to the 2D Heisenberg terms there is a coupling between spins in neighboring layers, made smaller because of frustration effects. Each spin has two



Figure 1.3: Crystal structure of the prototypical single-layer cuprates La_2CuO_4 and Nd_2CuO_4 [11].

parallel spins and two antiparallel spins that are equidistant in the tetragonal phase. In $La_{2-x}Sr_xCuO_4$ the small orthorhombic distortion lifts the frustration and results a residual antiferromagnetic coupling between layers. It is this interplanar coupling that allows true long-range order in the 2D plane, as otherwise via *Hohenberg* – *Mermin* – *Wagner* considerations the only long range ordered state would be at T = 0 [12]. In Eq. 1.2 the spin anisotropies are reflected by the fact that the exchange term **J** is a tensor. In a pure tetragonal structure, like K₂NiF₄, **J** would be diagonal and a vectorial representation would be possible.

The other distinct phase of the cuprate phase diagram is of course superconductivity. The superconducting state and symmetry of its order parameter will be discussed in more detail in Chapter 4, but let it suffice to say for now that these materials have properties different from typical low- T_c BCS superconductors. Most



Figure 1.4: The expulsion of magnetic field. i.e. the Meissner effect can float conventional magnets over a superconductor.

obvious is the symmetry of their order parameter, which is now more or less universally agreed to be of higher order $d_{x^2-y^2}$ symmetry. This has important implications for the low-energy properties of the superconducting state and it sheds light on the nature of the superconducting mechanism.

Aside from its symmetry, the superconducting state of the high- T_c 's may also differ from that of the BCS superconductors in its low superfluid density deriving from the low carrier density of the doped Mott insulator. This gives relatively small phase-stiffness and poor screening which leads to large phase fluctuations and a non-mean field superconducting transition. The small superfluid density has led to proposals that the phase coherence energy scale and the pairing energy scale are separated and have opposite doping dependencies. In the underdoped regime, "preformed pairs" may form at a higher temperature than T_c , and it is with the Bose condensation of these pairs that superconductivity occurs [13]. It is the fulfillment of both these conditions that allows the occurrence of superconductivity.



Figure 1.5: The phase diagram of the cuprate superconductors. Adapted from Ref. [15].

For the antiferromagnetic material, the Hamiltonian represented by Eq. 1.2 gives low-lying magnon excitations that well describe the low-energy degrees of freedom with the consideration of relevant anisotropies [14]. Not as clear is what happens to the normal state properties when the material is doped away from half-filling. In the discussion below, I will mainly consider the case of hole doping, as the vast majority of experiments have been done on the *p*-type compounds, their properties are the ones most modeled, and because it will serve as a counterpoint to the electron-doped compounds discussed in the next section. I will characterize the phenomenology of the doped compounds by breaking up the phase diagram into under-, optimal-, and overdoped regimes.

As holes are introduced to the CuO_2 planes the material quickly loses its antiferromagnetic phase and moves into a so-called "strange metal" phase. At very low doping levels, the materials resemble semiconductors with polaronic charge carriers. At slightly higher doping levels, but below the doping level that gives the highest T_c , these compounds can be characterized as metals. However, the description of this normal state escapes modeling by the conventional theory of metals. Inferred from a variety of probes is a large suppression in the low-energy density of states i.e. a pseudogap [16]. Pseudogap signatures are seen in ARPES, infrared, Raman, tunneling, DC resistivity, and specific heat measurements among others [16].

Most experiments sensitive to this pseudogap indicate a temperature (referred to as T^*) that it opens. Although techniques differ as to what the exact temperature is, they generally agree that the T^* line falls monotonically with increased doping and that it merges somewhat smoothly with T_c near the top of the superconducting dome.

The fact that the pseudogap appears to merge smoothly with T_c has led to proposals that it is intimately related to the superconducting gap. This is a point I will return to later as our measurements on $Nd_{2-x}Ce_xCuO_4$ may be able to shed light on it, but for now let me say that many measurements show there to be two distinct pseudogap energy scales, of which neither, one, or both may be related explicitly to superconductivity.

These energy scales are illustrated by what is seen in *p*-type angle resolved photoemission spectra near $(\pi, 0)$, as shown schematically in Fig. 1.6. For underdoped samples there is a clean leading edge gap in the normal state that has been posited to be indicative of pairing fluctuations [16, 17]. At higher binding energy (~ 200 meV) there is a large "hump" feature. Alternatively this high-energy pseudogap could be viewed as a suppression of spectral weight over a large energy range near- E_F . The fact that in *p*-type materials both of these features show a similar *d*-wave symmetry



Figure 1.6: The phase diagram of the hole-doped high-temperature superconductors showing the evolution of both pseudogap energy scales with doping. From Ref. [17]

and in the extreme underdoped samples the distinction between the two gets blurred has led to proposals that they share a common origin. I will have more to say about this in Chapter 5.

Neutron scattering and NMR show the large remnant of antiferromagnetic spin fluctuations that are still present in this underdoped regime. They are obviously weaker and broader than in the antiferromagnetically ordered state, but persist until the material is overdoped. There are differences between materials as to whether or not the fluctuations remain commensurate at (π, π) or not. In few materials (notably La_{2-x}Sr_xCuO₄) the incommensurability gives strong evidence for spin-charge ordering or fluctuations into one-dimensional stripes [18]. The incommensurability parameter δ of both x-ray (sensitive to charge) and neutron (sensitive to spin) has been shown to be proportional to the doping for x < 1/8. This is consistent with a picture where domains of one dimensionally ordered charge stripes are created. A similar incommensurability has also been found in Y123 [19].

As one moves towards optimal doping pseudogap effects get less pronounced, although they may still exist at the lowest energy scales. In the highest- T_c optimally doped *p*-type materials many of the temperature and frequency dependent probes (DC resistivity, optics, width of ARPES features) show a striking linear dependence up to many hundreds of degrees or meV in the normal state. Varma *et. al.* postulated that this linearity is due to a coupling of charge carriers to critical fluctuations from a nearby quantum critical point [20]. This was termed *marginal Fermi liquid*. However as pointed out by others (most recently by Allen [21]) the resistivity above T_c is actually well fit by conventional electron-phonon scattering theory as described by the Bloch-Grüneisen equations. It may be that the strikingly straight temperature dependence is due to the unfortunate occurrence of 90K superconductivity that obscures the normal metal low temperature behavior.

In the overdoped regime, the linear dependence of the resistivity begins to acquire a power law dependence with an exponent greater that 1. In well overdoped samples it may be roughly quadratic thereby having been termed *more Fermi liquidlike*. This is important because if the cuprates are Fermi liquids in the overdoped regime and there are no intervening phase transitions¹ as one underdopes then all the anomalous physics at low dopings are relegated to the category of messy details and not indicative of a new state of matter $a \ la \ RVB$.

1.2.2 The electron-doped compounds

 $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ is a member of the small family of cuprate superconductors that can be doped with electrons [23]. Other members of this material class with the chemical formula $Ln_{2-x}M_xCuO_4$ include substitutions where Ln=Pr, Nd, Sm or Eu and M=Ce or Th [24]. These are all single- layer compounds which, unlike their brethren 214 systems (for instance T crystal structured $La_{2-x}Sr_xCuO_{4\pm\delta}$), possess a T' crystal structure, characterized by a lack of oxygen in the apical position (see Fig. 1.3). It is found experimentally that only T' crystal structures appear to be dopable with electrons and structures with apical oxygen (like T) can only be doped with holes. This can be understood within a Madelung potential analysis, where strong modification of the local ionic potential on the Cu site is expected by the inclusion of an O^{-2} ion immediately above it [25]. As doped electrons are expected to primarily occupy the Cu site, while doped holes primarily occupy in plane O sites these considerations play a large role in the underlying physics.

The most dramatic difference between electron- and hole-doped materials is in

¹Reports of a quantum phase transition as a function of doping do exist; see Ref. [22].

their phase diagrams. Only an approximate symmetry exists about the zero doping line between p- and n-type, as the antiferromagnetic phase is much more robust in the electron-doped material and persists to much higher doping levels. Superconductivity occurs in a doping range that is almost five times narrower. In addition, these two ground states occur in much closer proximity to each other. From neutron scattering, in contrast to many p-type compounds, spin fluctuations remains commensurate where they can be resolved [26, 27].

One approach to understanding the differences in the extent of the antiferromagnetic region is to consider *spin-dilution models*. It was shown that Zn doping into La₂CuO₄ reduces the Néel temperature at a similar rate as Ce doping in Nd_{2-x}Ce_xCuO_{4±δ} [28]. Since Zn substitutes in a configuration that is nominally a d^{10} filled shell, it can be regarded as a spinless impurity. In this regard Zn substitution can be seen as simple dilution of the spin system. The similarity with the case of Ce doping into Pr_{2-x}Ce_xCuO_{4±δ} or Nd_{2-x}Ce_xCuO_{4±δ} implies that electron doping serves to dilute the spin system by neutralizing the spin on a d^9 site. It subsequently was shown that the reduction of the Néel temperature in these *n*-type compounds comes through a continuous reduction of the spin stiffness ρ_s which is consistent with this model [29].

This comparison of Ce with Zn doping is compelling, but cannot be exact as Zn does not add itinerant charge carriers like Ce does, as its d^{10} electrons are tightly bound and can more efficiently frustrate the spin order. That there is some validity in this point of view though can be seen by the fact that applied to hole doping it consistently explains the asymmetry of the AF phase on the two sides of the phase diagram. Aharony proposed that the reason *hole*-doping requires a much smaller density of holes is that they primarily exist on the in-plane oxygen atoms

and result in not spin-dilution but instead spin-frustration [30]. It was proposed that the exchange interaction between the doped hole on the oxygen site and the holes on either neighboring Cu site mediates an effective ferromagnetic interaction between Cu spins. The oxygen-hole/copper-hole interaction, whether ferromagnetic or antiferromagnetic, causes the spins of adjoining Cu-holes to align. This interaction competes with the antiferromagnetic superexchange and frustrates the Néel order; a small density of doped holes has a catastrophic effect on the long-range order. This additional frustration does not occur with electron doping as electrons are primarily introduced onto Cu sites and hence no frustration occurs.

The differences upon electron and hole doping have also been purportedly understood by considering the differences in sign of the higher-order hoppings within the context of t - t' - t'' - J models [31, 32]. A large next-nearest-neighbor hopping term t' can serve to stabilize the Néel state as it facilitates hopping on the same sublattice. As the parameterization of the hole-doped t - t' - t'' - J model has t' < 0 and the electron-doped t' > 0 the electron-doped material by these considerations has a greater stability of the Néel state. However, it may be that a complete treatment that includes t' explicitly, must also include next-nearest-neighbor spin-interaction $J' = t'^2/4$ (discussed below) which will frustrate the nearest-neighbor interaction [32].

Yet another scheme to understand the differences between the doping dependence of the magnetism with holes or electrons has been with spin fluctuations models that start from a Hubbard Hamiltonian in the weak coupling limit with t > U [33]. This approach assumes a Fermi Surface (FS) that changes volume with doping and typically neglects t'' terms. For electron doping this means that the FS just coincides with the AFBZ boundary near $(\pi/2, \pi/2)$. In the electron-doped compounds the magnetism is mediated by the nesting between these approximately flat sections of Fermi surface. The underlying band structure is such that the position of the FS near $(\pi/2, \pi/2)$ is relatively incompressible for electron addition and hence gives a large stability with doping and spin-fluctuations remain commensurate. In the holedoped compound the magnetism is mediated by nesting between the extended van Hove singularities near $(\pi, 0)$. In the *p*-type case the FS is rapidly "eaten-away" with doping near $(\pi, 0)$. This changes the nesting between Fermi patch regions and, in this picture, is the reason that the Néel temperature falls precipitously and the spin-fluctuations become incommensurate.

Experiments show other contrasting behavior between *n*-type superconductors and their *p*-type counterparts. There is a much touted T² dependence of the inplane resistivity that may be evidence for "more-Fermi liquid-like behavior" [34]. This behavior exists over a relatively large doping range as shown in Fig. 1.7 for $Pr_{2-x}Ce_xCuO_{4\pm\delta}$ This is in contrast to the *p*-type materials, which show such a T² dependence of the resistivity only in the very overdoped regime. It is interesting to note that many of the normal state properties of the highest T_c samples of the *n*-type materials are similar to those of the overdoped *p*-type compounds. Whether there is an intrinsic connection between them and the highest T_c samples of the *n*type materials can be seen as overdoped remains an open question. To investigate this, one must take into account the differences in FS shape and spin fluctuation spectrum.

In contrast to the *p*-types these materials possess a negative Hall sign over much of the superconducting doping regime. At first glance this confirms their *n*-type character, but is somewhat hard to understand given that ARPES measurements show the Fermi surfaces of electron and hole-doped materials to not have gratuitously



Figure 1.7: Temperature dependent resistivity for $Pr_{2-x}Ce_xCuO_{4\pm\delta}$ (b) plotted vs. T (b) plotted vs. T^2 . From Ref. [11]

different topologies. Moreover, they show an anomalous temperature induced sign reversal of the Hall coefficient near "optimal" doping that cannot be understood with conventional transport theory without invoking the existence of two bands [35, 36, 37]. Our ARPES measurements in Chapter 5 may shed some light on this.

For much of their history it was believed that the pairing symmetry in the electron-doped compounds was s-wave [38, 39, 40]. This picture has changed recently and now it seems the n- and p-type compounds appear to share a superconducting d-wave pairing symmetry (one of the subjects of this thesis) [41, 42, 43, 44]. Some differences in the superconductivity do exist, for instance the $2\Delta_{sc}/k_BT_c$ ratio of the n-type material is much smaller than that of its optimally-doped p-type counterparts [45].

Thus far, no signal resembling a "41 meV (π,π) resonance mode"² has been

 $^{^{2}}$ In fact, such a mode has not be seen in any single-layer cuprate. This may be a consequence

reported, although there is certainly much more to be done with neutron scattering [26, 27].

Another rarely mentioned aspect of the electron-doped system is the large magnetic moment developed in the crystal electric field by the core 4f electrons of the rare earth ions (Nd for instance). This large crystal field comes from the low positional symmetry at the rare earth site. Such a field strongly splits the energy levels of the 4f states and gives, with Hunds rule considerations, an electronic ground state with a large magnetic moment [46, 47]³. This magnetic ground state has complicated measurements of the penetration depth, as will be addressed in Chapter 4.

1.3 Theoretical models for the normal state

1.3.1 The Fermi liquid paradigm

Legend has it that shortly after the Schrödinger equation had been proposed and subsequently verified for small electron number systems like H_2 and He that P.M. Dirac declared that "chemistry had come to an end" as it was entirely specified by solutions to this equation. He continued that it was too bad that "in almost all cases this equation was far too complex to allow solution." It is a fortunate fact then for those who make a living studying the problem of 10^{23} interacting electrons, it is precisely this complexity that makes these systems so interesting. Since the beginning days of the subject, various approximate schemes have been proposed on how to deal with this formidable problem.

of low- T_c or the lack of interlayer effects

 $^{{}^{3}\}mathrm{Pr}_{2-x}\mathrm{Ce}_{x}\mathrm{CuO}_{4}$, despite its nominal $4f^{0}$ configuration, still has moment, albeit a very weak one, due to quantum fluctuations.

That many materials are relatively well described by the assumption that electronelectron interactions do not play a principle role in the essential physics is remarkable. Low-energy experiments (e.g. DC resistivity, specific heat) on materials like sodium, gold, or silicon, indicate that these systems can be well described by free-electron models. One assumes in modeling that the electrons only feel the static field of the ionic cores and the average of the other electrons. In other materials, experiments seem to indicate that the charge carriers are still free, but have masses many times larger than that of a bare electron. Even here at the lowest energy scales there are no clear signs that charge carriers are interacting with 10²³ other objects. It is surprising that considering the close proximity that many electrons have to each other that such interactions appear to be a weak perturbation on the free-electron physics.

In a system of interacting fermions, the relatively weak effect that even potentially strong interactions have on the underlying physics can be understood by realizing the strong constraint that a Fermi surface provides on the scattering kinematics. Consider an electron (1) that is inserted or excited some distance $\varepsilon_{\vec{k}}$ above the Fermi surface. This electron is constrained to scatter and impart energy only to another electron (2) that is within a thin shell $\varepsilon_{\vec{k}}$ of states below E_F , because electron (2) can only scatter into unoccupied states and therefore must receive at least enough energy to be promoted above E_F . As these electrons must conserve energy in their interaction, electrons (1) and (2) must end up again within $\varepsilon_{\vec{k}}$ of E_F . In three dimensions these two factors of $\varepsilon_{\vec{k}}$ means that the total phase-space available for scattering will go like $\sim \varepsilon_{\vec{k}}^2$. This in turn gives a scattering rate proportional to $\sim \varepsilon_{\vec{k}}^2$ and is related to the reason why the electronic contribution to the resistivity in a Fermi liquid goes like T^2 . In two dimensions a similar kinematic argument gives a small logarithmic correction. When the particle's scattering rate is less than its energy, i.e. $(\beta \varepsilon_{\vec{k}}^2 < < \varepsilon_{\vec{k}})$ one can say that the *quasiparticle* excitation is well-defined and scattering is a minor perturbation of free-electron physics. Such a perturbation renormalizes to zero in the $\varepsilon_{\vec{k}} \to 0$ limit. The effect of interaction can be subsumed into giving quasiparticle excitations a finite lifetime $(1/\beta \varepsilon_{\vec{k}}^2)$ and a renormalized energy parameterized by an effective mass m^* .

Landau hypothesized that if one imagines a gas of non-interacting electrons and envisions slowly turning on an interaction potential between them, some character of the original system would remain [48]. Specifically he conjectured that there would be a one-to-one correspondence between states and excitations of the non-interacting system and those of the interacting system. Since in the non-interacting electron gas, energy eigenstates were labeled by quantum number \vec{k} , there will be approximate eigenstates in the interacting system labeled by \vec{k} .

One can understand his point qualitatively by considering the first-year quantum mechanics example of a particle in a box. As is well known to all potential readers of this thesis, solutions to Schrödinger equation of a particle in an infinite square-well potential admit sine or cosine solutions. The various states of the system can be labeled by, for instance, how many nodes or wiggles the wave function has. If one imagines perturbing the square well by a weak potential that is peaked in the center of the box, one would expect that the wave function will change, but as long as the perturbing potential remains weak the number of wiggles or nodes will still be a good index for the hierarchy of states [49]. Such behavior is seen in Fig. 1.8 where a wavefunction is calculated within the WKB approximation for a weak perturbing potential that is peaked in the center of the box. The exact position of the peaks change (as the effective wave number gets bigger where the available kinetic energy


Figure 1.8: Perturbed square-well potential wavefunction calculated within WKB approximation.

is less) and the level spacing changes but the total number of wiggles is still a good quantum number.

The success of Fermi liquid theory comes, as detailed above, from the constraint on scattering kinematics for low-energy excitations. This gives the result that quasiparticle excitations are only defined at arbitrarily small energy scales. The condition for well defined quasiparticles to exist, $\beta \varepsilon_k^2 << \varepsilon_k$, means that as one increases the parameter β which characterizes the strength of electron-electron interactions, the maximum binding energy of well-defined excitations decreases, but well-defined quasiparticles still exist at progressively lower energies. Arbitrarily strong interactions just means that Fermi liquid behavior will only occur at arbitrarily low-energy scales i.e. at lower temperatures and excitation energies. As alluded to above with the case of phonons, it may be that the inopportune occurrence of superconductivity obstructs the view of low-energy quasiparticle behavior.

The vast majority of investigated metallic systems seem to obey the Fermi liquid paradigm, with the fractional quantum Hall effect being the only obvious case of where Landau's conjecture regarding a one-to-one correspondence of states has been *experimentally* falsified [50, 51]. On the theoretical side, exact solutions to 1-D interacting models show that the fundamental excitations in 1D are not electron-like at all, but fractions of electrons: spinons and holons that carry spin and charge separately [52]. This would be another case where the electronic quasiparticle concept is not valid, but thus far in real systems the residual higher dimensionality has been found to stabilize the Fermi liquid (see for instance Ref. [53]). It has been argued in *resonating valence bond* (RVB)-type models that the confusing phenomenology of the high- T_c 's comes from electron fractionalization occurring in the cuprates [54, 55]. Strong correlations models that may or may not exhibit these non-Fermi liquid effects are discussed below.

1.3.2 General considerations

P.W. Anderson pointed out soon after the discovery of the high- T_c superconductors that the likely key to understanding the unprecedentedly high-transition temperatures was understanding the anomalous properties of the normal state [54]. This is because in order for the question "what is the pairing mechanism;" to be well-posed one must assume the existence of quasiparticle electrons that can be paired. If the anomalous normal state implies the nonexistence of electronic quasiparticles then conventional BCS schemes based on electron pairing can not apply. It does appear that a straightforward application of Fermi liquid theory does not apply. Various theoretical models have been proposed for the underlying physics of the cuprate normal state.

Some theories fall into, what one might call, a "devil-in-the-details" approach [56]. These theories propose that the high- T_c 's are inherently very complex materials and that the peculiar properties of the normal state are a result of this complexity. For instance, nearly antiferromagnetic Fermi liquid (NAFL) and related theories emphasize the proximity of the material to the antiferromagnetic state and claim that residual antiferromagnetic fluctuations mediate interactions between electrons [57, 58, 59]. Here the fundamental excitations are quasiparticles that are electrons severely renormalized by magnons fluctuations. In contrast, polaronic theories emphasize the low carrier densities of these "almost-insulators" and the concominantly low ionic screening [60, 61]. Within this scheme the anomalous properties of the normal state are explained by the resulting large electron-lattice interaction. In general, this class of detail-oriented theories say that these materials can be understood within the Fermi liquid paradigm with interactions that are severely modified due to the peculiar properties of the parent materials.

Other theories posit that the anomalous properties of the cuprates are a quantum critical phenomenon that comes from the close proximity of the groundstate to some ordered phase. The fluctuations of this phase, being critical, are without an intrinsic length or time scale [20, 62]. Coupling of electrons to these fluctuations results in their anomalous properties and in so-called *marginal Fermi* liquid behavior. Interactions with typical non-critical fluctuations are *irrelevant* in a renormalization group sense, and renormalize away in the long-wavelength, low-frequency limit. Critical fluctuations do not renormalize to zero in the low-energy limit and are in the same renormalization group sense *marginal*. Electronic quasiparticle excitations do not exist as they immediately decay into a shower of lesser excitations. ARPES lineshapes that show evidence for non-critical modes will be discussed in Chapter 2.

Still another class of theories (RVB-type) propose that the normal state is a quantum disordered antiferromagnet which results in a new state of matter. This class of theories makes an analogy to 1D solutions of various interacting models that show that a 1D metal is a state of matter (called a Luttinger liquid) where spin and charge



Figure 1.9: Charge Transfer model. It is assumed that most of the "action" occurs in the CuO_2 plane and the intervening block layers serve as charge reservoirs and in giving structural stability. It is believed that their role can be subsumed into renormalizing effects of effective models of the CuO_2 planes and that they do not enter explicitly in the low-energy physics.

degrees of freedom are separated [52]. Here electrons decay into two separate welldefined particles (spinon and holon) that carry *fractions* of the original quantum numbers. Anderson has emphasized that the two different scattering rates extracted from the temperature dependence of the Hall angle are indicative of the existence of these two novel particles [55]. The striking linear dependence of the resistivity over many degrees (up to \sim 700K in LSCO) is taken to be another indication of these composite excitations. Holons and spinons cannot individually engage in scattering from conventional scattering sources as these only effect electronic quasiparticles and not the spinon and holon channels [55]. As the CuO₂ planes are a universal feature of all cuprates, the crystals are relatively two-dimensional, and band structure calculations show that intra-planar Cu and O orbitals are the majority states at E_F , most theories take as their starting point the CuO₂ planes in a charge transfer type of model. One assumes that most charge conduction happens in the CuO₂ planes and that the intervening block layers serve as charge reservoirs as shown in Fig. 1.9. It is believed that the role of the block layers can be subsumed into renormalizing effects on parameters in effective models and that they need not enter explicitly in the low-energy physics. This is the point of view taken by the strong correlation models discussed below.

1.3.3 Strong correlation models

I explained above that interactions in conventional metals can typically be considered as a perturbation to the kinetic energy Hamiltonian; this may or may not be possible in the cuprates. The best evidence for strong and unusual interaction effects in the cuprate superconductors comes from a close look at their undoped transitionmetal oxide parent compounds. These materials, which at low temperatures are antiferromagnetic, belong to a class of materials known as Mott insulators [63]. It was originally pointed out by de Boer and Verweij that a number of transition metal oxides, like NiO and CoO that are predicted to be metallic by band theory (as they have an odd number of electrons per unit cell) are in fact insulating [64]. Later it was explained that the very localized d orbitals have a large interaction energy for double site occupation and with one electron per site electrons are inhibited from hopping to an adjoining site due to the large energy cost to do so [65, 66, 67]. The low-energy physics attempting to model this behavior can be approximated by various effective Hamiltonians which are described below. But first: "Why effective Hamiltonians?" The full Hamiltonian relevant for solid-state physics is known exactly. Some wags have termed this "The-Theoryof-Everything" [68]. It is

$$H = \sum_{i} \frac{\vec{p_i}^2}{2m_e} + \sum_{i,j} \frac{e^2}{|r_i - r_j|} + \sum_{m} \frac{\vec{P_m}^2}{2M_m} + \sum_{m,n} \frac{Z_m Z_n e^2}{|R_m - R_n|} + \sum_{i,m} \frac{Z_m e^2}{|R_m - r_i|}$$
(1.3)

It is precisely the complexity of this equation that caused Dirac's lamentation recalled in a previous section. As it is too complicated to solve exactly, it is necessary in solid state physics to eliminate those aspects deemed least relevant to the lowenergy physics. Degrees of freedom are grouped together into effective parameters and Hamiltonians constructed that describe interactions between these parameters. Formally, this can be done through renormalization group methods, but is more often done through physical intuition. For example, in the Hamiltonian for tight binding models, $H = \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^{+} c_{j\sigma}$, the hopping parameters t_{ij} are single constants that represent the net effect of all kinds of messy hybridization between atomic orbitals. In the cuprates this term is the multisite overlap integral of the full complement of Cu 3d, Cu 4s and O 2p states, as well as weak components of (for NCCO) Nd 4f and 5s states. It is obviously much simpler to treat this as a single effective parameter t_{ij} than including each term explicitly.

The Hubbard model is the simplest example of an effective model that can include the strong on-site Coulomb repulsion that is considered at the heart of the properties of the cuprate oxides. In the three- band Hubbard model, one simplifies the square lattice of the CuO_2 plane by three hybridized bands $(d_{x^2-y^2}, p_x \text{ and } p_y)$ and an interaction term for double occupation on the Cu site. The model can be extended further by considering small interaction terms for double occupation of the O sites and intersite Cu-O interactions. These are typically neglected though as they are smaller perturbations. In its simplest form the Hamiltonian can be written [69].

$$H = \epsilon_d \sum_{i\sigma} n_{i\sigma}^d + \epsilon_p \sum_{j\sigma} n_{j\sigma}^p + t_{pd} \sum_{\sigma \langle ij \rangle} (p_{j\sigma}^{\dagger} d_{i\sigma} + \text{H.c.}) + t_{pp} \sum_{\sigma \langle jj' \rangle} (p_{j\sigma}^{\dagger} p_{j'\sigma} + \text{H.c.}) + U_d \sum_i n_{i\uparrow}^d n_{i\downarrow}^d$$
(1.4)

In an ionic picture (all t's = 0) one has a central oxygen band, and a Cu band that is split by the Hubbard U. It was proposed by Zhang and Rice that a strong hybridization between the $d_{x^2-y^2}$ and p bands results in a split-off state from the main manifold of central O states [70]. One imagines a doped hole delocalizing over a CuO₄ plaquette and in a sense forming a singlet bond with the hole already residing on the Cu site. If the doping of the system is such that the chemical potential lies between the energy of this Zhang-Rice singlet and the upper Hubbard band, the singlet may play the role of an effective Hubbard band with an effective Hubbard parameter U_{eff} proportional to the charge transfer energy ($\Delta = \epsilon_p - \epsilon_d$) and an effective hopping $t_{ij} = t_{pd}^2/\Delta$. The Hamiltonian is then

$$H = \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U_{eff} \sum_{i} n_{i\uparrow} n_{i\downarrow}$$
(1.5)

This is equivalent to reducing the three band Hubbard model to a one band model where each CuO_4 plaquette is real space renormalized to an effective site as shown in Fig. 1.10. The summation is now a sum of nearest neighboring plaquettes and as such t_{ij} is an effective hopping term that represents hopping between plaquettes.

The attentive reader will notice that my justification for the reduction of the three-band Hubbard model to a one-band model was very "hand-waving" and lacked rigor. It should be pointed out that while the one band Hubbard model (Eq. 1.5)



Figure 1.10: Schematic of antiferromagnetic half-filled square lattice. Electrons can hop to nearest neighbor sites only if the adjoining site's spin is anti-aligned.

is symmetric upon electron and hole doping, the more realistic three band model is **not** electron-hole symmetric. It may be that the assumptions that go into the three-band to one-band reduction are unrealistic and that this could be a starting point to justify the somewhat different phenomenology of the *p*- vs. *n*-type materials as electrons are doped onto Cu sites and holes onto O sites. The validity of the ZRS picture has been debated [71], but most workers agree that a split-off state is formed (as observed experimentally). As much of the debate revolves around the local spin character (singlet or doublet) I avoid the issue and will refer to the split-off oxygenderived band throughout this work as the charge transfer band (CTB).

The single-band Hubbard model, itself a low-energy approximation, can be further approximated at even lower energy scales. If one enforces a constraint of no double site occupation (the so-called Gutzwiller constraint) then the upper Hubbard band need not enter explicitly into the calculation. With the no-double-occupation constraint, electrons with oppositely aligned spins on neighboring sites can still lower their kinetic energy by undergoing virtual hopping to nearest-neighbor sites. Firstorder perturbation theory gives an energy lowering for oppositely directed spins

$$\Delta E_{\uparrow\downarrow} = \sum_{j} \frac{|\langle j | t_{ij} c_j^{\dagger} c_i | i \rangle|^2}{U}$$
$$\Delta E_{\uparrow\downarrow} = -4 \frac{t^2}{U}$$
(1.6)

Most of the following discussion will be in terms of the one band Hubbard model, but I should note that in the full three band model it is possible under similar considerations to derive a *superexchange* interaction given as

$$J_{se} = \frac{t_{pd}^4}{\Delta + U_{pd}^2} \left(\frac{1}{U_d} + \frac{2}{2\Delta + U_p} \right)$$
(1.7)

By Pauli principle considerations, an electron can not hop to a site already occupied by an electron of the same spin. This energy lowering can be subsumed into an effective spin interaction energy. U makes the material an insulator, but a remaining finite t makes it an antiferromagnet. In the limit where $t \ll U$ but is still finite for nearest neighbors, the effective Hamiltonian reduces to

$$H = \sum_{i,j} tc_i^+ c_j + \sum_{i,j} J(\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4}\mathbf{n}_i \cdot \mathbf{n}_j)$$
(1.8)

with the constraint on the Hilbert space of no double occupation. This t-J model is valid for calculating low-energy properties. It can be generalized further (and made to closer match experiment), by adding next-nearest (t') and next-next-nearest neighbor hopping terms (t''). The general systematics of the ARPES lineshapes and the difference between the photoemission spectra of hole- and electron-doped materials can be modeled successfully within a t-J context [72]. However, a question regarding its validity remains. The effective parameter J was derived for the insulating case with localized electrons. Is J still a valid parameter when many holes or electrons have been introduced? This question has not be satisfactorily addressed in the literature.

When t' = 0 and t'' = 0 the one band Hubbard Hamiltonian is particle-hole symmetric. This can be expressed formally as being invariant under the particlehole transformative operation

$$c_{i\sigma}^+ \to (-1)^i c_{i\sigma} \tag{1.9}$$

When $t' \neq 0$ the above transformation to the Hamiltonian with t' > 0 can be mapped onto its particle-hole symmetric one, but with the sign of t' reversed. This means that the results obtained for negative sign of t' for dopings below half-filling can be obtained from the results for positive filling. In this way t - J calculations that would represent the hole-doped case with a negative sign for t' can be made to represent the electron-doped case with a positive sign for t'.

There are many approximate solutions of the t - J model, which surprisingly lead to many similar answers [73]. A question remains for the extremely simplified and effective t - J model; Do solutions in the metallic regime give a Fermi liquid? Many workers have answered "no" to this question and have proposed the t - Jmodel natural leads to a RVB-type 2D generalization of the 1D spin-charge separated Luttinger liquid. It could be argued that the t - J model is the wrong starting point to model a Fermi liquid. In conventional Fermi liquid theory, one typically assumes that kinetic energy is the largest energy scale in problem and perturbs the bare wavefunctions with an interaction energy $U_{kk'}$. In the t-J model, we have started from localized states that are diagonal in the onsite interaction term U and perturbed them with the kinetic energy term t (Eq. 1.6). It is not obvious that a Fermi liquid can be recovered. This is a somewhat independent question to the one of "are the cuprates themselves Fermi liquids?", as there is no guarantee that the t - J model describes the cuprates.

1.4 The scope of this thesis

This thesis will attempt to address an number of the issues brought up above, specifically those concerning electron-doped cuprates. The high-temperature superconductors are known to be doped Mott insulators [63]. The symmetry, or lack thereof, between doping with electrons (n-type) or holes (p-type) has important theoretical implications as most existing models implicitly assume symmetry. Most of what we know about these superconductors comes from experiments on p-type materials. The comparatively fewer experiments on the n-types suggest that there is a substantial difference between these two sides of the phase diagram. Despite this, the issue of electron/hole symmetry has not been seriously discussed, perhaps because the existing database is rather limited.

Although *p*-type materials are interesting in their own right the major focus of this thesis will be to understand how or if their phenomenology fits into the somewhat established phenomenology of hole-doped compounds. I would like to address a number of questions. What is the symmetry of the order parameter? Many experiments indicate that it is *s*-wave; what does ARPES indicate? Is there a pseudogap? Does the close proximity of the highest T_c samples to the antiferromagnetic phase give us any insight into this enigmatic effect? What is the doping dependence of the density of states? As the *n*-type material provides a better opportunity to observe the Mott gap with ARPES it is interesting to see how it may evolve with doping. The fact that ARPES should be able to reveal in principle more of the relevant spectrum described by the Hubbard model in the *n*-type materials may be able to give us more insight into how the Mott insulator evolves into a metal. Can we discriminate between various models? It is usually claimed that the local character of the electrons is irrelevant to the low-energy fundamental excitations so that, despite the fact that doped electrons are thought to occupy Cu sites (as opposed to O sites for doped holes), this degree of freedom can be eliminated in effective models. In this regard can the three band Hubbard model really be reduced into a one band model?

Being very complex systems, the high-temperature superconductors are represented by models that are highly simplified abstractions of actual materials. It is hoped that these models capture the essence of the essential physics. As pointed out above, most are electron/hole symmetric. In as much as this symmetry is a natural result of these models, one might doubt their suitability or completeness if it is found that the symmetry is experimentally broken. This then raises the question: Do the real materials obey this symmetry or is it only a result of simple models?

Chapter 2

PhotoElectron Spectroscopy

The photoelectric effect was discovered by Hertz in 1887. The effect was inexplicable with then existing physics and its explanation by Einstein in 1905 was, along with Planck's work on black body radiation, instrumental in ushering in the quantum revolution. Hertz observed¹ that electrons emitted between two electrodes occur most readily when the cathode is illuminated with ultraviolet light [74]. At first glance this is not surprising, after all light carries energy and it is not unreasonable that some of the energy absorbed by a metal may reappear as kinetic energy of emitted electrons. However, a closer look shows that a classical picture cannot possibly describe the effect.

It was observed that the energy distribution of the photoelectrons was independent of the intensity of light. A stronger light beam yielded more electrons, but the average energy was the same for a given light frequency. Moreover, it was noticed that there exists a certain material-dependent critical light frequency below which photoelectrons were not produced no matter what the incident light intensity. At

¹More likely it was it a poor unappreciated, unheralded, but ultimately brilliant graduate student that made the observation; his(her) name is lost to history.

the same time a certain maximum energy of the electron distribution existed that was linearly proportional to the light frequency used.

Equally puzzling was that fact that within the experimental uncertainty (10^{-9} sec.) there was no time lag between the arrival of light at the metal and the detection of electrons at the collector. Again, a classical treatment could not explain the effect. A detectable photocurrent will result when $\sim 10^{-6} W/m^2$ of electromagnetic radiation is incident on the substrate [75]. There are about $\sim 10^{19}$ atoms in a monolayer of sodium 1 m². If all of the incident light is absorbed within this monolayer of sodium atoms, each atom will receive power at an average rate of 10^{-25} W. At this minuscule rate of energy transfer, it will take almost 2 weeks for an electron to receive the 1 eV of kinetic energy that it is measured to have outside the solid. If one adds in the typically 4-5 eV of potential barrier (work function) that the electron has to overcome, the time to acquire sufficient energy climbs to nearly 2 months. Conventional electromagnetic theory fails quite completely when trying to describe the photoelectric effect!

Einstein was able to provide a satisfactory explanation of the effect by carrying a proposal of Planck's just a bit further. Einstein conjectured that Planck's partitions of emitted energy from a black body cavity into equal quantized amount (quanta) were also valid for light as it traveled and was absorbed [76]. He hypothesized that the light was emitted, traveled, and ultimately absorbed as discrete packets (photons). The picture was one where electrons were not uniformly irradiated with UV light, but where *photons* individually impacted electrons and could impart them with their full energy which was sufficient to eject them from the solid. Einstein's empirical formula

$$E_{kin,max} = h\nu - \phi \tag{2.1}$$

where $E_{kin,max}$ is the maximum electron kinetic energy, h is the constant used by Planck, ν is the photon frequency, and ϕ is the work function, well described the data.

2.1 General description

In the years after its discovery and consistent description, the observation of the photoelectric effect evolved into a technique for the investigation of the fundamental electronic structure structure of solids. The simplest picture is one where the electron's initial energy E_i (where E_i includes both the electrons' initial kinetic energy and binding energy) and final energy E_f are related by

$$E_f - E_i - h\nu = 0 \tag{2.2}$$

Electrons in the solid with some initial state energy E_i (typically expressed as a negative number as the electrons are bound in the solid) are promoted into vacuum. If the illuminating photon energy is well known and monochromatic and the work function is well characterized, then we can get the electron's binding energy. In actuality one typically zeroes the energy to the measured Fermi energy of a noble metal (gold was used in the present case) that is in electrical contact with the sample. In this picture, the initial density of states in the material will get promoted to an energy that is higher by $h\nu$ as displayed in Fig. 2.1.

This picture where electron's initial and final state momenta are not explicitly taken into account is referred to as angle integrated photoemission. For materials



Figure 2.1: A simple density of states view of the photoemission process

with minimal correlations (e.g. alkali metals, semiconductors, band insulators, etc.) this provides the simplest and most direct method to image the density of states.

In addition to measuring the density of states it is, in principle, possible to measure band dispersions by discriminating an electron's angle of emission. I shall consider only the 2D case as the direct determination of the band structure of a 3D material is extremely difficult and requires an extensive study using multiple photon energies. The 2D case is also more relevant to the cuprates as inferred from the 2D nature of their transport.

Consider an electron with a well defined momentum \vec{k} parallel to the emission plane that is illuminated with monochromatic photons. This electron, if it absorbs a photon of sufficient energy to promote it to the vacuum, will conserve its momentum $\vec{k_{\parallel}}$ as shown in Fig. 2.2 with the approximate translational invariance in the parallel direction. It does not conserve its momentum in the perpendicular direction due to its interaction with the surface potential. This is not a consideration for electrons



Figure 2.2: Kinematics of an ARPES measurement. An electron with well-defined momentum parallel to the emission plane has its momentum conserved in the photoemission process.

in 2D metal whose $\vec{k_{\perp}}$ is undefined and is related to the reason that band mapping in a 3D material is so difficult. In an ARPES experiment one measures two things: the angle of emission of the electron θ and its kinetic energy. Knowledge of the photon energy $h\nu$, the electron's bare mass, and the workfunction ϕ allows one to work backwards as per the equations in 2.3 to determine the important quantities $E_{binding}$ and $\vec{k_{\parallel}}$.

$$E_{binding} = (h\nu - \phi) - E_{kin}$$
$$\vec{k_{\parallel}} = \sin\theta \sqrt{2mE_{kin}}$$
(2.3)

In a canonical ARPES experiment one sets the detector at a particular θ and scans kinetic energy. This gives a so called energy distribution curve (EDC). $I(E)_{max}$ as function of theta gives the band dispersion. This approach is valid for simple metals with minimal correlations. If one wants to map out the complete dispersion of a 2D material then of course one needs an additional degree of angular discrimination.

$$K_{x} = \frac{1}{\hbar} \sqrt{2m_{e}E_{kin}} \sin \vartheta \cos \varphi$$

$$K_{y} = \frac{1}{\hbar} \sqrt{2m_{e}E_{kin}} \sin \vartheta \sin \varphi$$

$$K_{z} = \frac{1}{\hbar} \sqrt{2m_{e}E_{kin}} \cos \vartheta$$
(2.4)

If the material in question is not a simple uncorrelated band metal or insulator then the above approach is not necessarily valid, although it may still provide a good 0-th order treatment. Electronic correlations can appear in the spectra in a number of ways. Both the initial states and final states are manifestly complicated many-body wavefunctions, but these complications carry intimate detail about the nature of the relevant interactions and lineshape analysis that machinery of manybody physics can shed light on. More problematic is the possibility of interactions between the outgoing electron or remaining photohole with the rest of the system. There are reasons to believe that these problems, while potentially severe, do not play a major role at typical excitation energies. This issue will be taken up below.

2.2 Three and one- step models

There is no exact tractable theory of the photoemission process. In principle, the so-called *one-step model*, where photon absorption, photoexcitation and electron emission are treated as a single coherent process should treat it exactly. However

the inclusion of bulk, surface, and vacuum effects into a Hamiltonian that already includes photoexcitation as well as the consideration of bulk, surface, and evanescent states make the problem one of considerable difficulty. For these reasons, photoemission is usually intuitively described in terms of the *three-step model*, where photoexcitation is factored into three discrete processes that each have their own probability functions. These steps are:

step 1: the optical excitation of an electron.

- step 2: the transport of the electron through the solid.
- step 3: the escape from the solid surface into the vacuum.

The photoemission intensity is given by the product of these three terms: the probability for optical excitation, a scattering probability for the electrons as they propagate to the surface, and a transmission function for escape into the vacuum through the surface barrier. Step 1 contains all the information intrinsic to the excitation process itself and will be addressed in detail below. Step 2 can be written as an effective mean free path, which is proportional to the probability that an electron will make it to the surface without a scattering. Such inelastic events are likely to be violent enough that these electrons will typically appear in the spectra as an angularly independent uniform background. The inelastically scattered electrons can be either modeled in a rough phenomenological way or for instance by a (slightly) more rigorous way with, for instance, a Shirley background [77]. The final transmission function is usually taken to be either 0 or 1 depending upon whether or not the electron has sufficient energy to overcome the work function.

Thus within the three-step model, it is the term representing the first step that has most of the interesting information in it. To treat optical excitation in the bulk we employ Fermi's golden rule.

$$I \propto \sum_{f,i} w_{fi} = \sum_{f,i} \frac{2\pi}{\hbar} |\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu)$$
(2.5)

Here $E_i^N = E_i^{N-1} + E_B^{\vec{k}}$ is the initial-state energy of the *N*-particle system and $E_f^N = E_f^{N-1} + E_{kin}$ is the final-state energy of the *N*-particle system ($E_B^{\vec{k}}$ is the initial binding energy of the photoelectron with kinetic energy E_{kin} and momentum \vec{k}). Ψ_i and Ψ_f are initial state and the final state wave-functions, respectively. H_{int} is the electron-photon interaction. It is:

$$H_{int} = \frac{e}{2mc} (\vec{A} \cdot \vec{p} + \vec{p} \cdot \vec{A}) = \frac{e}{mc} \vec{A} \cdot \vec{p}$$
(2.6)

where \vec{A} is the vector potential representing the photon field, \vec{p} is the electronic momentum operator, and the commutator $[\vec{p}, \vec{A}] = \hbar \vec{\nabla} \cdot \vec{A}$ was used. The use of this commutator is valid within the *dipole approximation* where one assumes \vec{A} is constant over atomic dimensions (true in the ultraviolet).

Then using $\vec{p} = \frac{-im}{\hbar} [\vec{r}, H]$ where H is the Hamiltonian without the interaction with the radiation field and since $|\Psi_f\rangle$ and $|\Psi_i\rangle$ are eigenstates of H, $\langle \Psi_f^N | \vec{A} \cdot \vec{p} | \Psi_i^N \rangle$ can be written as $-i\omega m \langle \Psi_f^N | \vec{A} \cdot \vec{r} | \Psi_i^N \rangle$. So then the optical excitation probability becomes

$$w_{fi} \propto |\langle \Psi_f^N | r | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu)$$
(2.7)

Within the sudden approximation (discussed below), we assume that the final state orbitals have minimal time to relax after photoexcitation and can write final and initial state wave functions as an appropriate product of single particle Slater determinants.

$$\Psi_i^N = \mathcal{A} \phi_i^{\vec{k}} \Psi_i^{N-1} \qquad \Psi_f^N = \mathcal{A} \phi_f^{\vec{k}} \Psi_f^{N-1}$$
(2.8)

where \mathcal{A} is the antisymmetrization operator. This means that one can write

$$\langle \Psi_f^N | r | \Psi_i^N \rangle = \langle \phi_f^{\vec{k}} | r | \phi_i^{\vec{k}} \rangle \langle \Psi_f^{N-1} | \Psi_i^{N-1} \rangle$$
(2.9)

In deriving the above we have been able to further distill the physics into a part concerned with the photoemission process itself $\langle \phi_f^{\vec{k}} | r | \phi_i^{\vec{k}} \rangle$ and a part that represent something of the intrinsic properties of the system under investigation $\langle \Psi_f^{N-1} | \Psi_i^{N-1} \rangle$.

In general Ψ_f^{N-1} will not be an eigenstate of the N-1 system and the final state of the system will be expressed as superposition of N-1 eigenstates i.e.

$$|\Psi_f^{N-1}\rangle = \sum_s |\Psi_s^{N-1}\rangle \langle \Psi_s^{N-1}|\Psi_f^{N-1}\rangle$$
(2.10)

$$|\Psi_f^{N-1}\rangle = \sum_s c_{s,i} |\Psi_s^{N-1}\rangle \tag{2.11}$$

Substituting 2.7, 2.9 and 2.11 into 2.5 one gets

$$I(\vec{k}, E_{kin}) \propto \sum_{f,i} w_{f,i} \propto \sum_{f,i} |M_{f,i}^{\vec{k}}|^2 \sum_{s} |c_{s,i}|^2 \delta(E_{kin} + E_{s,i}^{N-1} - E_i^N - h\nu)$$
(2.12)

Here $M_{f,i}^{\vec{k}}$ represents the $\langle \phi_f^{\vec{k}} | r | \phi_i^{\vec{k}} \rangle$ contribution. Neglecting the background contribution and within the sudden approximation the photoemission intensity can be seen to be proportional to the probability that the insertion of a photohole into the material results in leaving the system in a state Ψ_s^{N-1} (either the ground or one of the large manifold of excited states). Below I will show that $\langle \Psi_f^{N-1} | \Psi_i^{N-1} \rangle$ can be written formally as the single particle spectral function $A(\vec{k},\omega)$ and therefore the photoemission intensity can be written as

$$I(\vec{k}, E_{kin}) \propto \sum_{f,i} |M_{f,i}^{\vec{k}}|^2 A(\vec{k}, \omega)$$
 (2.13)

This a helpful simplification as it means that one can bring to bear the considerable mathematical machinery of many-body physics for intuition and analysis. Most of the analysis for the remainder of this thesis will rest heavily on the assumption that the above expression is at least qualitatively true.

2.3 Sudden approximation

A remaining difficulty in the analysis of ARPES spectra is that the incorporation of interactions effects between both the outgoing electron and the remaining N-1 system and the interaction between the photohole and the system is not straightforward. As argued above, the effect of photoelectron interactions are somewhat "self-selecting" and in much analysis can be neglected or incorporated as a uniform background.

Interpretation involving photohole/N-1 system interactions are most easily dealt with by *ignoring* them. This assumption was what enables us to write Eq. 2.8. Typically, this neglect is justified by invoking the *sudden approximation* where one makes the supposition that relaxation effects of the excited N-1 state do not have time to occur before the electron leaves the solid. Strictly speaking, this is only valid in the high photon energy limit. In the 15-30 eV range typically used in ultra-high resolution ARPES, it is not obvious that this is a good description of the underlying physics.

We can make some simple estimates of the time scales involved [78]. Roughly

speaking, one can compare the time that the electron spends escaping from the solid to the intrinsic time scales for photohole interactions. An electron moving with a kinetic energy of 20 eV has a velocity of ~ 3×10^8 cm/s (assuming a ~free electron mass). The appropriate length scale (l) is the smaller of either the screening radius of the photohole or the escape depth. This gives a time scale in which "dressing" interactions need to happen of $l = 3 \times 10^{-16}$ seconds or quicker. The frequency scale for such electron-electron interaction effects are on the order of the plasma frequency $\omega_p \simeq 10^{15}$ sec⁻¹, using the typical plasmon energies of ~ 1 eV for the cuprates. This very rough estimate gives 4×10^{-15} sec. for the electronic screening time. A more exact treatment would require a more rigorous analysis, but the factor separating these time scales (~ 1/10) may convince us that a sudden approximation approach is not without some validity [78].

2.4 Single particle spectral functions

Green's functions techniques are one particular methodology that has been employed to treat a system of interacting fermions. One envisions a many-body strongly interacting ground state where one introduces a single electron (hole) into a single particle wave function (labeled \vec{k}) at a time t and asking what is the probability amplitude that one will find the electron (hole) occupied in \vec{k} at some later time t'? The quantity describing this is the single particle propagator $G(\vec{k}, t, t')$ or time ordered Green's function. It represents the sum over the amplitudes of all intermediates states that the particle could undergo in a time t' - t. By taking a Fourier transform, one may express this quantity in ω -representation where $G(\vec{k}, \omega) = G^+(\vec{k}, \omega) + G^-(\vec{k}, \omega)$, with $G^+(\vec{k}, \omega)$ and $G^-(\vec{k}, \omega)$ indicating the one-electron addition and removal Green's function, respectively (with $\hbar = 1$).

$$G^{\pm}(\vec{k},\omega) = \sum_{s} \frac{|\langle \Psi_{s}^{N\pm1} | c_{\vec{k}}^{\pm} | \Psi_{i}^{N} \rangle|^{2}}{\omega \mp E_{s}^{N\pm1} \pm E_{i}^{N} \pm i\eta}$$
(2.14)

where ω is the excitation energy from the chemical potential and $c_{\vec{k}}^+$ and $c_{\vec{k}}^-$ are the electron creation and annihilation operators respectively. The summation runs over all possible $(N\pm 1)$ -particle eigenstates $\Psi_s^{N\pm 1}$ with eigenvalues $E_s^{N\pm 1}$, and η is a small positive number ² needed to ensure that the reverse Fourier transform is still valid.

One can express the relation for the single particle spectral function from the Green's function formalism using the relation

$$A(\vec{k},\omega) = A^{+}(\vec{k},\omega) + A^{-}(\vec{k},\omega) = -(1/\pi) \operatorname{Im} G(\vec{k},\omega)$$
(2.15)

In the limit $\eta \to 0$, $(x \pm i\eta)^{-1} = \mathcal{P}(1/x) \mp i\pi \delta(x)$, with \mathcal{P} denotes the principle part one has

$$A^{\pm}(\vec{k},\omega) = \sum_{s} |\langle \Psi_{s}^{N\pm1} | c_{\vec{k}}^{\pm} | \Psi_{i}^{N} \rangle|^{2} \delta(\omega \mp E_{s}^{N\pm1} \pm E_{i}^{N})$$
(2.16)

Despite its theoretical interest a direct calculation of the spectral function for even the simplest interacting case is a formidable exercise. In practice the single particle Green's function is typically more amenable to calculation through the use of Feynman diagrams and other perturbation techniques. The spectral function can be directly expressed in terms of the Green's function through relation 2.15.

The attentive reader should have more that a passing sense of deja v \dot{u} when

²Perhaps a philosophical point could be made here, where η represents the fact that electronic excitations can be only arbitrarily well defined, but cannot be absolutely well-defined by having a scattering rate that is identically zero.

seeing Eq. 2.16. With $c_{\vec{k}}^{\pm}|\Psi_i^N\rangle = |\Psi_i^{N\mp 1}\rangle$ it is precisely the one electron removal or addition function defined as $|c_{s,i}|^2$ in 2.12. It is through this relation that one can equate the photoemission spectra with the single particle spectral function.

Formally it can be shown that if in Eq. 2.14 $|\Psi_i^N\rangle$ is the ground state, then the sum over energy $|\Psi_s^N\rangle$ eigenstates can be replaced by representing the many-body interaction effects by a complex *self-energy* $\Sigma(\vec{k},\omega) = \Sigma'(\vec{k},\omega) + i\Sigma''(\vec{k},\omega)$ [79]. $G(\vec{k},w)$ and $A(\vec{k},\omega)$ can be represented compactly then as

$$G(\vec{k},\omega) = \frac{1}{\omega - \epsilon_{\vec{k}} - \Sigma(\vec{k},\omega)}$$
(2.17)

$$A(\vec{k},\omega) = \frac{1}{\pi} \frac{\Sigma''(\vec{k},\omega)}{[\omega - \epsilon_{\vec{k}} - \Sigma'(\vec{k},\omega)]^2 + [\Sigma''(\vec{k},\omega)]^2}$$
(2.18)

In a Fermi liquid $\Sigma(\vec{k},\omega)$ can be given direct physical meaning. In its simplest form Fermi liquid theory says the electronic excitations still have integrity at low energies despite strong interactions i.e. their scattering rate is much less than their binding energy. For self-energies where $\epsilon_{\vec{k}} + \Sigma'(\vec{k},\omega) >> \Sigma''(\vec{k},\omega)$ for energies $\omega \to 0$ one is in the Fermi liquid regime. One views the excitation much as a normal electron except with its binding energy shifted by an amount $\Sigma'(\vec{k},\omega)$ and with a finite lifetime $1/\Sigma''(\vec{k},\omega)$. In such a case $G(\vec{k},w)$ and $A(\vec{k},\omega)$ can be broken up into separate parts that represent the kernel of the electron excitation as well as a cloud of renormalizing incoherent excitations.

$$G(\vec{k},\omega) = \frac{Z_{\vec{k}}}{\omega - E_{\vec{k}} - i\Gamma_{\vec{k}}} + G_{inc}$$
(2.19)

$$A(\vec{k},\omega) = Z_{\vec{k}} \frac{\Gamma_{\vec{k}}/\pi}{(\omega - E_{\vec{k}})^2 + \Gamma_{\vec{k}}^2} + A_{inc}$$
(2.20)

Here $Z_{\vec{k}}$ is the overlap of the quasiparticle wavefunction with a bare electron wave

function with momentum \vec{k} . It represents the fact that there are still well-defined electronic excitations despite the strong interactions.

The interaction of the electrons with various bosonic modes can be expressed compactly with self-energies. This has been an area of much current focus in the ARPES community with the observance of bosonic effects confirmed in strongly coupled electron-phonon systems (Be and Mo) [80, 81, 82] and CDW systems (Nb₂Se₃) [83]. The case of the Be (0001) surface state is a beautiful example of this kind of analysis [80, 81]. A two peak structure (Fig. 2.3) in the spectral function is indicative of strong electron-phonon coupling. LaShell *et. al.* showed from a lineshape analysis how one could reasonably extract parameters like the Debye energy (ω_D) and the dimensionless electron-phonon coupling parameter (λ). The imaginary part of the self-energy $|\Sigma''(\omega)|$ when coupled (by a constant α^2) to a bath of dispersionless bosons $F(\omega)$ can be expressed

$$|\Sigma''(\omega)| = \pi\hbar \int_0^{|\omega|} \alpha^2 F(\omega') d\omega'$$
(2.21)

They assume the Debye model and have

$$|\Sigma''(\omega)| = \frac{\pi\hbar\lambda}{3} \frac{|\omega|^3}{\omega_D^2} \qquad \omega < |\omega_D|$$
$$|\Sigma''(\omega)| = \frac{\pi\hbar\lambda}{3} \omega_D \qquad \omega > |\omega_D|$$
$$\Sigma'(\omega)| = -(\frac{\hbar\lambda}{3}\omega_D) * [(\omega/\omega_D)^3 ln |(\omega_D^2 - \omega^2)/\omega^2| +$$

$$ln[(\omega_D + \omega)/(\omega_D - \omega)] + \omega/\omega_D]$$
(2.23)

for imaginary and real parts of the self-energy. $\Sigma'(\omega)$ is obtained by a Kramers-Kronig transform of the imaginary part. Using these model self-energies and plugging into the canonical form for the spectral function Eq. 2.18 they were able to reproduce the EDCs using parameters of $\omega_D = 65$ meV and $\lambda=0.65$. To obtain the best agreement with experiment a constant of 54 meV was added to $\Sigma''(\omega)$ that represents the (unphysically large) contribution from impurity scattering. These parameters in the Debye model reproduce the interesting features of Fig 2.3, i.e., the two component structure indicative of two excitation branches and non-quasiparticle behavior for $E(\vec{k})$ near the characteristic phonon frequency.

Although the case of electrons coupled to a bosonic mode are made explicit through the above consideration of the case of phonons, this treatment is generally valid, whether the bosons in question are magnons, plasmons, or some other collective mode.

The self-energy formalism is very general. In the case of marginal Fermi liquid (discussed in the previous chapter), it is proposed that the system is tuned arbitrarily close to a quantum critical point and as such there are no relevant energy scales (for instance ω_D in the phonon example above) excepting the temperature itself. The bosonic spectrum, to which the electrons couple, reflects an approach to order and manifests the underlying criticality with fluctuations on all length and time scales. Spin and charge polarizabilities (proportional to the bosonic spectral density) of the form $ImP(\omega) = -N(0)(\omega/T)$ for $|\omega| < T$ and $-N(0)sgn\omega$ for $|\omega| > T$ were proposed by Varma *et. al.* in which physically relevant self-energies can be derived [20]. Famously then $\epsilon_{\vec{k}} + \Sigma'(\vec{k}, \omega) \propto \Sigma''(\vec{k}, \omega)$ and quasiparticles excitations are not well-defined $[Z_k \propto 1/ln(\omega_c/E_{\vec{k}})$ so that $Z_k \to 0$ as $E_{\vec{k}} \to 0$; ω_c is an ultraviolet cutoff]. A MFL system is not a Fermi liquid in the sense that introduced photoholes



Figure 2.3: Be surface state interacting with phonons. The two peak structure is indicative of two excitation branches. The lower energy one corresponds to the excitation of a polaronic-like quasiparticle. The higher energy one is the excitation of a similar polaronic-like quasiparticle *and* a real photon. Figure adapted from Ref. [80].

break up into a shower of lesser excitations none of which have integrity.

The use of spectral functions in ARPES analysis and interpretation is particularly advantageous when one can exploit the use of various sum rules. If one had access to reliable inverse photoemission data then one could make powerful use of the relation.

$$\int_{-\infty}^{+\infty} d\omega A(\vec{k},\omega) = 1$$
(2.24)

In actuality the relation for the momentum distribution $n(\vec{k})$ is more useful.

$$\int_{-\infty}^{+\infty} d\omega f(\omega) A(\vec{k}, \omega) = n(\vec{k})$$
(2.25)

In this case, if $|M_{f,i}^{\vec{k}}|^2$ in Eq. 2.13 is a smooth function along the Fermi surface (FS) then one can use Eq. 2.25 and identify the locus of steepest descent of n(k) $(\max|\nabla n(\vec{k})|)$ with the Fermi surface.

2.5 Key experimental ARPES cuprate results

ARPES has been one of the key experimental probes in the investigation of the cuprate superconductor problem. Phil Anderson's early optimism that for the high- T_c 's photoemission will "play the role that tunneling played for BCS" [63] may have been a tad optimistic, but it is indisputable that such studies have contributed immensely. The fact that these materials are approximately two dimensional and cleave relatively easily has made them particularly amenable to study.

Most of the valuable contributions of ARPES have been on the *p*-type materials. One of the earliest achievements was the demonstration of a structure in momentum space that resembled a large Fermi surface (at least for overdoped compounds) [84, 85]. This was a confirmation that the FS had a volume that scaled with doping as 1-x as a metal would, instead of scaling with x as a Mott insulator or semiconductor would be expected to be. This was an initial challenge to theory and one that has not been satisfactorily addressed. Moreover, as regards the general band structure it was observed that since the "band" at the $(\pi, 0)$ position is not degenerate with that at $\approx (\pi/2, \pi/2)$ higher order hopping terms must be relevant (t' and t'') [72, 86]. It was also noticed that the overall bandwidth is much reduced from the expected $\sim 8t$ and seems to be controlled instead by the nearest neighbor magnetic interaction J [86, 87]. This bandwidth reduction points to the strong role of correlations and perhaps the necessary use of strong correlation models of the t - J variety.

In some of the earliest ARPES work on the cuprates, the superconducting gap was seen [85]. This was the first detection of superconductivity by photoemission. The initial angle resolved work was confusing with many contradictory reports regarding the symmetry of the gap [88, 89, 90]. With careful measurements and increased sample quality, results converged so that now the community more or less agrees on a superconducting gap with at least a major component of $d_{x^2-y^2}$ symmetry [86, 91, 92, 93].

The detection of the superconducting gap of an exotic symmetry, while novel, was not totally unexpected with the emphasis on spin-fluctuation models that naturally give such a momentum-space dependence. More unexpected was detection of pseudogap features (mentioned in Chapter 1) in the spectrum of underdoped and optimally-doped samples. There is a partial gap in the EDCs that that appeared to have the same functional form as the *d*-wave superconducting gap, but occurred *above* T_c . It can be characterized in two ways, by the position of the leading edge midpoint of the spectra (in a similar way to the SC gap) giving a energy scale of ~ 30 meV, or by the higher energy hump ~ 200 meV that appeared in underdoped samples [17]. Although both seemed to follow the *d*-wave functional form, it is possible that they are of different origin. More recently, with advent of new analyzers and techniques novel features have been found in the low-energy spectra. A "kink" in the dispersion is seen ubiquitously in the *p*-type materials [94, 95] and at the time of this writing its origin is a matter of heated debate [95, 96, 97]. Some groups have pointed to a many-body electronic source, perhaps related to the magnetic resonance mode discovered via neutron scattering [96, 97]. Others have argued that its universality shows it is likely caused by a coupling to phonons and indicates the strong (and largely neglected) role that lattice effects have on the low-energy physics [95].

Chapter 3

Experimental Issues

The major difference between a thing that might go wrong and a thing that cannot possibly go wrong is that when a thing that cannot possibly go wrong goes wrong it usually turns out to be impossible to get at or repair. - Douglas Adams, Hitchhiker's Guide to the Galaxy

3.1 Experimental apparatus: BL 5-4 at SSRL

Through much of its history, photoemission was considered a technique best suited for qualitative verification of calculated band structures and density of states for simple metals and semiconductors [98]. These measurements were primarily performed with lab-based XPS and UV excitation sources and analyzers based on cylindrical mirror (CMA) technology. Performance of such setups (resolutions of $\Delta E \approx 0.5$ eV and $\Delta \theta \approx \pm 5^{\circ}$) constrained the technique to answering questions on only the grossest energy scales relevant to solid-state materials. However, advances in the 80's and early 90's allowed angle resolved measurements to be performed with ~ 40 meV and $\pm 1^{\circ}$ resolution and ushered in an era were photoemission could begin to be considered a true many-body probe. This was due to, not only new methods and designs of photoelectron analyzers, but also to the increasing prevalence and use of tunable synchrotron radiation sources. As detailed in the previous chapter, this allowed photoemission to see the anisotropic *d*-wave superconducting gap [86, 93], as well as shed light on issues such as heavy fermion and Kondo physics [99].

Further changes in the technology in the last six years have again changed the kind of experiments and measurements that are proposed and carried out. This has come primarily with the advent of *Scienta*-style analyzers, but also with new beamline technologies and the implementation of third generation synchrotron sources and their insertion devices such as undulators and "wigglers". The newly commissioned beamline 5 - 4 (Fig 3.1) of the Stanford Synchrotron Radiation Laboratory (SSRL) (where the majority of experiments described in this thesis were carried out) makes use of both these advances in analyzers and beamlines. An upgrade to the SSRL ring in January of 2003 will bring it up to specification as a third-generation source.

The system installed at SSRL as a permanent endstation at beamline 5-4 is a Scienta SES 200 electron spectrometer coupled to a normal incidence monochromator (NIM). Both of these elements make crucial improvements over previously conventional apparatuses for ARPES experiments at SSRL. The NIM monochromator is a significant advance over previous "grasshopper" or glancing incidence designs for photons in the UV range. Glancing incidence geometry monochromators were originally designed to have a large dynamic working range (20-1000 eV), however they result in large sacrifices in intensity when trying to decrease the photon contribution to the total energy resolution. There is also their large background signal due to the contribution of higher-order light. In NIM monochromators the geometry



Figure 3.1: Bird's eye view of Beamline 5-4 at Stanford Synchrotron Radiation Laboratory. The experienced VUV eye will notice a familiar scene; the chamber is baking.

is such that the dispersion, i.e. the angular spread of the monochromatized light per unit λ , is maximized. This results in much higher throughput of photons at a particular beamline energy resolution setting (i.e. beamline entrance and exit slit widths). These potential gains are somewhat countered by the low reflectivity in the UV range for normal incidence. For this reason NIM designs are limited to photons < 30 eV. This doesn't present an appreciable problem for most measurements of high-T_c and related materials as they have large cross-section for photo-ionization in the ~ 20 eV range. At the end of the day, the intensity gain over a comparable glancing incidence setup is approximately a factor of five.

In the typical operating configuration the beamline contribution to the system's energy resolution is on the order of 2 meV. It can be independently measured by a gas-phase cell. In Fig. 3.2 absorption results are shown for the He $1s \rightarrow np$ transition for the beamline 5-4 NIM during its commissioning. The absorption was measured in a simple ion cell, whereby a high-energy photon is absorbed by the He atom causing an ionization which is detected as a current between two high voltage plates. As expected, the progression between energy levels becomes narrower and narrower before ultimately the electron is excited to the continuum. As the energy levels themselves are narrow as compared to other energy scales in the problem, the fringe pattern disappears when the incident photon energy spread becomes approximately equal to the level spacing. This gives a beamline contribution of approximately 2 meV.

The advantages of the NIM design notwithstanding, the primary advances in the photoemission technique have come with the development of Scienta-style analyzers. These hemispherical analyzer differ from older style hemispherical ones by having both a sophisticated electron lens at the entrance to the hemispheres and a two



Figure 3.2: He $1s \rightarrow np$ transition for independent beamline resolution calibration. When the spread in incident energies becomes equal to the level spacing of the transition the fringe pattern disappears.

dimensional multichannel plate detection system. The electron lens allows much more intricate focusing of electron trajectories, allowing sequential angle scanning (detailed below) and more precise retardation potential control, increasing energy resolution as shown in Fig. 3.3. The 2D multichannel plate replaces resistive anode style detection in conventional older detectors. A two stage electron amplification system sits before a phosphor screen, which is then imaged by an $ex\ situ$ digital camera.

In a canonical angle-resolved photoemission experiment, angular selection is made by the presence of an aperture that only allows electrons within a certain solid angle to be admitted. Angular resolution is determined by aperture size and angular discrimination is done by either moving the analyzer or by turning the sample. This method, although straightforward, discards those electrons that do not enter the


Figure 3.3: Photoemission spectrum of the Ar $3p_2^3$ core level taken with 25 eV synchrotron radiation from beamline 10.0.1 at the Advanced Light Source. The full width at half maximum of the main peak is 8 meV. After taking into account the intrinsic excitation lifetime and Doppler broadening of the Ar $3p^3$ line, the total contribution from the beamline and the analyzer is 3 meV. Similar performance is seen at the beamline 5-4 system at SSRL.

detector. This is unfortunate and inefficient, particularly in low-signal experiments like those described in later chapters on the $Nd_{2-x}Ce_xCuO_4$ material system. The Scienta analyzer's operation when being run in this manner is termed *Transmission* mode. Here the electron lens potentials are configured such that they focus what is essentially a real space image of electron intensities of the sample onto the analyzer entrance slits (see Fig. 3.4 for a diagram). Spatial resolution in the horizontal direction across the sample corresponds to points on the entrance slit. By virtue of the hemispherical geometry there is a one-to-one correspondence of points of the analyzer entrance slit to the electron multichannel plate detector (see the electron trajectories in the hemispheres in Fig. 3.4).

The greatest qualitative advantages of the Scienta system is an ability to run in socalled "Angle" mode. In this case, the voltages of the electron lens (run apertureless)



Figure 3.4: The Scienta hemispherical analyzer

are configured such that instead of focusing at a finite distance from the sample to a real image on the slit, the lens focuses *from* infinity to the entrance slit. In this way, all electrons inside a large solid angle are collected and those with parallel trajectories are collimated to specific points on the entrance slit and thereby a specific point on the multichannel detector. The reason for operating in this manner is multifold. Firstly, it allows angle resolved parallel scanning in a large angular range, in this way making use of the maximum number of photoemitted electrons and drastically increasing statistics and/or decreasing acquisition time. Secondly, angular resolution is decreased significantly, as it is largely limited by the chosen horizontal bin size of the multichannel plate detector. Thirdly, since the apparatus discriminates electrons according to their angle relative to the lens axis and **not** according to their admission through an aperture, a sample's finite surface area does not give a extra contribution to the angular resolution.



Figure 3.5: Gold Fermi edge scan comparing the resolution of two generations of photoemission systems.

In the Scienta's Angle mode, in principle, an angular range of $\pm 7^{\circ}$ can be imaged simultaneously. For the 16.5 eV photon energy used primarily in these measurements this corresponds to 52% of the Brillouin zone quadrant width $(\pi/a, 0)$. In practice, we commonly only use the middle $\pm 5^{\circ}$. In order to image a comprehensive region in momentum space, one still needs to be able to manipulate the angle of the sample's normal to the analyzer's axis. To avoid the complexities of moving a large Scienta chamber with UHV couplings we have constructed a custom dual-axis lowtemperature sample manipulator. The coordinate system of this manipulator could be described as equatorial spherical i.e. the sample normal at $\theta = 0, \phi = 0$ lies on the equatorial plane. This is in contrast to coordinate systems that are typically used in photoelectron diffraction systems where the coordinate system is polar spherical $(\theta = 0, \phi = 0$ at the north pole). In our geometry (to first order i.e. $sin\zeta \approx \zeta$) the two perpendicular momentum are $\vec{k_x} \propto \theta$ and $\vec{k_y} \propto \phi$. All of the above features make for substantial improvements over previously existing technology. Energy resolution has improved by approximately a factor of 10 and angular resolution by a factor of 15. Typical gold Fermi edge scans for the two generations of photoemission systems is shown in Fig. 3.5.

Systems all over the world are being improved dramatically. In September of 1999, I reported at a conference in Hvar, Croatia that our system was capable of 4 meV resolution as measured on a gold Fermi edge. At the time this was, to the best of our knowledge, a world record. Less than a year later a group in Japan was reporting measurements of the superconducting gap of the BCS materials Pb and Nb [100]. These measurements were done at 2.3 meV resolution! This may be close to the limit with existing technology. Further improvements may require going to time-resolved spectrometers. Hopefully with the SPEAR 3 upgrade to SSRL the beamline 5-4 system will begin to approach the limits of the theoretical performance.

3.2 Experimental details

The majority of measurements reported in this thesis were performed at the above described Stanford Synchrotron Radiation Laboratory's Beamline 5-4. The photons in the SSRL measurements had an energy of 16.5 eV, which has been found empirically to give good cross-section in the relevant binding energy range. Data were taken with an incidence angle of approximately 45 degrees and with the in-plane polarization either along or at 45 degrees to the the Cu-O bond direction.

As it is imperative to determine which characteristics of the data are intrinsic and which are possible artifacts due to, for instance, the matrix elements for photoexcitation, data was also collected on beamline 10.0.1 at the Advanced Light Source



Figure 3.6: Laué pattern of Nd_{1.85}Ce_{0.15}CuO₄

(ALS). Our measurements at ALS used an incident energy of 55 eV in a glancing incidence geometry with the in-plane polarization along and at 45 degrees to the Cu-O bonds.

Data reported here was collected with 10-20 meV energy resolution and an angular resolution $0.14^{\circ} - 0.56^{\circ}$ except where indicated. Sample temperatures were 10-30K to prevent problems with physioabsorbed gases reacting with the sample surfaces. Surprisingly, this presented no charging problems even for the x=0 insulator reported in Chapter 6, indicating the nominally undoped sample is probably slightly doped. The chamber pressure was lower than 4 x 10⁻¹¹ torr. No signs of surface aging were seen for the duration of the experiments(~24 hours).

Samples were oriented $ex \ situ$ to the analysis chamber by the Laué method. A typical pattern for a x=0.15 sample taken on the University of Tokyo Laué machine



Figure 3.7: LEED pattern of $Nd_{1.85}Ce_{0.15}CuO_4$ cleaved in situ at 10K.

is shown in Fig. 3.6. Due to the extreme surface sensitive nature (probing depth of 20 Angstroms) of measurements in the UV range, great care must be taken with regards to surface quality and cleanliness. Cleaving the samples at low temperature *in situ* results in shiny flat surfaces of which low-energy electron diffraction (LEED) [Fig. 3.7] reveal clean and well ordered with a symmetry commensurate with the bulk. This also served as a good cross-check of sample alignment.

3.3 Materials growth

As is well known to anyone working in the field of solid-state physics, all real progress comes from the advent of new materials. The discovery of superconductivity in the $Nd_{2-x}Ln_xCuO_4$ (where Ln=Lanthanide) material class was serendipitous. Along with the flurry of work on the hole-doped compounds in the late 1980's, a number of groups had looked into the possibility of *n*-type substitutions. These efforts were given up as there were no signs of superconductivity and with the pace of research and discovery being what it was they couldn't afford to pursue non-fruitful directions for long. The work on the $Nd_{2-x}(Ln)_x CuO_4$ system was motivated after the discovery of 20K superconductivity in $Nd_{2-x-y}Sr_xCe_yCuO_4$, by J. Akimitsu¹. There it was found that higher cerium concentrations actually reduced and eventually killed the superconducting T_c .

As no one had found a superconducting electron-doped cuprate, the original extensive work on NCCO at the University of Tokyo was done with the likely result in mind that the material when doped with electrons may become an *n*-type metal, but it would not become a *superconductor*. This would point to the special role played by superconducting holes. Initial work seemed to back up this prejudice. The group found that indeed the conductivity seemed to rise when increasing cerium concentration and that for well-doped samples the behavior was metallic $(d\rho/dT > 0)$ for much of the temperature range. Hall effect measurements confirmed the presence of mobile electrons. This underscored the suspicion that cerium was substituting tetravalently for trivalent neodymium and was donating electrons for conduction.

At the lowest temperatures the materials were **not** good metals and showed residual semiconducting tendencies with $d\rho/dT < 0$. In an attempt to create a true metallic state at low temperature, various growth conditions and sample compositions were tried. A breakthrough occurred when a student, H. Matsubara, accidently quenched a sample in air from 900°C to room temperature. This sample, presumed to be destroyed by such a violent process, actually showed superconductivity at 10K.

 $^{^1\}mathrm{J.}$ Akimitsu was to make another fortuitous discovery of 39K superconductivity in MgB_2 earlier in this present year.

Further work showed that in samples with x=0.15 cerium concentration superconductivity could be induced at 20K, by oxygen *reducing* them in a flowing argon (or similar) environment. Later it was found that by optimizing the conditions T_c could be pushed as high as 24K. N-type superconductivity was subsequently discovered by other workers in a number of related compounds based on rare-earths lanthanides [24].

An interesting question regards the role of oxygen reduction. Naively one may think that the role of extra oxygen in the crystal is to reduce the electron carrier concentration (oxygen doping in the *p*-type crystals increases the hole concentration). Some effects of this kind may play a role, but this does not seem to be the whole story as superconductivity has not been observed in any electron-doped compound without post-growth annealing of the crystals. It does not seem to be possible to make up for an electron deficiency with excess cerium. Typically the total oxygen removed is very very small (on the order of 0.25% per unit cell.) Neutron scattering studies have pointed to the fact that this removed oxygen is likely excess oxygen that occurs naturally in the as-grown crystal as an interstitial apical impurity site |101|. Impurity oxygens in the apical position with nominal valence -2 would be expected to strongly effect the local Madelung potential at the Cu site. It is believed that the lack of an O^{-2} in the apical position for the pure T' structure is the very feature that allows electron doping onto the Cu site in this crystal structure, as discussed in Chapter 1. For these reasons, it is believed that oxygen may act more as a scattering impurity or pinning center than as a provider of charge carriers. Several studies suggest that this is the case [102, 103, 104].

Early crystals of $Nd_{2-x}Ce_xCuO_4$ were grown by the so-called flux method where one prepares the desired composition in a crucible with excess CuO as flux. In the



Figure 3.8: The view inside a traveling solvent floating-zone furnace. From Ref. [14]

growth of cuprates, the exess CuO typically serves two functions. First, it decreases the melting temperature so that crystals can be grown at relatively low temperatures (~ 1200°C). Second, some crystals ($La_{2-x}Sr_xCuO_4$) can not be grown uniformly in a stoichiometric melt. The advantages of the flux method are that, with a proper temperature gradient, large flat crystals can be grown and that the equipment involved is relatively straightforward. The disadvantages are that the crystals can be contaminated by crucible material, and for some materials (like $Nd_{2-x}Ce_xCuO_4$), the tendency for dopant segregation may increase. Contamination problems are so severe that the use of platinum crucibles can completely suppress T_c (with Pt incorporated only at the 1% level) and necessitates the use of YSZ and Al_2O_3 crucibles [105].

Dopant segregation problems in the $Nd_{2-x}Ce_xCuO_4$ system were shown by Skelton *et. al.* [106]. Using micron-sized x-rays, they observed segregation of cerium on length scales of 100nm, indicating that the material grows layer by layer with



Figure 3.9: Meissner transition of $T_c = 25 \text{K Nd}_{1.85} \text{Ce}_{0.15} \text{CuO}_4$

smoothly varying Ce for Nd. Many of the above problems with the flux-based crucible method can be overcome, or at least addressed more systematically, using traveling floating-zone techniques.

The traveling-solvent floating-zone method avoids contamination by growing crystal without a crucible. A ceramic rod of the appropriate concentration is joined to a rod with excess CuO. This excess melt constituent is required for maintaining the proper growth conditions. Using high-intensity halogen lamps, the small region of the two rods where they are originally joined together is melted while they are counter-rotated to each other. Typically, the halogen light is focused by putting the melt zone in one focus of an ellipsoid mirror with the bulb at the other focus. The melt zone is then moved slowly up the rod. With luck, skill and good bit of magic, large nearly contaminant-free crystals can be grown. In the $La_{2-x}Sr_xCuO_4$ system single crystals of greater than 1 cm³ have been grown.

The $Nd_{1.85}Ce_{0.15}CuO_4$ crystals used in this thesis were grown by the traveling solvent floating-zone method in 4 ATM of O_2 at Stanford University and the University of Tokyo by the Greven and Tokura groups, respectively. Crystals with x=0, 0.04 and 0.1 doping levels were also grown at Stanford University under similar conditions to the x=0.15 samples. For the x=0.15 samples, the c-axis lattice constants agree well with previously reported values, confirming the desired Ce concentration. The as-grown boules are not superconducting and must be post-growth annealed to remove the impurity apical oxygen. Tokyo samples were heated in flowing argon gas for 100 hours at 1000° C. For the x=0.15 samples, both resistivity and magnetic susceptibility measurements show an onset of the superconducting transition at 25 K. A superconducting volume (Meissner shielding) of almost 100% at 20K is a testament to their extremely high quality. In Fig. 3.9, a magnetization curve for a typical transition in our crystals is displayed. It shows a transition width of \sim K. Stanford University grown samples were annealed in Ar for 10 hours at 930°C and then 20 hours at 500°C in flowing O_2 . These show an onset of superconductivity at 24K and similarly narrow transition widths. The photoemission data obtained between the two batches are identical. Lower doping samples grown at Stanford University were subjected to gentler reducing conditions as there appears to be a relation between Ce concentration and O content.

Chapter 4

The Superconducting Gap^{\perp}

4.1 Background

This chapter deals with the symmetry of the superconducting gap and order parameter in $Nd_{1.85}Ce_{0.15}CuO_4$. This is a matter of much recent interest due to the conflicting pictures coming from different experimental probes. A correct determination of the order parameter is of fundamental importance, as an asymmetry between the two sides of the phase diagram could shed light on the nature of the superconducting mechanism.

The normal metal to superconductor transition is characterized by the emergence of a macroscopic phase coherent pairing state, manifested by the bosonic occupation by paired electrons (Cooper pairs) of a single $\vec{k} = 0$ quantum state. As in all ordered states, it can be parameterized by an order parameter that, in this case, represents the degree of macroscopic phase coherence in the system. The concept of an order parameter was first applied to superconductivity by Ginzburg and Landau in their

¹The main contents of this chapter were published as N.P. Armitage et. al., Phys. Rev. Lett. 86 1126 (2001)

phenomenological free-energy functional description of the superconducting state using the Landau theory of 2nd-order phase transitions [3]. The superconducting order parameter written as a Ginzburg-Landau local variable has both a spatially dependent amplitude and phase $\Psi(\vec{r}) = |\Psi(\vec{r})|e^{i\phi(\vec{r})}$. As $|\Psi(\vec{r})|^2$ is a measure of the local condensate fraction [107], it is suggestive that the $\Psi(\vec{r})$ is the pairing wave function.

These ideas can be, perhaps, best expressed through the concept of off-diagonal long-range order, a necessary condition for such macroscopic quantum phenomena. This is where the two particle density matrix

$$\rho_2(\vec{r}, \vec{r'}) = \langle \Psi^{\dagger}_{\alpha}(\vec{r}) \Psi^{\dagger}_{\beta}(\vec{r}) \Psi_{\alpha}(\vec{r'}) \Psi_{\beta}(\vec{r'}) \rangle$$
(4.1)

acquires a finite off-diagonal expectation value. In a momentum space representation the expression becomes, after some simplification for the relevant case of spin-singlet pairing

$$\rho_2(\vec{k}, \vec{k'}) = \langle \Psi_{\uparrow}^{\dagger}(\vec{k}) \Psi_{\downarrow}^{\dagger}(\vec{k}) \rangle \langle \Psi_{\uparrow}(\vec{k'}) \Psi_{\downarrow}(\vec{k'}) \rangle \tag{4.2}$$

where the off-diagonal terms can be constructed out of the expression for the condensate fraction in the Ginzburg-Landau formalism. One can see that nonvanishing off-diagonal terms are a prerequisite for finite condensate fraction. Such off-diagonal long-range order means that macroscopic quantum mechanical aspects like flux quantization can be conceivably derived without knowing anything at all about the microscopic mechanism driving the condensed state. This approach is taken advantage of in those probes that couple to topological excitations of the system such as the tri-crystal experiments described below.

The order parameter can have different symmetries that are associated with the different internal degrees of freedom of the Cooper pairs i.e. angular momentum, parity etc. Conventional BCS electron-phonon mediated superconductors have an almost isotropic s-wave symmetry. These are s = 0, l = 0 states. Other higher angular momentum symmetries are possible of which various s = 1, l = 1 pairing channels in superfluid He-3 are the canonical examples, but have also been suggested for Sr_2RuO_4 [108]. It has been proposed, and indeed seems to have been confirmed in hole-doped compounds, that the cuprate superconductors have a $d_{x^2-y^2}$ order parameter (s = 0, l = 2). This order parameter changes sign with a rotation of $\pi/2$. Different symmetries have different momentum space structures associated with them. For isotropic s-wave, the order parameter is constant in momentum space. A $d_{x^2-y^2}$ order parameter in a 2D plane can be represented as $\cos(k_x a)$ - $\cos(k_y a)$. This expression comes from the projection of an even superposition of the $l=2, m=\pm 2$ spherical harmonic as it is defined on a sphere of radius 1/a down onto plane of the same units and analytically continued to r > 1/a. Similarly an d_{xy} (odd superposition) order parameter can be shown to have a momentum space structure $\sin(k_x a)\sin(k_y a).$

Knowing the symmetry of the order parameter is important as it can rule out various candidates for superconducting mechanisms. For instance, a purely phononic interaction cannot create an order parameter other than relatively isotropic s-wave and therefore the existence of a d-wave symmetry, if it exists in the cuprates, points to at least the partial contribution of electronic mechanisms to pairing [109].

When a material undergoes a superconducting transition an energy gap in its excitation spectra develops at E_F . This is shown in Fig. 4.1 where the gap opens and the electron and hole dispersions bend back at $\vec{k_F}$ by virtue of particle-hole



Figure 4.1: Upon passing below the superconducting transition, the free particle dispersion acquires a gap in it. The "bending-back" of excitation branches reflects particle-hole mixing.

mixing.

In a BCS superconductor the energy dispersion curves change from the free particle dispersions $E(\vec{k})$ to

$$E_{\vec{k}} = \sqrt{\Delta_{\vec{k}}^{2} + [E(\vec{k}) - E_{F}]^{2}}$$
(4.3)

It is this gap which is responsible for the remarkable stability of the superconducting state and that the low-energy properties of the system are most sensitive to. In a very simple sense the energy gap Δ represents the binding energy of the Cooper pairs. However, the fact that this gap energy is proportional to the order parameter i.e. the many-body wave-function through the BCS relation given in Eq. 4.4 shows the nontrivial nature of such a parameter. It appears explicitly in this expression of the order parameter because it represents the first excitations out of the many-body



Figure 4.2: s- and d-wave symmetric gap

bosonic ground-state.

$$\Delta_{\vec{k}} = 2E_{\vec{k}}\Psi(\vec{k}) \tag{4.4}$$

It is through this relation that most experimental probes are sensitive to the order parameter. As the order parameter itself can have momentum structure, thereby, so can the superconducting gap.

As shown schematically in Fig. 4.2 an s-wave order parameter will have an isotropic gap and a pure d-wave one such as $d_{x^2-y^2}$ will have nodes where excitations are possible with infinitesimally small energy. It is these nodes which give signatures of d-wave that can be detected by low-energy probes. As they are proportional to each other, in the remainder of this chapter I shall use the terms "energy gap" and "superconducting order parameter" somewhat interchangeably.

The momentum dependence of the superconducting gap is perhaps most directly imaged in ARPES, which is the only momentum sensitive single-particle probe. It samples the N-1 excitation spectra of the system as an inserted photohole has no partner to pair with and most overcome Δ_k as the lowest energy electron-hole addition state.

It is now generally agreed that the hole-doped (*p*-type) cuprate superconductors have an order parameter whose majority component is of $d_{x^2-y^2}$ symmetry. As mentioned previously, angle resolved photoelectron spectroscopy (ARPES) provided a key piece of early evidence by the demonstration of a large momentum space anisotropy of the electronic excitation gap [93]. In Fig. 4.3 ARPES data from optimally-doped Bi2212 are displayed that was taken near $(\pi/2, \pi/2)$ and near $(\pi, 0)$ the minimum and maximum respectively of the $d_{x^2-y^2}$ functional form above and below T_c . There is not a large temperature induced change in the spectra above and below T_c along the zone diagonal. However near the $(\pi, 0)$ position, the energy distribution curves (EDCs) show a dramatic difference. Firstly, a sharp "superconducting" peak develops which appears in the spectra as the famous peak-hump-dip structure. Also, notably the leading edge midpoint of the superconducting spectra is pulled back from that of the normal state spectra of about $\sim 12 \text{ meV}$ while the spectra from along the zone diagonal have a shift of 0-0.5 meV. These energy scales represent the energy cost to break a Cooper pair apart. The large anisotropy in this gap was interpreted as being consistent with a $d_{x^2-y^2}$ order parameter.

Other probes have contributed to the understanding of the superconducting gap symmetry. Quantum interference devices have given a definitive attestation to the existence of an order parameter that changes sign in momentum space [110, 111]. These measurements have been so convincing because they measure the magnetic flux that occurs in amounts topologically stabilized by the uniform phase of the superconducting order parameter. It is in this way the only probe that directly couples to the order parameter as the pairing wave function.



Figure 4.3: The prototypical $d_{x^2-y^2}$ gap in Bi2212 by Shen et. al. [93]. The first definitive proof for d-wave superconductivity in the cuprates.

Corroborating evidence for *d*-wave superconductivity has been provided by a number of other techniques [91, 92]. These are in no particular order: a power-law behavior of the low temperature penetration depth (indicative of nodes in the gap function) [112], NMR (absence of a Hebel-Slichter peak) [113], the presence of the so-called zero-bias Andreev bound state on the (110) surfaces (a consequence of a momentum space sign change in the order parameter) [114], thermal conductivity (where $\frac{v_{parallel}}{v_F}$ at the node can be reasonably extracted and compared with that extracted from ARPES) [115, 116] and specific heat which also shows a power-law dependence on temperature [117]. In a messy materials-based field like high- T_c it is a remarkable convergence of experimental data, although there are unexplained results such as c-axis SIS tunneling [91].

In contrast, the experimental and theoretical situation on the small family of electron-doped (*n*-type) cuprate superconductors, such as the subject of this thesis $Nd_{1.85}Ce_{0.15}CuO_4$, has not reached a similar détente. Since its discovery, tunneling [45], microwave penetration depth [38], and Raman [40] measurements all have given evidence for some kind of nearly uniformly gapped Fermi surface. In addition, $Nd_{1.85}Ce_{0.15}CuO_4$ is the only measured cuprate superconductor that does not exhibit a zero-bias Andreev bound state on its (110) surface [118, 119], However, recent work has called this picture of a uniformly gapped Fermi surface into some doubt.

There have been recent reports of the existence of a (110) zero-bias anomaly[120]. There is evidence from measurements using scanning SQUID microscopy on tricrystal films, that the electron-doped materials have an order parameter with a large d-wave component [41]. In addition, there has been speculation that the ordering at low temperature of the free 4f moments on the rare earth Nd ions affects the usual microwave penetration depth measurements by altering the low temperature magnetic permeability [121, 122]. A Néel antiferromagnetic ordering of temperature of 0.5-1.5K has been estimated from neutron scattering [123]. Since it is at such low temperatures that these measurements need to be performed, such an ordering is obviously problematic.

A recent reanalysis of existing microwave data that incorporates a correction for the Nd spin ordering by J.R. Cooper [121] has been interpreted as being consistent with "dirty *d*-wave behavior." The DC value, extracted from magnetic susceptibility experiments is substituted for the finite-frequency permeability. While suggestive, is not clear that this analysis is valid as it may be possible that the susceptibility at microwave frequencies (10 GHz) might not be as significant as the zero frequency (DC) value. However, this picture of dirty *d*-wave behavior appears to hold, as experiments on the related paramagnetic material $Pr_{2-x}Ce_xCuO_4$ seem to be consistent with a *d*-wave scenario [42, 43].

On the theoretical side, there have been problems reconciling the s-wave experimental results with current models. As in the hole-doped case, strong on-site Coulomb repulsion in the copper oxygen plane strongly favors an anisotropic order parameter that has positive and negative lobes. In Hubbard models, U the onsite repulsion creates an effective spin-dependent repulsive potential that oscillates in real space with characteristic wave vector (π, π) . For such a repulsive positive interaction $V_{\vec{k}\vec{k'}}$ peaked at (π, π) , a superconducting order parameter with $d_{x^2-y^2}$ symmetry such as $cos(k_x) - cos(k_y)$ is a solution to the self-consistent BCS gap equation 4.5 for typical Fermi surface shapes, although other d-wave symmetries are possible.

$$\Delta_{\vec{k}} = -\sum_{\vec{k'}} V_{\vec{k}\vec{k'}} \frac{\Delta_{\vec{k'}}}{2E_{\vec{k'}}}$$
(4.5)

On general grounds Eq. 4.5 mandates that for a purely positive interaction

the order parameter must have positive and negative lobes as a consequence of the negative sign prefactor. If the $V_{\vec{k}\vec{k}'}$ is negative then s-wave solutions are possible, as is the case with the attractive interaction of the conventional electron-phonon mediated superconductors.

The fact that the *n*-type cuprates have, for most of their history, appeared to posess a symmetry other than $d_{x^2-y^2}$ has led to proposals on why they may be different. As was seen in the initial ARPES work [124] on this system, the dispersive feature in NCCO near $(\pi, 0)$ is flat and has a saddle point ~300 meV below E_F . This contrasts with virtually all the *p*-type compound which show a large flat band region in an "extended Van-Hove singularity" near $(\pi, 0)$ at E_F [86]. It has been proposed that one reason $d_{x^2-y^2}$ superconductivity is favorable in the hole-doped cuprates is that there is a particularly large local low-energy density of states in this region of the Brillouin zone that a $|cos(k_x) - cos(k_y)|$ proportional order parameter gaps for a particularly large energy savings. This argument would not hold in the electron-doped materials where the flat band is electronically inert at ~300 meV below E_F .

4.2 Experiment

In this chapter, I focus on an energy scale much lower than that of the rest of the thesis (below 5 meV). The central intellectual issue is the anisotropy of the superconducting gap, which should manifest itself in the ARPES spectra as a displacement of the leading edge to higher binding energy as a gap opens up.

These ARPES measurements of the superconducting gap were performed at beamline 5-4 of the Stanford Synchrotron Radiation Laboratory. Data were taken

in Scienta "Angle" mode. The sample temperature was measured by a calibrated diode mounted near the measurement position. The temperature difference between the diode position and the actual measurement position was found to be negligible from previous measurements on another diode that had been mounted to a sample holder in a identical fashion as the samples. All measurements were taken with 16.5 eV photons. For each measurement set, the temperature was cycled a number of times to ensure repeatability and an absence of problems from surface aging. No such problems were detected over the typical measurement time of 7 hours per \vec{k} -space cut. To improve statistics of these intrinsically low signal experiments the same temperature spectra were summed together.

In order to see signatures of superconductivity on a system with an expected small gap, it is crucial that one compare leading edge midpoints (LEMs) from the same sample above and below T_c . In many past studies it has been standard practice to simply compare LEMs of the spectral weight onset to the Fermi energy of a reference gold sample, but this kind of analysis is not reliable in the small gap *n*-type systems. To make this point more clear, in Fig. 4.4 I compare the trend of the LEMs of $Nd_{1.85}Ce_{0.15}CuO_4$ referenced to the Fermi energy to that of one plane bismuth based cuprates with similar T_c 's as our $Nd_{1.85}Ce_{0.15}CuO_4$ sample. All spectra were taken at approximately 11 meV resolution and with the polarization parallel to the Cu-O bond. The bismuth cuprate data are adapted from Ref. [125]. A few distinct trends are evident in the hole-doped compounds. There is a notable decrease in the maximum gap as one proceeds from underdoping to overdoping. This is consistent with previous ARPES results as well as with other techniques. There is a definite increase in the LEMs as one goes around the Fermi surface in accordance with one's d-wave expectation. Similar behavior is seen in YBa₂Cu₃O_{7-x} and La_{1.85}Sr_{0.15}CuO₄



Figure 4.4: Plot of the leading edge midpoint around the apparent Fermi surface of a few cuprate superconductors of comparable T_c 's in units of the fractional distance from $(\pi/2, \pi/2)$ to $(\pi, 0.3\pi)$.

[126, 127]. In contrast, this analysis which reveals a large anisotropy on the holedoped compounds, does not reveal any clues as to anisotropy in $Nd_{1.85}Ce_{0.15}CuO_4$ as the LEM referenced to E_F shows no systematic trends along its Fermi surface. This is a consequence of the fact that the superconducting gap by any measure is much smaller than in the hole-doped materials and hence is obscured due to finite resolution and subtle changes in the lineshape around the Fermi surface. If the systematics of the lineshape did not change very much around \vec{k} , one would still have a good measure of relative changes in the gap energy, despite not being able to measure its absolute magnitude exactly. This was been done, for example, in the imaging of a gap in Bi2212 and YBa₂Cu₃O_{7-x} that follows the *d*-wave functional form, despite large measured negative gap energies in the nodal region [126, 128]. In the present case, due to a weaker component in the spectra that appears near $(\pi, 0)$ (which will be dealt with in more detail later on) the systematics of the lineshape do change and a simple comparison with E_F is not valid. One must then compare the shift of LEMs from spectra above and below T_c at the same momentum space point on the same sample in order to accurately measure the gap value. This should remove extraneous effects of the final state and otherwise eliminate effects (e.g. photoionization matrix elements) other than a gap opening up.

Much lip service has been paid to the importance of good resolution in performing superconducting gap measurements. Equally important however are statistics. The essential condition for a reliable measurement is for the horizontal fluctuations of the spectrum's leading edge to be at least as good as the expected gap magnitude $(F_h < \Delta_{sc})$. As the slope of the leading edge is $\sim N/\Delta E$ where N is the measured intensity and ΔE is the total resolution, then

$$F_h = \frac{\Delta N}{N/\Delta E} < \Delta_{sc} \tag{4.6}$$

with ΔN equal to \sqrt{N} the stability condition for an accurate gap measurement

$$\frac{\Delta E(N)}{\sqrt{N}} < \Delta_{sc} \tag{4.7}$$

It is this relation that quantifies how good the resolution must be to do an accurate measurement. As $\Delta E(N)$ is a positive increasing function of N, it is the interplay of this factor and the \sqrt{N} compensating term that determines the optimal operating conditions.

4.3 Results

is

Coarse energy resolution data at 10K was taken with over 500 energy distribution curves (EDCs) over a Brillouin zone octant and symmetrized across the zone diagonal. Fig. 4.5 shows a 30 meV integration about the Fermi energy of these EDCs plotted over a Brillouin zone quadrant. This gives a measure of the locus of \vec{k} -space points that contribute the most to the low-energy properties of the material i.e. the Fermi surface. The details of the Fermi surface will be dealt with in more detail in Chapter 5.

Along the roughly circular shaped Fermi surface, one sees three regions of high intensity. The central one corresponds to the previously mentioned broad, highly dispersive feature moving into the integration window. The other two are the intensity maxima of the smaller low binding energy feature. I took high resolution angle resolved cuts at two temperatures through $\vec{k_F}$ points in two different regions of



Figure 4.5: A 30 meV integration around the Fermi energy of each EDC plotted over the Brillouin zone quadrant. Two high resolution angle resolved cuts [labeled (a) and (b)] were taken as marked by the arrows. These are displayed in Fig. 4.6. In the inset is the LEED pattern of the sample cleaved *in situ* at 10K.

momentum space as shown by the arrows in the figure [$(0.46\pi, 0.46\pi)$ and $(\pi, 0.27\pi)$ exactly, but hereafter referred to as near $(\pi/2, \pi/2)$ and $(\pi, 0.3\pi)$]. In both cases the photon energy was 16.5 eV, polarization was parallel to the cut direction, and the energy resolution was 11 meV.

In Fig. 4.6a and 4.6b, I present false color scale plots of the spectral function in a $\pm 5.5^{\circ}$ ($\pm 21\%$ π) angular windows from the cuts near ($\pi/2, \pi/2$) and ($\pi, 0.3\pi$) respectively. In the spectra near ($\pi/2, \pi/2$), I find a dispersion which is universal for the cuprates in this region of the Brillouin zone. A large broad feature disperses towards the Fermi energy, sharpens, and then disappears as it passes above E_F . In Fig. 4.6b, which is a cut through $\vec{k_F}$ at approximately $(\pi, 0.3\pi)$, the spectra are best characterized by a large hump feature that disperses only slightly while the smaller low-energy feature disperses toward E_F , loses weight, and then disappears. This behavior is characterized in more depth in Chapter 3. In Figs. 4.6c and 4.6d, I compare spectra at 0.5° steps taken at 30K (red) and 10K (blue) at a few near- $\vec{k_F}$ positions for each cut. In Fig. 4.6c from the spectra near $(\pi/2, \pi/2)$ we see that, aside from some small thermal broadening, there is no temperature induced change. This is quite different from that of spectra from the $\vec{k_F}$ crossing near $(\pi, 0.3\pi)$ (Fig. 4.6d) where there is a systematic displacement by ~1.5-2 meV of the leading edge to higher binding energy in the superconducting state.

In Fig. 4.7 there is an expanded image of a spectrum with one of the large temperature induced shifts in Fig. 4.6d. To more systematically quantify the result, I fit the lineshape with a simple phenomenological model. For broad spectral features at the Fermi level, the superconducting state spectra can be approximated by a 10K Fermi function multiplied by a linear spectral function whose onset edge is displaced from the Fermi energy by the superconducting gap energy. Likewise, the normal state spectra can be modeled as that of a 30K Fermi distribution at finite temperature multiplied by the same (but non-displaced) linear spectral function. These model spectra are convolved with a Gaussian of FWHM of 11 meV to simulate the experimental resolution. The agreement between the experimental curves and the fits are quite good within this picture with a gap parameter of 1.9 meV.

The above temperature dependent measurements were repeated on 7 different samples [4 samples at both $\vec{k_F}$ positions, two only at $(\pi, 0.3\pi)$ and one just at $(\pi/2, \pi/2)$]. In Fig. 4.8 I plot the temperature dependent shift of the LEM at both $\vec{k_F}$ crossings for all samples. Although there is some scatter in the data, one



Figure 4.6: (color). At the top labeled (a) and (b) are false color plots representing the intensity of the spectral function in a $\pm 5.5^{\circ}$ angular windows ($\pm 21\% \pi$) near ($\pi/2, \pi/2$) and ($\pi, 0.3\pi$) respectively. In (c) and (d) I compare EDCs taken at 30K (red) and 10K (blue) from the \vec{k} -E regions represented by the horizontal bars in panels (a) and (b) respectively. Arrows denote the direction that angular cuts are displayed as referenced to the arrows in insets of the Brillouin zone. Gap values represent the results of the fitting procedures for the curves.



Figure 4.7: At the bottom of the panel are EDCs from k_F near $(\pi, 0.3\pi)$ which is curve 2 in from Fig. 4.6d. They are plotted along with a simple fit convolved with the resolution. At the top is the same fit unconvolved with the experimental resolution. The fitted gap parameter is 1.9 meV.

can see that, with the exception of one sample, they all show a 1.5-2 meV shift at the $(\pi, 0.3\pi)$ position and a negligible one at the $(\pi/2, \pi/2)$ position. This shift anisotropy is interpreted as a consequence of the opening of a superconducting gap that is maximal near $(\pi, 0)$ and minimal or zero along the zone diagonal. This is consistent with the presence of a $d_{x^2-y^2}$ superconducting order parameter. I cannot rule out a very anisotropic s-wave order with a small gap along the zone diagonal that is below our detection limit [approximately the same as the scatter in the data at $(\pi/2, \pi/2)$, < 0.3meV]. The reason for the lack of a temperature dependent shift on the one sample is unknown. Its spectral features and dispersions were consistent with the others. It is possible that it suffered from being in poor thermal contact with the cold stage.



Figure 4.8: The temperature dependence data from all 7 samples taken near $(\pi/2, \pi/2)$ and $(\pi, 0.3\pi)$. The data are slightly offset from each other in the horizontal direction for display purposes.

4.4 Discussion

The $2\Delta/k_BT_c$ ratio in the narrow doping range of superconducting *n*-type materials is typically measured by tunneling to be smaller than those in the hole-doped ones when comparing the highest T_c samples from both material classes. There may be a closer correspondence if the highest T_c samples of the *n*-type compound could be viewed as being more overdoped-like, as the *p*-type materials typically show lower $2\Delta/k_BT_c$ ratios in the overdoped regime. This conjecture is supported by the fact that the resistivity of the electron-doped system shows a quadratic temperature dependence like the overdoped *p*-type. In this case one may expect a low $2\Delta/k_BT_c$ ratio. In our particular case the gap value of 1.5-2 meV obtained with our technique is consistent with, but slightly smaller than, the gap values reported by other techniques [38, 40, 45]. There are a few possibilities for this. Firstly, it is well documented that photoemission analysis based on LEMs consistently underestimates the maximum gap value (in some cases by as much as a factor of 2) as compared to the intrinsic value defined as the quasiparticle energy at the antinodal position [128]. LEM analysis does not necessarily measure any intrinsic quantity, as it is only a convenient parameterization. Moreover, other measurement techniques (like tunneling) typically take place at 4.2 K (0.15 T_c), in contrast to our measurement at approximately 0.5 T_c. At our intermediate temperatures the superconducting gap may not have opened fully, as there is no reason to believe that the gap will open up in a mean field-like way. We cannot rule out the possibility is there may be some background contribution that partially obscures the gap signal.

In summary, I performed angle resolved photoelectron spectroscopy on the electrondoped cuprate superconductor Nd_{1.85}Ce_{0.15}CuO₄. A comparison of the leading edge midpoints between the superconducting and normal states reveals a small, but finite shift of 1.5-2 meV near the $(\pi,0)$ position, but no observable shift along the zone diagonal near $(\pi/2,\pi/2)$. This is interpreted as evidence for an anisotropic superconducting gap in the electron-doped materials, which is consistent with the presence of *d*-wave superconducting order in this cuprate superconductor. Despite the strong differences between the p- and *n*-type compounds in the larger scale electronic structure(~1 eV) which will be detailed in later chapters, their superconductivity appears to share the same symmetry and is therefore possibly of similar origin.

Chapter 5

Normal State Electronic Structure¹

5.1 Background

The electron-doped cuprate superconductors provide a unique opportunity to study the physics of doped Mott insulators and high- T_c superconductors. In addition to possessing interesting physics in their own right, the *n*-type materials, with their different normal state properties and phase diagram, offer an alternative venue to test various theories of high- T_c superconductivity.

One might hope that an in-depth ARPES study of the normal-state of the highest T_c electron-doped compound may provide insight into some of the issues that ARPES has contributed to in the past: band structure, high-energy pseudogap, low-energy pseudogap, scattering rate etc. [86]. A comparison to the *p*-type materials may point to possible origins of these anomalous features. Moreover it may give a route towards

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rationalizing some of the confusing experimental aspects of the *n*-type compounds; for instance a negative Hall coefficient for a material with a hole-like Fermi surface and large pseudogap effects in the optical spectra [35, 36, 37, 129, 130].

As pointed out in previous chapters, $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ is a member of the small family of cuprate superconductors that can be doped with electrons [23]. Only an approximate symmetry in the phase diagram exists about the zero doping line between p- and n-type, as the antiferromagnetic phase is much more robust in the electron-doped material and persists to much higher doping levels. Superconductivity occurs in a doping range that is almost 5 times narrower. In addition, these two ground states occur in much closer proximity to each other, only being separated by 1% neodymium concentration and/or 0.5% oxygen concentration. This proximity of the highest- T_c sample to antiferromagnetism may, in particular, lend insight into the origin of the pseudogap phase. Experiments show other contrasting behavior between *n*-type superconductors and their *p*-type counterparts, for instance a T^2 dependence of the in-plane resistivity [34] and the lack of incommensurate neutron scattering peaks [26, 27]. As pointed above, one particularly difficult to understand phenomenon, in light of ARPES data that shows the Fermi surfaces of electron- and hole-doped materials to not have gratuitously different topologies, is an apparent temperature induced sign reversal of the Hall coefficient [35, 36, 37].

In this chapter, an ARPES study of the electronic structure of the highest T_c cerium concentration (x=0.15) sample of Nd_{2-x}Ce_xCuO₄ is reported. Significant differences are found between it and the *p*-type materials that shed light on a number of important topics in the high-T_c superconductors. Previous work on this material's general band structure are confirmed. In addition, I found that the Luttinger-volumed Fermi surface is truncated into several pieces with a high-energy "pseudogap"-like suppression that forms, not at the maximum of the *d*-wave functional form as in the underdoped *p*-type materials, but near the intersections of the Fermi surface with the antiferromagnetic Brillouin zone (AFBZ) boundary.

5.2 Experiment

The discussion of the following data will rely on arguments for expected intensities of the near- E_F spectra in the Brillouin zone (BZ). Because is important to determine which characteristics of the data are representative of the spectral function itself and which are possible artifacts of, for instance, the matrix elements for photoexcitation, data were collected on two different photoemission systems. As detailed previously, on beamline 5-4 at the Stanford Synchrotron Radiation Lab (SSRL), data were taken at 16.5 eV photon energy ($\hbar\omega$) with an incident angle of approximately 45 degrees (Energy resolution $\Delta E \simeq 10$ meV and angular resolution $\Delta \theta \simeq 0.5^{\circ}$). At beamline 10.0.1 at the Advanced Light Source (ALS) an incident energy of 55 eV was used in a glancing incidence geometry with in-plane polarization at 45 degrees to the Cu-O bonds ($\Delta E \simeq 20$ meV, $\Delta \theta \simeq 0.25^{\circ}$). All displayed spectra were taken at low temperature (10 - 20K) in the superconducting state; this does not change the conclusions I make regarding the larger scale normal state electronic structure as the changes in spectra with the onset of superconductivity are very subtle in NCCO [44].

5.3 Results

In Fig.'s 5.1a - c energy distribution curves (EDCs) are displayed from high symmetry lines in the Brillouin zone (BZ) taken on the SSRL apparatus. In Fig. 5.1a, one sees

a dispersion along the Γ to (π, π) direction which is ubiquitous among the cuprates. A broad feature disperses quickly towards the Fermi energy (E_F) , sharpens to a peak at $\vec{k_F}$ (0.46 π , 0.46 π), and then disappears. Along the Γ to $(\pi, 0)$ direction, the *n*-type spectra are quite different from their *p*-type counterparts. While the lowenergy feature in the optimally doped *p*-type compounds disperses quite close to E_F and forms a flat band region with a correspondingly high density of states close to E_F , in NCCO this flat band region is at about 300 meV higher energy [124]. This aspect of the *n*-type/*p*-type asymmetry has been identified by a number of workers as a possible route to understanding the different low-energy properties from the two sides of the phase diagram. Along $(\pi, 0)$ to (π, π) [Fig. 5.1c] the peak disperses to E_F and gives a small peak at $\vec{k_F}$. The spectra also possess a large background contribution that has a weak maximum at 300 meV, as seen in the 100% curves in Figs. 5.1a and 5.1c.

In addition to the spectra from the high-symmetry directions, more comprehensive intensity maps were obtained over a large region in momentum space at both photon energies. In Fig. 5.2a and 5.2c I have plotted the integrated spectral weight of the EDCs ($\hbar \omega = 16.5$ and 55 eV respectively) from within a 30 meV window about E_F as a function of \vec{k} . This gives a measure of the regions in momentum space that dominate the low-energy properties of the material i.e. the Fermi surface. The expected large Fermi surface has a volume greater than 1/2 (measured filling level $\delta = 1.12 \pm 0.05$) and has a shape consistent with the LDA band calculations [131]. Interestingly however, it shows two regions of suppressed spectral weight near ($0.65\pi, 0.3\pi$) and ($0.3\pi, 0.65\pi$). Although there is obviously some modulation of the intensity due to matrix elements, as some of the details of the intensity pattern are different between the two excitation energies, the gross features are the same. In



Figure 5.1: Energy distribution curves from various symmetry directions in the Brillouin zone of Nd_{1.85}Ce_{0.15}CuO₄ taken with $\hbar\omega = 16.5$ eV at SSRL. (a) $\Gamma - (\pi, \pi)$, (b) $\Gamma - (\pi, 0)$, (c) $(\pi, 0)$ - (π, π) .


Figure 5.2: (color). (a) and (b) Fermi surface of the partial Brillouin zone of NCCO taken with $\hbar \omega = 16.5$ eV with the incoming photon polarization along and at 45° to the Cu-O bonds respectively. (c) 55 eV photon energy with polarization at 45° to the Cu-O bonds In all graphs the plotted quantity is a 30 meV integration about E_F of each EDC plotted as a function of \vec{k} . 16.5 eV data were taken over a Brillouin zone octant and symmetrized across the Γ to (π, π) line, while the 55 eV data were taken over a full quadrant, except for a line of symmetrized data points that were used immediately below and parallel to the zone diagonal as these points were missing from our initial data set. The polarization direction is denoted by the double arrow. The dotted line is the antiferromagnetic Brillouin zone boundary.

addition, data (Fig 5.2b) from SSRL at 16.5 eV with the sample turned so that the polarization is at 45° to the Cu-O bond reveals a similar pattern. The fact that the same systematics are see with different configurations and excitation energies gives us confidence that we are measuring intrinsic properties, a fact which will be substantiated by lineshape analysis below.

A detailed look at $\hbar \omega = 16.5$ eV EDCs through the suppressed region of the Fermi surface [Fig. 5.3] reveals that the peak initially approaches E_F and then monotonically loses weight despite the fact that its maximum never comes closer than ~100 meV to E_F . This results in features which are quite broad, even at $\vec{k_F}$. Such behavior is similar to the high-energy pseudogap seen in the underdoped ptype materials although in the present case it is observed near $(0.65\pi, 0.3\pi)$ and not at $(\pi, 0)$ the maximum of the *d*-wave functional form. In Fig. 5.4, I show EDCs



Figure 5.3: EDCs through the "hot spot" region. $(0.65\pi, 0)$ - $(0.65\pi, \pi)$

adapted from Ref. [132] that compares both over and underdoped spectra of two Bi2212 samples at the $(\pi, 0)$ and $(\pi/2, \pi/2)$ positions. The underdoped spectra near $(\pi, 0)$ are qualitatively similar to the 32% curve in Fig. 5.3.

An additional important difference between the *p*-type and *n*-type compounds is that a true clean gap at the very lowest energies cannot be defined, because the continually decreasing slope of the EDCs at $\vec{k_F}$ gives a leading edge midpoint that is within a few meVs of E_F . A distinction must be made between high-energy pseudogap behavior [the conversion of an expected sharp peak at E_F to a broad feature over a large-energy range (~100 meV) and the suppression of low-energy spectral weight] and low-energy pseudogap behavior which is the clean leading edge gap seen in the normal-state of underdoped and optimally doped *p*-types near (π , 0)



Figure 5.4: Bi2212 EDCs showing both over and underdoped spectra and comparing them in the $(\pi, 0)$ and $(\pi/2, \pi/2)$ positions. In overdoped Bi2212, the spectra show qualitatively similar lineshapes in the two regions of the BZ. In the underdoped materials they are very anisotropic with the $(\pi, 0)$ spectra showing a high-energy pseudogap. Adapted from Ref. [132].

that has been posited to be reflective of pairing fluctuations in the normal state. Both gaps can be distinguished in moderately doped samples. The fact that they share the same *d*-wave functional form and that the low-energy pseudogap appears to evolve somewhat continuously with underdoping into the high-energy pseudogap of the underdoped superconductor and AF insulator has lead to proposals that the pairing gap in the superconductor is an inherited property of the insulating state [133, 134, 135]. These distinctions are important ones that I will return to later.

In Fig. 5.5a and 5.5c I plot $\hbar\omega$ =55 and 16.5 eV EDCs from around $\vec{k_F}$ from

 $(\pi/2,\pi/2)$ to $(\pi,0.3\pi)$ as shown in the inset. Consistent with the intensity maps in Fig 5.2a and 5.2c the data show a well defined and intense peak at E_F in momentum space regions close to the Γ to (π,π) Fermi surface crossing and the $(\pi,0)$ to (π,π) Fermi surface crossing. In between these regions, corresponding to where the maps in Figs. 5.2 show suppressed intensity, the spectra are rather different [see curves 4 of Fig. 5.5a and 7-9 of Fig. 5.5c] with no well defined peaks. These different spectral lineshapes prove that the major effects seen in the intensity plots are not due to matrix elements which will not change the shape of the spectra drastically. This assertion receives further support from the measurement of EDC widths in Fig. 5.5b. Here I plot the width in energy of the EDCs (defined as the FWHM/2 of the actual features and not the output of a fitting parameter) in Fig. 5.5a This quantity, which can be viewed as an average over the low-energy scattering rate (Im Σ) is largest in the momentum region of interest along k_F where the near- E_F spectral weight is suppressed maximally as shown in Fig. 5.2. Those regions along the FS that show the anomalous low-energy spectral weight suppression are subject to the strongest scattering effects.

I take the view that this anomalous electronic structure in the suppressed region is reflective of the transfer of spectral weight from a near- E_F peak to a large broader incoherent maximum at higher energy. As one moves along the Fermi surface from $(\pi/2, \pi/2)$ to $(\pi, 0.3\pi)$, this high-energy part at first gains intensity and shifts the global maxima to higher energy. In the intermediate region along the $\vec{k_F}$ contour, the near- E_F weight is suppressed maximally with a plurality of spectral weight at higher energy. Moving towards $(\pi, 0.3\pi)$ the high-energy part still forms a maximum at ~100 meV but the low-energy peak begins to recover at E_F and the two features can be seen simultaneously in a single spectrum. The low-energy peak continues to



Figure 5.5: (a) EDCs from along the $\vec{k_F}$ contour for $\hbar\omega=55$ eV. The graph plots $(\pi/2,\pi/2)$ on the bottom and $(\pi,0.3\pi)$ at the top along the $\vec{k_F}$ contour given in the inset. (b) ΔE (defined as FWHM/2) for EDCs in Fig. 3(a). (c) $\hbar\omega=16.5$ EDCs along the same $\vec{k_F}$ contour. The large momentum independent background [defined as the signal at (π,π)] has been subtracted out.

gain weight until the zone edge at $(\pi, 0.3\pi)$, while the high-energy part loses intensity and disappears. The point of view that the two features are part of a single spectral function is supported by the fact that I observe only a single Fermi surface with the expected Luttinger volume.

5.4 Discussion

Note that the regions of momentum space with the unusual low-energy behavior fall intriguingly close to the intersection of the underlying FS with the AFBZ boundary as shown by the dashed lines in Fig. 5.2. This suppression of low-energy spectral weight and large scattering rate in certain regions on the FS bears resemblance to various theories that emphasize a coupling of charge carriers to a low-energy collective mode. Central to these schemes is the supposition that there exists an anomalous low-energy scattering channel with typically (π, π) momentum transfer. A simple phase space argument such as that shown in Fig. 5.6 shows that those charge carriers which lie at the intersection of the FS with the AFBZ boundary will suffer the largest effect of anomalous (π, π) scatterings as these are the only FS locations that can have low-energy coupling with $\mathbf{Q} = (\pi, \pi)$. These heavily scattered regions of the FS have been referred to in the literature as "hot spots". It has been suggested that the large back-scattering felt by charge carriers in the hot spots is the origin of the pseudogap in the underdoped hole-type materials [57, 58].

An alternative and somewhat equivalent way to look at the data is to consider a mean-field calculation of the effect of a reduction in the real-space symmetry of the unit cell on a simple tight binding band. This distortion would be such that the BZ decreases in volume by 1/2 and rotates by 45° . In surface science parlance such a distortion is referred to as $\sqrt{2} \times \sqrt{2}$ and is equivalent to reducing the BZ to the AFBZ. It is not relevant what the source of the reduced symmetry is, only that it couples to the charge carriers and is relatively weak as compared to other relevant energy scales. If one starts with a simple tight binding model with nearest and next-nearest neighbor hopping (simplest parameterization of the band structure that reproduces a hole-like FS)



Figure 5.6: Schematic showing only those regions of FS near the black circles can be coupled with a (π, π) scattering. The smaller inner square is the quadrant that most of the FS data is displayed in.

$$E_{\vec{k}}^{0} = t[\cos(k_{x}a) + \cos(k_{y}a)] + t'[\cos(k_{x}a) \times \cos(k_{y}a)]$$
(5.1)

and considers the addition of an identical band displaced by $\vec{q} = (\pi, \pi)$, as $\vec{k} = (\pi, \pi)$ and Γ are now symmetry points via the crystal distortion.

$$E^{0}_{\vec{k}+\pi,\pi} = -t[\cos(k_{x}a) + \cos(k_{y}a)] + t'[\cos(k_{x}a) \times \cos(k_{y}a)]$$
(5.2)

The energy eigenvalue solution to a coupling $|V_{\vec{k}-\vec{k'}}|$ between these two bands is expressed through standard degenerate perturbation theory for a two-level system as

$$\frac{E_{\vec{k}}^{0} + E_{\vec{k'}}^{0}}{2} \pm \sqrt{\left(\frac{E_{\vec{k}}^{0} - E_{\vec{k'}}^{0}}{2}\right)^{2} + \left|V_{\vec{k}-\vec{k'}}\right|^{2}}$$
(5.3)



Figure 5.7: Schematic showing how new Fermi surfaces are formed with a weak $\sqrt{2} \times \sqrt{2}$ reconstruction

For our particular case of $E^0_{\vec{k}}$ and $E^0_{\vec{k}+\pi,\pi}$ Eq. 5.3 reduces to

$$E_{\vec{k}}^{\sqrt{2}\times\sqrt{2}} = t'[\cos(k_x a) \times \cos(k_y a)] \pm \sqrt{\left(t[\cos(k_x a) + \cos(k_y a)]\right)^2 + |V_{\pi,\pi}|^2}$$
(5.4)

The even and odd solutions correspond to new band sheets that appear due to the additional Bragg scattering potential. With realistic parameters for the cuprates for t and t' (as they are defined above) a hole pocket centered around $(\pi/2, \pi/2)$ and an electron pocket around $(\pi, 0)$ appears. This is sketched roughly in Fig. 5.7 where the hatch regions represent filled states and the double-hatch regions represent two filled band sheets at a particular \vec{k} .

The above solution Eq. 5.4 only gives the energy eigenvalues of the new dispersions, it says nothing about the coherence factors (intensities) associated with the bands. If $|V_{\pi,\pi}|$ is very weak then the (π,π) back reflections of FS will be weak and possibly undetectable (by ARPES).

The above picture allows us to understand the apparent asymmetry in the evolution of the EDCs around $\vec{k_F}$ going $(\pi/2, \pi/2)$ towards $(\pi, 0.3\pi)$ vs. going from $(\pi, 0.3\pi)$ towards $(\pi/2, \pi/2)$, as well as the qualitative manner that the spectra could be effected by a low- energy mode in places of the BZ away from the "hot spots". In particular when going from $(\pi/2, \pi/2)$ to $(\pi, 0.3\pi)$ the feature at E_F pulls back to higher binding energy while another feature pushes up at E_F . The spectra are **not** characterized by a single sharp feature that simply gets broad in the "hot spot". In the language of the mean-field calculations, one inadvertently jumps from one band sheet to another. This is easy to do as the spectra are broad at the intersection of FS with the AFBZ boundary and the backfolded bands are weak and cannot be easily resolved. The presence of two features in the spectra near $(\pi, 0.3\pi)$ is the result of the two band sheets near $(\pi, 0)$.

The above derivation is for a potential with long-range order. More relevant to the current case may be a situation where true long range order of the $\sqrt{2} \times \sqrt{2}$ phase does not exist, but where the material still has strong fluctuations of this order. In this case the potential will acquire a frequency dependence in addition to its momentum dependence. An analysis in the spirit of the above is much harder, but as long as the fluctuations are slow, it may be that some aspects of the above zone folding picture remain.

For instance depending on their relevant time scales, some experiments may be sensitive to the proto-electron pocket around $(\pi, 0)$. This may be the origin of the negative sign in the Hall coefficient experiments. For finite frequency fluctuations the picture of sharp quasiparticles may break down where the kinematics for low-energy scattering are strong i.e. where the underlying FS crosses the AFBZ boundary.

A few candidates for such a scattering channel or $\sqrt{2} \times \sqrt{2}$ phase have been proposed. One realization would be a strong coupling of the charge carriers to (π, π) magnetic fluctuations. Indeed, strong AF fluctuations have been found at (π, π) , as may have been expected in a material that is as close to the antiferromagnetic phase as this one [26, 27]. In this context the pseudogap is seen as a precursor to spin density wave formation. Other possibilities include coupling to short range fluctuations of the CDW, DDW, or phononic type. A great deal of theoretical effort has been devoted to schemes based on the above general considerations [57, 58, 136, 137]. Of course a combination of effects cannot be ruled out.

Alternatively large effective (π, π) scatterings could be caused by umklapp (U) processes which are only allowed for charge carriers on the on the umklapp surface. In tetragonal crystals the umklapp surface coincides with the AFBZ boundary. It has been suggested that these U processes create anomalously large effective backward scattering that leads to hot-spot phenomena and the creation of a non-Fermi liquid without an additional broken symmetry [138, 139].

For the sake of completeness, I should mention that there have been reports of a peak at the forbidden Bragg reflections of (π, π) (among others) from x-ray diffraction [140, 141]. Its intensity (~ 1/100 of main Bragg peak intensities) seems to indicate that it is an elastic peak (inelastic cross-sections being much lower). As it only appears in annealed crystals and has a unusual c-axis incommensurate structure, its origin and relation to our observations is unclear; it seems likely that it is related to off-planar oxygen ordering [140].

In the underdoped *p*-type materials, due to band filling considerations, the underlying Fermi surface's area is smaller and hence its intersection with the AFBZ boundary is closer to $(\pi, 0)$. This, along with the existence of the near- E_F $(\pi, 0)$ extended saddle points, would cause these regions of the Brillouin zone to feel the largest effect of (π, π) couplings if such processes exist [132]. As alluded to earlier, this may lead to the formation of a pseudogap whose momentum dependence closely mimics and can be confused with the functional form of the *d*-wave superconducting gap. In the present case of NCCO, the underlying Fermi surface is more distant from the $(\pi, 0)$ regions and the band there is flat 300 meV below E_F . In this scenario, this would move the pseudogap regions away from $(\pi, 0)$ on the FS and along $\vec{k_F}$ towards $(\pi/2, \pi/2)$, as observed.

The above considerations may provide a route towards understanding the different transport properties between electron and hole doping. Transport theories based on hot/cold spot models predict very different contributions from the hot vs. cold regions [57, 58, 142]. If I consider as cold spots those regions that are not connectable by a (π,π) scattering vector then there appear to exist two different types of cold spots and a single type of hot spot in the BZ of NCCO. This may be one reason that the transport phenomena differ so markedly in the two materials classes despite their similar FS topologies [143]. In particular, if the fluctuations of the order associated with the characteristic wavevector (π,π) become enhanced as the temperature is lowered, the systematics of the temperature dependent transport would change greatly.

Similarly in the above model where I considered long range order and a real BZ size reduction, a large change in the Hall coefficient terms would be expected as the large hole pocket centered around (π, π) is turned into a small hole pocket around $(\pi/2, \pi/2)$ and a small electron pocket around $(\pi, 0)$.

The class of theories that predict pseudogap formation at the intersection of the AFBZ boundary with the FS contrast with those that explain high-energy pseudogap and hot spot effects to result from fluctuations of a very large energy superconducting pairing scale that has been inherited from the AF insulator. The latter class of theories predict that the momentum dependence of the pseudogap will follow the general

trend of the d-wave superconducting gap i.e. attaining a maximum value at $(\pi, 0)$ [133, 134, 135]. The advantage of the present experiments on the electron-doped material is that the two different origins for pseudogaps give different functional forms, whereas they will give similar ones in the p-type materials as detailed above. In the very underdoped regime in the *p*-type materials, ARPES measures a high-energy d-wave like pseudogap on the order of 100 meV near the $(\pi, 0)$ region [144]. As I observe a high-energy pseudogap in NCCO of a similar energy scale, but with a very different momentum dependence, our results demonstrate the possibility that this very large d-wave-like pseudogap in the extreme underdoped p-type materials may not be related to preformed pairs, but instead may be due to pre-emergent magnetic order or similar phenomena. Our observation still allows for the existence of a normal state low-energy pseudogap (defined by the leading edge) that may be related to the existence of pairing fluctuations above T_c . In this regard it appears that one must carefully discriminate between high-energy pseudogap behavior, which may be caused by the effects discussed above and is tied to the intersection of the FS with the AFBZ boundary, and pairing fluctuations that may cause pseudogap behavior on a lower energy scale and should follow the *d*-wave functional form. If one wishes to interpret the physics of the p- and n-type cuprates in a comprehensive fashion then our results suggest that some of the confusing pseudogap phenomenology regarding energy scales and doping dependencies may be reconciled by distinguishing effects of these kinds.

Chapter 6

Doping Dependence of $NCCO^{\perp}$

6.1 Background

It generally agreed that the high-temperature superconductors belong to a class of materials known as Mott insulators [63]. At half-filling (one charge carrier per site) these materials, predicted to be metallic by band theory, are insulating due to the large on-site Coulomb repulsion that inhibits double site occupation and hence charge conduction. The half-filled material, with its gapped charge excitations, only has antiferromagnetic spin degrees of freedom. These cuprates become metals and then superconductors when doped with charge carriers (holes or electrons). Although the general systematics of Mott insulators and certainly normal metals are understood, the question of how one may proceed from a half-filled Mott insulator with only low-energy spin degrees of freedom to a metal is unclear. Even after 15 years of research into this fundamental solid state issue in the cuprates, the manner in which this evolution occurs and the nature of electronic states at the chemical potential is

¹The main contents of this chapter have been submitted as N.P. Armitage *et. al.* Phys. Rev. Lett. (2001)

unresolved.

In actuality the high- T_c and cuprate materials are not Mott insulators per se, but are more properly characterized as charge transfer insulators. It is believed that such systems can be described by a Hubbard Hamiltonian, where oxygen derived Zhang-Rice singlet states substitute for the lower Hubbard band and the charge transfer gap Δ plays the role of an effective U. In the following discussion I will use the terms Mott and charge transfer insulator somewhat interchangeably.

As detailed in previous chapters, within the Hubbard model, Mott insulators are described as a single metallic band that is split into an upper Hubbard band (UHB) and a lower Hubbard band (LHB) by a correlation energy U that represents the energy cost for a site to be doubly occupied, as shown in the top panel of Fig. 6.1. Thus, at half-filling the LHB (UHB) is totally occupied (unoccupied) with the chemical potential inside the insulator's gap. In the simplest picture, the chemical potential shifts into the LHB or UHB respectively with a concomitant transfer of spectral weight across the correlation gap [145], as the material is doped away from half filling with a few holes or electrons (middle panel of Fig. 6.1).

A transfer of spectral weight occurs due to the many body nature of these correlated bands. The upper and lower Hubbard bands are not bands *per se*, but are more properly excitation spectra that represent the total weight for N+1 or N-1 excitations respectively (electron addition and subtraction spectra). If the system was a semiconductor, the chemical potential would move into the UHB as electrons are doped. For x doped electrons one would obviously observe occupied spectral weight=1 in the LHB, occupied weight x in the UHB and unoccupied weight 1-x in the UHB. In a purely ionic picture (t=0) the occupied weight of the lower Hubbard band and the unoccupied weight of the upper Hubbard band are both proportional



Figure 6.1: A Hubbard model schematic. The top panel represents the half-filled case. In the middle panel is the simplest scenario where the chemical potential moves into the upper Hubbard band with electron doping. The green shaded area represents impurity states or excitonic effects that do not play a direct role in the low-energy properties. The bottom schematic shows "states" being created inside the insulator's gap. Yellow represent N+1 excitation spectra and blue represents N-1 excitation spectra.

to the number of sites that are singly occupied. As one dopes electrons to the material the number of singley occupied sites decreases and therefore the occupied weight of the lower Hubbard band decreases. If we doped x electrons into the system, the number of electrons on singly occupied sites become 1 - x and the number of electrons on doubly occupied sites becomes 2x (there are x sites with 2 electrons each). This conserved spectral weight reappears as additional *occupied* weight of the upper Hubbard band. Every doped electron counts double in the upper Hubbard band (one doped electron can be added to an already filled site, but two electrons can be removed from the site with the same energy). A symmetric situation exists for hole-doping.

In an alternative scenario the act of doping creates "states" inside the insulator's gap and as a result the chemical potential is more or less pinned to these states inside the gap (bottom panel of Fig. 6.1). It has been proposed that these states can be created in a number of ways. These may be impurity states created by doping that become metallic when some sort of percolation threshold is reached. However, it is difficult to see how this may happen in some samples with metallic conduction for very low dopings as well how a universal mechanism for creating these states could exist across all the cuprates with very different doping requirements [146] Phase separated systems (stripes or otherwise) may also show in-gap states. A thermodynamically necessary requirement for phase separation is that the chemical potential must be constant for a large region of doping. For the chemical potential to be constant, a mechanism must exist for the creation of intragap states. In dynamic mean field theory (DMFT) it is proposed that the Mott insulating state breaks down by the creation of coherent spectral weight in the gap [147].

Some aspects of this picture of a doped Mott insulator have been confirmed

in the cuprates. In particular, high-energy spectroscopies such as EELS and XAS have clearly shown a transfer of spectral weight from lower Hubbard band (LHB) to upper Hubbard band (UHB) or vice versa with electron or hole doping respectively [148, 149]. However, because the location of the chemical potential can be judged only approximately from XAS and EELS as the degree that excitonic effects play in the core hole excitation spectrum is unknown, the question of whether or not the chemical potential actually sits in either of these Hubbard bands or instead lies in "mid-gap" states is an open question. A definitive answer has been hampered by a lack of reliable inverse photoemission measurements, that in principle, coupled with photoemission could show where the E_F states exist with respect to the upper and lower Hubbard band. Thus far, this information has been culled from photoemission measurements only. Predictably, this information has been both contradictory and confusing [150, 151, 152].

Allen *et. al.* concluded from their valence band measurements of LSCO and NCCO that the chemical potential didn't move appreciably when going from $La_{1.85}Sr_{0.15}CuO_4$ to La_2CuO_4 to Nd_2CuO_4 to $Nd_{1.85}Ce_{0.15}CuO_4$ and that it was stabilized in the middle of the gap by impurity states. This was a somewhat suspect conclusion because of the large occupation of Nd 4*f* states in NCCO that makes the maximum of the valence band a very poor zero for the binding energy. Ino *et. al.* concluded from their doping dependence of the near- E_F weight of $La_{2-x}Sr_xCuO_4$ that weight was transferred from a CTB singlet like object at ~ 600*meV* binding energy to the chemical potential and that this was consistent with the existence of phase separation. Due to the strong evidence for stripe fluctuations in this system, they concluded in favor of a stripe midgap state scenario.

More recently, the successful doping of $Ca_2CuO_2Cl_2$ single crystals with Na has

allowed ARPES doping dependence measurements in a new material class. These quite clearly show the chemical potential in the hole-doped material moves to the top of the CTB although there are also other states created at E_F [153]. There has also been work investigating the singlet character of the near- E_F states of the *p*-type compounds. These spin-polarized photoemission measurements concluded in favor of almost a pure singlet state at E_F [154]. Both of these measurement are consistent with the chemical potential moving into the CTB derived lower Hubbard band upon the act of hole doping.

The vast majority of photoemission experiments on the high-temperature superconductors have been performed on hole-doped materials [86, 155]. In contrast, the electron-doped materials have been relatively unexplored [44, 124, 150, 156, 157, 158]. The issue of how a Mott insulator evolves into a metal may be better explored with photoemission in the electron-doped case, as a greater portion of the relevant spectrum is occupied. In fact, one may consider that for electron-hole symmetric Hubbard models, photoemission on the electron-doped material should be equivalent to *inverse photoemission* on the hole-doped material.

In this chapter we report results of an angle-resolved photoemission spectroscopic (ARPES) study of the electron-doped cuprate superconductor $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ at concentrations x = 0, 0.04, 0.1, and 0.15. For the first time, we are able to isolate and resolve the contribution to the spectra from the CTB on the x = 0 sample as has been observed in hole-dopable materials thereby demonstrating the universality of the electronic structure of the CuO₂ plane. More importantly in NCCO this feature appears ~1.3 eV below the Fermi energy, making almost the entire Mott gap visible with our experiment. Upon doping, spectral weight is shifted from the CT band to form states near E_F . At very low doping, these states are centered

around $(\pi,0)$ forming a small Fermi surface with volume $\sim x$. Simultaneously, there is an appearance of spectral weight at higher energy that begins to span and fill the insulator's gap. At greater doping levels this higher energy feature moves to E_F near $(\pi/2,\pi/2)$ and thereby connects with $(\pi,0)$ derived states to form an LDA-like Fermi surface with volume $\sim 1 + x$. For the x = 0.15 sample it is only states at the intersection between the FS and antiferromagnetic Brillouin zone boundary that retain their unusual properties. This evolution provides a natural explanation for the confusing transport data from electron-doped materials, and is qualitatively similar to what one expects from the t - t' - t'' - U model.

6.2 Experimental details

Single crystals of $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ were grown by the traveling solvent floating zone method in 4 ATM of O₂. Details of this growth may be found in Chapter 3. The displayed x = 0.15 spectra were grown at the University of Tokyo and show an onset of superconductivity at 25K and a superconducting volume (Meissner shielding) of almost 100% at 20K. A second batch of crystals, grown at Stanford University under similar conditions, showed an superconducting onset at 24K with similarly narrow transition widths. The photoemission data obtained between the two batches are identical. Crystals with x = 0, 0.04, and 0.1 doping levels were grown at Stanford University under similar conditions to the x = 0.15 samples. Samples of x = 0.1and 0.15 concentrations were oxygen reduced. In addition some data was taken for reduced samples on x = 0.04 samples and were found to have features intermediate to unreduced x = 0.04 and reduced x = 0.1. Measurements were performed at the Stanford Synchrotron Radiation Laboratory's Beamline 5 – 4. Data reported here was collected with 10-20 meV energy resolution and an angular resolution of as good as 0.25 degrees (~ 1% of the Brillouin zone) except where indicated. The photons in all measurements had an energy of 16.5 eV, which has been found empirically to give good cross-section in the relevant binding energy range. The chamber pressure was lower than 4 x 10⁻¹¹ Torr. Sample temperatures were uniformly 10-20K. Surprisingly, this presented no charging problems even for the x = 0 insulator. Cleaving the samples *in situ* at 10K resulted in shiny flat surfaces of which LEED revealed them clean and well ordered with the same symmetry as the bulk [156, 44]. No signs of surface aging were seen for the duration of the experiments(~ 24 hours).

6.3 Results

Previous photoemission measurements on the prototypical half-filled parent Mott insulators Ca₂CuO₂Cl₂ (CCOC) and Sr₂CuO₂Cl₂ (SCOC) have shed light on the dispersive behavior of the low-energy charge transfer band (CTB) [87, 159]. In Fig. 6.2 [159] some of these data from Ronning *et. al.* is shown. It represents the energy for a single photohole inserted into and propagating in a Néel antiferromagnet. The dispersion is a nearly perfectly symmetric "cone" peaked at $(\pi/2,\pi/2)$, with \vec{k} points Γ , $(\pi,0)$, and (π,π) all being nearly degenerate. As pointed out by Laughlin [160] this remarkable symmetry is interesting as the dispersion seemed to be controlled in all directions by either only J or by a unlikely coincidence of parameters t - t' - t''. Being set by J points to the possibility that the measured dispersion is actually one of a spinon and not of a true electron. Interestingly, previous photoemission



Figure 6.2: Dispersion of the charge transfer band in $Ca_2CuO_2Cl_2$ in the BZ quadrant. From Ref. [159].

measurements on undoped Nd_2CuO_4 (NCO) did not reveal a similar feature [161]. This is surprising as one might expect that the half-filled CuO_2 planes in both cases would exhibit generalities independent of material class.

Here, we have reinvestigated NCO in a comprehensive momentum space survey. In Fig. 6.3, we show the results of these measurements along high symmetry directions with polarization of the incoming photons at 45° to the Cu-O bonds. Along the Γ to (π,π) cut, a large broad feature disperses out from under the main valence band, reaches a maximum near $(\pi/2,\pi/2)$, and then disperses back to higher energy. As a very similar dispersion can be seen in the perpendicular direction (Fig. 6.3b) this feature's dispersion is near perfectly symmetric around $(\pi/2,\pi/2)$. A dispersion with a similar shape and energy scale has been seen in CCOC and SCOC as shown



Figure 6.3: (color) (a) Dispersion of charge transfer band (CTB) in Nd₂CuO₄ along zone diagonal from 25% to 75% of Γ to (π,π) distance. (b) Dispersion of charge transfer band from $(\pi/2,\pi/2)$ to 50% of the $(\pi/2,\pi/2)$ to $(\pi,0)$ distance.



Figure 6.4: (color) Comparison of the charge transfer band dispersion of Nd₂CuO₄ and Ca₂CuO₂Cl₂ (a) (π ,0) to (0, π) cut (b) zone diagonal Γ to (π , π) cut

in Fig. 6.2. Like in CCOC and SCOC there is some variability between cleaves and the CTB is found at a distribution of binding energies (1.2-1.4 eV). The energy scale for the data in Fig. 6.3 is set at the average energy. In Fig. 6.4 I explicitly compare the dispersions (the feature's energy defined as the maximum curvature from 2nd derivative plots) along the two symmetry diagonals for NCO and CCOC. The agreement in both total energy scales and symmetry is striking. Due to this similarity as well the fact that the feature's average position relative to the chemical potential (minimum binding energy of its centroid ~1.3 eV) is approximately the same as this material's optical gap (~1.5 eV) we make the assignment of this feature as the CTB. This assertion is supported below by its dramatic doping dependence.

The CTB in NCO may not have been resolved previously for a number of reasons. In contrast to CCOC and SCOC, the CTB in NCO is partially degenerate with the main valence band and hence is obscured over part of its energy range. The valence band onset may be slightly different due to the different non-bonding Cu-O states



Figure 6.5: (color) Intensity of CTB feature (integrated from 1 eV to 1.7 eV binding energy) with polarization along Cu-O bonds.

from NCCO's T' structure as well as the large occupation of 4f electron states from Nd. Although the polarization dependence is qualitatively what one expects for a $d_{x^2-y^2}$ symmetric initial state for the displayed NCO EDCs (with polarization at 45° to the Cu-O bonds), another likely reason for it previously going unobserved is an anomalous polarization dependence of the feature's intensity in the more typical geometry with the incoming light polarized along the Cu-O bonds. This can be seen in Fig. 6.5 where the integrated spectral weight (1-1.7 eV binding energy) is plotted as function of \vec{k} for a polarization of light along the Cu-O bonds. The intensity dependence is counter to one's naive expectation for a $d_{x^2-y^2}$ initial state in this geometry where one would expect the highest intensity to be in the upper octant of the displayed quadrant [86]. At the band structure level, this may be explained by differences in the hybridization of Cu $d_{r^2-z^2}$ orbitals with oxygen p_z orbitals because of the absence of apical oxygen [162]. Having identified the CTB singlet in Nd₂CuO₄, it is interesting to track it as the cerium concentration is increased and spectral weight appears in the near- E_F region. In Figs. 6.6a and 6.6b we plot quasi-angle integrated EDCs from regions near $(\pi/2,\pi/2)$ and $(\pi,0.3\pi)$ respectively. In Fig. 6.6a one can see that as the electron concentration increases the CTB spectral weight decreases and intensity develops at energies near- E_F . This is suggestive of the kind of transfer of spectral weight from high energies to low energies that one qualitatively expects when doping a Mott insulator [145]. The CTB singlet is not resolved near $(\pi,0.3\pi)$, irrespective of its intrinsic intensity at any doping level, as it has dispersed back near the main valence band onset and has a strong matrix element suppression in this region of the BZ as detailed above.

A closer look at Fig. 6.6a reveals that the nondispersive near- E_F spectral weight that has developed along the zone diagonal for the x = 0.04 sample is gapped by ~ 100meV. This is in contrast to the behavior near $(\pi, 0.3\pi)$ (Fig. 6.6b) where there is spectral weight at E_F for x = 0.04 doping levels. For x = 0.1 the zone diagonal spectral weight has moved to E_F and even stronger E_F intensity has formed near $(\pi, 0.3\pi)$. A weak dispersion is evident along the zone diagonal for the x = 0.1 sample. At x = 0.15 there is large near- E_F weight and a strong dispersion throughout the zone as detailed Chapter 5.

Following our previous analysis of the optimally-doped compound [156], we construct the Fermi surfaces for the materials by integrating EDCs in a small window about E_F (+20 meV, -40 meV) and plotting this a function of \vec{k} . Consistent with our above observation that spectral weight along the zone diagonal is gapped for x = 0.04 sample, one can see that it is only those states at (π ,0) that can contribute



Figure 6.6: (a) EDCs integrated from near $(\pi/2,\pi/2)$ position (b) EDCs integrated from near $(\pi,0)$ position

to the low-energy properties. Here a Fermi "patch" indicates that there is an extremely low-energy shallow band in this part of the BZ. At x = 0.1 near- E_F weight with low intensity begins to appear along the zone diagonal. Near $(\pi, 0)$ the "band" becomes deeper and the Fermi patch becomes a Fermi surface. At x = 0.15 the zone diagonal region has become intense and only in the intensity suppressed regions near $(0.65\pi, 0.3\pi)$ (and its symmetry related points) does the underlying Fermi surface keep its anomalous properties as per Chapter 5 [156].

We can gain more insight by looking at plots of the EDCs around the putative Fermi surface for the x = 0.15 sample as shown in Figs. 6.8a-6.8c. In Fig. 6.8c for the x = 0.04 sample a large broad feature is gapped from E_F by ~ 100 meV. As one proceeds around the ostensible $\vec{k_F}$ of the x = 0.15 sample the high-energy feature loses spectral weight and may disappear while another feature pushes up at lowenergy. It is this second component that contacts E_F to form the small Fermi surface for the x = 0.04 sample. Similar two component behavior is seen in the x = 0.1 and 0.15 plots; the lowest energy features become progressively sharper as one gets closer to and enters the metallic state. The fact that there are two components supports our conjecture that at low dopings the spectra can be characterized by a Fermi patch around $(\pi, 0)$ with doping induced spectral weight at higher energy elsewhere in the zone. As the carrier concentration is increased a Fermi surface begins to form with a volume 1.12 ± 0.05 near that appropriate for the highest T_c samples. This comes about by the zone diagonal feature moving to the Fermi energy as seen from the bottom EDC of Figs. 6.8a-6.8c.

In Figs. 6.9, 6.10, and 6.11, I show EDCs from along the high symmetry directions $\Gamma \to \pi, \pi$ and $\pi, 0 \to \pi, \pi$ on the three doped samples. Strong near- E_F dispersions are not seen on the x = 0.04 samples. It is only a higher doping levels that a



Figure 6.7: (color) Fermi surface plots of (a) x = 0.04,(b) x = 0.1, and (c) x = 0.15. EDCs integrated in 60 meV window (-40 meV,+20 meV) plotted as a function of \vec{k} . Data was typically taken in the upper octant and symmetrized across the zone diagonal. (d) Slices in momentum space of E_F intensity.



Figure 6.8: EDCs from around the putative Fermi surface for (a) x = 0.04, (b) x = 0.10, and (c) x = 0.15 samples respectively

dispersion emerges.

Interestingly the FS, where it is observed, does not appear to shift appreciably with doping. In Fig. 6.7d we show cuts through the intensity plots of Figs. 6.7a-6.7c to illustrate more precisely where the FS forms as a function of doping. Along the $(\pi, 0) - (\pi, \pi)$ cut one can see that the FS is developing at the same place in momentum space for all samples. In the $\Gamma - (\pi, \pi)$ cut for the x = 0.04 sample the spectra were integrated not at E_F , but instead in a 60 meV window at the onset of spectral weight as the spectra do not reach E_F in this momentum region. Intriguingly even for this sample, the maximum of the low-energy spectral weight is developing near the same \vec{k} space location as the FS is located for the x = 0.15 sample.



Figure 6.9: EDCs of x=0.04 sample along high symmetry directions (a) $\Gamma\to\pi,\pi,$ (b) $\pi,0\to\pi,\pi$



Figure 6.10: EDCs of x = 0.10 sample along high symmetry directions (a) $\Gamma \to \pi, \pi$, (b) $\pi, 0 \to \pi, \pi$



Figure 6.11: EDCs of x = 0.15 sample along high symmetry directions (a) $\Gamma \to \pi, \pi$, (b) $\pi, 0 \to \pi, \pi$

6.4 Discussion

The existence of a Fermi patch at $(\pi, 0)$ at x = 0.04 is consistent with t - t' - t'' - Umodels which predict that the lowest electron addition states for the insulator are near $(\pi, 0)$ [164]. This confirms an electron-hole asymmetry (broken by the higher order hopping terms) [164] as the lowest hole addition states for the insulator are near $(\pi/2, \pi/2)$ [87, 159, 72] and is the first direct evidence of an indirect CT gap in the cuprates. However, the spectral weight that appears in the the CT gap is not explained within a simple LHB/UHB picture. Exact t - t' - t'' - U model numerical calculations have shown evidence for intrinsic excitations to lie in the insulators gap at low dopings [164]. These calculations show features with only low spectral weight with the majority contribution at $(\pi, 0)$ as is observed. In addition, the detailed evolution of the electronic structure with doping does bear clear resemblance to theoretical models that allow the effective U to decrease with doping [162]. Within these models, the CT gap closes with increasing doping and the Fermi level now cuts not only the bottom of the conduction band near $(\pi, 0)$, but also the top of the valence band near $(\pi/2, \pi/2)$ because of the indirect gap [162]. Fermi surface plots generated by this model bear a striking resemblance to our experiemntal data as shown in Fig. 6.12. Speaking against this point of view is that fact one can see near- E_F spectral weight forming along the zone diagonal at the same time the CTB still exists at higher energy in Fig. 6.6. It does not appear that the CTB moves smoothly to E_F .

Starting from the metallic side, an alternative approach may be one that emphasizes a coupling of electrons to magnetic fluctuations with characteristic wavevector (π, π) . Within this picture, as the antiferromagnetic phase is approached and antiferromagnetic correlations become stronger the "hot spot" regions (intersection of the



Figure 6.12: Fermi surface plots of doping dependent U_{eff} model. (a) x = 0.01 (b) x = 0.04 (c) x = 0.1 (d) x = 0.15. From Ref [162].

FS and antiferromagnetic Brillouin zone boundary [156]) spread so that the states near $(\pi/2, \pi/2)$ are gapped by the approximate nesting of the $(\pi/2, \pi/2)$ section of FS with the $(-\pi/2, -\pi/2)$ section of FS. This scheme obviously breaks down as one gets close to the Mott state.

Our finding explains the long standing puzzle that while the materials exhibit unambigous n-type carrier behavior at low doping, one has to invoke both electron and hole-carriers to explain data near optimal doping [35, 36, 37].

It appears that elements of both the scenarios, laid out in the introduction, can explain our data, as we find evidence for new spectral weight being created in the insulator's gap with the chemical potential appearing to stay relatively fixed, but at an energy near that expected for the UHB. At low carrier concentrations electrons are doped into regions close to $(\pi, 0)$ (confirming a particle-hole asymmetry) near the energy of the UHB and form a small Fermi surface. Simultaneously, there is an appearance of spectral weight at higher energy that begins to span and fill the insulator's gap. At greater electron doping levels more states are created in this midgap region and it is this high-energy spectral weight that moves to the chemical potential and completes the k_F segment to form a large Fermi surface with a volume close to the expected Luttinger volume. It is interesting to note that the full Fermi surface forms near the concentration where the long range order of the antiferromagnetic phase disappears.

Chapter 7

Conclusion

Sir, I have found you an argument, I am not obliged to find you an understanding.

- Samuel Johnson

The electron-doped compounds have different experimental properties than their *p*-type counterparts. In the introduction, I stated that the major goal of this work was to see how or even if these compounds could be understood within the established phenomenology and models of the *p*-type materials. I wanted to understand if the difference that experiments told us existed between electron- and hole-doping, was important; could the same models be applied in both compounds and hence the experimental differences were only due to the role of complicating details or was there something fundamentally different about electron doping? After extensive ARPES study of these compounds it can be concluded that, indeed, their electronic structure can be understood in terms of the same models. At the same time, our investigation of this underexplored side of the phase diagram has gained additional information on the nature of the Mott metal-insulator transition.
Although some differences exists in their superconductivity (a smaller energy gap), the important details regarding the symmetry of their order parameters appear to be the same. On both sides of the phase diagram, I have found evidence for $d_{x^2-y^2}$ superconductivity by the observation of an anisotropic superconducting gap.

In the normal state of the highest T_c samples I have found evidence for a pseudogap in the low-energy spectrum. Unlike the *p*-type material, where this pseudogap is maximal near $(\pi, 0)$, I found that it is maximal at the incommensurate positions near $(0.65\pi, 0.3\pi)$. We can understand the universal formation of a pseudogap (*p*- and *n*type) by realizing that in both cases the maximum of this gap falls at the intersection of the underlying Fermi surface with the antiferromagnetic Brillouin zone boundary. These differences point to the fact that the the pseudogap in the *p*-type compounds may be related to the presence of antiferromagnetic (or similar) correlations and not to the existence of large energy scale preformed pairs. This is a textbook example of how the same underlying physics can manifest itself very differently due to the details of the specific material.

The doping dependent study shows that to some extent these materials can be viewed as electron-doping into an upper Hubbard band and in this regard there may be a similarity in the underlying models with the *p*-type. It appears that the threeband Hubbard model may be reduced (at least qualitatively) to a one-band model. Since I find for low-doped samples that the lowest energy states are near $(\pi, 0)$, it confirms models that predict an exact electron-hole symmetry is broken, between *p*and *n*-type compounds, by higher order hopping terms. This is, in my opinion, the first unambigous evidence that Mott gap is indirect. I also find that there is spectral weight that develops in the insulator's gap. As one moves towards optimal doping this spectral weight moves towards E_F and completes the zone diagonal Fermi surface section to make the large Fermi surface of the optimally-doped material. Here it is difficult to make direct comparisons to the behavior of the *p*-type compounds because in-gap spectral weight will be unoccupied and hence unobservable by photoemission. This study does give some insight as to how the large Fermi surface of the hole-doped material can develop from the small Fermi surface of the Mott insulator.

There are a number of unanswered questions and directions for future research. It would be interesting to do a temperature dependent study of the "hot spot" regions. If indeed they are due to a coupling with antiferromagnetic fluctuations, then one may expect that a simple Fermi surface will recover as the samples are warmed and such correlations become weaker. Although important, this is a very technically demanding experiment as the surfaces of the high- T_c 's are intrinsically unstable. Samples are typically cleaved at low temperatures (10K) and are kept cold and in ultra-high vacuum. Such surfaces can be irreversibley damaged by warming them, as gases physioabsorbed at low temperatures can acquire sufficient activation energy to chemically react. In doing the superconducting gap measurements, I was able to reproducibly temperature cycle to 30K and back; going to higher temperatures may be more difficult and such studies need to be done carefully.

It would also be interesting to do a more in-depth study of the role of oxygen impurities. As stronger antiferromagnetism is found in the non-superconducting x = 0.15 samples, one may expect "hot spot" effects to be stronger in these unreduced samples. Additionally I might expect that going to higher doping levels (x = 0.17) should move the hot spots along $\vec{k_F}$ towards ($\pi/2, \pi/2$) as the Fermi surface expands to incorporate additional electrons. Such studies would be an important confirmation of pseudogap models based on a coupling of charge carriers to antiferromagnetic fluctuations.

Appendix A

Spectral Function Analysis of $Nd_{1.85}Ce_{0.15}CuO_4$

It is now possible in photoemission to do simultaneous parallel angle scanning and generate direct 2D $E - \vec{k}$ images of the ARPES spectral function. Although ARPES data has been typically displayed in terms of energy distribution curves (EDCs) where the photoemission intensity is plotted as a function of energy for a specific angle, ARPES data can now be displayed in terms of these detailed image plots and in analogy with EDCs, complementary momentum distribution curves (MDCs) can be generated. Using these new techniques, a preliminary ARPES lineshape analysis of the electron-doped (*n*-type) cuprate superconductor Nd_{1.85}Ce_{0.15}CuO₄ was performed.

As detailed previously in Chapter 2, within the sudden approximation, ARPES measures the single particle spectral function $A(\vec{k}, \omega)$. It can be represented compactly in terms of a complex self-energy $\Sigma = \Sigma' + i\Sigma''$ as

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

In momentum regions where $\Sigma''(\vec{k},\omega)$ is a weak function of \vec{k} and the bare dispersion can be linearized as $\epsilon_{\vec{k}} = v_F^0(\vec{k} - \vec{k}_F)$ then $A(\vec{k},\omega)$ at constant ω can be put in the form of a Lorentzian that is centered at $\vec{k}_F - \Sigma'(\vec{k},\omega)/v_F^0$ with width $\Sigma''(\vec{k},\omega)/v_F^0$. As detailed in Chapter 2, such analysis in a number of compounds has recently lead to the observance of novel features indicative of many-body correlations [80, 81, 82, 83, 95, 96, 97].

Angle-resolved photoemission data were recorded at beamline 10:0:1:1 of the Advanced Light Source with a photon energy of 55 eV in a glancing incidence geometry. Polarization angles were both along and at 45° to the Cu-O bonds. Energy resolution was typically 18 meV and angular resolution was 0.14° (corresponding to 0.5% of the Brillouin zone size). Samples were cleaved *in situ* at low temperatures in vacuums better than 4 x 10⁻¹¹ Torr. As there are only minor changes to the spectra when entering the superconducting state [44], all displayed data were taken at low temperature (10 - 20K) in the superconducting state.

In Figs. A.1 and A.2 we show the raw data 2D image plots of the spectral function and the corresponding EDCs for \vec{k} -space cuts along the Γ to (π, π) and the $(\pi, 0)$ to (π, π) directions. In the Γ to (π, π) direction, a large broad feature disperses out of the background and sharpens to a sharp peak at E_F and then disappears.

In the $(\pi, 0)$ to (π, π) direction an almost perfectly parabolic shaped band is seen. A similar sharpening of the feature is seen here as well, as it disperses to E_F , but not to the same extent.

The MDCs from the raw image plots were fitted to Lorentzians as detailed above. These position fits are displayed in Fig. A.3 along with the corresponding energy



Figure A.1: (a.) Image of spectral function along Γ to (π, π) direction. (b.) EDCs from (a.).



Figure A.2: (a.) Image of the spectral function along the $(\pi, -\pi)$ to (π, π) direction. (b.) EDCs from (a.). The lower piece of the parabola is slightly distorted from its real shape as this data was at the very edge of the detector multichannel plate and there are problems from astigmatic effects in the electron lens.



Figure A.3: Dispersions fitted from spectral function analysis. (a.) $\Gamma - (\pi, \pi)$ (b.) $(\pi, 0)$ - (π, π) . The straight lines are simple fits.

widths in Fig. A.4. Along the zone diagonal there is no mass-renormalization or "kink" behavior as seen in the *p*-type materials. By comparing to a parabolic fit, one may see that along the $(\pi, 0)$ - (π, π) cut there may be a very small mass renormalization around 75 meV. This may be related to the kink behavior reported in the *p*-type and perhaps due to phonons. However, we cannot rule it out as an artifact of the magnetic effects discussed in earlier chapters.

As far as widths are concerned, our data indicates a drop in the scattering rate along the zone diagonal, but not near $(\pi, 0)$. This is similar to the case of CDW formation in Nb₂Se₃ where a mass renormalization in one place in the Brillouin zone is accompanied by scattering lifetime effects elsewhere in the zone.

More work needs to be done with this spectral function analysis. Particurally it needs to be confirmed that the drop in the scattering rate along the zone diagonal and the "kink" near $(\pi, 0)$ is real and not an artifact of non-many-body origin. This may be possible by taking into account models that incorporate some of the possible momentum-dependent self-energy effects.



Figure A.4: Energy widths fitted from spectral function MDCs and multiplied by velocity. (a.) Γ - (π, π) (b.) $(\pi, 0)$ - (π, π) .

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