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**AN ANGLE RESOLVED PHOTOEMISSION STUDY OF A
MOTT INSULATOR AND ITS EVOLUTION TO A HIGH
TEMPERATURE SUPERCONDUCTOR***

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AN ANGLE RESOLVED PHOTOEMISSION STUDY OF A
MOTT INSULATOR AND ITS EVOLUTION TO A HIGH
TEMPERATURE SUPERCONDUCTOR

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

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September 2001

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Abstract

One of the most remarkable facts about the high temperature superconductors is their close proximity to an antiferromagnetically ordered Mott insulating phase. This fact suggests that to understand superconductivity in the cuprates we must first understand the insulating regime. Due to material properties the technique of angle resolved photoemission is ideally suited to study the electronic structure in the cuprates. Thus, a natural starting place to unlocking the secrets of high T_c would appear to be with a photoemission investigation of insulating cuprates.

This dissertation presents the results of precisely such a study. In particular, we have focused on the compound $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$. With increasing Na content this system goes from an antiferromagnetic Mott insulator with a Néel transition of 256K to a superconductor with an optimal transition temperature of 28K. At half filling we have found an asymmetry in the integrated spectral weight, which can be related to the occupation probability, $n(\mathbf{k})$. This has led us to identify a d -wave-like dispersion in the insulator, which in turn implies that the high energy pseudogap as seen by photoemission is a remnant property of the insulator. These results are robust features of the insulator which we found in many different compounds and experimental conditions. By adding Na we were able to study the evolution of the electronic structure across the insulator to metal transition. We found that the chemical potential shifts as holes are doped into the system. This picture is in sharp contrast to the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ where the chemical potential remains fixed and states are created inside the gap. Furthermore, the low energy excitations (ie the Fermi surface) in metallic $\text{Ca}_{1.9}\text{Na}_{0.1}\text{CuO}_2\text{Cl}_2$ is most well described as a Fermi arc, although the high binding energy features reveal the presence of shadow bands. Thus, the results in

this dissertation provide a new avenue for understanding the evolution of the Mott insulator to high temperature superconductor.

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Chapter 1

Introduction

1.1 A General Overview

Understanding high temperature superconductivity is an extremely complex and interesting problem. In this section I will introduce this subject by reviewing some of the basic properties of the high temperature superconductors. The remainder of this introduction will present a more detailed picture of the current state of the field, and will identify the specific questions which this dissertation addresses.

In normal materials a single electron will bump into other electrons over a million times a second, but in superconducting materials, electrons have amazingly found a way to avoid one another entirely. This dissertation is one part of a global effort to understand how this phenomenon occurs in a particular class of materials called the cuprates.

The term cuprates is used to describe all ceramic crystals that have the common feature of layers of copper and oxygen atoms. (See figure 1.1) Before the discovery of superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ in 1986,[1] superconductivity could only be found below 23 degrees Kelvin (-250C)[2] (see figure 1.2). In the cuprates, transitions into the superconducting state have now been found as high as 138K(-135C) under atmospheric conditions,[3] and can be pushed even higher by applying pressure to the sample. The dramatic increase in transition temperature compared to previously known crystals gave these materials the title of "high temperature superconductors".

Figure 1.1: Crystal structure of $A_2CuO_2Cl_2$ ($A = Sr, Ca$), a typical cuprate. By substituting Na for Ca one can create a high temperature superconductor. The complicated structure on the left can be simplified by considering only the CuO_2 layers as relevant, and the remaining atoms, called charge reservoir layers, simply provide or remove electrons from the CuO_2 planes. Due to the two dimensional nature of the cuprates the structure can be further reduced to a simple single CuO_2 unit cell shown on the right.

Although, to put this in perspective, this temperature still lies $46^\circ C$ below the coldest temperature ever recorded on Earth (Antartica in 1983).[4] In 1956 J. Bardeen, L.N. Cooper, and J.R. Schrieffer developed a model now known as BCS (after their last names), which explains superconductivity from a microscopic point of view for the lowest temperature superconductors.[5] However, under this theoretical framework superconductivity at “high” temperatures is inconceivable. Obviously, a new microscopic understanding is necessary. Over the past 15 years more research has been

Figure 1.2: A historical perspective of the rising maximum superconducting transition temperature. “High T_c ” began with the discovery of superconductivity in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. [1] The dotted red line indicates the boiling point of liquid nitrogen, a relatively cheap coolant. For perspective the lowest temperature recorded on the earth’s surface (in Antartica, 1983) is also indicated. (Figure courtesy of D.H Lu)

done in this field than in any other area of physics. Despite many accomplishments, the fact that we still lack an understanding of the cuprates hints at the complexity of this problem.

The cuprates actually come in many varieties. One way to characterize them is by the average number of conduction electrons per copper atom. Conduction electrons are those electrons which are able to move throughout the solid. By chemically substituting the atoms which surround the copper-oxygen layers the number of conduction electrons can be changed. Remarkably, when there is an average of one conduction

electron per copper atom, as in $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (Calcium copper oxychloride), the material is an electrical insulator; however, $\text{Ca}_{1.85}\text{Na}_{0.15}\text{CuO}_2\text{Cl}_2$, for example, has an average value of 0.85 conduction electrons per copper atom and becomes superconducting at low enough temperatures. [See figure 1.4] To find that the best conductors of electricity to date are so closely related to insulators was one of the most shocking discoveries in this field.

Aside from the fundamental interest of this problem to physicists, the cuprates also have great technological potential. It is hoped that by understanding the microscopic mechanism of the cuprates, scientists will be able to synthesize new materials which superconduct at room temperature and above. One could then easily exploit their fantastic characteristics. For example, since superconducting electrons do not collide with one another, they will not lose any energy. As a result, one could use energy much more efficiently, and a natural consequence would be that the cost of electricity would drop. Superconductors also have the potential to be great magnets, leading to, among other things, faster trains, better computers, and more powerful scientific probes including those used for medical diagnosis. In fact, anything that uses electricity or magnetism has the potential for improvement. It should be noted that while some applications may be more of a dream than potential reality, others are already in use. As an example, high temperature superconductors are playing a large role in improving cellular phones.

How then does one begin to attempt to understand the cuprates? For physicists, one of the most important properties of a material is something called its electronic structure. This structure contains a wealth of information, describing the physical properties, such as the energy and momentum, of every electron inside the solid. From this microscopic knowledge, many macroscopic physical properties can be understood. Among other things, one can predict the color of a material, whether or not it is fluorescent, transparent, or shiny, and how well it can conduct electricity. In fact, all physical properties including superconductivity are dependent on the electronic structure of a material in some way. For example, in the BCS model, in order to calculate the temperature at which the electrons will begin to superconduct, one needs to know the energy distribution of the electrons; this information is contained

Figure 1.3: A schematic of Angle Resolved PhotoEmission Spectroscopy(ARPES). While a synchrotron facility is often the preferred light source, there are many alternatives. The wavelength of light is chosen by a monochromator. The photons are then absorbed by the sample and electrons are thus emitted. An electron analyzer measures the Kinetic energy of the out going electrons. From the position of the detector and using the fundamental conservation laws of energy and momentum, one can then extract the dispersion relation $E(\mathbf{k})$ which gives the energy of an electron inside the sample as a function of its momentum. (For details see chapter 2)

in a materials electronic structure. So to discover the microscopic nature of the high temperature superconductors, a good starting point would be to determine the electronic structure of the cuprates.

The technique of Angle Resolved Photoemission (ARPES) is ideally suited for this task. The origin of this technique can be traced to Hertz's discovery of the photoelectric effect.[6] By shining light with sufficient energy on a material, electrons are emitted from the surface. We can detect the energy and momentum of these out going electrons. Then by using fundamental laws of physics, we can deduce the energy and momentum distribution of the electrons from when they were in the sample, thereby directly probing its electronic structure. For a schematic illustration of ARPES, see figure 1.3. Thus, by performing ARPES on cuprates we hope to determine any peculiarities in their electronic structure that would result in such high transition temperatures into the superconducting state.

This dissertation presents ARPES results on cuprates such as $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ and related materials. I will demonstrate how the electronic structure changes when a cuprate goes from an insulator to a superconductor. In following this evolution, I

have noticed that certain features of the electronic structure are remarkably similar in both the insulator and the superconductor. We hope that this will provide a guide to the theorists in developing a new theory of superconductivity.

1.2 Solving High T_c

An important aspect of “solving” high temperature superconductivity is equivalent to trying to explain the phase diagram of the cuprates. Of course the phase diagram is dependent on the particular cuprate system being studied, but the general features which are common to all systems are shown in figure 1.4. The parameter x refers to the number of doped holes into the CuO_2 plane. At $x=0$, also known as half filling, the material is an antiferromagnetic insulator with a Néel temperature of roughly 300K. As the number of holes increases the antiferromagnetic phase is quickly destroyed, and the cuprates become “strange” metals characterized by a pseudogap. The pseudogap has been identified by many different experimental techniques including ARPES, Nuclear Magnetic Resonance (NMR), tunneling spectroscopy, transport measurements, specific heat, optical conductivity, and Raman scattering. This phase is extremely poorly understood, due to its many anomalous properties. For a review see [7]. At very large hole doping the metallic phase returns to more conventional behavior expected by Fermi liquid theory. However, it is unclear whether a true phase transition exists between the two metallic “phases” or if it is simply a crossover regime. Finally, between $x \approx 0.07$ and $x \approx 0.25$, at low enough temperature, the system becomes superconducting. The maximal T_c is achieved at $x \approx 0.15$, also referred to as optimal doping, while lower(higher) hole doping is referred to as underdoped(overdoped).

The superconducting state is far from conventional. The isotope effect, partly responsible for identifying the electron-phonon coupling as the mechanism for conventional superconductivity, is weak in the cuprates.[8] The order parameter for the high T_c superconductors has an amplitude and a phase which has $d_{x^2-y^2}$ symmetry as opposed to s-wave symmetry for most other known superconductors. This perhaps is considered the strongest evidence against a conventional electron-phonon mediated theory of high T_c , although there is now evidence that electron-phonon coupling may

Figure 1.4: A simplified phase diagram of the cuprates. At half filling the cuprates are antiferromagnetic insulators (AFI). As holes are doped into the CuO_2 plane (increasing x) the system becomes a poor metal, which has been characterized by many unusual properties. At very large hole doping more typical metallic properties associated with a Fermi liquid exist. The hashed line indicates the ambiguity as to whether there is a true phase transition between the two metallic regimes, or whether it is simply a crossover of differing energy scales. Red is the region of superconductivity, and some terminology is indicated at the bottom.

not necessarily compete against d -wave superconductivity [9, 10]. It should also be noted that the weak isotope effect is not an open and shut case either. Crawford *et al.*[11] showed using the LSCO and LBCO systems that there exists a considerable doping dependence of the isotope effect which is greatest when the LTO to LTT structural phase transition is maximal. Aside from the electron-phonon coupling question, attempts to explain superconductivity given any coupling mechanism within the conventional BCS framework have failed [12]. The phase diagram is further complicated when considering electron doping to the CuO_2 plane (ie $x < 0$; not shown). Qualitatively it appears symmetric with respect to half filling, but a closer inspection reveals that this symmetry is only approximate. The antiferromagnetic phase is more robust, and superconductivity is limited to a smaller doping range than on the hole doped side. The symmetry or lack thereof is crucial to theories of high temperature superconductivity. Although many implicitly assume an electron-hole symmetry there is clearly much to be understood on this issue.

The crystal structure of the cuprates at first glance is even more complicated than the phase diagram. However, both experiments and theory agree that the low energy physics of the cuprates is dominated by the CuO_2 planes, which are common to all cuprates. Thus the crystal structure can be thought of as layers of CuO_2 planes separated by charge reservoir layers, the details of which simply act to supply more or less holes into the CuO_2 plane. The extreme two dimensional nature of the cuprates means that theoretically, we can focus our attention on a single CuO_2 plane. This is illustrated in figure 1.1. In this case the three relevant orbitals are the oxygen p_x, p_y and copper $d_{x^2-y^2}$ orbitals. Performing a simple tight binding calculation, one gets a nonbonding band ($E_k = \epsilon_p$) as well as bonding and antibonding bands of the form

$$E_k = \frac{\epsilon_p + \epsilon_d}{2} \pm \sqrt{\left(\frac{\Delta}{2}\right)^2 + 4t_{pd}\left(\sin^2 \frac{k_x a}{2} + \sin^2 \frac{k_y a}{2}\right)} \quad (1.1)$$

where t_{pd} is the hopping integral from a copper d orbital to a neighboring oxygen p orbital, ϵ_p and ϵ_d represent the energy of putting an electron on the respective orbitals, $\Delta = \epsilon_p - \epsilon_d$ is the charge transfer energy, and a is the lattice constant. At $x=0$ there are 5 electrons per unit cell to fill these bands, which results in a half-filled

antibonding band as shown in figure 1.5. A more complete band calculation also finds a metal resulting from the CuO_2 plane.[13] However, this is wrong! Experimentally, at half filling these crystals are insulators with a charge gap of roughly 1.5 to 2eV.[14, 15] Clearly, electron correlations which are neglected in the band calculations must be taken into account. Specifically, the insulating nature is a result of the energy cost, U , associated with putting two electrons in the copper $d_{x^2-y^2}$ orbital. This can be qualitatively understood by considering a chain of hydrogen atoms as described by

Figure 1.5: Band structure along high symmetry directions. Left is a simple tight binding model using only $\text{Cu}d_{x^2-y^2}$, $\text{O}p_x$, and $\text{O}p_y$ orbitals as a basis. The relevant parameters are indicated in the figure. Right is the complete band structure calculation of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ using the linear augmented plane-wave method.[13] Clearly both predict a metal at half-filling.

Mott.[16] Band theory predicts the chain to be metallic independent of the separation between atoms. However, in the limit of large atomic separation the electrons will be localized on each atom resulting in an insulating state. As the hopping integral becomes infinitesimally small at large separation, it is no longer valid to ignore the energy associated with putting two electrons on a single atom (since it is comparable to the kinetic energy, proportional to t). In the cuprates, the Cu d orbitals are highly localized; hence, large atomic separation is not necessary for electron correlations to be relevant.

Theoretically, we need a model which can capture the physics at hand. We begin with one of the simpler models, the one band Hubbard model[17], which was first argued by Anderson to capture the essential properties of the cuprates.[18]

$$H = t \sum_{\sigma \langle ij \rangle} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (1.2)$$

where $c_{i\sigma}^\dagger$ creates an electron with spin σ on the i th site of a square lattice (for now the oxygen sites have been ignored). The first sum is over nearest neighbor sites $\langle ij \rangle$ only, t is the effective hopping integral, U is the energy cost of putting two electrons on the same site, and $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ is the electron occupation operator. This simple Hamiltonian is deceptively complex, and has only been solved for special cases. At half filling and $U=0$ one recovers the tight-binding result, while for $t=0$, one can see that the ground state is 2^N degenerate with a single, localized electron per site. Since for large U , doubly occupied sites are energetically very costly, one can project out the doubly occupied states for small t/U and arrive at an effective Hamiltonian, known as the t - J model:

$$H = t \sum_{\sigma \langle ij \rangle} (\tilde{c}_{i\sigma}^\dagger \tilde{c}_{j\sigma} + \text{H.c.}) + J \sum_{\langle ij \rangle} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} n_i n_j) - \frac{t^2}{U} \sum_{\sigma \langle ijk \rangle} (\tilde{c}_{k\sigma}^\dagger n_{j-\sigma} \tilde{c}_{i\sigma} - \tilde{c}_{k\sigma}^\dagger \tilde{c}_{j-\sigma}^\dagger \tilde{c}_{j\sigma} \tilde{c}_{i-\sigma} + \text{H.c.}) \quad (1.3)$$

where $\tilde{c}_{i\sigma} = c_{i\sigma}(1 - n_{i-\sigma})$ is an electron creation operator which prevents double occupation, $J=4t^2/U$, $\bar{\mathbf{S}}_i = c_{i\alpha}^\dagger \bar{\sigma}_{ij} c_{j\beta}$ with $\bar{\sigma}_{ij}$ being the Pauli spin matrices, and where

the final term is a three site term which is usually neglected. Note that although $\tilde{c}_{i\sigma}^\dagger$ represents the creation of an electron when possible, it no longer satisfies the fermionic commutation relations. At half filling, hopping is not possible as every site contains one spin, and double occupancy is not allowed. Thus for $x=0$, the t - J model reduces to a spin 1/2 Heisenberg antiferromagnet. Indeed the half filled cuprates are one of the best experimental realizations of the spin 1/2 Heisenberg antiferromagnet with $J=130\text{meV}$ determined by neutron and two magnon Raman scattering [19, 20].

However, photoemission experiments have shown that the $\text{Cu}d^8$ state is 8eV below the $\text{Cu}d^9L$ state, where L refers to the ligand(which in this case are the oxygen atoms).[21] This is large with respect to Δ , and classifies the cuprates as charge transfer insulators($\Delta < U$) rather than Mott insulators($\Delta > U$). Thus it is not clear whether or not one may neglect the oxygen sites when constructing an effective Hamiltonian for the low energy physics. So Emery proposed the more comprehensive three band Hubbard model[22]:

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

where p and d refer to oxygen p and copper d orbitals, respectively. Unfortunately, it is not apparent how one reduces this Hamiltonian to the one band Hubbard model. However, the pioneering effort by Zhang and Rice has made this Hamiltonian a manageable starting place.[23] They applied the three band Hubbard model to a single CuO_4 cluster containing two holes (see figure 1.6). They found that one hole located on the Cu site would hybridize most strongly with a hole located on a linear combination of the four surrounding oxygen hole states forming what they termed a singlet, a nonbonding, and a triplet state. The large energy separation between the singlet and the triplet, which has been calculated by Eskes and Sawatzky to be 3.5eV,[24] implied that the triplet state could be projected out. Note that the Zhang-Rice singlet states

Figure 1.6: From ref. [23]. Schematic of the hybridization of a hole on the Cu site with a hole on the four surrounding oxygens.

on neighboring sites are not orthogonal. An effective Hamiltonian can then be constructed to allow the “Zhang-Rice singlet” to hop over the entire CuO_2 plane. The impressive result is that the effective Hamiltonian is again the t - J model, which was also the effective Hamiltonian for the single band Hubbard model. In this sense, it is tempting to think of the Zhang-Rice singlet as forming an effective lower Hubbard band, thus lending more credibility to starting from an effective one band Hubbard model to begin with. Finally, we note that the one band Hubbard model possesses electron hole symmetry while the three band Hubbard model does not which is relevant in trying to understand the electron doped as well as hole doped side of the phase diagram.

Early angle resolved photoemission results on $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ showed that the Hubbard model is indeed a reasonable starting point.[25] The overall bandwidth is similar to the t - J prediction of $2.2J$, which contrasts to the $8t_{pd}$ prediction from band theory. The discrepancy however lies in the dispersion from $(\pi, 0)$ to $(\pi/2, \pi/2)$. The t - J model predicts all the states along the antiferromagnetic zone boundary, $(\pi, 0)$ to $(0, \pi)$, to be degenerate. However, the actual dispersion is on the order of the total band width. The solution to this problem has been to add second and third nearest neighbor hopping terms, t' and t'' which lifts this degeneracy [26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36].

Figure 1.7: From ref. [37]. Spectral weight (proportional to the radius of the circle) from exact diagonalization calculations of 16, 18, and 20 site clusters of the one band Hubbard (left) and t - J (right) models. $U/t=10$.

1.3 Doping Evolution

Although the Hubbard models correctly predict an antiferromagnetic insulator at $x=0$ it is still unclear how the Mott insulator evolves across the metal to insulator transition. For a material where band theory is valid, it is known that the Fermi surface will shrink to a point and then disappear. For a Mott insulator though it is still unknown. This is the main question which this dissertation addresses. The Fermi surface is one of the most characteristic properties of a metal. How, then, does it vanish as a system becomes an insulator? Numerical calculations show that in the intermediate coupling regime of the Hubbard model, the occupation probability, $n(\mathbf{k})$, survives in the insulating state, while this is not true in the t - J model.[37, 38, 39](See figure 1.7) Chapters 3 and 5 will investigate this issue from the experimental point of view of angle resolved photoemission.

Alternatively, one can flip the question around, and ask how the insulator evolves to the metal. In particular, how does the chemical potential shift upon doping? First let us compare a band insulator, a Mott-insulator and a charge-transfer insulator (shown in figure 1.8). Upon doping the band insulator with either holes or electrons

the chemical potential simply shifts. The Mott-insulator is similar, but with one significant difference: when a hole is doped into the system it removes one doubly occupied state. This is a state in the upper Hubbard band. A state from the lower Hubbard band is also removed. Hence, spectral weight is transferred from the upper and lower Hubbard bands as the chemical potential shifts to the lower Hubbard band. The situation is analogous when an electron is doped into the system. For a charge-transfer insulator, the electron doped picture remains the same, although note that the spectral weight which is lost still comes from the lower Hubbard band, not the

Figure 1.8: The effect of doping three kinds of insulators: A band-insulator, a Mott-insulator, and a charge-transfer insulator. The electron removal spectra (ie. photoemission) are indicated by the shaded regions, while the electron addition spectra (ie. inverse photoemission) are dotted. The top shows the undoped insulator while the middle and bottom spectra are for a single doped hole or electron, respectively. (after ref [40])

charge transfer band. In the case of hole doping, an occupied state in the charge transfer band simply becomes unoccupied, and nothing else happens. This is what happened in the case of the band insulator. Thus there is a distinct asymmetry between the effects of hole doping and electron doping. The charge-transfer scenario was drawn in the limit of negligible hopping ($t_{pd} \rightarrow 0$). As the hybridization is increased between the oxygen p and copper d orbitals, the charge-transfer band will also transfer spectral weight, and thus look increasingly more like the lower Hubbard band[40]. Thus we again recover a scenario which appears more like the one band Hubbard model out of the original charge-transfer insulator.

The above description however, fails to capture another possibility which appears to have been realized in the cuprates. Namely, in the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ it is believed that the chemical potential remains fixed inside the gap upon doping [41]. These states are presently believed to be related to stripe formation.[42] The additional scenario along with the case described above is shown in figure 1.9. Again, we start at half filling where the chemical potential in the absence of any impurities is undefined as the energy to add an electron greatly differs from the energy to remove an electron. However, upon doping one can imagine that states are created which fix the chemical potential inside the gap. This is a strongly differing view from the case where the chemical potential shifts upon doping. Note that in the scenario where states are created inside the gap, it is assumed that by doping the system, one changes the Hamiltonian of the system. Otherwise, this scenario is not possible. In chapter 6 we will present ARPES results on $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$, which in contrast to $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, shows that the chemical potential shifts with doping akin to a band material. We will discuss the remarkable finding that two similar systems could show differing evolutions across the metal insulator transition.

Studying the evolution across the metal to insulator transition has also allowed us to make several interesting observations on the origin of various aspects of the electronic structure in the cuprates. Throughout this dissertation we will demonstrate that the high energy pseudogap as seen by ARPES is indeed a property of the insulator. This was first conjectured to be the case by Laughlin.[44] Furthermore, in chapter 3 we find that the dispersion of the insulator can be characterized by a

Figure 1.9: Two possible evolutions of the chemical potential upon hole doping. a) The undoped Mott insulator. b) The chemical potential shifts upon doping causing a transfer of spectral weight. c) Doping creates states inside the gap which are filled. (After ref. [43])

d -wave like modulation, the details of which will be investigated in chapters 4 and 5. Thus, an interesting link between the antiferromagnetic insulator and the d -wave superconductor is formed. A consequence of the chemical potential shift observed in chapter 6 is the existence of shadow bands[45] in a hole doped sample; however, the low energy excitations appear more well described as a Fermi arc[46] than as a hole pocket centered about $(\pi/2, \pi/2)$ as one would naively expect. We will conclude with a discussion on some of the theoretical implications of our results, and other prospects for future work in this exciting field.

1.4 System of Choice

As mentioned earlier, the cuprates come in many varieties. While each are unique in their own way, they all share the common feature of CuO_2 planes. So the first task is

to decide which system will be the most effective in answering the questions discussed above. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, with its high transition temperature and extremely good cleavage plane, is almost the ideal system for photoemission. It has only a few minor drawbacks. First is the presence of “superstructure” caused by a modulation in the BiO layer, which clouds the interpretation of the data near $(\pi, 0)$. The second is the relatively poor spectral quality of the data as half filling is approached. The reason for this is unclear, but may be due to the sample quality. This is a significant set back for trying to address the issues concerning the metal to insulator transition. There have been two approaches to fill this void. One is to study the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system which is grown equally well over the entire doping range. Unfortunately, it does not have a very good cleavage plane, and the resulting spectra are also quite broad.¹ The alternative approach is to study the oxyhalide system, which until very recently had not been successfully doped to produce single crystals. The later approach has been taken in this dissertation.

The oxyhalide compounds, $\text{M}_2\text{CuO}_2\text{X}_2$ ($\text{M}=\text{Sr}, \text{Ca}, \text{Ba}$; $\text{X}=\text{F}, \text{Cl}, \text{Br}$) and variations thereof have been known since the 1970’s. For a review of the various structures see ref [49]. The compound $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ is considered one of the best realizations of the $\text{S}=1/2$ Heisenberg quantum antiferromagnet [50, 51]. The difference of these single layer cuprates to others is the presence of an apical halide as opposed to an apical oxygen for other hole doped cuprates. The discovery of superconductivity in the oxyhalide, $\text{Sr}_2\text{CuO}_2\text{F}_{2.6}$ ($T_c=46\text{K}$), suggested that the apical site was not intimately connected with hole doped superconductivity [52]. Indeed we find, that the electronic structure is independent of the apical atom (See chapter 4). The good cleavage plane of the oxyhalides makes them a potentially ideal system to study with photoemission. Indeed the ARPES data on $(\text{Sr}, \text{Ca})_2\text{CuO}_2\text{Cl}_2$ produces the highest quality spectra from any half filled cuprate.[25, 26, 53, 54, 55] This facilitates a comparison across the metal insulator transition with data from the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ system. After attempts by many institutions, Kohsaka *et al.* have successfully produced hole doped single crystals of $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ [56]. The photoemission study of this compound

¹Recent measurements on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ are now revealing sharper structure when the experimental conditions are properly tuned.[47, 48]

is presented in chapter 6. With the oxyhalide systems and the technique of angle resolved photoemission we are now ideally prepared to tackle the issues of the insulator to metal transition in the cuprates.

Chapter 2

ARPES: a technique to probe the electronic structure

Angle Resolved Photoemission (ARPES) is a powerful tool for studying the electronic structure of solids. Its origin can be traced back to Hertz's discovery of the photoelectric effect in 1887,[6] which was subsequently explained under the postulates of quantum mechanics by Albert Einstein in 1905.[57] Today it is used in condensed matter physics to probe the electronic structure of solids.

2.1 Photoemission Energetics

To illustrate the usefulness of photoemission to solid state physics we begin by demonstrating how the electronic density of states can be obtained from a photoemission experiment. In a photoemission experiment we illuminate a sample with monochromatic light of energy, $h\nu$. If this energy is greater than the work function of a material then an electron will be emitted. Conservation of energy tells us that

$$E_{final} = E_{initial} + h\nu \tag{2.1}$$

$E_{final}(E_{initial})$ is the final(initial) state of the entire N particle system. The final state is a product of a free electron and the remaining N-1 particle system, Ψ^{N-1} . If we

assume a single particle picture, as is often done (although we will reexamine this point shortly), then the energy of the N particle system can be described as the sum of N individual states: $E^N = \sum_k \epsilon_k$. Thus one will see that $E^N = \epsilon_k + E^{N-1}$. So equation 2.1 can now be rewritten as:

$$E_{p.e.} + E^{N-1} = E^N + h\nu \quad (2.2)$$

$$E_{p.e.} = \epsilon_k + h\nu \quad (2.3)$$

where $p.e.$ stands for the photoelectron. Taking the chemical potential to be the zero of energy we get

$$KE_{p.e.} + \Phi = \epsilon_k + h\nu \quad (2.4)$$

where KE is the kinetic energy of the emitted electron, and Φ is the work function of the sample. If we further assume that the cross section for emitting an electron is independent of it's initial state and final momentum¹ then we can see that the ratio of the number of electrons emitted with KE_A versus the number of electrons emitted with KE_B will be equal to the number of states at energy $\epsilon_k = KE_A + \Phi - h\nu$ divided by the number of states at energy $\epsilon_k = KE_B + \Phi - h\nu$. Thus it is apparent that a photoemission spectra $I(KE)$ will be proportional to the density of electronic states which are occupied. This is illustrated in figure 2.1. In practice these spectra, also known as angle integrated spectra, are obtained by collecting a finite solid angle of electrons emitted from a polycrystalline surface. Note that in the figure the photoemission spectra has additional weight indicated by the hashed region. These electrons are termed secondary electrons and result from those which incur multiple scattering events, and thus lose a fraction of their energy inside the solid before they are emitted.

¹This is an unjustified assumption. We will in see subsequent sections that photoemission cross sections have a large k dependence. Thus, one should always be wary of detailed fits to angle integrated data.

Figure 2.1: Energetics of the photoemission process showing how photoemission maps out the density of states. The hashed region is due to “secondary” electrons which are the result of multiple scattering events. Φ is the work function, and $h\nu$ is the photon energy.

2.1.1 Measuring the Chemical Potential

From above we can see that the electron with the maximum kinetic energy will originate from the highest occupied orbital. However, one would often like to know whether this electron lies at the chemical potential, or alternatively, if there is an energy gap in the system. As work functions are not very precisely known, the question of calibrating one’s photoemission spectra is an important yet subtle one. To do so, we must first understand precisely what is measured in the experiment. An illustration of this process is shown in figure 2.2. It is important that the sample and the detector are in electrical contact, so that the chemical potential of the two will be equal. It is entirely possible that the work functions of the two are different. In this event a potential, V_{S-D} , will be established between the sample and the detector.

Figure 2.2: An illustration of the energies involved in determining a reference energy in photoemission. Note that a potential V_{S-D} is created to account for the difference in work functions between the sample and the detector. For this reason the chemical potential as measured for two different samples will be the same.

This prevents a violation to the law of conservation of energy. Otherwise, one can see that if the work function of the sample and the detector are different, then in the absence of the potential V_{S-D} , an electron would lose an amount of energy $= \Phi_{\text{sample}}$ when emitted by the sample and gain an energy $= \Phi_{\text{detector}} \neq \Phi_{\text{sample}}$ when absorbed by the detector. The potential, V_{S-D} , causes the measured kinetic energy to be different from the kinetic energy which the electron had as it left the sample by an amount V_{S-D} . Therefore the energy of the free electron can now be written as

$$E_{p.e.} = KE_{\text{init}} + \Phi_{\text{sample}} = KE_{\text{measured}} + \Phi_{\text{detector}} \quad (2.5)$$

Thus using equation 2.3 we get

$$E_{\text{initial}} = KE_{\text{measured}} + \Phi_{\text{detector}} - h\nu \quad (2.6)$$

The importance of this is to note that the relevant work function is that of the detector, and not of the sample. Thus, independent of what sample is emitting the electrons, so long as the the detector is in electrical contact with the sample, the reference point will be the same. In our case, we use a polycrystalline sample of gold in electrical contact to form a reference. The acquired photoemission spectra from

the gold sample is fit to the Fermi-Dirac function:

$$I(KE_{measured}) \propto \frac{1}{(1 - \exp(E_{initial} - \mu)/kT)} \quad (2.7)$$

where k is Boltzmann's constant and T is the temperature of the gold sample. The fit gives us the kinetic energy of an electron at the chemical potential $= \mu - \Phi_{detector} + h\nu$, which is independent of the sample being measured. Thus we can study a sample of interest with the chemical potential predetermined by our gold reference. From now on we will no longer make the distinction between the measured kinetic energy and the kinetic energy of the electron as it is emitted from the sample. This distinction was only necessary to understand how one can identify the chemical potential in a photoemission experiment. On a side note, the fit to the Au spectra will also give us a measure of our experimental energy resolution.

2.2 ARPES

We now turn our attention to Angle Resolved Photoemission. So far we have only used the conservation of energy and have neglected the conservation of momentum. In the photoemission process the component of momentum perpendicular to the surface is not conserved; although there is a one-to-one correspondence of $k_{\perp}$ inside the sample to $k_{\perp}$ outside the sample. A simple way to think of this is that the work function creates a potential perpendicular to the surface, and thus a force is applied in this direction to the electron as it escapes from the solid. As a result, momentum conservation is no longer valid. However, assuming that the surface barrier is uniform across the sample, the inplane component of momentum is conserved up to a reciprocal lattice vector G .

$$k_{i\parallel} + k_{\gamma\parallel} = k_{pe\parallel} + k_{system\parallel} + G_{\parallel} \quad (2.8)$$

where the momentum of the photon, k_{γ} , can be ignored for low photon energies (for $h\nu=20\text{eV}$; $|k|=0.01\text{\AA}^{-1}$ which is roughly 1% of the Brillouin zone in cuprates). To extract the inplane component of momentum one uses:

$$\begin{aligned}
k_{pe_{\parallel}} &= k_{pe} \sin \theta = \frac{\sqrt{2m_e K E}}{\hbar} \sin \theta = 0.512 \sqrt{E} \frac{\text{\AA}^{-1}}{\text{eV}} \\
k_{pe_x} &= k_{pe_{\parallel}} \cos \phi; \quad k_{pe_y} = k_{pe_{\parallel}} \sin \phi
\end{aligned} \tag{2.9}$$

ARPES becomes even more powerful when studying one- or two-dimensional systems, since in this instance the dispersion is fully characterized by $k_{\parallel}$ which, contrary to $k_{\perp}$, is conserved in the photoemission process. Figure 2.3 demonstrates how ARPES can be used to determine the electronic structure by again examining a system of non-interacting particles, this time in two dimensions. The electron analyzer measures the kinetic energy of the outgoing electron. From the position of the analyzer, the angles θ and ϕ are also known. From these two pieces of information and using equations 2.4 and 2.9 the energy of the state ϵ_k is uniquely determined. By changing the position of the analyzer relative to the surface normal the entire k -space can be mapped out to give the full dispersion. Figure 2.3 also illustrates the typical fashions in which photoemission data is presented. Kinetic energy scans at constant θ and ϕ are called energy distribution curves (EDCs). Note that as long as the kinetic energy range of the scan is small compared to the kinetic energy, then curves which are taken at constant (θ, ϕ) are equivalent to a hypothetical scan taken at constant (k_x, k_y) . Alternatively, the energy can be held constant and the angle can be varied. The resulting curves are known as momentum distribution curves (MDCs).[58] In both cases the peak position of a curve gives us ϵ_k while the peak width gives information on the interactions as will be discussed below.

2.3 Correlations and Approximations

Now having a general feel for the concepts used in photoemission we will construct here a more formal approach to the subject. For a detailed derivation the reader is referred to more comprehensive works such as the one by Almladh and Hedin and references therein [59]. In this way we can also begin to take electron correlations into account. There are several approximations used in analyzing photoemission spectra and for many of them there appears little justification other than the fact that the

Figure 2.3: ARPES is an ideal technique for probing the electronic structure. This illustration assumes a non-interacting two dimensional electron gas shown in (a). The detector in photoemission measures the kinetic energy and angle of the photoemitted electron. By scanning energy and changing angles one can generate an intensity plot as shown in (b) (yellow is maximum intensity). Using standard conservation laws the energy and momentum of the photoelectron yields the energy and momentum of the initial state from which it came. By performing many two dimensional cuts as the one shown in (b) for different ϕ angles, one can reconstruct the full dispersion information presented in (a). The red and blue curves illustrate typical ways in which ARPES data is presented known as EDCs and MDCs respectively. The curves correspond to slices taken out of the neighboring image plot along the thin lines. By tracking the peak position one can again recreate the dispersion seen in (a), in this case for $k_y=0$.

resulting equations manage to describe the experimentally measured spectra quite well. Specifically, we will work under the sudden approximation, where it is assumed that the electron is removed quickly enough from the sample so that the system is unable to adiabatically evolve into its new state.

Calculating the photoemission intensity is equivalent to determining the cross-section for starting in an initial N particle state Ψ_i^N and ending in a N particle final state Ψ_f^N which consists of a photoemitted electron and the remaining $N-1$ particle

system. This can be expressed as:

$$\sigma_{fi} = \frac{2\pi}{\hbar} |\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu) \quad (2.10)$$

This is the perturbative result where the bare Hamiltonian consists of the system alone, and the delta function ensures energy conservation. In the presence of electromagnetic radiation the momentum operator changes from $\mathbf{p} \rightarrow (\mathbf{p} - \frac{e}{c}\mathbf{A})$. For a system where the potential terms only depend on $\mathbf{x}$ and not on $\mathbf{p}$

$$H = H_{system} + H_{int} \quad (2.11)$$

where

$$H_{int} = \frac{e}{2m_e c} (\mathbf{p} \cdot \mathbf{A} - \mathbf{A} \cdot \mathbf{p}) + \frac{e^2}{c^2} \mathbf{A}^2 \quad (2.12)$$

For current photoemission experiments, the amplitude, $|\mathbf{A}|$, of the incident light is small enough that one can ignore two photon processes and hence drop the $\mathbf{A}^2$ term. Furthermore, if the wavelength of light is large compared to atomic dimensions then one can use the commutation relation $[\mathbf{p}, \mathbf{A}] = -i\hbar \nabla \cdot \mathbf{A} \approx 0$. Thus H_{int} reduces to $\frac{e}{m_e c} \mathbf{A} \cdot \mathbf{p}$ and the cross section can now be expressed as

$$\sigma_{fi} \propto |\langle \Psi_f^N | \mathbf{A} \cdot \mathbf{p} | \Psi_i^N \rangle|^2 \quad (2.13)$$

This is commonly referred to as the dipole approximation. We note that there is no reason for neglecting the $\nabla \cdot \mathbf{A}$ term in photoemission. At the surface of the sample, $\mathbf{A}$ will have a strong spatial variation, while for an electron with an energy of 20eV the escape depth is only 5-10Å.

We will now work out the formula for the photoemission intensity in terms of the single particle spectral function, $A(\mathbf{k}, \omega)$. First we assume that the final state containing the photoelectron possesses the same boundary conditions as the time-reversed LEED state, and thus can be written as:

$$|\Psi_f^N\rangle = |k; N-1, s\rangle \quad (2.14)$$

where s is an excited eigenstate of the $N-1$ particle system. Far from the solid, where the photoelectron is detected this can be expanded as:

$$\Psi_{k,s}^N(r, r_1, r_2, \dots, r_N) \approx \frac{1}{\sqrt{N}} (e^{ik \cdot r} + f_s^-(\hat{k}) \frac{e^{-ik \cdot r}}{r}) \Psi_s^{N-1}(r_1, r_2, \dots, r_N) \quad (2.15)$$

where $f_s^-(\hat{k})$ is the usual scattered wave amplitude. Next, by using a second quantization approach, and using the field operator $\hat{\psi}(r) = \sum_j \varphi_j(r) \hat{c}_j$ we can write [60]

$$\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle = \int dr \langle k; N-1, s | \hat{\psi}^\dagger(r) \hat{\psi}(r) | N, 0 \rangle H_{int}(r) \quad (2.16)$$

and by inserting a complete set of states of the $N-1$ system we get

$$\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle = \sum_j \int dr \langle k; N-1, s | \hat{\psi}^\dagger(r) | N-1, j \rangle \langle N-1, j | \hat{\psi}(r) | N, 0 \rangle H_{int}(r) \quad (2.17)$$

This equation is often broken up into two pieces. An “intrinsic” contribution is obtained by setting $j, j' = s$, while $j, j' \neq s$ are considered “extrinsic” processes, and can be thought of as the outgoing photoelectron changing the state of the $N-1$ system from j to s . By considering only the intrinsic processes we arrive at the desired result as the photoemission intensity can be written as [61]:

$$I(k, E) \propto \int \int dr dr' \langle k; N-1, s | \hat{\psi}^\dagger(r) | N-1, s \rangle H_{int}(r) A^-(r, r', E - h\nu) \\ H_{int}(r') \langle N-1, s | \hat{\psi}(r') | k; N-1, s \rangle \quad (2.18)$$

where $A = A^- + A^+$ is the spectral function:

$$A^-(r, r', E) = \sum_s \langle N-1, s | \hat{\psi}(r) | N, 0 \rangle \langle N, 0 | \hat{\psi}^\dagger(r') | N-1, s \rangle \delta(E - (E_0^N - E_s^{N-1})) \quad (2.19)$$

Note that in this formulation creation and annihilation operators inherently imply

that we are operating under the sudden approximation, as the system is not permitted to relax while the electron is being removed. In an independent particle picture the above expressions reduce to

$$I(k, \omega) = I_0(k, \nu, \mathbf{A}) f(\omega) A(k, \omega) \quad (2.20)$$

where $f(\omega)$ is the fermi function and I_0 is termed the matrix element.

2.3.1 Sudden approximation versus the adiabatic limit

As the standard interpretation assumes the sudden approximation let us examine it here in more detail. Physically, the sudden approximation says that the optically excited photoelectron does not interact with the remaining N-1 particle system. This is certainly true for very high energy photons, but at lower energies it is not as clear. For the moment let us consider the opposite extreme: the case where the photoelectron moves so slowly through the sample that the N-1 particle system is able to fully relax before the electron leaves the sample (the adiabatic limit). In this picture, if the initial N particle state was in the ground state of the N particle Hamiltonian, then the final state will also be in the ground state of the N-1 particle Hamiltonian. To illustrate this idea, in figure 2.4 we consider the simple case of a H_2 molecule. The full Hamiltonian will consist of two electrons, two nuclei, and all the interactions between them. This however, is a complex many body problem to solve. We simplify the problem by considering the nuclei as fixed and neglect the interactions between the electrons. Thus the eigenstates $\{\psi_m(\mathbf{R}_i)\}$ will be solely due to the potential determined by the positions of the nuclei $\{\mathbf{R}_i\}$. Conversely, we must keep in mind that the equilibrium position of the nuclei are determined by the potential created by the surrounding charge density. Thus if the photoelectron is slowly leaving the molecule the nuclei will have a chance to adjust to the potential which is slowly changing about them. In turn, as long as the nuclei positions are changing adiabatically the eigenstates of both the excited electron and the one remaining behind will adjust accordingly. This will continue until the photoelectron is far enough removed from the molecule, that we can consider the photoemission process over. If the H_2 molecule (initial state of the N

Figure 2.4: a) shows the initial state of a H_2 containing two electrons. b) In the sudden limit the photoelectron is removed so quickly that the hydrogen nuclei are unable to respond in time, and hence are left in an excited state of the H_2^+ Hamiltonian. If we further assume that the excited state is equal to simply annihilating a single electron from the original H_2 molecule then we are left with the frozen orbital approximation (bottom). c) In the adiabatic limit the H_2^+ molecule has time to respond to the changing potential created as the photoelectron slowly escapes from the system. Thus the final state will end up in the ground state of the H_2^+ Hamiltonian assuming that the molecule was in its ground state to begin with.

particle system) began in its ground state, then in the adiabatic limit just described, the resulting H_2^+ molecule (final state of the $N-1$ particle system) will also be in its respective ground state. Thus the photoemission spectra would consist of a single peak at an energy $E_{H_2}^0 - E_{H_2^+}^0 + h\nu$.

Now let us consider the other extreme. If the electron is removed quickly enough, the system will not have a chance to relax. In the H_2 example the nuclei will remain at their initial equilibrium position. The resulting final state will be in some excited state. It is important to note that this excited state will most likely not even be an eigenstate of the $N-1$ particle system. For the case where the electron of the H_2^+ remains in the same state as it began we are considered to be in the frozen orbital approximation ($|\Psi_f^{N-1}\rangle = \hat{c}|Psi_i^N\rangle$). This corresponds again to a single peak in the excitation spectrum, but in general the final state of the H_2^+ system will be in a superposition of several excited states resulting in multiple peaks in the photoemission spectra.

2.4 Analysis methods

2.4.1 $n(\mathbf{k})$

A consequence of the sudden approximation is that photoemission can be used to measure the occupation probability, $n(\mathbf{k})$, of a system. This can be seen by noting that $n(\mathbf{k}) = \int_{-\infty}^{\infty} A^-(k, w) dw$. In an actual experiment one must be careful, as the photoemission intensity is modulated by the matrix element (See eq. 2.20). However, for a Fermi liquid system there is a discontinuity in $n(\mathbf{k})$ of magnitude Z_k , at the Fermi surface [62]. Z_k is the renormalized quasiparticle weight. If the matrix elements can be assumed to be smoothly varying functions of k then the contour of steepest descent in $n(\mathbf{k})$ as measured by photoemission will correspond to the Fermi surface, provided that Z_k is large enough. Note there is evidence that even in the case of correlated systems, where the Fermi liquid picture is no longer valid, the contour of steepest descent may still correspond to the tight binding Fermi surface before correlations were turned on. This is indeed the case for a Luttinger liquid. We will use this type of analysis for studying the Mott insulator $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ in chapter 3.

2.4.2 MDC analysis

As photoemission is directly related to the spectral function, it in principal can be used to extract the real and imaginary parts of the self energy, which contains the information on the interactions in the solid. To see how to do this we return to the single particle spectral function, which can be expressed in terms of the self energy:

$$A(k, \omega) = \frac{1}{\pi} \frac{\Im m \Sigma(\omega, \mathbf{k})}{\omega - \epsilon_k + \Re e \Sigma(\omega, \mathbf{k})^2 + \Im m \Sigma(\omega, \mathbf{k})^2} \quad (2.21)$$

ϵ_k is the bare electron energy before correlations were turned on (ie. the tight binding solution). Thus, close to the chemical potential, ϵ_k can be expanded $\epsilon_k = v_F(k - k_F) + \beta(k - k_F)^2$. However, extracting $\Sigma(\omega, k)$ is still a non-trivial task. If the functional form of the self energy is known apriori then the spectra can be fit to extract the relevant parameters. The quality of the fit is thus indicative of the applicability of the particular model to the system under investigation. This is done, for example,

in testing systems which are believed to be ideal Fermi liquids such as Mo and Be surface states as well as in TiTe_2 [63, 64, 65]. In these cases one typically assumes that the scattering rate determined from the self energy can be broken into three separate terms: $\Sigma = \Sigma^{el-el} + \Sigma^{el-ph} + \Sigma^{imp}$ which refer to the electron-electron, electron-phonon, and impurity contributions respectively. It is not clear that this separation can still be done in highly correlated systems, nor are there any agreed upon models for the self energy.

However, by making a few simplifications we can extract the general properties of the self energy. We start by recalling our knowledge on Fermi liquid systems. Even in these ideal cases, the ω dependence of Σ is non-trivial such that an expansion in ω would necessarily contain many terms. Thus an EDC analysis (constant k scan) is not particularly useful for extracting the self energy. However, unless there is significant k dependence of the scattering potential, one can safely Taylor expand the real and imaginary parts of the self energy in k . $\Sigma(\omega, \mathbf{k}) = \Sigma(w, k_F) + (k - k_F)\Sigma'(w, k_F) + \dots$. This can be inserted into equation 2.21.

Typically one retains only the zeroth order term (ie. no k dependence) of Σ and a linear bare dispersion ($\beta=0$), resulting in

$$A(k, \omega) = \frac{1}{\pi} \frac{\Im m \Sigma(w, k_F)}{(\omega - v_F(k - k_F) + \Re e \Sigma(w, k_F))^2 + \Im m \Sigma(w, k_F)^2} \quad (2.22)$$

By setting $\omega=E_k=\text{constant}$ (as is the case for MDCs) a lorentzian lineshape is obtained whose peak position, k , satisfies the equation: $E_k = v_F(k - k_F) + \Re e \Sigma(\omega, k)$. E_k is the renormalized quasiparticle energy, and the half width at half maximum of the lorentzian is equal to $\Im m \Sigma/v_F$. Given that the high temperature cuprate superconductors are known to have d -wave pairing, it does not seem apparent that the simplification performed above is valid. However, it turns out that the MDC line-shapes in the cuprates are indeed well fit by lorentzians, which in turn is the strongest justification for the validity of this analysis.

There are several explanations for a deviation from a perfect lorentzian. To begin with one may need to include the higher order terms which were neglected. This will clearly cause an asymmetric lineshape. The above analysis was also done under the

assumption that only a single band is involved. Bands which are similar in energy including bands created by umklapp scattering will also need to be considered in the fitting. Finally, we have neglected the matrix element in all of this. One would hope that the variation of the matrix element is small. Again, the lorentzian lineshapes support this claim, but observed deviations could easily be a result of the matrix element.

It should also be kept in mind that due to causality the real and imaginary parts of the Greens function are related by the standard Kramers Kronig relation. Thus the real and imaginary parts of the self energy are similarly related. If the entire spectral function were known (ie for $-\infty < \omega < \infty$) then the self energy could be extracted without the use any approximations or fits.[66] Although determining the entire spectral function in this way can not be done with out some new assumptions.

2.4.3 Matrix elements

Equation 2.20 shows that the matrix element is the term which prevents the ARPES intensity, $I(k, \omega)$, from being exactly proportional to the single particle spectral function, $A(k, \omega)$. However, the presence of matrix elements in photoemission is not entirely bad news. In fact, they can be used to probe the symmetry of the initial state wave function. Consider an experimental geometry where the detected outgoing electron and the incident photon beam form a plane perpendicular to the surface of the sample. Now examine each term in the general expression for the transition probability shown in equation 2.10 with respect to this mirror plane. The outgoing electron is of the form $e^{ik \cdot r}$. Thus the final state is even with respect to this plane. The $\mathbf{A} \cdot \mathbf{p}$ term is even or odd depending on the polarization of the incoming radiation (even if the polarization is in the plane; odd if it is perpendicular to it). Thus there are two cases which will result in a vanishing cross section:

$$\langle \Psi_f^N | H_{int} | \Psi_i^N \rangle = \begin{Bmatrix} \langle + | - | + \rangle \\ \langle + | + | - \rangle \end{Bmatrix} \Rightarrow \sigma_{fi} = 0 \quad (2.23)$$

where $+$ ($-$) indicates even(odd) symmetry with respect to the mirror plane defined by the incident photon and outgoing electron. Thus by rotating the polarization

from even to odd, one can determine whether the symmetry of the initial state being probed is even or odd with respect to the mirror plane defined by the orientation of the crystal. If one does not have the capability of rotating the polarization of the light, one can alternatively rotate the mirror plane by 90° by moving the analyzer (one must also rotate the sample, if it is not 4 fold symmetric). This however requires that the incident beam is at normal incidence, which is rarely the case for a photoemission setup. In these situations, as the incident beam is moved off normal the selection rules will become less rigorous. Although beamlines V-3 and V-4 at SSRL where the work for this dissertation was performed falls into this latter category, we found that the measurements on the cuprates were consistent with the above selection rules and a $d_{x^2-y^2}$ initial state.

2.5 Practical issues

In the analysis of photoemission spectra several practical issues must also be considered which we discuss here. As $k_{\parallel}$ is determined by equation 2.9, the k -space resolution due to the finite acceptance angle, $\Delta\theta$, of the analyzer is given by:

$$\Delta k_{pe\parallel} = \frac{\sqrt{2m_e K E}}{\hbar} \cos \theta \Delta \theta \quad (2.24)$$

From this it is clear that the momentum resolution is improved by reducing the kinetic energy which is accomplished by reducing the photon energy. Lowering the photon energy will also improve the energy resolution; however, it also creates some concerns. Namely, the escape depth of an electron from a sample reaches a minimum of 5-10Å in the photon energy range from 20 to 100eV (the standard operating energies for high resolution ARPES studies). Thus photoemission is probing only a small surface layer. So in addition to signal from bulk excitations there can also be several other excitation due to the surface. For example, there are electronic states which are created due to the loss of translational symmetry and exist solely at the surface. The short escape depth also implies that the sample surface must be atomically clean in order to see anything. Note that a monolayer of “junk” will be deposited within one

hour at 10^{-9} torr assuming everything which hit the sample stuck to its surface. This requires that measurements be done in Ultra High Vacuum (UHV) where pressures are typically on the order of 10^{-11} torr. The low photon energy also brings into question the validity of the sudden approximation, on which, the entire analysis above was based. Fortunately, Randeria showed in YBCO that $n(\mathbf{k})$ as determined by ARPES was temperature independent using 19eV photons[67]. Although this does not conclusively prove the validity of the sudden approximation it certainly does provide support for it.

Assuming that the approximations are valid, and that the resulting signals are truly bulk signals, we can ask what systems apriori appear promising for photoemission. In principle, dimensionality is not an issue, as methods have been developed to compensate for the non-conservation of $k_{\perp}$ in photoemission, although large amounts of data are often required. Thus, lower dimensional systems are typically much easier to handle. In addition, the $k_{\perp}$ dispersion of the hole created by photoemission typically creates large widths in three dimensional systems, and thus the detailed dispersion is difficult to extract. Clearly single crystals are also required to utilize the angle resolved capability of photoemission. The photon beam at beamline V-4 of SSRL is $0.2 \cdot 1\text{mm}^2$. Thus a sample which has a cross-sectional area of roughly 1mm^2 is considered ideal for photoemission. As mentioned above ARPES also requires flat, atomically clean surfaces. Maintaining such a surface requires UHV conditions, but the preparation of such a surface is also non-trivial. *In situ* annealing is a possible solution, provided that the high temperatures will not destroy the good vacuum conditions. One must also be careful that the high temperatures do not alter the chemical composition of the compound. In the cuprates the concern is over the loss of oxygen which will alter the doping level. The alternative to annealing is to cleave the sample. However, the average sample does not break to provide an atomically flat surface. This is true, even for some two dimensional systems. However, some systems do contain natural cleavage planes, where the bonding is very weak, such as in the Bi-O layers of Bi2212. Thus, we conclude that in principle, photoemission is the most powerful tool to study the electronic structure, but in practice, one needs some luck to find a system which utilizes the full potential of ARPES. Fortunately,

the cuprates fall into this category.

Finally, it should be noted that when performing ARPES measurements on insulators charging is a serious issue. By removing an electron from the sample photoemission leaves a positively charge hole behind. If the sample resistance is high enough a net positive charge will accumulate on the surface. Therefore when mounting samples care should be taken to minimize the contact resistance. This is accomplished by freshly cleaving the sample prior to epoxying it to the metallic sample holder. Also, since the resistance is linear with the thickness of the sample, a thinner sample

Figure 2.5: Two samples of $\text{Ca}_2\text{CuO}_2\text{Br}_2$ which were cleaved and measured at 300 and 372K are shown in the left and right panels respectively. The height of each spectra has been normalized to 1. To determine whether or not a sample is charging, one varies the photon flux incident on the sample $\propto I_0$ one checks if the spectra are pushed to lower kinetic energies with increasing flux. The sample on the left is charging significantly, even causing the lineshape to be somewhat distorted as the flux is increased. The sample on the right shows much less charging, probably due to the increased conductivity at higher temperature. One effect of aging is shown by the spectra taken with the smallest flux, but is pushed to higher binding energy than any other spectra.

will tend to have less charging problems than a thicker one. This is not a concern for metals as the conductivity quickly fills the vacant hole. To check for charging one must vary the incident photon flux and examine the effect on the photoemission spectra. For a small amount of charging, increasing the flux will create a uniform potential across the sample, and thus the spectra will simply shift to higher binding energy. However, if the charging is non-uniform, which is typically the case when the resistance is very high, the spectra will not only shift to higher binding energy, but also become heavily distorted. An example of a sample which demonstrates charging is shown in figure 2.5.

Chapter 3

Evidence for a Remnant Fermi Surface and a d -Wave-Like Dispersion in Insulating $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ ¹

In this chapter an angle resolved photoemission study on $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, a parent compound of high T_c superconductors is reported. Analysis of the electron occupation probability, $n(\mathbf{k})$, from the spectra shows a steep drop in spectral intensity across a contour that is close to the Fermi surface predicted by the band calculation. This analysis reveals a Fermi surface remnant even though $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ is a Mott insulator. The lowest energy peak exhibits a dispersion with approximately the $|\cos k_x a - \cos k_y a|$ form along this remnant Fermi surface. Together with the data from Dy doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ these results suggest that this d -wave like dispersion of the insulator is the underlying reason for the pseudo gap in the underdoped regime.

¹The contents of this chapter were published in Science **282**, 2067 (1998)

3.1 Background

A consensus on the $d_{x^2-y^2}$ pairing state and the basic phenomenology of the anisotropic normal state gap (pseudo gap) in high- T_c superconductivity has been established[68], partially on the basis of angle-resolved photoemission spectroscopy (ARPES) experiments [69, 70, 71, 72], in which two energy scales have been identified in the pseudo gap, a leading-edge shift of 20-25 meV and a high-energy hump at 100-200 meV.[71] Both of these features have an angular dependence consistent with a *d*-wave gap. For simplicity in the discussion below, we refer to these as low- and high-energy pseudo gaps, respectively, in analogy to the analysis of other data.[73] The evolution of these two pseudo gaps as a function of doping are correlated[74], but the microscopic origin of the pseudo gap and its doping dependence are still unestablished. Theoretical ideas of the pseudo gap range from pre-formed pairs or pair fluctuation [75, 76, 77, 78, 79, 80, 81] and damped spin density wave (SDW) [82, 83] to the evidence of the resonating valence bond (RVB) singlet formation and spin-charge separation [84, 85, 86, 87, 44]. To further differentiate these ideas, it is important to understand how the pseudo gap evolves as the doping is lowered and the system becomes an insulator. We present experimental data from the insulating analog of the superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ which suggest that the high energy pseudo gap is a remnant property of the insulator that evolves continuously with doping, as first pointed out by Laughlin.[44]

The compound $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, a half-filled Mott insulator, has the crystal structure of La_2CuO_4 [88] and it can be doped by replacing Ca with Na or K to become a high-temperature superconductor.[89] As with the case of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ has a much better surface property than La_2CuO_4 and thus is better suited for ARPES experiments. Although the data from $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ are consistent with earlier results from $\text{Sr}_2\text{CuO}_2\text{Cl}_2$,[25, 26, 54] the improved spectral quality obtainable from this material allows us to establish that: (I) the Fermi surface, which is destroyed by the strong Coulomb interactions, left a remnant in this insulator with a volume and shape similar to what one expects if the strong electron correlation in this system is turned off; (II) the strong correlation effect deforms this otherwise iso-energetic contour (the

non-interacting Fermi surface) into a form that matches the $|\cos k_x a - \cos k_y a|$ function very well, but with a very high energy scale of 320 meV. Thus, a *d*-wave like dispersive behavior exists even in the insulator.

Comparison with data from underdoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212) with T_c 's of 0, 25 and 65 K indicates that the high energy *d*-wave like pseudo gap in the underdoped regime originates from the *d*-wave like dispersion in the insulator. Once doped to a metal, the chemical potential drops to the maximum of this *d*-wave like function, but the dispersion relation retains its qualitative shape, albeit the magnitude decreases with doping. Thus, only the states near the *d*-wave node touch the Fermi level and form small segments of the Fermi surface, with the rest of Fermi surface gapped. In this way, the *d*-wave high energy pseudo gap in the underdoped regime is naturally connected to the properties of the insulator. Since the high energy pseudo gap correlates with the low energy pseudo gap which is likely to be related to superconductivity [70, 71, 72, 74, 90], it is likely that the same physics that controls the *d*-wave dispersion in the insulator is responsible for the *d*-wave like normal state pseudo gap and the superconducting gap in the doped superconductors.

3.2 Experimental

Experiments were performed at beamline V-3 of the Stanford Synchrotron Radiation Laboratory (SSRL). $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ single crystals grown by a flux method[88] were oriented before the experiments by the Laue method and were cleaved in situ by knocking off the top posts that were glued to the samples, giving flat fresh surfaces suitable for ARPES experiments. The base pressure was better than 5×10^{-11} torr. With the photon energies used in the experiments, the total energy resolution was typically 70 meV. The angular resolution was $\pm 1^\circ$. The spectra from $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ reported here were all taken at 100 K with 25.2 eV photons.

3.3 Methodology for analyzing the data

To investigate the strong correlation effect, we contrast our experimental data with the conventional results for the case when the correlation effects are neglected. As discussed in chapter 2 we can obtain the occupation probability, $n(\mathbf{k})$, by integrating $A(\mathbf{k}, \omega)$, obtained by ARPES, over energy [91, 67]. Experimentally $A(\mathbf{k}, \omega)$ can not be integrated over all energies due to contributions from secondary electrons and other electronic states. Instead an energy window for integration must be chosen, and the resulting quantity we define as the *relative* $n(\mathbf{k})$. Fortunately, the features we are interested in are clearly distinguishable from any other contributions. We note

Figure 3.1: Illustration of the Fermi surface determination. (A) The case for band metal. Electrons occupy states only up to a certain momentum, showing a sharp drop in $n(\mathbf{k})$. (B) Band insulator case. Electrons occupy all possible states and do not show a drop in $n(\mathbf{k})$. (C) Fermi liquid with electron correlation. Note that electrons that used to occupy the states below k_F have moved above k_F . However, it still shows a discontinuity at k_F . (D) For a strongly correlated non-Fermi liquid $n(\mathbf{k})$ does not show discontinuity, yet there exists $n(\mathbf{k})$ drop showing the remnant Fermi surface.

that $n(\mathbf{k})$ is a ground state property, and hence is different from the integration of the single-particle spectral weight, $A(\mathbf{k}, \omega)$, over energy. However, under the sudden approximation integration of $A(\mathbf{k}, \omega)$ as measured by ARPES gives $n(\mathbf{k})$ [91, 67]. We then use the drop in the relative $n(\mathbf{k})$ to determine the Fermi surface as illustrated in figure 3.1. For a metal with non-interacting electrons, the electron states are filled up to the Fermi momentum, k_F , and the $n(\mathbf{k})$ shows a sudden drop (figure 3.1A). As more electrons are added, the electron states are eventually filled and the system becomes an insulator with no drop in $n(\mathbf{k})$ (figure 3.1B). Therefore, the drop in $n(\mathbf{k})$ characterizes the Fermi surface of a metal with non-interacting electrons. When correlation increases, $n(\mathbf{k})$ begins to deform (figure 3.1C), although there is still some discontinuity at k_F when the correlation is moderate. Note that the electrons that used to occupy states below k_F have moved to the states that were unoccupied. For a non-Fermi liquid with very strong correlation, $n(\mathbf{k})$ drops smoothly without a discontinuity (panel (D)). Several theoretical calculations using very different models have found that $n(\mathbf{k})$ of the interacting system mimics that of the non-interacting system, even when the material is fully gapped [37, 38, 39, 92]. Hence we can recover the remnant of a Fermi surface or an underlying Fermi surface by following the contour of steepest descent of $n(\mathbf{k})$ even when correlation is strong enough that the system becomes a Mott insulator.² The volume obtained by this procedure is consistent with half-filling as expected in a Mott insulator.

We now apply this method to determine the Fermi level crossing of a real system. The traditional way (figure 3.2A) is shown for the ARPES spectra on the $(0,0)$ to (π, π) cut taken from Bi2212 which is metallic. As we move from $(0,0)$ toward (π, π) , the peak disperses to the Fermi level, E_F . As the peak reaches E_F and passes it, it begins to lose spectral weight (this again is k_F). Alternatively, we simply integrate the spectral function from 0.6 eV to -0.1 eV relative to the E_F , and the resulting relative $n(\mathbf{k})$ is plotted in figure 3.2C. We can now define k_F as the point of steepest descent in the relative $n(\mathbf{k})$. The same conclusion can be drawn here independent of the method we use. Note that the $n(\mathbf{k})$ also drops as we approach $(0,0)$; this is a

²A key difference between a Mott insulator and a band insulator is that $\sum_{\mathbf{k}} n(\mathbf{k}) / (\text{Brillouin zone volume})$ equals 1 for a Mott insulator, and equals 2 for a band insulator.

Figure 3.2: Application of the method described in figure 3.1. (A) Spectra along the (0,0) to (π, π) cut from Bi2212. The peak disperses towards the low energy side and reaches the Fermi level at k_F , $(0.43\pi, 0.43\pi)$. (B) Spectra along the $(\pi, 0)$ to (π, π) cut from metallic $\text{La}_{3-x}\text{Sr}_x\text{Mn}_2\text{O}_7$. The peak disperses toward the low energy side, but never reaches the Fermi energy. However, it loses intensity as it crosses the position where the band calculation predicts the Fermi surface, showing an underlying Fermi surface. (C) and (D) plots of the relative $n(\mathbf{k})$ for the data in (A) and (B), respectively, show a sudden drop around k_F , essentially showing the two methods give the same Fermi momentum k_F .

photoemission artifact, because the photoemission cross-section of the $d_{x^2-y^2}$ orbital vanishes due to symmetry.

We can show that the $n(\mathbf{k})$ procedure is still valid for strongly correlated systems with gapped Fermi surface by presenting ARPES spectra on ferromagnetic $\text{La}_{3-x}\text{Sr}_x\text{Mn}_2\text{O}_7$ on the $(\pi, 0)$ to (π, π) cut (figure 3.2B)[93]. It shows a dispersive feature initially moving toward E_F and then pulling slightly back away from E_F around $(\pi, 0.27\pi)$, but never reaching the E_F . However, the feature suddenly loses its spectral weight when it crosses $(\pi, 0.27\pi)$ as if it crosses the Fermi surface as shown in panel D. Furthermore, the Fermi surface determined by a local density approximation calculation coincides with the Fermi surface determined by the $n(\mathbf{k})$ despite the spectra of this ferromagnetic metallic state material having a significant gap. Thus, the underlying Fermi surface can survive a strong interaction, and the $n(\mathbf{k})$ method is effective in identifying it even when the peak does not disperse across E_F .

3.4 Results from an insulator

The low-energy feature along the $(0,0)$ to (π, π) cut in $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (figure 3.3A) has the same origin as the low-energy peak seen in Bi2212, the Zhang-Rice singlet on the CuO_2 plane. As k increases from $(0,0)$ toward (π, π) , the peak moves to lower energy and subsequently pulls back to higher energy as it crosses $(\pi/2, \pi/2)$. Its spectral weight increases as it moves away from the $(0,0)$ point for the reason described earlier, and then drops as it crosses $(0.43\pi, 0.43\pi)$. These changes along the $(0,0)$ to (π, π) cut are consistent with the earlier reports on $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ [25, 26, 54]. Similar to the drop of $n(\mathbf{k})$ across the Fermi surface seen in Bi2212, $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ also shows that the intensity of the peak $n(\mathbf{k})$ drops as if there is a crossing of E_F even though the material is an insulator. The intensity along the $(0,0)$ to $(\pi, 0)$ cut (figure 3.3B) goes through a maximum around $(2\pi/3, 0)$ as in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$. This behavior is also seen in superconducting cuprates.[94] Earlier works on $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ show the spectral weight along the $(\pi, 0)$ to (π, π) cut is strongly suppressed. However, for $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, the improved spectral quality allows us to clearly observe the spectral weight drop along

Figure 3.3: (A) $(0,0)$ to (π,π) cut. The peak disperses towards the low energy side and loses intensity near the $(\pi/2, \pi/2)$ point. (B) $(0,0)$ to $(\pi,0)$ cut. The lowest energy peak shows little dispersion. The spectral weight initially increases and then decreases again after $(0.67\pi, 0)$ as in the $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ case [26, 54]. However, note that there is appreciable spectral weight at $(\pi, 0)$ contrary to the $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ case. (C) $(\pi, 0)$ to (π, π) cut. The spectral weight drops as we move to (π, π) . (D) Another cut (as marked in the inset) showing the $n(\mathbf{k})$ drop. (E) relative $n(\mathbf{k})$ s constructed from the spectra in panels A-D. The relative increase of spectral weight above 0 is caused by emission from second order light. The insets and labels show where the spectra were taken in the Brillouin zone.

the $(\pi, 0)$ to (π, π) cut (figure 3.3C)³. Note that the spectral weight drops as we move toward the (π, π) point, which we attribute to the crossing of a remnant Fermi surface. We also show another cut (figure 3.3D) which exhibits essentially the same behavior.

³As generally found in photoemission experiments, the change of photoemission cross-section for each sample is hard to calculate quantitatively. At the qualitative level, data from $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ are consistent with each other.

The relative $n(\mathbf{k})$ s of the cuts are summarized in figure 3.3E in arbitrary units. The relative $n(\mathbf{k})$ here and in figure 3.4 were obtained by integrating from 0.5 eV to -0.2 eV relative to the peak position at $(\pi/2, \pi/2)$. All of the $n(\mathbf{k})$ s show a drop (after the maximum) as we cross the remnant Fermi surface. Here we emphasize that we are using the same method as we do for metals, where the identification of a Fermi surface is convincing.

The remnant Fermi surface can be identified in the relative $n(\mathbf{k})$ contour plot of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (figure 3.4A). The little crosses in the figure denote the k -space points where spectra were taken. The data points here and in figure 3.4C have been reflected about the line $k_y=k_x$ to better illustrate the remnant Fermi surface. Again, it should be emphasized that the suppressed $n(\mathbf{k})$ near (0,0) comes from the vanishing photoemission cross section due to the $d_{x^2-y^2}$ orbital symmetry rather than a remnant Fermi surface crossing. For the same reason, the photon polarization suppresses the overall spectral weight along the (0,0) to (0, π) line as compared with the (0,0) to (π , 0) line. In figure 3.4B we present the relative $n(\mathbf{k})$ of an optimally doped Bi2212 sample in the normal state. In this case the identification of the Fermi surface is unambiguous, but the same matrix element effects that were seen in the insulator can be seen in the metallic sample as well. However, for both samples, the drop in $n(\mathbf{k})$ near the diagonal line connecting (π , 0) and (0, π) can not be explained by the photoemission cross section. In the metallic case, the Fermi surface is clearly identified (the white-hashed region in figure 3.4B). For the insulator, the drop is approximately where band theory predicts the Fermi surface.[95] Therefore, we attribute the behavior in the insulator to a remnant of the Fermi surface that existed in the metal. The similarity of the results in the insulator and the metal makes the identification of the remnant Fermi surface unambiguous. The white hashed area in figure 3.4A represents the area where the remnant Fermi surface may reside as determined by the relative $n(\mathbf{k})$. Although there is some uncertainty in the detailed shape of this remnant Fermi surface, this does not affect the discussion and the conclusions drawn below. The relative $n(\mathbf{k})$ we presented is a very robust feature. In metallic samples with partially gapped Fermi surfaces, underlying Fermi surfaces have also been identified in the gapped region[93, 96, 97]. This effect is similar to what we report here in the insulator. The remnant Fermi

Figure 3.4: Contour plot of the relative $n(\mathbf{k})$. (A) $n(\mathbf{k})$ from the spectra shown in figure 3.3. The color scale on the right represent $n(\mathbf{k})$. The spectra were taken only in the first octant of the first Brillouin zone (crosses). The $n(\mathbf{k})$ plot was folded to better represent the remnant Fermi surface. Note, the $n(\mathbf{k})$ drops as we cross the approximate diagonal line connecting $(0, \pi)$ and $(\pi, 0)$. The hashed area represents approximately where the remnant Fermi surface exists. (B) An identical plot for an optimally doped Bi2212 sample in the normal state. (C) Contour plot of the lowest energy peak position from the spectra in figure 3.3 relative to the $(\pi/2, \pi/2)$ peak. The hashed area is from (A), showing the remnant Fermi surface. The color scale on the right indicates the relative binding energy of the peak. (D) The 'gap' versus $|\cos k_x a - \cos k_y a|$. The straight line shows the *d*-wave line. The inset is a more illustrative figure of the same data as explained in the text.

surface in the underdoped Bi2212 was also identified at similar locations to the $n(\mathbf{k})$ drop in these materials with a different criteria of minimum gap locus[96, 97]. Calculations also show the Fermi surface defined by $n(\mathbf{k})$ is robust in the presence of strong correlation[37, 38, 92]. Given that there is a remnant Fermi surface as shown by the white hashed lines in figure 3.4, A and C, the observed energy dispersion along this line has to stem from the strong electron correlation. In other words, the electron correlation disperses the otherwise iso-energetic contour of the remnant Fermi surface. This dispersion is consistent with the non-trivial *d*-wave $|\cos k_x a - \cos k_y a|$ form[84, 85, 86, 87, 44]. These results also support our identification of the remnant Fermi surface in a Mott insulator.

Figure 3.4C plots the energy contour of the peak position of the lowest energy feature of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ referenced to the energy of $(\pi/2, \pi/2)$ peak. The hashed area indicates the remnant Fermi surface determined in figure 3.4A. The 'Fermi surface' is no longer a constant energy contour as it would be in the non-interacting case. Instead it disperses as much as the total dispersion width of the system. In figure 3.4D we plot the dispersion at different points on the remnant Fermi surface referenced to the lowest energy state at $(\pi/2, \pi/2)$. The dispersion of the peaks along the Fermi surface is plotted against $|\cos k_x a - \cos k_y a|$. The straight line shows the *d*-wave dispersion function at the 'Fermi surface' with a *d*-wave energy gap. The figure in the inset presents the same data in a more illustrative fashion. On a line drawn from the center of the Brillouin zone to any point either experimental (blue) or theoretical (red), the distance from this point to the intersection of the line with the antiferromagnetic Brillouin zone boundary gives the value of the 'gap' at the k -point of interest. The red line is for a *d*-wave dispersion along $(\pi, 0)$ to $(0, \pi)$. The good agreement⁴ is achieved without the need for free parameters. This *d*-wave like dispersion can only be attributed to the many-body effect. The relative energy difference between the energy at $(\pi/2, \pi/2)$ and $(\pi, 0)$ has been referred to as a gap[44], which we follow.

This gap differs from the usual optical Mott gap (figure 3.5) and may correspond to the momentum dependent gap once the system is doped. This gap monotonically

⁴The details on whether or not the dispersion near the *d*-wave node is a cusp is addressed in chapter 5. The motivation to compare the data with the *d*-wave function stems from the fact that the insulator is related to a *d*-wave superconductor (and thus a *d*-wave gap) by doping.

Figure 3.5: An illustration showing the two experimental features presented in this chapter on the insulator, and the similarity they show to a slightly overdoped Bi2212 sample. (A) The bottom half shows the relative $n(\mathbf{k})$, and above it lies the approximate remnant Fermi surface derived from it. However, there is much dispersion over the entire Brillouin zone, and the remnant Fermi surface is no longer an iso-energetic contour as can be seen by the quasiparticle dispersion (energy relative to the valence band maximum). Here the remnant Fermi surface is shown as a black and white line running over the visible portions of the dispersion contour. For clarity, a portion of the dispersion along the remnant Fermi surface is shown in the top half. Note the idea presented that the isoenergetic contour (dashed black line) is deformed by strong correlation to the observed red curve. The *d*-wave like 'gap' referred to in the text is the quasiparticle energy deviation from the dashed black line set at the energy of the $(\pi/2, \pi/2)$ point. The difference between this 'gap' and the Mott gap can now be seen clearly. (B) For overdoped Bi2212, $n(\mathbf{k})$ defines the actual Fermi surface. The quasiparticle dispersion (binding energy) shows states filled to an isoenergetic Fermi surface. In the top panel one is reminded that below T_c , a *d*-wave superconducting gap opens. This is an intriguing similarity between the insulator and the metal.

increases when we move away from $(\pi/2, \pi/2)$ as also reported earlier[25]. As well as summarizing the data presented, figure 3.5 also shows the intriguing similarity between the data from the insulator and a slightly overdoped *d*-wave superconductor (Bi2212), and thus gives the reason for comparing the dispersion along the remnant Fermi surface with the $|\cos k_x a - \cos k_y a|$ form. In the superconducting case, $n(\mathbf{k})$ helps determine the Fermi surface. The anisotropic gapping of this surface below T_c reveals the *d*-wave nature of the gap. In the insulator, $n(\mathbf{k})$ helps determine the remnant Fermi surface. The *k*-dependent modulation along this surface reveals the *d*-wave like dispersion. Whether this similarity between the insulator and the doped superconductor is a reflection of some underlying symmetry principle is a question which needs to be investigated [98, 99].

The above analysis is possible only because we now observe the remnant Fermi surface. Although the dispersion for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ was similar to the present case, the earlier results did not address the issue of a remnant Fermi surface because the smaller photoemission cross section along the $(\pi, 0)$ to (π, π) cut prevented this identification. Therefore the analysis shown above was not possible. With only the energy contour information (such as in Fig 4C), it is plausible to think that the Fermi surface evolves to a small circle around the $(\pi/2, \pi/2)$ point.[100] However, with the favorable photoemission cross section, the results from $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ show that the Fermi surface leaves a clear remnant, although it may be broadened and weakened. Therefore, the energy dispersion along the original Fermi surface of a non-interacting system is due to the opening of an anisotropic 'gap' along the same remnant Fermi surface.

The same analysis is shown in figure 3.6 for Bi2212 with different Dy dopings together with $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ results. The corresponding doping level and T_c as a function of Dy concentration are also shown. The energy for $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ is referenced to the peak position at $(\pi/2, \pi/2)$ and that for Dy doped Bi2212 is to E_F . However, the two energies essentially refer to the same energy since the peak on the $(0,0)$ to (π, π) cut for all Bi2212 samples reaches the Fermi level. Note that the gaps for Dy doped Bi2212 data also follow a function that is qualitatively similar to the *d*-wave function with reduced gap sizes as shown with the $(\pi, 0)$ spectra in figure 3.6B. This result suggests that the *d*-wave gap originating in the insulator continuously evolves

Figure 3.6: (A) Combined *d*-wave plot of the data from $Ca_2CuO_2Cl_2$ and Bi2212 with various Dy dopings. (B) The spectra at $(\pi, 0)$, showing the evolution of the high energy pseudo gap as a function of doping, as previously stressed by Laughlin[44].

with doping, but retains its anisotropy as a function of momentum and that the high energy pseudo gap in the underdoped regime is the same gap as the *d*-wave gap seen in the insulator as discussed above. Of course, the high energy pseudo gap in the underdoped regime is smaller than the gap in the insulator. In a sense, the doped regime is a diluted version of the insulator, with the gap getting smaller with increasing doping. The two extremes of this evolution are illustrated in the quasiparticle dispersions shown in figure 3.5. The insulator shows a large *d*-wave like dispersion along the remnant Fermi surface. In the overdoped case, no gap is seen in the normal state along an almost identical curve in *k*-space; however, a *d*-wave gap is observed in the superconducting state. Although their sizes vary, the *d*-wave superconducting gap, and the *d*-wave 'gap' of the insulator have the same non-trivial form, and are thus likely to stem from the same underlying mechanism.

3.5 Implications of a remnant Fermi surface in a Mott insulator

We do not know the full implications of the data we report, but can offer the following possibilities. First, we compare the experimental dispersion with a simple spin-density wave picture. Starting with the Hubbard model

$$H = \sum_{\sigma k} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (3.1)$$

with

$$\begin{aligned} \epsilon_k = & -2t(\cos(k_x a) + \cos(k_y a)) - 4t'(\cos(k_x a)\cos(k_y a)) - \\ & 2t''(\cos(2k_x a) + \cos(2k_y a)) \end{aligned} \quad (3.2)$$

and adding a SDW picture, the following dispersion relation will be found

$$E_{k\pm} \approx -4t'(\cos(k_x a)\cos(k_y a)) - 2t''(\cos(2k_x a) + \cos(2k_y a)) \pm [U/2 + J(\cos(k_x a) + \cos(k_y a))^2] \quad (3.3)$$

with $J = t'^2/U$. With realistic values for t' and t'' , and an experimental value for J of -0.12 eV, 0.08 eV, and 0.125 eV respectively,[26] we find that the experimental dispersion deviates significantly from this mean field result giving a bandwidth of 1.1 eV. It is crucial to note the observed isotropic dispersion around the $(\pi/2, \pi/2)$ point, with almost identical dispersions from $(\pi/2, \pi/2)$ to $(0,0)$ and from $(\pi/2, \pi/2)$ to $(\pi, 0)$. This result is unlikely to be a coincidence of the parameters t' , t'' , and J as suggested by the SDW picture above.

We now compare the data with numerical calculations that, unlike the mean field SDW picture, appropriately accounts for the dynamics. Being mainly concerned with the dispersion relation, we concentrate our discussion on the t - J model as more extensive literature exists and as J can be independently measured.[38] Qualitatively, the same conclusion is expected for the Hubbard model[101], which has the added advantage of yielding $n(\mathbf{k})$, but has more uncertainty in the parameter U . Although the t - J model correctly predicts [38] the dispersion along $(0,0)$ to $(\pi/2, \pi/2)$ quantitatively[25], with the band width along this direction solely determined by J , it incorrectly predicts the energy of $(\pi, 0)$ to be nearly degenerate to $(\pi/2, \pi/2)$. This is a serious deficiency of the t - J model, because the evolution of the $(\pi, 0)$ feature is crucial to understand the *d*-wave-like pseudo gap. The inclusion of the next nearest neighbor hoppings of t' and t'' can resolve this problem [101, 32, 102, 29, 103, 27, 104, 28, 33, 31]. In fact, the t - t' - t'' - J model can account for both the dispersion and lineshape evolution over all doping levels, which is a remarkable success of this model.[26, 32] With a J/t ratio in the realistic range of 0.2 to 0.6, the t - t' - t'' - J model shows that the dispersion from $(\pi/2, \pi/2)$ to $(0,0)$ and to $(\pi, 0)$ are equal and scaled by J . [105, 106] This result supports the notion that the isotropic dispersion is controlled by a single parameter, J , as stressed by Laughlin.[44]

The above discussion indicates that we have a model, when solved by Monte Carlo or exact diagonalization, that can account for the data, but what does the

data fitting the non-trivial $|\cos k_x a - \cos k_y a|$ function so well mean? As pointed out [26], the key to the inclusion of t' and t'' is that the additional hole mobility destabilizes the one-hole Néel state with the hole at $(\pi, 0)$ and makes the system with one-hole move closer to a spin liquid state rather than to a Néel state that is stable in the t - J model. This point is relevant to some early literature of the resonating valence bond (RVB) state [18, 107]. Anderson conjectured that the ground state of the insulator at half filling is a RVB spin liquid state. [18] This idea was extended in the context of a mean field approach to the t - J model that yields a d -wave RVB or flux phase solution. [84, 85, 86] The mean-field solution also predicts a phase diagram similar to what is now known about the cuprates, with the d -wave like spin gap in the underdoped regime being the most successful example. The problem with the mean-field solution of the t - J model is that it does not agree with exact numerical calculation results [38], and the half-filled state was found by neutron scattering to have long range order [108, 109]. If these numerical calculations are right then the d -wave RVB is not the right solution of the t - J model. However, the d -wave RVB like state may still be a reasonable way to think about the experimental data that describes the situation of the spin state near a hole [110]. It is just that one has to start with a model where the single hole Néel state is destabilized, as in the t - t' - t'' - J model. We leave this open question as a challenge to theory.

The presence of d -wave like dispersion along the remnant Fermi surface shows that the high energy pseudo gap is a remnant of the d -wave 'gap' seen in the insulator. The details of the evolution of this gap, and its connection to the low energy pseudo gap (which is likely due to pairing fluctuations) as well as the superconducting gap is unclear at the moment. However, we believe that there has to be a connection between these gaps of the similar $|\cos k_x a - \cos k_y a|$ form, as their presence is correlated with each other [74].

Chapter 4

Universality of the Electronic Structure from a Half Filled CuO_2 Plane

4.1 Introduction

One approach to unraveling the mysteries of the High T_c superconductors is to understand how the electronic structure evolves from an antiferromagnetic insulator to a superconductor upon doping. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) is the one system which has been successfully grown from half filling to heavily overdoped; however, Angle Resolved Photoemission (ARPES) results on these crystals remain somewhat controversial due to the poor surface quality obtained in the experiments. $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ (YBCO), which can cover the range of half-filling to optimal doping, might appear as the next suitable candidate, but the presence of a surface state and the existence of one dimensional chains has clouded the interpretation of its bulk electronic structure. In this regard, the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi2212) system, with its extremely good cleavage plane, has been ideal for ARPES. For precisely this reason, the majority of ARPES data on the High T_c 's to date have come from Bi2212. Unfortunately, high quality Bi2212 crystals at very low dopings have not been achieved. On the other hand, $\text{A}_2\text{CuO}_2\text{Cl}_2$ ($\text{A}=\text{Sr}, \text{Ca}$) also cleaves extremely well and gives high quality ARPES

data comparable to that seen in optimally doped Bi2212, but in this case, single crystals have only been available at half filling. As a result there exists no single system to study the electronic structure from the antiferromagnetic insulator to the heavily over doped metal.¹

The solution to this problem has been to make the reasonable assumption, that the low energy physics of the Bi2212 and A₂CuO₂Cl₂(ACOC) systems are identical due to the fact that the CuO₂ planes are common to both structures. Thus the entire doping range can be studied. However, these two systems also have several differences. Bi2212 is a bilayer system compared with the single CuO₂ plane per unit cell of ACOC. (Although the single layer compound Bi₂Sr₂CuO_{6+δ}(Bi2201) can also be studied, but has similar problems to Bi2212.) Sr₂CuO₂Cl₂(SCOC) and Ca₂CuO₂Cl₂(CCOC) have a Cu-O-Cu distance of 3.97Å and 3.87Å respectively[49], compared to 3.83Å for Bi2212 [111], and they also do not possess any orthorhombic distortion or superstructure effects which plague Bi2212. Finally, the most striking difference in ACOC is that the apical oxygen has been replaced with a halide atom, in this case chlorine. Given these differences, it is important to test whether or not they can have an effect on the low energy electronic structure.

In this chapter I will justify the assumption that low energy ARPES data on the oxychlorides are representative of photoemission from a generic, half-filled CuO₂ plane, and thus may be reasonably compared with ARPES data on hole doped Bi2212. This will be done by showing that replacing the apical chlorine with bromine has no effect on the low energy electronic structure. Furthermore, it will also be shown that heavily underdoped Bi2212, near half filling, despite having relatively poor spectral quality is qualitatively consistent with the results on the oxyhalides. Finally, ARPES on Sr₂Cu₃O₄Cl₂, which contains an additional copper atom in every other CuO₂ plaquette, demonstrates that the Zhang-Rice singlet is surprisingly unaffected by even a seemingly large modification of the CuO₂ plane.

¹Recently, hole doped Ca_{2-x}Na_xCuO₂Cl₂ single crystals have been grown[56]. ARPES results on these crystals will be presented in chapter 6.

4.2 Experimental

$\text{A}_2\text{CuO}_2\text{X}_2$ (A=Sr, Ca; X=Cl, Br) and $\text{Bi}_2\text{Sr}_2\text{MCu}_2\text{O}_8$ (M=Er, Dy) single crystals were grown by a flux method described elsewhere.[88, 112] ARPES experiments were performed at beamlines V-3 and V-4 of SSRL. Crystals were oriented prior to the experiment by Laue back reflection, and cleaved *in situ* at a base pressure better than 5×10^{-11} torr. The energy and angular resolution was $\leq 70\text{meV}$ and $\pm 1^\circ$, respectively. The measurement temperature differs between samples to account for charging issues, and the photon flux was then varied to determine whether or not the sample was charging. Slight charging was in fact observed for the presented $\text{Ca}_2\text{CuO}_2\text{Br}_2$ and $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ samples, but the results were reproducible and the spectra simply shifted to higher binding energy with increased flux indicating a uniform potential barrier due to charging.

4.3 $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$

Figure 4.1 presents a comparison between SCOC and CCOC along the high symmetry directions. The two are almost identical. This is to be expected as Sr and Ca are isovalent and lie in the charge reservoir layer. Along (0,0) to (π, π) both show a feature which emerges from the background, disperses towards the chemical potential, reaches a maximum at $(\pi/2, \pi/2)$ and then loses weight rapidly as it pushes back to higher binding energy. We note that the centroid of the feature at $(\pi/2, \pi/2)$ still lies well below the chemical potential, indicative of the fact that these crystals are Mott insulators. The precise value ranges from 0.3eV to 1.8eV depending on where the chemical potential has been pinned for a particular cleave of the insulator. Along the (0,0) to $(\pi, 0)$ cut a more intense and significantly more asymmetric peak is observed. Under certain experimental conditions it becomes clear that this strong asymmetry is due to the presence of a second feature which lies approximately 600meV below the main band.[26] The dispersion of this second feature appears similar to that of the lower binding energy feature, although the intensity is not. The features along the $(\pi, 0)$ cuts do not show much dispersion, and lie approximately 300meV below

Figure 4.1: EDCs of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ (a) and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (b) along the high symmetry direction indicated in the insets. The final panel indicates the magnitude of the d -wave-like dispersion seen in the oxyhalides, and the difference in lineshape exhibited as a function of k . The measurement conditions were $T=150\text{K}$, $E_\gamma=22.4\text{eV}$ and $T=100\text{K}$, $E_\gamma=25.2\text{eV}$ for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, respectively.

the maximum in dispersion at $(\pi/2, \pi/2)$. The one significant difference between SCOC and CCOC is the observed spectral weight at $(\pi, 0)$ in CCOC which is absent in SCOC. On going from $(\pi, 0)$ to (π, π) it can be seen that this weight vanishes quickly. Although it is not clear why the matrix elements would favor CCOC over SCOC in the $(\pi, 0)$ region, it is this difference which facilitated the identification of a remnant Fermi surface in CCOC which was not observed in previous studies on SCOC. One of the most significant features of the insulator is the dispersion between $(\pi/2, \pi/2)$ and $(\pi, 0)$. The right panels makes a clear illustration of this. There are two aspects to notice here. The most important of which is clearly the difference of roughly 350meV in dispersion. This is the magnitude of the *d*-wave-like modulation seen in the insulator. The second is the strong difference in lineshape. At $(\pi/2, \pi/2)$ the spectra show a clear peak which resembles a quasiparticle like peak, albeit with a *very* large width, while at $(\pi, 0)$, the spectra merges more continuously into the high energy background, somewhat resembling a step function. These will be the benchmarks to which the other compounds will be compared in determining whether or not the data from SCOC and CCOC are representative of a single CuO_2 plane.

4.4 $\text{Ca}_2\text{CuO}_2\text{Br}_2$

The biggest difference between ACOC and other high T_c cuprates is the presence of chlorine as opposed to oxygen in the apical site. To see whether or not the apical site has an effect on the electronic structure we present in figure 4.2 ARPES data from $\text{Ca}_2\text{CuO}_2\text{Br}_2$ where bromine has replaced chlorine in the apical site. On the cut from $(0,0)$ to (π, π) a dispersive feature is clearly observed with a minimum in binding energy at $(\pi/2, \pi/2)$ and an overall bandwidth of approximately 300 meV. In panel (b) the spectra at $(\pi/2, \pi/2)$ and $(\pi, 0)$ are compared. This data looks almost identical to CCOC which was shown in figure 4.1. Specifically, the lineshape at $(\pi/2, \pi/2)$ is quite sharp and well defined compared with the broad feature seen at $(\pi, 0)$. The energy difference of 270 meV is also consistent with that seen in CCOC. We also took a limited amount of data on $\text{Sr}_2\text{CuO}_2\text{Br}_2$. The general features were consistent with that of the other oxyhalides, although significant charging was observed. The data

Figure 4.2: a) EDCs of $\text{Ca}_2\text{CuO}_2\text{Br}_2$ from $(0,0)$ to (π, π) taken with 16.5eV photons at $T=372\text{K}$. b) Comparison of $(\pi/2, \pi/2)$ and $(\pi, 0)$.

on the oxybromides is strong evidence that the low energy excitations are relatively independent of the apical atoms and the observed spectral function in ACOC thus originates from the half filled CuO_2 plane. Consequently, the comparison of ARPES data on ACOC at $x=0$ with Bi2212 data at finite doping is valid.

4.5 $\text{Bi}_2\text{Sr}_2\text{ErCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{DyCu}_2\text{O}_8$

Of course the ideal scenario to examine the doping evolution is to study the same system through the entire doping range. Therefore, we also present Er and Dy doped Bi2212 crystals grown near half filling. Figure 4.3 shows the valence band spectra of Er doped Bi2212 at $(0.63\pi, 0)$ and $(0, 0.63\pi)$. The valence band spectra are comparable to those of Bi2212 at various other dopings[113]. The spectra have been normalized only by the incident flux, and one clearly sees that the low energy spectral weight within 1.5eV of E_F is suppressed in the $(0, 0.63\pi)$ spectra relative to the $(0.63\pi, 0)$ spectra. As these two locations are at equivalent points in the CuO_2 Brillouin zone, one can conclude that the wave function at $(0.63\pi, 0)$ is symmetric with respect to a mirror plane parallel to the Cu-O bond direction. [For a more complete description of such an analysis, see chapter 2.] This is consistent with results on the oxychlorides and Bi2212[114, 113], and is the expected result for a wavefunction with $d_{x^2-y^2}$ symmetry.

Figure 4.3: Valence band spectra of $\text{Bi}_2\text{Sr}_2\text{ErCu}_2\text{O}_8$ at equivalent k points $(0.63\pi, 0)$ and $(0, 0.63\pi)$. The inplane polarization is indicated in the figure. $E_\gamma=22.4\text{eV}$ and $T=230\text{K}$.

The lack of a complete suppression at $(0, 0.63\pi)$ may be due to a combination of superstructure effects, a non zero out of plane component of the vector field, and hybridization with alternative symmetry states.

Figures 4.4 and 4.5 show the EDCs for these samples along the high symmetry directions. The low energy features are not nearly as well defined as in the oxyhalides;

Figure 4.4: EDCs of $\text{Bi}_2\text{Sr}_2\text{ErCu}_2\text{O}_8$ along the high symmetry directions as indicated in the cartoons. Below is a plot of the second derivative of the above EDCs, from which one can trace out the dispersion. $E_\gamma=22.4\text{eV}$ and $T=100\text{K}$.

Figure 4.5: EDCs of $\text{Bi}_2\text{Sr}_2\text{DyCu}_2\text{O}_8$ along the high symmetry directions as indicated in the cartoons. Below is a plot of the second derivative of the above EDCs, from which one can trace out the dispersion. $E_\gamma=22.4\text{eV}$ and $T=75\text{K}$.

however, a clear shoulder does emerge from the background. The poor definition of these features is consistent with previous studies on underdoped Bi2212 which show that the low energy excitation spectra become smeared out as one proceeds toward half filling.[71, 113] In fact, this is precisely the reason why ARPES data on the oxychlorides has been so valuable to the study of high T_c superconductivity. The reason for the relatively poor spectral quality of heavily underdoped Bi2212 is an open question, although it is possibly simply an issue of sample quality.

Examining the low energy spectra from $(0,0)$ to (π, π) of Er doped Bi2212 we see that the shoulder is most pronounced at $(\pi/2, \pi/2)$ with a minimum binding energy of -0.27 eV. From $(0,0)$ to $(\pi, 0)$ the shoulder develops at higher binding energy with a value of -0.49 eV at $(\pi, 0)$ and then disappears again as one travels from $(\pi, 0)$ to (π, π) . Although there is significant ambiguity in identifying the binding energy of these features, the fact that the shoulder has a dispersion of roughly 0.22eV between $(\pi, 0)$ and $(\pi/2, \pi/2)$ can be clearly seen in the final panel. Another way to attempt to systematically track the dispersion is with the use of a second derivative plot also shown in figure 4.4. One will notice that the dispersion found with this method reproduces the above description. Results on Dy doped Bi2212 shown in figure 4.5 clearly mimic the behavior seen in the Er doped Bi2212 including the 0.22eV difference in energy between $(\pi/2, \pi/2)$ and $(\pi, 0)$. The overall features of the dispersion and the resulting energy difference of roughly 220 meV between $(\pi/2, \pi/2)$ and $(\pi, 0)$ in Er and Dy doped Bi2212 is qualitatively consistent with the dispersion and the 350 meV d -wave-like modulation seen in CCOC. Thus, despite the poor definition, the electronic structure is still qualitatively consistent between the oxyhalide and Bi2212 systems. This result along with our data on CCOB justifies the long standing assumption that the ARPES data from SCOC and CCOC are representative of a half filled CuO_2 square lattice.

4.6 $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$: Cu_3O_4 plane

$\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ is a particularly remarkable example of the apparent robustness of the Zhang-Rice singlet. This system deviates from the other cuprates due to an additional Cu atom located in every other CuO_2 plaquette resulting in an in-plane stoichiometry of Cu_3O_4 . The resulting crystal structure has a unit cell twice as large as in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and rotated by 45 degrees (see figure 4.6). Thus $(\pi, 0)$ of the CuO_2 unit cell is now equivalent to (π, π) in the Cu_3O_4 system, and similarly $(\pi/2, \pi/2)$ for $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ is equivalent to $(\pi, 0)$ for $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$. However, instead of presenting results in the new Cu_3O_4 basis, we will continue to present all momentum values in the original CuO_2 basis. This will make for a simpler comparison between the two

Figure 4.6: Real space(a) and Reciprocal space(b) cartoons of the unit cell of Cu_3O_4 (dashed line). The unit cell of the CuO_2 (solid line) is shown for comparison.

systems.

Sample valence band spectra at four high symmetry points of $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ are shown in figure 4.7. Note the strong momentum dependence of the features. In fact these spectra are quite similar to the valence band of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ [114]. We will however, continue to focus on the low energy excitations contained in the “foot” of the valence band and expanded in the following panel for clarity. Note that the spectra at $(+\pi/2, -\pi/2)$ shows a clear suppression of weight with respect to the equivalent Brillouin zone location of $(+\pi/2, +\pi/2)$. As the polarization of the incident light is horizontal, this suppression of spectral weight at $(+\pi/2, -\pi/2)$ relative to $(+\pi/2, +\pi/2)$ indicates that the wave function at $(\pi/2, \pi/2)$ is odd with respect to a mirror plane at 45° to the Cu-O bond direction. As would be expected for a Zhang-Rice singlet state, this observation is consistent with a $d_{x^2-y^2}$ orbital character.

In figure 4.8, two perpendicular cuts through $(\pi/2, \pi/2)$ are shown. Note that the lowest energy feature is most well defined near $(\pi/2, \pi/2)$, the dispersion is isotropic about its minimum at $(\pi/2, \pi/2)$, and as can be seen in the final panel, $(\pi, 0)$ lies approximately 320 meV below $(\pi/2, \pi/2)$. From the image plot normalized at high binding energy along the antiferromagnetic zone boundary one can observe that the lowest

Figure 4.7: a) Valence band spectra of $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ at four high symmetry locations. b) An expanded view of the low energy spectra. A comparison of the spectra at $(+\pi/2, +\pi/2)$ and $(+\pi/2, -\pi/2)$ indicates that the wavefunction responsible for the low energy excitations is odd with respect to a 45° line relative to the Cu-O bond direction. $E_\gamma=16.55\text{eV}$ and $T=293\text{K}$.

energy excitations have a smooth rounded dispersion about $(\pi/2, \pi/2)$. These observations including the polarization dependence are identical to the case of ACOC.[114] These results are also consistent with earlier reports on the isostructural compound $\text{Ba}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ taken at a different photon energy.[115, 116] Although, here we neither confirm nor deny their interpretation for the existence of two Zhang-Rice singlets on differing sublattices. However, we do confirm the observation that the spectral features about $(\pi/2, \pi/2)$ have a remarkable resemblance to those in $\text{Sr}_2\text{CuO}_2\text{Cl}_2$, which have been attributed to the Zhang-Rice singlet.[23] It is astounding that the

Figure 4.8: a) and b) EDCs of $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ along two high symmetry directions as indicated in the inset. c) Image plot corresponding to the data in (b) where white is maximum and blue is minimum. d) comparison of the spectra at $(\pi/2, \pi/2)$ and $(\pi, 0)$. $E_\gamma=16.5\text{eV}$ and $T=293\text{K}$.

properties of the Zhang-Rice singlet seen in ACOC are almost undisturbed by the drastic change to the CuO_2 lattice in the case of $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$.

The biggest difference between $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ and $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ is the “background”, or in other words, the spectral weight at binding energies above the lowest energy feature. The background is much greater in $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$. This is apparent when comparing the $(\pi/2, \pi/2)$ spectra of both systems, but perhaps is best exemplified by the spectra at (π, π) , which in the case of $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ has no weight. The reason for this is unclear, but some insight may be hidden in the spectra at $(0,0)$. In contrast to data from all other cuprates at $(0,0)$, in the case of $\text{Sr}_2\text{Cu}_3\text{O}_4\text{Cl}_2$ significant spectral weight is observed. In fact, it is comparable to the spectra at $(\pi, 0)$. This would point to the possibility that the background is the result of an angle integrated contribution. However, a laser reflection off the sample surface showed no divergence due to a less than perfect cleave. Furthermore the strong angular dependence of the spectra are

also indicative of a well ordered surface. Thus the origin of this spectral weight remains unclear, although one can not help but wonder if the strain induced by the additional copper atoms in the CuO₂ plane are responsible, or alternatively comes from the additional copper atoms themselves.

4.7 La_{2-x}Sr_xCuO₄, Nd₂CuO₄, and Other Cuprates

In attempts to further check the universality of the insulating features on ACOC, we also tried to perform ARPES on YBa₂Cu₃O₆ and isostructural GaBa₂Cu₃O₆ at half filling. Unfortunately, the results were inconclusive, as not even a shoulder could be resolved in the data. This indicates that we were likely cleaving the samples where flux inclusions had mechanically weakened the sample.

Finally, La_{2-x}Sr_xCuO₄ and Nd_{2-x}Ce_xCuO₄ near half filling have been studied as well.[42, 117, 118] In LSCO at x=0.03, a broad shoulder exists at ($\pi/2, \pi/2$) at 0.5eV which disperse by roughly 200meV to higher binding energy as it approaches ($\pi, 0$). For Nd₂CuO₄ a shoulder on the edge of the valence band exists and exhibits a minimum binding energy at ($\pi/2, \pi/2$). Both of these observations further support the universality to all cuprates of the dispersion of the lowest energy feature seen in Sr₂CuO₂Cl₂ and Ca₂CuO₂Cl₂.

4.8 Discussion

Let us return to the data of the heavily underdoped Bi2212 crystals. One observation on the data is the apparent small size of the Mott gap relative to the oxychlorides. A possible explanation for this is that the chemical potential has been pinned slightly above the top of the occupied band, and thus the large Mott gap would have been seen in an Inverse Photoemission(IPES) experiment which measures the unoccupied states. However, the fact that charging is not as great of an issue for the Bi2212 crystals as it is in the oxyhalide systems indicates that the Mott gap has been significantly reduced. See figure 4.9 for the lack of temperature dependence down to 11K. Thus, an alternative explanation is that the Mott gap has already been almost

Figure 4.9: Temperature dependence of the valence band(a) and low energy(b) spectra of $\text{Bi}_2\text{Sr}_2\text{ErCu}_2\text{O}_8$ normalized by the incident photon flux. Note the lack of temperature dependence in the low energy spectra down to 11K. This is also evidence that the system is not charging. $E_\gamma=22.4\text{eV}$

completely destroyed by doping simply a few holes into the system. This is somewhat counterintuitive if the samples are truly at half filling, as one would not expect the Mott gap, which is created by strong electron correlations to be destroyed so easily with the addition of a few holes. However, this becomes much more plausible when considering that there is a reasonable amount of uncertainty as to the exact doping level particularly at the surface of doped Bi2212 samples.[112, 119] This may also explain why the d -wave-like modulation is smaller in Er and Dy doped Bi2212 relative to ACOC, as it has been shown that the high energy pseudogap originates as the d -wave modulation in the insulator whose magnitude decreases upon doping.[74, 53] Furthermore, the Er doped crystals seem to have a smaller Mott gap than the Dy

Figure 4.10: A comparison of the various half-filled cuprates taken from the figures throughout this chapter.

doped crystals, as evidenced by the minimum binding energy at $(\pi/2, \pi/2)$ of -0.27 eV for the Er doped Bi2212 sample compared with -0.41 eV for the Dy doped Bi2212 sample. This may be accidental as the absolute value of the gap is known to vary from cleave to cleave in insulators, but is consistent with previous work measuring the dielectric constant indicating that the Dy crystals are indeed closer to half filling than the Er doped Bi2212 crystals.[119] We have found that the oxychlorides typically have a minimum binding energy at $(\pi/2, \pi/2)$ which varies from -0.5eV to -0.8eV between different samples. The reason for this is unknown, but may have to do with differing pinning sites on the surface and the overall crystal quality.

To summarize, we have studied the Mott-insulating cuprates: $\text{Ca}_2\text{CuO}_2\text{Br}_2$, $\text{Bi}_2\text{Sr}_2\text{ErCu}_2\text{O}_8$, $\text{Bi}_2\text{Sr}_2\text{DyCu}_2\text{O}_8$, and $\text{Sr}_2\text{Cu}_3\text{O}_2\text{Cl}_2$. The lowest energy excitations measured by ARPES are the same in these compounds as for the prototypical insulators: $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$. The spectra from $(\pi/2, \pi/2)$ and $(\pi, 0)$ for each sample are compiled in figure 4.10. Other studies on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and Nd_2CuO_4 produce similar results.[42, 117, 118] This shows that the low energy excitations are indeed independent of the apical atom, and that the results from $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ are truly representative of a half-filled CuO_2 plane.

Chapter 5

A Detailed Study of $A(\mathbf{k}, \omega)$ at Half Filling

Having shown that the ARPES results of the half filled Mott insulating cuprate are not system dependent, we turn our attention to the physics of the half filled CuO_2 plane contained in the single particle spectral function, $A(\mathbf{k}, \omega)$. Unfortunately, extracting the single particle spectral function from ARPES measurements is complicated by the fact that the measured photoemission intensity is a product of the single particle spectral function and the matrix element (See chapter 2). In interacting electron systems, it is impossible to calculate the matrix element exactly, thus further complicating the ARPES analysis. Although we note that symmetry arguments can be very powerful in understanding some properties of the matrix element.[114] In general it is a function of the experimental geometry, photon energy, and the electronic wave function. Since its details are not well understood, the objective in a given photoemission study must be to focus on only those features of the data which are robust against variations in the matrix element.

With this in mind let us review the general features of the oxychlorides by previous ARPES studies which have assumed that the matrix elements are not responsible for the gross aspects which they report. The first studies on SCOC showed that the lowest energy excitations consist of a broad feature whose width and overall dispersion

are both approximately 300meV. [25, 55, 26] The dispersion is isotropic about its minimum at $(\pi/2, \pi/2)$. An important characteristic of the dispersion of the insulator is that the energy at $(\pi, 0)$ lies approximately 300meV below $(\pi/2, \pi/2)$. The t - J model which successfully accounted for the overall bandwidth of the insulator, required the addition of next nearest neighbor hopping terms to account for this fact.[26] Subsequently, we found in CCOC that the $n(\mathbf{k})$ pattern determined by ARPES was not isotropic about $(\pi/2, \pi/2)$, rather it beared a striking resemblance to that seen in optimally doped Bi2212.[53] Thus we were able to identify a “remnant” Fermi surface in the insulator. Much of this could be seen in figure 4.1 which presented ARPES data on SCOC and CCOC along the high symmetry directions. Each of the studies referenced above used only a single photon energy and experimental geometry. Thus, individually they could not determine whether or not the matrix element has an effect, but no two studies of those referenced above were taken with the same photon energy thus suggesting that the agreement between the different studies implies that matrix element effects are negligible.

However, photon energy dependent studies designed specifically to test the influence of the matrix element on both the dispersion, $E(\mathbf{k})$, [120, 114] and the intensity, $n(\mathbf{k})$, [121] have conflicting reports on the magnitude of variations caused by matrix elements. It is important to clarify this issue before extracting physics from the spectra of the half-filled insulator. So to test whether or not the dispersion and the remnant Fermi surface are impressive manifestations of matrix element modulations we have performed ARPES $n(\mathbf{k})$ mappings over the entire Brillouin zone for 5 different photon energies, and examined the $(0,0)$ to (π, π) cut for 14 photon energies. We find that the dispersion is independent of photon energy as one might expect, and that with few exceptions, the remnant Fermi surface is robust despite observing strong variations in spectral weight caused by matrix elements.

With an understanding of the matrix element we can finally turn our attention to the physics contained in the ARPES spectral function. Specifically, we will focus on the d -wave-like dispersion found in the insulator.[53] This observation allows for a natural connection between the d -wave form of the high energy pseudogap seen in underdoped Bi2212 and the dispersion of the insulator as first suggested by Laughlin.[44]

This connection is particularly intriguing in light of the fact that the high energy pseudogap and low energy pseudogap appear to be correlated.[74] The latter of which is directly related to the superconducting gap, thus linking antiferromagnetism which is responsible for the dispersion of the insulator to d -wave superconductivity. The original data on CCOC however left some ambiguity as to whether or not the dispersion near the node exactly fit the d -wave functional form. A linear dispersion away from the node of the form $E(\pi/2, \pi/2) - E(\mathbf{k}) \propto ||\mathbf{k} - (\pi/2, \pi/2)||$ is highly nontrivial and several theories which attempt to connect the insulator to the superconductor predict precisely such a nonanalytic behavior in the vicinity of the node[44, 122, 123]. However, the t - J model with next nearest neighbor hopping terms, t' and t'' , has a functional form of $\cos 2k_x a + \cos 2k_y a$ which is analytic at $k_x = k_y$. To investigate this issue we performed ultra high resolution ARPES experiments along the antiferromagnetic Brillouin zone (AFBZ) to determine the exact nature of the dispersion near $k_x = k_y$. From this we find that the dispersion near the node is non-linear and thus can not be fit by the simple d -wave functional form of $|\cos k_x a - \cos k_y a|$.

5.1 Experimental

$A_2CuO_2Cl_2$ ($A = \text{Sr, Ca}$) single crystals were grown by a flux method described elsewhere [88]. ARPES experiments were performed at beamlines V-3 and V-4 of SSRL. Crystals were oriented prior to the experiment by Laue back reflection, and cleaved *in situ* at a base pressure better than 5×10^{-11} torr. The energy and angular resolution indicated in the first figure caption for each data set presented was better than 70 meV and 1° , respectively. The measurement temperature differs between samples to account for charging issues, and the photon flux was then varied to ensure that the sample was not charging.

5.2 E_γ Dependence on $E(k)$ and $n(k)$

Here we present a photon energy dependence study of this issue to extract the intrinsic $E(k)$ and $n(k)$ structure from the raw data which can be affected by matrix

elements. In figure 5.1 EDCs from a single cleave of CCOC taken along the nodal direction through $(\pi/2, \pi/2)$ for fourteen different photon energies are presented. The morphology of the spectra are consistent, of which there are two features to be noted. First, is that the minimum binding energy occurs near $(\pi/2, \pi/2)$ for all the photon energies studied, and second, with a few exceptions the intensity profile begins to lose weight before the minimum in binding energy is reached. We will address the latter point in more detail below. To determine if the dispersion is indeed independent of photon energy we plot the peak position versus k for each photon energy in figure 5.2. The peak positions were found by taking the minimum of the second derivative of each spectra. One can see that to within our experimental limits, which were determined by the reproducibility of the dispersion on subsequent scans under identical conditions, the dispersion is independent of photon energy. This agrees with most of the previous reports on SCOC[25, 55, 26] including one very detailed, recent study[114], but contrast with the results from Ref. [54, 121], the latter of which report that the minimum binding energy position shifts by approximately 10% of the $(0,0)$ to (π, π) distance to $(0.39\pi, 0.39\pi)$ when using 35eV photons. (note that this is outside of our error bars) They attribute this change to matrix elements whose binding energy dependence varies as a function of photon energy.

Aside from indicating the expected two dimensional nature of the dispersion, our photon energy dependence has also clearly resolved the presence of a second component in the low energy electronic structure of the half filled insulator.[26] Figure 5.3 presents EDCs in the nodal direction for six photon energies from 16.5eV to 17.5eV. Aside from the feature typically associated with the Zhang-Rice singlet, a second component is observed at approximately 600meV higher binding energy. In the nodal direction this feature is most clearly resolved at 17eV. From this data it is clear that when attempting to model the data on the insulator, one can not simply treat the high energy spectral weight as a featureless incoherent background. Although the dispersion of this feature is difficult to track it appears to mimic the dispersion of the low energy feature. This may be the first experimental data that clearly show features predicted by string resonances. String resonances occur when a hole, created in an antiferromagnetic background, experiences a confining potential

Figure 5.1: EDCs from a single cleave of CCOC along $\Gamma \rightarrow (\pi, \pi)$ for 14 different photon energies indicated in each panel, respectively. The bold spectra indicates $(\pi/2, \pi/2)$. The angular separation between the top and bottom spectra in each panel is 11.4° with an energy resolution, $\Delta E \leq 50\text{meV}$. $T=200\text{K}$.

Figure 5.2: $E(\mathbf{k})$ obtained by the minimum of the second derivative from the EDCs in figure 5.1. The shaded blue bar represents the momenta error bars.

Figure 5.3: EDCs from a single cleave of CCOC along the nodal direction for $E_\gamma=16.5\text{eV}$ to $E_\gamma=17.5\text{eV}$ as indicated in each panel. The bold spectra indicates $(\pi/2, \pi/2)$. The angular separation between the top and bottom spectra in each panel is 13° with an energy resolution, $\Delta E = 70\text{meV}$. $T=293\text{K}$.

due to the energy cost associated with disrupting the antiferromagnetic order as it hops away from its original location. The lowest energy state for the hole in this potential corresponds to the Zhang-Rice singlet, while the first excited state is predicted to lie roughly $1.8(J/t)^{2/3} \approx 0.5\text{eV}$ higher in energy.[124] Although we are not certain of the origin of the higher energy feature, the string resonance concept provides an intriguing possibility for further study.

Having examined the dispersion, we now look at the more difficult problem of extracting the underlying $n(\mathbf{k})$ structure. It is of particular interest to determine

Figure 5.4: a) EDCs and b) corresponding image plot of CCOC taken along the nodal direction with 23.5eV photons from figure 5.1. The bold spectra indicates $(\pi/2, \pi/2)$. $T=200\text{K}$.

whether or not the underlying intensity profile of $A(\mathbf{k}, \omega)$ has an asymmetry with respect to the antiferromagnetic zone boundary as this would put constraints on the valid coupling regime for different models. In figure 5.1 we noticed that for the majority of photon energies the intensity of the lowest energy excitation begins to lose weight before $(\pi/2, \pi/2)$. This can be seen even more clearly in an image plot for a characteristic set of data in figure 5.4. This has also been observed previously by several authors with isolated photon energies.[25, 55, 54, 26, 120] In figure 5.5 the $n(\mathbf{k})$ curves obtained by integrating the EDCs in figure 5.1 from -0.5 to 0.3eV relative to the valence band maximum for each photon energy are shown.¹ Clearly, with the

¹the energy integration window was chosen so as to minimize the contribution from the second component seen at higher binding energy, but we note that the results are independent of the specific energy window chosen

Figure 5.5: $n(\mathbf{k})$ obtained by integrating the EDCs in figure 5.1 from -800meV to E_F . The maxima of each curve were normalized to each other for display. The blue bar represents the momenta error bars.

exception of 16.5, 32, and 33eV the intensity profile peaks well before $(\pi/2, \pi/2)$, which can also be seen from the EDCs themselves. This is evidence that a true asymmetry exists in the data. This differs from the conclusions of a similar study on SCOC, which used five photon energies from 20 to 24eV.[121] They observe the intensity profile to be more heavily weighted towards (0,0) at $E_\gamma=24\text{eV}$ which then gradually shifts until at $E_\gamma=20\text{eV}$ the profile is more heavily weighted towards (π, π) . From this one would conclude that the matrix elements are strong enough that the true underlying $n(\mathbf{k})$ can not be determined. However, the data from Figure 5.5 and the majority of single photon energy studies on SCOC[25, 55, 54, 26, 120] suggests otherwise.

As all of the above studies were only from a single cut through the Brillouin zone we now examine a more global perspective of the intensity profile. Figure 5.6b)-f),

presents relative $n(\mathbf{k})$ patterns of CCOC over a Brillouin zone quadrant for five different photon energies while panel a) is of an optimally doped Bi2212 sample. Spectra are taken at the crosses and except for panel (c), the data has been symmetrized about $k_x=k_y$ and the geometry of the experimental setup was identical. The first two panels reproduce the original comparison of metallic Bi2212 and insulating CCOC from which the initial identification of a “remnant Fermi surface” was made.[53] For a state with $d_{x^2-y^2}$ orbital symmetry the suppression of weight as one approaches the line $k_x=0$ is expected. In Bi2212 the only drop in intensity which is not naturally explained by matrix elements is where a Fermi surface crossing has occurred. As seen in the figure the intensity drop matches the traditional method for determining a Fermi surface crossing by following the dispersion by eye and is indicated by the dots. A similar drop in intensity is observed in the insulator. Although the feature is less well defined here, the striking resemblance it bears to the metal suggests that the origin is similar, and hence it was qualitatively described as a remnant Fermi surface.[53] [Note that the remnant Fermi surface is fully gapped by the large Mott gap.]

Here we examine the effect of changing the photon energy. From panels (b) through (f) one immediately notices that the intensity pattern varies tremendously for the five photon energies: 25.2, 16.5, 29, 32.3, and 41eV. However, the variations appear predominantly parallel to the $(\pi, 0)$ to $(0, \pi)$ direction, while perpendicular to this there exists relatively little variation as we noted above in figure 5.2. The exact shape of the remnant Fermi surface may change, but at all photon energies used there is a loss of spectral weight as one crosses the approximate antiferromagnetic zone boundary from $(0, \pi)$ to $(\pi, 0)$. It may appear that the remnant Fermi surface is more hole-like or electron-like depending on the photon energy chosen, but the broadness and the variability due to matrix elements prevent one from clearly identifying the intensity profile as either case. However, the point which is clear from the data is that globally, there is always an asymmetry in intensity stronger towards $(0,0)$ than towards (π, π) as one crosses the region spanned by the black lines in the Brillouin zone which is also coincident with the antiferromagnetic zone boundary.

Figure 5.6: (color) Integrated spectral weight. The crosses indicate where spectra were taken. Except for (C) the data is symmetrized about the $k_x=k_y$ line. Red is maximum. (A) optimally doped Bi2212 at $E_\gamma=22.4\text{eV}$. The white hashed region indicates the approximate location of the Fermi surface determined from $n(\mathbf{k})$. The dots illustrate the position of the Fermi surface as determined by the traditional method for analyzing ARPES data. (B) CCOC shows a striking similarity of the insulator to the metal allowing the identification of the white hashed region as a remnant Fermi surface. Comparison of (B) through (F) show CCOC taken at photon energies of 25.2, 16.5, 29, 32.3, and 41eV. The intensity maxima varies between different panels, but the loss of intensity as one approximately crosses the antiferromagnetic zone boundary is a consistent feature. The cumulative boundary of the remnant Fermi surface is drawn with black lines on panels (B) through (F). $\Delta E \leq 70\text{meV}$.

Although the $n(\mathbf{k})$ image plots can provide a wealth of information and are extremely good for summarizing data, it is important to look at the raw data to fully appreciate the information being given by the image plots. This is done in Figure 5.7. Panels (a) and (b) plot respectively, the EDCs from $(0,0)$ to (π, π) and $(\pi/2, \pi/2)$ to $(\pi, 0)$, from the data sets used to create the intensity maps in figure 5.6b-f). We find the spectra are qualitatively similar. This is true even at 41eV where the peak is poorly defined throughout the zone. To examine them more closely, Figure 5.8 plots both the dispersion of the peak position and $n(\mathbf{k})$ together for all the cuts shown in figure 5.7. As we saw before only slight differences exist in $E(\mathbf{k})$ and $n(\mathbf{k})$ among the five different photon energies along $(0,0)$ to (π, π) . This however, contrasts sharply with the $(\pi, 0)$ to $(0, \pi)$ cut. While the dispersion is again identical, the intensity varies seemingly randomly. In the extreme case between 25.2eV and 29eV the intensity is increasing as one approaches $(\pi/2, \pi/2)$ for the former, and decreasing for the latter.

Even for the case of a single two dimensional plane, the wavefunctions will have some finite extent in the z -direction. Thus, the outgoing photoelectrons resulting from photons with different wavelengths will necessarily have a different overlap, and hence different cross-section, with the initial wavefunctions of the system. This is impossible to avoid unless the initial wavefunctions z dependence were unrealistically proportional to $\delta(z)$. The ideal way to eliminate such matrix element effects is to average over all possible photon energies, and experimental geometries. Here we have observed large variations along the antiferromagnetic zone boundary that are manifestations of the matrix element, while the asymmetric shift of weight towards $(0,0)$ with respect to the $(\pi, 0)$ to $(0, \pi)$ line is found to be a robust feature of the underlying spectral function. Our initial report implied that the underlying $n(\mathbf{k})$ structure matched that of the LDA Fermi surface at half filling without correlations.[53] It is now clear, that the matrix elements are strong enough to make such a precise identification nearly impossible. However, we still conclude that an underlying asymmetry exists in the spectral function about the antiferromagnetic zone boundary which is robust despite variations with photon energy. Whether it truly lies along the LDA Fermi surface, the antiferromagnetic zone boundary, or some other contour is an open

Figure 5.7: (color) ARPES spectra along 2 cuts, $(0,0)$ to (π, π) and $(\pi/2, \pi/2)$ to $(\pi, 0)$, and 5 different photon energies (16.5, 25.2, 29, 32.3, and 41 eV). The intensities of the features vary, but the dispersion remains the same.

Figure 5.8: (color) Plots the peak position and $n(\mathbf{k})$ from the spectra in figure 5.7. For both cuts the dispersion is independent of photon energy. The data along $(\pi, 0)$ to $(0, \pi)$ has been symmetrized. Along $(0, 0)$ to (π, π) the intensity has minor shifts, but is overall consistent indicating robustness of the remnant Fermi surface. For $(\pi/2, \pi/2)$ to $(\pi, 0)$ the intensity varies randomly indicating that this modulation in intensity is due to matrix elements. Filled symbols indicate $E(\vec{k})$ while open symbols are for $n(\mathbf{k})$.

question.

5.2.1 E_γ Discussion

What is the significance of this underlying intensity modulation? The question of how a metal evolves into an insulator is one of the most fundamental in solid state physics, and information on the evolution of $n(\mathbf{k})$ would certainly provide insight on this issue. For the case of non-interacting electrons, the Fermi surface shrinks and eventually disappears as a band is filled. When electron-electron interactions dominate, the situation is less clear. By considering the strong Coulomb interaction,

Mott qualitatively described how a material predicted by band theory to be a metal would in fact be an insulator.[16] However, it remains unclear as to how the details of the electronic structure evolve from a half-filled metal to a Mott insulator. As the Fermi surface which can be defined by the surface of steepest descent in the electron momentum distribution function, $n(\mathbf{k})$, is a characteristic features of any metal, an equivalent question to the one above is how does the Fermi surface of a metal vanish as strong electron correlations drive the system into an insulator?

In the context of specific many-body models such as the Hubbard model, it has been shown that a structure in $n(\mathbf{k})$ survives even when the on site Coulomb U drives the system insulating, albeit the discontinuity in $n(\mathbf{k})$ which existed in the metal has been washed out.[38, 37, 39] This effect is linked to the fact that $n(\mathbf{k})$ reflects the underlying Fermi statistics of the electronic system. For the specific case of a two dimensional square lattice that resembles the CuO_2 planes of the cuprates, there is a drop in $n(\mathbf{k})$ across a line that is close to the antiferromagnetic zone boundary.[38, 37] This is contrary to generalized t - J models where the structure in $n(\mathbf{k})$ is washed out.[37, 34]

By presenting $n(\mathbf{k})$ we have implicitly used the sudden approximation to extract the momentum distribution function, $n(\mathbf{k})$, from ARPES data via the relation $n(\mathbf{k}) = \int A(\vec{k}, \omega) f(\omega) d\omega$ where $f(\omega)$ is the Fermi function.[67] In the metallic state of optimally doped Bi2212 the steepest descent of $n(\mathbf{k})$ gives a Fermi surface consistent with traditional ARPES analysis methods, despite the complication of matrix elements as shown in figure 5.6. The intriguing result is that the $n(\mathbf{k})$ pattern of the insulator, CCOC, is strikingly similar to the $n(\mathbf{k})$ pattern seen in Bi2212.[53] This realization, coupled with many-body theoretical calculations on various forms of the Hubbard model[38, 37], suggests that the insulator pattern contains information that is related to a Fermi surface which has been destroyed by strong electron-electron interactions thus giving a qualitative concept of a remnant Fermi surface as the surface of steepest descent in $n(\mathbf{k})$. In this chapter we have found that the remnant Fermi surface acts to emphasize a robust feature which we observe in the insulator, although its precise shape is uncertain. While this may not be a rigorous definition, as the Fermi surface is only defined for a metal, this idea allows a practical connection from the pseudogap

seen in underdoped cuprates to the properties of the insulator.[44]

However, the fact that the antiferromagnetic Brillouin zone boundary is quite similar to the underlying Fermi surface (See figure 5.9a) will mean that the true origin of this asymmetry will be uncertain. Therefore we suggest here a few ideal tests for the RFS. One idea is to find a system whose non-interacting Fermi surface is radically different from the antiferromagnetic Brillouin zone. For a hypothetical example see figure 5.9b. To find such a single band strongly correlated two-dimensional system compatible with ARPES may be a dream, particularly when considering that the magnetic properties are a result of the electronic structure, but should at least be kept in mind. Perhaps a more realistic approach will be to find a system similar to the cuprates, but where the antiferromagnetic correlations are much smaller, such that, at the measured temperature effects due to antiferromagnetic correlations could be ruled out. We leave this as a hope for the future.

Returning to the photon energy dependence of the cuprates, we know they are generally believed to be two dimensional electronic systems. However, as mentioned above, only in the artificial case where the wavefunctions of each plane are proportional to $\delta(z)$ will the electronic states probed by ARPES be independent of photon energy. In reality the wavefunctions have some finite z extent, and even if they are highly localized will have some finite overlap with neighboring planes. In fact such a coupling must be present to create the observed three dimensional long range magnetic order seen at half filling. Thus there exist several reasons which could cause $E(\mathbf{k})$ to depend on photon energy. Certainly, if the wave function overlap were large enough to create a small dispersion as a function of k_z such an effect would be expected. Alternatively, if the matrix element had a significant dependence in the binding energy of the feature which varied with photon energy, a photon energy dependent dispersion would also result. Along similar reasoning, if there are multiple excitation branches there is no reason to expect that the matrix elements dependence on photon energy would be the same for each branch. Most likely an observed variation with photon energy would be caused by a combination of several of these factors. However, in figures 5.2 and 5.8 we have shown that the dispersion of the insulator is independent of photon energy to within our experimental uncertainty. Three dimensionality

Figure 5.9: Cartoons to illustrate differing ideas of the remnant Fermi surface as correlations are turned on ($U \neq 0$). Shaded regions indicate larger occupancy. Experimentally it is difficult to distinguish in the CuO_2 plane whether the Fermi surface simply becomes washed out or whether the asymmetric $n(\mathbf{k})$ is solely due to the antiferromagnetism present in the system. b) is a hypothetical case which could easily distinguish between the two cases, although it is questionable whether such a structure could even produce an antiferromagnetic ground state.

may still play a role in causing a small shift in dispersion with photon energy, but it is a safe assumption to treat the electronic structure of the half filled insulator as essentially two dimensional.

Recently, the role of the matrix element effects is also under examination regarding the Fermi surface of Bi2212.[125, 126, 127] Several groups have reported the existence of an electron-like Fermi surface centered at $(0,0)$. [125] These groups report a subtle change of dispersion near the flat band region around $(\pi, 0)$, causing a change in the

shape of the Fermi surface. Largely due to the difficulty in understanding the effects caused by photoelectron matrix elements, there is no consensus in attempting to resolve this issue.[126] However, it would be very surprising to find the matrix element purely responsible for causing an apparent change of the Fermi surface from hole-like to electron-like with varying photon energy. More likely explanations include: dispersion in k_z , bi-layer splitting[128, 129, 130], and phase separation. With the exception of Pb doped samples Bi2212 also has the additional complication of superstructure in the Bi-O planes. In Bi2212, it would be surprising for the dispersion in k_z to have a large effect considering the two dimensional nature of the cuprates. In reality though, it is likely that all of these effects play roles which result in a potentially very complex picture.

Interestingly, models which have multiple component electronic structures where the wavefunctions and dispersions differ could have a simple explanation for the observed controversy.[128, 129, 130] In such a case, variations in the matrix element could now lead to different interpretations of the observed ARPES spectra at different photon energies. This is possible because there may now be a different matrix element for each component, and each matrix element may vary differently with photon energy. Thus causing one component to be more dominant at one photon energy while hidden at another. This would naturally lead to different interpretations as a function of photon energy. Thus we see that matrix element effects are not unique to the oxchlorides, and care must be taken to extract the underlying single particle spectral function from the ARPES data.

We have shown that the loss in intensity as one crosses the antiferromagnetic zone boundary is a robust feature of the insulator, $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, which can not be explained solely by matrix element effects. However, the photon energy dependence does underscore the qualitative rather than quantitative nature of the remnant Fermi surface concept. We argue that much physics can be learned in spite of the effect which matrix elements can have in ARPES, as long as care is taken to properly sort out the intrinsic versus the extrinsic physics. In particular, the resulting connection between the d -wave like dispersion and the pseudogap in the underdoped regime is robust.

5.3 Rounded Node

Indeed, the greatest significance of the remnant Fermi surface as it pertains to the high temperature superconductors is that a d -wave-like dispersion was identified in the insulator, which could thus provide a natural connection between antiferromagnetism and d -wave superconductivity. However, the earlier study on CCOC left some ambiguity as to the precise nature of the dispersion near the nodal line, $k_x=k_y$. [53] A simple d -wave dispersion proportional to $|\cos k_x a - \cos k_y a|$ would produce a linear dispersion with a discontinuous derivative perpendicular to the nodal direction at $k_x=k_y$. This is most easily seen by the fact that along the antiferromagnetic zone boundary the above function reduces to $|\sin(k_x a - \pi/2)|$. Such a non-analytic dispersion is non-trivial, and hence the presence or absence of such a dispersion is of great significance to theories which attempt to unify the antiferromagnetic insulator with the d -wave superconductor.

In figure 5.10 we present EDCs taken at 0.6° intervals along the antiferromagnetic zone boundary and through $(\pi/2, \pi/2)$. One observes a smooth round dispersion through $(\pi/2, \pi/2)$. This is even more evident in the image plot of the same data. To compare with the d -wave functional form we must quantify the dispersion seen in the raw spectra. From the data one can see that the low energy features seen in the insulator are inherently very broad. The half width at half max at $(\pi/2, \pi/2)$ is 100meV, which is on the order of the total dispersion seen in this material. Due to this and the fact that the higher energy spectral weight is also dispersive and of unknown origin, the significance of any particular fit to the data is questionable. For this reason we have chosen to quantify the dispersion using three methods: the peak maximum, the location of maximum curvature, and the leading edge midpoint. We compare these quantities against $|\cos k_x a - \cos k_y a|$ in figure 5.11. The straight line represents the simple d -wave scenario. Near the node it is clear that the dispersion is rounded in each case.

One plausible explanation for the flatness of the dispersion near $(\pi/2, \pi/2)$ could be the dirty d -wave scenario. Previous ARPES work on underdoped Bi2212 samples also found a flattened dispersion near the node of the superconducting and normal

Figure 5.10: EDCs and corresponding image plot of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ data taken along the antiferromagnetic zone boundary at 0.6° intervals. $(\pi/2, \pi/2)$ is indicated by the bold EDC and the dotted line in the image plot. Data was taken at $T=200\text{K}$, 25.5eV photons, $\Delta E = 40\text{meV}$, and 0.8° angular resolution

state low energy pseudo gap [70, 97, 131]. In the earlier works this was mentioned to be consistent with dirty d -wave since a finite density of states with zero excitation energy would result in a flattening of the node region. However, Mesot *et al.* argue that the flattening due to impurities can be ruled out since the pair breaking due to impurities would cause the overall magnitude of the gap to decrease, while they observe the opposite.[131] In other words, as the node region becomes flatter the maximum gap value increases. Furthermore, we note that ACOC is very stable and must be very

Figure 5.11: Three methods for characterizing the dispersion of the data in figure 5.10 plotted with the original data from ref. [53]. A straight line corresponds to a simple d -wave dispersion. Each curve was offset to zero at the node. Note that the d -wave-like gap is in addition to the Mott gap which is not shown. The increased scatter as one approaches $(\pi, 0)$ is indicative of the increased difficulty in tracing the dispersion away from $(\pi/2, \pi/2)$.

chemically pure as evidenced by many unsuccessful attempts by many institutions to dope the oxychlorides under atmospheric conditions[56]. The broadness of the peaks can not be used as evidence for impurities since the same feature seen to be almost equally broad in Bi2212 samples contain nearly resolution limited quasiparticle peaks in their spectra in the superconducting state.[132] So, although one can not rule out the possibility that the observed dispersion is due to impurities we will suffice it to say that it remains a possibility, and will now focus our attention for the remainder of this chapter on the more interesting assumption, that the observed rounding is intrinsic to the undoped insulator.

In an attempt to quantify the deviation from a simple d -wave picture we fit the data to $\Delta|B \cos(2\phi) + (1-B) \cos(6\phi)|$ in figure 5.12, where ϕ is described in the figure.

Figure 5.12: Fits of the data in figure 5.11 to $\Delta|B \cos(2\phi) + (1 - B) \cos(6\phi)|$ where ϕ is indicated in the figure. B characterizes the deviation from a simple d -wave.

$\cos(2\phi)$ is approximately $|\cos k_x a - \cos k_y a|$ and $\cos(6\phi)$ is the next allowable harmonic for d -wave symmetry. An increase in the $\cos(6\phi)$ term (smaller B) corresponds to a flatter nodal region. We find $B=0.81 \pm 0.01$. This is smaller than any underdoped sample measured by Mesot *et al.*, and thus is consistent with their interpretation that the rounding is a result of increasing antiferromagnetic correlations.[131]

Finally we note that the above data was taken at $E_\gamma=25.5\text{eV}$. Identical results were obtained at $E_\gamma=29\text{eV}$, on a second cleave of CCOC at $E_\gamma=25.5\text{eV}$, and on SCOC using 22.4eV photons. Improving the angular resolution by a factor of 4 by narrowing the slits of our analyzer also had no effect.

5.3.1 Dispersion Discussion

We now address the significance of the rounded dispersion at $(\pi/2, \pi/2)$. On simple grounds, a sharp feature in k -space implies long range interactions in real space. Considering that we are dealing with an antiferromagnet below the Néel temperature,

this is what one might expect. However, we have found this not to be the case for the dispersion in the nodal region. As a result, the photoemission spectrum, which measures an excited state property, seems more to resemble a spin liquid state, where the short range antiferromagnetic interactions are extremely important.

Numerical calculations show that the t - J model describes the dispersion from $(0,0)$ to (π, π) well, but incorrectly predicts the energy at $(\pi/2, \pi/2)$ and $(\pi, 0)$ to be equal [38]. The addition of t' and t'' corrects this problem, and furthermore, for realistic values of these parameters, shows that the dispersion is isotropic and scaled by a single parameter, J . [105] The effect of adding t' and t'' to calculations is to destabilize the single hole Néel state about $(\pi, 0)$. The resulting state appears to be a spin liquid state which may display spin charge separation, but this only occurs about $(\pi, 0)$. [105, 106] Perhaps this explains why RVB theories, which assume spin charge separation throughout the entire zone, incorrectly predict a cusp at $(\pi/2, \pi/2)$ in the spinon dispersion while still correctly describing the overall dispersion on a qualitative level. [44, 122]

The mean field treatment in a simple SDW applied to the Hubbard model which includes up to third nearest neighbor hopping, fails. [105] The dispersion along $(\pi, 0)$ to $(0, \pi)$ is much too great for realistic values. However, the dispersion does contain a rounded node region. If one can argue why one should renormalize these parameters as done by Nuñez-Regueiro then it is possible to obtain a very good fit to the experimental data. [133] Furthermore, they show that the magnitude of the overall dispersion decreases with doping as has been seen in the high energy pseudogap. Alternatively a diagrammatic expansion of the Hubbard model containing t' and t'' also reproduces the observed dispersion. [134] Finally, the $SO(5)$ theory predicts a $|\cos k_x a - \cos k_y a|$ dispersion for the insulator when the superconductor has simple d -wave pairing. [123] However, in the projected $SO(5)$ the observed flattening of the node in the insulator is consistent with a flattened dispersion observed near the node of the superconducting gap as well. [99]

5.4 Conclusions

In conclusion, our photon energy dependent study to extract the intrinsic spectral function shows that the dispersion is indeed independent of photon energy, and that despite a few exceptions an asymmetry exists in the $n(\mathbf{k})$ about the line from $(\pi, 0)$ to $(0, \pi)$. We also find that the dispersion along this contour does not fit a simple d -wave dispersion, but is flattened near $(\pi/2, \pi/2)$ consistent with similar rounding observed in underdoped Bi2212 samples.[70, 97, 131] Numerical calculations on the t - t' - t'' - J model which match all aspects of the insulator dispersion including the rounded nodal region, show that the antiferromagnetic correlations are destroyed near $(\pi, 0)$, indicating that a spin liquid picture may be more appropriate for interpreting the ARPES data.[105, 106] However, generalized t - J models fail to reproduce the observed asymmetric intensity profile which is produced in the Hubbard model.[37, 38] Possibly the Hubbard model including next nearest neighbor hopping terms [134] will be able to capture all the physics of a single hole in the half-filled CuO_2 plane.

Chapter 6

Na-doped $\text{Ca}_2\text{CuO}_2\text{Cl}_2$

This chapter presents Angle Resolved Photoemission (ARPES) results on the doped oxy-halide system, $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$. This is an ideal system to study the evolution of the electronic structure across the metal to insulator transition, which may be the key to unlocking the mystery of why the high temperature superconductors originate as antiferromagnetic insulators. Due to material limitations $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ (LSCO) is the only system to have been studied across the metal to insulator transition to date. In this case, a two component electronic structure is observed, which is attributed to microscopic phase separation.[42] It is currently still controversial whether the behavior seen in LSCO is general to all the cuprates. Due to its superior surface quality, the doped oxy-halides are a more natural choice to investigate these issues.

From ARPES we have found that Na-doped $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ contains fingerprints of the parent insulator. This manifests itself in the form of “shadow bands”, a chemical potential shift to the top of the valence band, and an extremely large pseudogap. In addition, the low energy excitations (ie the Fermi surface) are best characterized as a Fermi arc about $(\pi/2, \pi/2)$. We also find evidence for an additional energy scale of roughly 50meV in the hole-doped oxychloride.

6.1 Experimental

Na-doped CCOC single crystals were grown by a flux method under high pressure, by using a cubic anvil type pressure apparatus.[56] A powder mixture of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$, NaCl , NaClO_4 , and CuO (1:0.2:0.2:0.1 molar ratio), sealed in a gold tube, was heated up to 1250°C and then slowly cooled down to 1050°C under a high pressure (on the order of 4 GPa). Uniform samples of varying Na concentration were achieved by using different pressures during the synthesis. Crystals with a maximum dimension of $1.5 \cdot 1.5 \cdot 0.1 \text{ mm}^3$ were obtained and cleaved easily in situ. The Na content, x , was estimated by comparing the c -axis lattice constant with powdered ceramic samples.[89] Magnetization measurements of T_c gave results consistent with the assigned doping concentration. The Na concentrations used in this study were $x=0.10$ ($T_c=13$) and $x=0.12$ ($T_c=22\text{K}$), which lie in the underdoped regime. As a reference, optimal T_c in powder samples has been found to be 28K.[89] ARPES measurements were performed solely on beamline 5-4 of SSRL. The measurement conditions are indicated in the first caption of each new cleave which is presented.

6.2 Valence Band Comparison

Our investigation on Na-doped $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ begins with a comparison of the valence band of the half-filled insulator and the metallic sample. In figure 6.1 valence band spectra along the nodal direction are compared for $x=0$ and $x=0.1$. The data on the insulator is consistent with previous reports,[114, 55] while the data for the Na-doped $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ was reproduced on multiple cleaves. The low energy excitations within 1eV of the chemical potential which the bulk of this chapter will focus on are barely visible in this expanded scale. Generally, the two data sets are quite similar, although differing relative intensities for a few of the bands about (0,0) can be seen. The other difference is that the insulator is sharper than the metal, particularly near (π, π) . Perhaps this is an indication that the surface of Na-doped $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ is not as well ordered as the pure sample grown under atmospheric conditions. Panel 6.1c plots the second derivative of the above spectra, which can be used to identify

the dispersion of various features in the data. This method agrees with the visually determined dispersion of the various bands in the insulator and the metal as shown in panel 6.1d. With one minor exception, the resolved bands appear to have shifted to lower binding energy with doping, as would be expected if this were a simple band material. The discrepancy is from the metallic band at 5.5eV binding energy near (0,0). However, due to the broadness of the metallic features, it is likely that this band is a superposition of several peaks, and can not be rigorously compared to the insulator. Note that several insulating bands are resolved in this same region. Thus, the overall picture from the valence band data is suggestive of a chemical potential shift with doping. The most convincing demonstration for this is at (π, π) where the peaks for both hole concentrations are most clearly resolved. Here, the peak positions indicate that the insulator is shifted to higher energy by roughly 300meV relative to the metal. The naive expectation based on band structure calculations, which are shown in figure 1.5, is a shift of roughly 100meV for an increased hole concentration of 10%. [13, 95] The specific value of 300meV depends on which insulating data set is used, since the chemical potential in the insulator can vary as much as the magnitude of the Mott gap due to different pinning sites which exist for the different cleaved surfaces. One could imagine that if the chemical potential of the insulator were pinned at the peak position of the Zhang-Rice singlet at $(\pi/2, \pi/2)$ then there would be no shift of the chemical potential upon doping. However, this scenario is unphysical, as the broad lineshapes of the insulator would then extend above the chemical potential, which would imply that the system is metallic. This is clearly not the case. Thus, a shift of 300meV is actually the minimum value one could get by comparing an insulating data set to the data of the doped metallic sample presented in figure 6.1.

The valence band of our Na-doped CCOC crystals has a final peculiarity not illustrated in the spectra discussed thus far. Namely, from 8 to 13eV binding energy there exists several pronounced features which vanish extremely quickly with time. This is shown in figure 6.2. The spectra from the cleave where these features were most prominent is shown in the top panel. Features at 9, 10, and 12eV are visible which we have never observed in the parent compound, CCOC. These features, however, do not survive very long. 6.2b reveals that within 90 minutes following the initial cleave,

Figure 6.1: Valence band spectra along the nodal direction for a) $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ and b) 10% Na-doped CCOC. c) is a second derivative plot of a) and b) retaining only points with negative curvature, and d) maps the dispersion of the various features seen in the first two panels. The measurement conditions are identical except for the temperature of the insulator which is raised to avoid electrostatic charging during the photoemission process. Resolution $\Delta E \leq 30\text{meV}$, $E_\gamma = 25.5\text{eV}$, $T = 200\text{K}$ and 17K for $x=0$ and $x=0.1$, respectively. The data is consistent with a shift of the chemical potential with doping as discussed in the text.

Figure 6.2: a) reveals three features, at 9, 10, and 12 eV, in Na-doped CCOC not present in the pure sample. the time elapsed between the initial cleave and the time the spectra were recorded is indicated in the figure. b) illustrates, with a different cleave, how the features vanish within 90 minutes of the initial cleave. The photon energy was 25.5 eV and the temperature was 10 K and 20 K for panels (a) and (b) respectively. The Fermi cutoff on the low energy spectral weight is too small to be visible in this expanded scale. For comparison XPS spectra of NaClO_4 (c) and NaCl (d) are also shown (from ref [135]), which are used in excess in the sample growth.

these features have vanished. For binding energies less than 7 eV no change in the spectra was ever observed over these time scales where particularly close attention was paid to the near E_F features. The photon energy was adjusted to ensure the high binding energy features were not excited by a contribution of second order light from the monochromator. Comparing the spectra in panels a) and b) suggests a dispersive nature of these features. However, it was also observed that these features shift to lower binding energy as they age. We tentatively assign the origin of these features to molecules, such as NaCl and NaClO_4 which are used in excess during the synthesis. These loosely bound molecules are subsequently photodesorbed following the cleave. Despite the uncertain nature of these high energy features, the fact that the low energy features of the spectra have no variation over the short time scale where the high energy features vanish, gives us confidence in our results on the Na-doped CCOC crystals which follow below.

6.3 Shadow bands

We now focus on an examination of the raw low energy spectral weight of a representative cleave, which contain the features common to all cleaves. In this case the Na concentration, x , is 0.10, which results in a T_c of 13.5K ($\Delta T_c = 3.5K$). The spectra taken along (0,0) to (π, π) with a photon energy of 25.5eV are plotted in figure 6.3a. One can observe a broad feature develop near (0,0) and disperse toward the Fermi level with increasing k . The crystal momentum with maximal intensity at the Fermi energy occurs at $(0.43\pi, 0.43\pi)$ which naturally coincides with the observed sharp Fermi cutoff in the EDC. This coupled with a loss of spectral weight at larger k values is representative of a band crossing the Fermi energy. However, this is not the end of the story. Instead, as indicated by the tick marks, a feature is observed which disperses away from the Fermi level as it loses weight rapidly. This feature is identified as a shadow band as it resembles the half filled insulator in which a band folding about $(\pi/2, \pi/2)$ occurs due to the long range antiferromagnetic ordering which exists at half filling. In the insulator the magnetic order doubles the size of the unit cell which, in turn, reduces the Brillouin zone by a factor of two. In actuality, the term shadow band originates from calculations which show a similar folding of a band as expected for long range order in a model where only short range correlations were included.[45] Previously, Aebi *et al.* reported evidence for shadow bands in underdoped Bi2212.[136] However, one is unable to distinguish whether or not the features they observe result from a structural distortion or from underlying antiferromagnetic fluctuations.[137] By contrast, to our knowledge, no structural distortion has ever been reported on any of the doped or undoped oxy-halides.

Further examining the features about $(\pi/2, \pi/2)$, figure 6.3b presents an image plot of the data shown in figure 6.3a. One will notice, as seen in the EDCs, that there is substantial weight after the Fermi crossing. Figure 6.3d shows MDCs at 300 and 600meV binding energy taken from the image plot in figure 6.3b. From this it is clear that a single lorentzian will not suffice to properly fit the data. A second lorentzian is necessary, indicating that the band disperses back as the separation between the two lorentzians grows with increasing binding energy. Finally, the shadow band will also

Figure 6.3: a) and c) EDCs of Na-doped CCOC along high symmetry directions as shown in the cartoon. b) An intensity plot from the spectra shown in a). d) MDCs along $(0,0)$ to (π,π) revealing a band dispersing back. Resolution $\Delta E \leq 23\text{meV}$, $x=0.10$, $T=10\text{K}$, and $E_\gamma=25.5\text{eV}$

Figure 6.4: Comparison of EDCs at selected k points of 10% Dy-doped Bi2212 (taken from ref [71] and 10% Na-doped CCOC (from figure 6.3). The Na-doped CCOC system suggests a much larger pseudogap than in Bi2212, both for the low energy pseudogap (thick bars) and the high energy pseudogap (triangles).

be apparent in the second derivative plot shown in figure 6.5. This demonstrates that a broad feature in Na-doped CCOC pulls back and loses weight rapidly after reaching a maximum near $(\pi/2, \pi/2)$, which we identify as evidence for a shadow band.

Along with the unusual features from $(0,0)$ to (π, π) we also find some surprises in the data from $(0,0)$ to $(\pi, 0)$ to (π, π) which are displayed in figure 6.3c. Although a broad feature is apparent, it never seems to reach the Fermi energy. Instead it simply appears to lose weight as it reaches $(\pi, 0)$ and vanishes completely on its approach to (π, π) . This is in sharp contrast to the data along the nodal direction where a clear Fermi cutoff indicating a Fermi level crossing is observed. In comparison with other

cuprates, the lack of a Fermi cutoff would normally be identified as an extremely large pseudogap, the origin of which, remains as a longstanding question. In an attempt to quantify this suppression of weight, we compare 10% Na-doped CCOC to 10% Dy doped Bi2212[71] in figure 6.4. One clearly observes the loss of spectral weight at the Fermi energy for the Fermi momentum of $(\pi, 0.3\pi)$ when compared to the respective Fermi crossings along the nodal direction near $(0.4\pi, 0.4\pi)$. There are two common methods for characterizing the pseudogap with ARPES. The first, is by the shift of the leading edge midpoint of a spectra to higher binding energy relative to the chemical potential as indicated by the dashed lines. This is typically referred to as the low energy pseudogap. For Dy-doped Bi2212 this is reasonably well defined, and gives a value of 30 meV. For the Na-doped CCOC sample, we find a value of 65 meV at $(\pi, 0.3\pi)$ and 130 meV at $(\pi, 0)$. However, this result is a bit tenuous, as the Na-doped CCOC spectra in figure 6.4 do not provide us with a clear leading edge. In this case we are more inclined to characterize the pseudogap by the high energy pseudogap which is the identification a larger energy scale in the spectra about $(\pi, 0)$, and is sometimes referred to as a “hump”.[74] Here, we find a high energy pseudogap of roughly 300meV for Na-doped CCOC, compared with 120meV for Dy doped Bi2212 as indicated by the triangles in figure 6.4. Independent of the method chosen, the pseudogap for Na-doped CCOC appears significantly larger than that of Bi2212 at a comparable doping level. Notice though, that the pseudogap of 300meV at $(\pi, 0)$ in Na-doped CCOC is comparable to the d -wave gap modulation seen in the half-filled insulator. Indeed, the overall features observed in Na-doped CCOC are quite reminiscent of the features of the insulator.

A final characterization of the data, is that in the vicinity of $(\pi/2, \pi/2)$, the spectra indicate the presence of two components as noted by the tick marks. We will come back to this point in the section on lineshapes.

6.4 Chemical potential shift

As the Na-doped CCOC data suggests a similarity to the half filled insulator we now focus on a more detailed comparison of the doped and undoped oxy-chloride.

Figure 6.5: Second derivative intensity plots of the $x=0.10$ data shown in figure 6.3 and of a half filled sample taken from ref [53]. The dispersion is nearly identical aside from the fact that the insulator lies roughly 700meV below the chemical potential. This suggests a shift of the chemical potential upon doping the antiferromagnetic insulator.

Figure 6.5 plots the second derivative in gray scale of the doped sample first shown in figures 6.3a and 6.3c along side the second derivative of the undoped data in color originally presented in ref [53]. Immediately one will notice that the dispersion is nearly identical. Along $(0,0)$ to (π, π) a band disperses towards the Fermi level, is maximum near $(\pi/2, \pi/2)$, and loses weight rapidly as it pulls back to higher binding energy. Meanwhile, the minimum binding energy along $(0,0)$ to $(\pi, 0)$ to (π, π) lies roughly 300meV below the minimum of the nodal direction. In fact, the only difference between the insulator and the metal seems to be that the band in the metal intersects the Fermi energy near $(\pi/2, \pi/2)$ while the minimum binding energy of the insulator at $(\pi/2, \pi/2)$ lies 700meV below the chemical potential. It appears that the broad features seen in the metal originate from the insulator.

To further support this idea figure 6.6 presents spectra along the entire $(0,0)$ to $(\pi, 0)$ and $(0,0)$ to (π, π) lines, with the chemical potential of the insulator shifted by 650meV. Along $(0,0)$ to $(\pi, 0)$ the spectra are remarkably similar. In many instances fine details of the line shape match perfectly. For example, a second broad component in the electronic structure can be observed at roughly 600meV higher binding energy

from the first feature.¹ This indicates that upon doping, the chemical potential simply drops to the top of the valence band similar to the case of an ordinary band material. This would naturally explain the large high energy pseudogap seen at $(\pi, 0)$ as a remnant property of the insulator as first suggested by Laughlin.[44, 53] The apparent discrepancy between 650meV and 300-400meV obtained by the low energy and valence band spectra, respectively, is due to different pinning sites for different insulating data sets as discussed earlier.

Along $(0,0)$ to (π, π) the situation is less clear. As the feature moves towards lower binding energy a sharp Fermi cutoff appears in the metallic samples, as anticipated by the large peak at the Fermi level from the energetically shifted spectra of the insulating sample. However, the match between the spectra becomes increasingly worse as $(\pi/2, \pi/2)$ is approached. The weight at $(\pi/2, \pi/2)$ is simply suppressed relative to the insulator, perhaps simply indicating that a Fermi crossing has indeed occurred before $(\pi/2, \pi/2)$. The Na-doped CCOC sample was even rotated by 45 degrees for the $(0,0)$ to (π, π) cut relative to the other three sets of data so as to maximize the cross section along the nodal direction for an initial state with $d_{x^2-y^2}$ symmetry. Perhaps this indicates that increased scattering which could effectively smear out the k resolution, and thus have the greatest effect where the dispersion is the steepest, is responsible for this suppression. However, this would require a nontrivial scattering mechanism, which does not simply produce an angle averaged background. Also, the cleavability of the Na-doped compounds is the same as the parent insulator, and laser reflections from the sample indicate flat surfaces, which argue against angle averaging as the cause for the observed suppression of weight. Typically, highly angle dependent valence band spectra as shown in figure 6.1 are indicative of a good surface, although the Na-doped valence band features are somewhat broader than in the case of the insulator. In this regard, a broadened feature at $(\pi/2, \pi/2)$ is not unexpected considering the observation by Pothuizen *et al.* who noted that in SCOC the lineshape of the 2eV binding energy peak at (π, π) is identical to the lineshape of the Zhang-Rice singlet at $(\pi/2, \pi/2)$. [55] This suggests that the small differences between the doped system and the half filled insulator may indeed result from a difference in sample

¹A brief discussion on this high energy feature is in chapter 5

Figure 6.6: EDCs of $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ (blue) taken from ref [53] are shifted by 650meV and are compared with EDCs of 10% Na-doped CCOC (black). The overlap is extremely good with the exception of the features near $(\pi/2, \pi/2)$. The data is normalized at high binding energy for comparison. The slight rise in spectral weight above E_F observed in some EDCs of CCOC is due to the presence of a core level excited by second order light. This is not present in the metallic sample where the second order light contribution is heavily suppressed by the use of a normal incidence monochromator as opposed to a grazing incidence monochromator for the insulating data. $E_\gamma=25.5\text{eV}$, $T=100\text{K}$ and 10K for $x=0$ and $x=0.1$, respectively.

quality.

6.4.1 E_γ dependence versus the Insulator

Considering that the features of hole doped CCOC track the dispersion of the features in the half filled insulator, one might wonder exactly how similar the electronic states are for the two doping levels. As previously discussed in this dissertation, the spectral function of interest is modulated by a matrix element which under the dipole approximation can be written as $|\langle \Psi_f | A \cdot p | \Psi_i \rangle|^2$ where $\Psi_{i,f}$ are the initial and final state wavefunctions, and $A \cdot p$ is the perturbing Hamiltonian (See chapter

Figure 6.7: Photon energy dependence along the nodal direction for $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ for $x=0.1$ and $x=0$. For each doping, the same k range is shown, while the photon energy is indicated in each panel. $T=10\text{K}$ and 293K for $x=0.1$ and 0.0 , respectively. Notice, that the modulation of intensity varies with photon energy in a similar fashion for both dopings.

2 for more details). Practically, this means that the cross section of all the initial states will depend on the photon energy and experimental geometry. In chapter 5, we showed that CCOC experiences a fairly sharp modulation of intensity along the nodal direction from 16.5 to 17.5eV. In figure 6.7, we compare the EDCs along the nodal direction of a 10% Na-doped CCOC sample and undoped CCOC using 16.5eV and 17.5eV photons. We notice that the change in the modulating intensity on going from $E_\gamma=16.5$ to 17.5eV is similar for both samples. Namely, for 16.5eV there is much more intensity at $(\pi/2, \pi/2)$ and higher k values, which vanishes on going to 17.5eV. Even the existence of the second feature at 600meV higher binding energy from the lowest energy feature can be seen in the Na-doped sample along the nodal direction. These results show that the wavefunction of the electronic states within 2eV of the chemical potential discussed thus far are remarkably similar. Along with the shift in dispersion of the low energy states and the valence band on the order of 0.5eV, this data shows conclusively that the chemical potential indeed shifts upon doping the half filled insulator, $\text{Ca}_2\text{CuO}_2\text{Cl}_2$.

6.5 Fermi Surface Arc

Naively, in a simple band picture, a rigid chemical potential shift to the top of the valence band of the insulator would thus result in a Fermi surface consisting of four small hole pockets centered at $(\pm\pi/2, \pm\pi/2)$. Figure 6.8 presents an intensity plot of the low lying excitations (ie the Fermi surface) of a $x=0.10$ Na-doped CCOC sample by integrating the photoemission spectra with a $\pm 10\text{meV}$ window about the Fermi energy. The plot shows a maximum slightly before $(\pi/2, \pi/2)$ indicative of a Fermi level crossing. On going from the nodal direction towards $(\pi, 0)$ the intensity is quickly suppressed as the large pseudogap removes the majority of low energy spectral weight. The dotted line indicates the identifiable Fermi crossings for cuts perpendicular to the antiferromagnetic zone boundary. Note that this low energy integration window gives no indication of a second crossing on the opposite side of the antiferromagnetic zone boundary. There are a few possible explanations for this absence. The shadow band may be asymmetric about the antiferromagnetic zone boundary, causing its

Figure 6.8: Intensity Plot of the low energy excitations. (red is maximum) The dotted line is a guide to the eye, indicating where a clear Fermi cutoff was identified. The black lines mark high symmetry directions through the Brillouin zone. Resolution $\Delta E \leq 14\text{meV}$, $x=0.10$, $T=22\text{K}$, the integration window is $\pm 10\text{meV}$ about the Fermi energy, and $\text{HeI}\alpha$ radiation ($E_\gamma=21.2\text{eV}$) was used as the photon source.

Fermi crossing to occur at the same momenta as the main band. Alternatively, the coherence factors associated with the shadow band are possibly such that the second crossing is indistinguishable from the background signal.[45] The latter scenario would be surprising considering that the shadow band is clearly evident at higher binding energies. This suggests that perhaps the shadow band and the low energy excitations responsible for the image in Figure 6.8 result from two separate components of the spectral function: a high energy one associated with the observed shadow band, and a separate component responsible for the Fermi surface which is most well described

as a Fermi Arc about $(\pi/2, \pi/2)$. Below we will see more evidence for this picture.

6.6 Lineshapes and Dispersion

We begin an examination of the lineshapes with another look at the spectra near $(\pi/2, \pi/2)$. From the earlier cleave presented in figure 6.3 we alluded to the existence of two components in the electronic structure near $(\pi/2, \pi/2)$. Figure 6.9 presents EDCs perpendicular to, and along the Fermi arc shown in figure 6.8. Now, in the

Figure 6.9: EDCs perpendicular to and along the Fermi arc of figure 6.8, as indicated by the cartoon above the respective stack of EDCs. Note that two components can be seen for the spectra in the vicinity of k_F along the nodal direction. $x=0.10$, $T=22\text{K}$, and $\text{HeI}\alpha$ radiation ($E_\gamma=21.2\text{eV}$) was used as a photon source.

vicinity of the Fermi crossing in the nodal direction, two components in the EDCs are clearly observed. The higher energy feature loses weight rapidly as it pulls back away from the Fermi surface in a fashion reminiscent to the insulating feature as discussed earlier, while the sharper, lower energy feature appears to have a more conventional behavior associated with a Fermi crossing. From $(0,0)$ to (π,π) this feature emerges from the higher energy feature on its approach towards $(\pi/2, \pi/2)$, sharpens, and then, crosses the Fermi level. The loss of the two component structure as one approaches $(\pi,0)$ is again indicative of the observed large pseudogap, which precludes the identification of any similar structure in the low energy excitations near $(\pi,0)$. The reason for the difference in clarity of this structure between cleaves is unknown, but may be due to a variation of inhomogeneities and experimental conditions between different cleaves. Note, that the presence of the sharp low energy feature is a tribute to the high quality of these samples.

An alternative method to study the electronic structure is through the use of MDCs. In figure 6.10a we present MDCs along the nodal direction for the same data presented in figure 6.9 as EDCs. The red curves show the quality of single lorentzian fits to selected MDCs. Similar good agreement in other cuprates has been used as justification for extracting self energies from the fit parameters, as discussed in chapter 2 [138, 139, 140]. In the following section we will perform a similar analysis, but here they simply serve as a method for parameterizing the observed dispersion. Figures 6.10b and 6.10c plot the peak positions and widths as a function of the binding energy of the corresponding MDCs. A change of slope in the dispersion of the peak positions at 56meV is indicated by the arrow. This value is attained from the intersection of two linear fits ranging from 0 to 30meV and 100 to 200meV. We shall refer to this feature as a “kink”. A similar kink in other cuprate systems has received significant attention in recent ARPES literature.[139, 140, 141, 142] Another change in slope at roughly 350meV is ignored as it is likely to be an artifact of matrix elements and contributions from a broad band roughly 600meV higher in binding energy. Note, that the width of the peak is roughly linear at very high energy, but there also appears to be a more rapid change in width at approximately 80meV binding energy.

A peculiar feature of the MDCs in figure 6.10 is that the shadow band which we

Figure 6.10: a) Sample MDCs of the nodal direction data from figure 6.9. Single lorentzian fits to selected MDCs are overlayed in red. Respectively, b) and c) give the peak positions and widths (half width at half maximum) from the MDC analysis. The arrow in b) indicates the kink energy, as discussed in the text.

had discussed before is not evident in this set of data. To understand this, one must realize that the photon energy was different between the two cleaves shown in figure 6.3 and figure 6.9. This indicates that matrix elements are responsible for determining the relative intensity between the main band and the shadow band. Thus, by varying the photon energy we may hope to bring to light all the different excitations in the system even if they are not all present at one single photon energy. In figure 6.11 EDCs of yet another cleave, this time a $x=0.12$ Na-doped CCOC sample, is presented along the nodal direction for two different photon energies. At $E_\gamma=16.5\text{eV}$ the peak-dip-hump structure is clearly observed, while at $E_\gamma=21.0\text{eV}$ the hump is suppressed

Figure 6.11: EDCs from a $x=0.12$ sample along the nodal direction for two different photon energies. Note that the broad high energy hump is suppressed upon changing to the higher photon energy. The dashed lines mark the dip position in the $E_\gamma=16.5\text{eV}$ data, and are redrawn on the $E_\gamma=21.0\text{eV}$ data. Resolution $\Delta E \leq 15\text{meV}$, and $T=8\text{K}$. Other than the photon energy and an adjustment of the outgoing electron angles in order to measure the same k range, the measurement conditions are identical.

to the extent that a dip is no longer observed at k_F . Although we can not distinguish whether the hump feature has been suppressed or the sharp peak has been enhanced, it is clear that the ratio of the two peaks varies significantly with photon energy.

Next, let us examine the MDC analysis which further illustrates the differences between the two photon energies. From the MDCs in figure 6.12 it is clear that two lorentzians are necessary for a reasonable fit to the $E_\gamma=16.5\text{eV}$ data, while a single lorentzian is sufficient at $E_\gamma=21.0\text{eV}$. Again we see an instance where the shadow band is present under one set of experimental conditions and not the other. What is remarkable is that the shadow band in the $E_\gamma=16.5\text{eV}$ data becomes weaker as one approaches the Fermi energy, while the main band sharpens and is more well defined. This is completely counterintuitive. One would expect that the coherence factors

Figure 6.12: Sample MDCs from the data in figure 6.11. Fitting curves are in color. Note that two lorentzians are necessary to fit the $E_\gamma=16.5\text{eV}$ data, while a single lorentzian is sufficient for the $E_\gamma=21.0\text{eV}$ data.

which regulate the intensity of the shadow band to become stronger, not weaker, as the Fermi energy is approached. Thus, either the low and high energy parts of the shadow bands have different origins, or their wave functions have significantly different character which permits one to find a photon energy where the low energy portion of the shadow band is suppressed relative to the high energy part. In the latter case, one would expect that by searching hard enough one should be able to find a situation where the converse is true, which to this point we have not. In any event, this certainly is not a typical shadow band.

From the MDCs one can extract the dispersion of the various features by fitting the peaks to one or more lorentzians. The peak positions from the fits to the data in figure 6.12 are shown in figure 6.13. If one could legitimately identify the peak positions with a single dispersing band with a corresponding shadow, then the $E_\gamma=16.5\text{eV}$ data would be quite remarkable. It shows a kink in the main band near 50meV as observed before, while the shadow band exhibits a much steeper dispersion, a Fermi crossing which is not symmetric to the main band with respect to the antiferromagnetic zone boundary, and a possible kink, which is very difficult to identify if it exists at all. Meanwhile, the MDC data in figure 6.10 and the $E_\gamma=21.0\text{eV}$ data in figure 6.12 lack the second component expected for a band which is bending back. A second lorentzian indicating the existence of a shadow band can not be ruled out, but the quality of the single lorentzian fits implies that the matrix elements conspire such that it does not give a significant contribution under these experimental conditions. Note that when using polarized 21eV photons, the sharp feature which appears to cross the Fermi energy is significantly enhanced relative to the hump like feature as seen by the EDCs in figure 6.11. This fortuitous photon energy is thus the best opportunity for an MDC analysis to examine the details of the dispersion of this seemingly isolated band. In figure 6.13 the $E_\gamma=21.0\text{eV}$ peak position data also show a rounded kink at 50meV. This suggests that an energy scale of roughly 50meV indeed exists in Na-doped CCOC as indicated earlier in figure 6.10. It is remarkable that despite the tremendous variation in photon energy which calls into question the assignment of a single feature in the MDC analysis, particularly at $E_\gamma=16.5\text{eV}$, the kink in the main band lies at the same energy independent of the conditions.

Figure 6.13: Peak positions of the lorentzian fits of the MDCs shown in figure 6.12 for a $x=0.12$ sample. The blue lines are guides to the eye. Note the “kink” position of roughly 50meV in the main band dispersion at both photon energies, while the shadow band has a significantly steeper dispersion. The dashed lines are the same as those in figure 6.11 where they were marking the boundary of the dip location in the $E_\gamma=16.5$ eV data. Here they serve well to mark the approximate kink position of the main band.

The k dependence of the kink is not clear. It appears to be washed out as one moves away from the nodal direction, but this may be a combination of two effects. First, the dispersion flattens out at higher energy as one approaches the Van Hove singularity, and second the high energy pseudogap removes spectral weight which prevents a clear identification of the dispersion near E_F . Samples where the high energy pseudogap is not as imposing will be necessary to elucidate the k dependence of the kink.

6.6.1 Temperature dependence of the peak-dip-hump

The peak-dip-hump structure in Na-doped CCOC may remind one of the peak-dip-hump structure first seen in Bi2212[143, 144], and now in YBCO[145] and Bi2223[146] as well. The striking aspect of this feature in Bi2212, Bi2223, and YBCO is that the peak appears to turn on at T_c . However, one should note that the peak-dip-hump structure observed here is along the nodal direction, while in the others it is seen at $(\pi, 0)$. So one would like to know if the peak-dip-hump structure observed in Na-doped CCOC is at all related with T_c . Figure 6.14 shows a temperature dependence of EDCs along the nodal direction which display the peak-dip-hump structure at 10K. It is clear that this structure survives well past the transition temperature of 22K all the way to 75K, after which it becomes smeared out. The temperature was then cycled back down to 10K to ensure that the broadening was not due to an aging

Figure 6.14: Temperature dependence of EDCs along $k_x=k_y$ taken with $E_\gamma=16.5\text{eV}$, and $\Delta E \leq 15\text{meV}$. The spectra were taken from left to right as a function of time. As $T_c=22\text{K}$ for this $x=0.12$ Na-doped CCOC sample, we see that the two component structure observed here is not related to superconductivity.

sample. Therefore the peak-dip-hump structure in the nodal direction of Na-doped CCOC is certainly not a result of superconductivity. The MDC analysis of this data is similar to the $E_\gamma=16.5\text{eV}$ data shown in figures 6.12 and 6.13. The peak position of the main band as a function of temperature is shown in figure 6.15, from which, it can be seen that the kink is also unaffected through T_c .

Figure 6.15: Peak positions of the main band in an MDC analysis of the data shown in figure 6.14. They have been offset in k for clarity, and the second band necessary for a reasonable fit to the data is not shown. The solid lines are guides to the eye, and the dashed lines give estimated limits for the energy of the “kink”, and the data were taken from left to right as a function of time.

6.6.2 Self Energy, Σ

As the $E_\gamma=21.0\text{eV}$ data suggests that only a single component has a significant contribution to the observed spectra, it is tempting to assign the lorentzian fit parameters to expressions containing the real and imaginary parts of the self energy, as discussed in chapter 2. To do this one must first make an assumption on the form of the bare dispersion, ϵ_k . Here, we let $\epsilon_k = v_F \cdot (k - k_F)$, and determine v_F by setting $\text{Re}\Sigma(-0.2\text{eV}) = \text{Re}\Sigma(E_F) = 0$. The choice of -0.2eV is arbitrarily chosen so as to

lie at a higher binding energy than the kink energy scale, but at energies less than where the fits give a non-sensical dispersion. This choice is consistent with previous studies [140, 142], where -0.2eV is chosen because at higher binding energy a single lorentzian no longer produces a satisfactory fit. The quality of the single lorentzian fits here up to 500meV is likely to be accidental, as a second high energy component exists. The fact that we can not identify a clear point at which the MDC analysis begins to fail brings into question the validity of this procedure as a whole. However, we proceed on the assumption that setting $\text{Re}\Sigma = 0$ as done for Bi2212 and LSCO is also reasonable for Na-doped CCOC. This gives $v_F = 4.93\text{eV}\text{\AA}$, and the resulting real and imaginary parts of the self energy are shown in figure 6.16.

From $\text{Re}\Sigma$ we see the effect of the kink near 60meV, and the arbitrary nature of setting $\text{Re}\Sigma = 0$ at -0.2eV. Note however, that setting $\text{Re}\Sigma = 0$ at any other value would not affect the qualitative features observed here. Now, let us assume that we can break up the self energy into three terms: electron-electron, electron-phonon and impurity scattering. For the imaginary part of the self energy we can take the impurity contribution to be a constant, and in a simple model the electron-phonon term will also be a constant above the Debye frequency. Thus electron correlations are solely responsible for the high energy part of $\text{Im}\Sigma$ under these approximations. In figure 6.16 we fit the imaginary part of Σ from -0.2 to -0.3eV with both a quadratic term and a linear term. The former being representative of a Fermi liquid scenario, while the latter is expected for a marginal Fermi liquid. Aside from the constant impurity term determined by $\text{Im}\Sigma(E_F)$, the residual contribution, given by the dotted lines, is presumably purely an electron-phonon scattering term. Interestingly, the point of steepest descent of the electron-phonon contribution, independent of using the quadratic or linear fit, is roughly 50meV, which is equal to the kink energy which we identified earlier. The near linear scattering rate seen here in $\text{Im}\Sigma$ up to high energies is reminiscent of marginal Fermi liquid behavior.[147] However, if a pure marginal Fermi liquid picture were responsible for the observed behavior of the self energy then a sharp kink can not exist as there is no additional energy scale associated with such a picture. The sharpness of the kink is currently under debate in the Bi2212 system,[140, 142, 148] and unfortunately, is equally unclear here. Note that although

Figure 6.16: Self energy extracted from the lorentzian fits of the $E_\gamma=21.0\text{eV}$ MDCs shown in figure 6.12. The bare dispersion was taken to be $\epsilon_k = 4.93\text{eV}\text{\AA}(k - k_F)$. The solid blue and red curves are quadratic and linear fits, respectively, to $\text{Im}\Sigma$ from -0.3 to -0.2eV, and the dashed curves are the residual contributions taking into account a constant impurity scattering term and shifting the solid fit curves to 0 at E_F . As discussed in the text, the solid and dashed curves refer to the electron-electron, and electron-phonon scattering terms respectively.

both electron-phonon scattering and marginal Fermi liquid have been proposed to explain the MDC dispersion separately, they are not mutually exclusive.

Finally, in comparing the $\text{Im}\Sigma$ from Na-doped CCOC and that of Bi2212 we find that the magnitude of the scattering rate is much larger in the oxychloride. There are two reasons for this. The first is clearly that the MDC width is somewhat broader than in Bi2212. The larger widths are also apparent in an EDC comparison. However, as great a factor as the broad widths, is the value for v_F . The dispersion here is much steeper than that found in Bi2212, by almost a factor of 2. Since $\text{Im}\Sigma = v_F \cdot \Delta k$ this will result in significantly larger scattering rates. It is amazing that the present value of $4.93\text{eV}\text{\AA}$ is roughly equal to the band calculation result of $5\text{eV}\text{\AA}$ [13, 95]. Typically, smaller values will be found when using data sets where the shadow band is seen clearly. This suggests that the shadow band may act to give a steeper dispersion if one is forced to use only a single lorentzian to fit the broad MDCs.

6.7 Doping Evolution

We now focus on the limited doping dependence data we have. The two concentrations studied aside from the half filled insulator were $x=0.10$ and $x=0.12$ samples with superconducting transitions of 13K and 22K respectively. The results are so similar that they have been used interchangeably in the previous sections. Figure 6.17 compares E_F intensity plots for the two different dopings under identical experimental conditions. The plots were oriented by symmeterizing dispersive features about high symmetry points. The three local maxima near $(+\pi/2, +\pi/2)$ for $x=0.12$ is an artifact of the linear interpolation used to generate the plots. Otherwise, they

Figure 6.17: Intensity plots of the low energy excitations for two different dopings indicated in the plots. The bold lines mark the Brillouin zone boundary, while the thinner lines are guides to the Γ to $(\pi,0)$ direction. The integration window for the $x=0.10$ ($x=0.12$) sample was $\pm 20\text{meV}$ ($\pm 15\text{meV}$) about the Fermi energy, and the sampling density was roughly $3000\text{pts}/(2\pi/a)^2$. The two sets of data were taken at 10K with 25.5eV photons and with the in-plane component of the electric field along the horizontal axis.

give nearly identical results. Even the asymmetry of intensity about $(0,0)$ to (π,π) due to the matrix elements is the same. An interesting difference is that the maximum intensity along the nodal direction occurs at 43% of the cut for $x=0.10$ and at 41% for $x=0.12$. This may be a fortuitous result given the uncertainty in orienting the samples, but none the less, is consistent with an increased hole concentration. In figure 6.18 EDCs for the $x=0.12$ sample are compared with the $x=0.10$ data shown in figure 6.3 taken under identical conditions. From $(0,0)$ to $(\pi,0)$ to (π,π) the spectra are similar, while indicating that the pseudogap is closing for increased hole doping as is seen universally in the cuprates. For $(0,0)$ to (π,π) , the $x=0.12$ sample shows a more well defined Fermi crossing and more intense structure at k_F . Also, the suppression of the shadow band like feature with increased hole doping is consistent with the idea that it originates from the antiferromagnetic correlations which are reduced with doping. Finally, the MDC analysis showed no difference in v_F , the kink position, or the widths over this very limited doping range.

6.8 Temperature Dependence

The lack of temperature dependence of the peak-dip-hump like structure through T_c has already been discussed. Here we make a careful comparison to see if any temperature dependence can be observed other than the expected thermal broadening. The data in figure 6.19 shows that there is no temperature dependence up to 150K along $(0,0)$ to (π,π) other than thermal broadening of the Fermi cutoff. This observation is consistent with the idea that the temperature dependence which is observed in the insulator is a result of antiferromagnetic correlations causing a transfer of spectral weight observable with changing temperature.[149] In this picture the amount of temperature dependence should decrease with decreasing correlations as observed. In reality, other factors are also necessary to account for the full temperature dependence observed.

As a longshot, we tried to find evidence for a gap opening with T_c at the edge of the Fermi arc, which might distinguish the superconducting gap from the pseudogap. This is the most likely location to find such a dependence as further towards $(\pi,0)$

Figure 6.18: a) and b) EDCs of a Na-doped $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ sample with $x=0.12$ ($T_c=22\text{K}$) along high symmetry directions. The measurement conditions were identical as for the data presented in figure 6.3 on a sample with $x=0.10$ which is compared along the nodal direction in c) by normalizing at -0.7eV . For $x=0.12$ the Fermi level crossing along the nodal direction is more well defined, and the shadow band like feature is more difficult to detect. d) demonstrates that the high energy pseudo-gap closes with increased doping, but is still much larger than the Dy-doped Bi2212 sample with $T_c=65\text{K}$.

Figure 6.19: Temperature dependence through k_F along the nodal direction of a $x=0.10$ Na-doped CCOC. The broadened spectral features relative to other cleaves presented in this chapter indicate that this surface was not as clean or well-ordered as the others. The photon energy was 25.5eV , and $\Delta E \leq 20\text{meV}$.

the large pseudogap prevents us from identifying a well defined leading edge, while along $k_x = k_y$ no gap is detected as would be expected if Na-doped CCOC is indeed a d -wave superconductor. Figure 6.20 shows the lack of temperature dependence on the leading edge of the spectra at the edge of the Fermi arc. The small size of the Fermi step is a result of examining the Fermi crossing away from the nodal direction. Had we moved any further towards $(\pi, 0)$ the high energy pseudogap would have suppressed all the weight at the chemical potential, and no Fermi cutoff would be visible.

Figure 6.20: Temperature dependence of the leading edge midpoint at k_F near the edge of the arc(as illustrated by the cross in the cartoon). $T_c=13\text{K}$ and the photon energy was 25.5eV , and $\Delta E \leq 15\text{meV}$.

6.9 Discussion with other Cuprates

There are several unusual features in the photoemission data of $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$. In this discussion we will focus on the large pseudogap, the origin of the peak-dip-hump like structure in the nodal direction, the observation of shadow bands with some strange features, as well as the chemical potential shift as a function of doping, and the resulting Fermi surface. We begin with the extremely large pseudogap in $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ as seen in figure 6.4. What is the implication for such a large pseudogap relative to the Bi2212 system at comparable doping? The high energy pseudogap may simply indicate that the Van Hove singularity is located at higher binding energy in Na-doped CCOC compared with Bi2212. If the condensation energy for superconductivity is acquired by the gapping of low energy states near $(\pi, 0)$, then this would result in superconductivity being less favorable as evidenced by the smaller optimal T_c (28K and 90K for NaCCOC and Bi2212, respectively). With regards to the low energy pseudogap, some believe that its existence is a result of preformed Cooper pairs which lack the phase coherence necessary for superconductivity.[150, 75, 78] In contrast with the aforementioned optimal transition temperatures for the two systems,

a simple BCS picture expects that stronger pairing leads to a larger T_c . However, the low energy pseudogap in the cuprates has been observed to increase even though T_c decreases in the underdoped regime. Thus the larger low energy pseudogap in $\text{Ca}_{2-x}\text{Na}_x\text{CuO}_2\text{Cl}_2$ is also consistent with the phenomenology of the cuprates. We note that a smaller low energy pseudogap in the data is still quite conceivable, as the high energy pseudogap may have completely suppressed all low energy spectral weight near $(\pi, 0)$. Only after the high energy pseudogap vanishes could one then clearly identify the low energy pseudogap. This obviously would necessitate differing origins for the high and low energy pseudogap. We leave this as an open question.

The high energy pseudogap seen in Bi2212 was first conjectured by Laughlin to be a result of the d -wave-like modulation of the dispersion which is seen in the insulating oxy-halides.[44, 53] Due to the observed shift of the chemical potential it is clear that the high energy pseudogap indeed directly results from the dispersion seen in the parent compound, although it appears that the energy scales of the high energy pseudogap have a small system dependent variation. Furthermore, the doping dependence reveals that the high energy pseudogap in Na-doped CCOC is closing with increased hole concentration in agreement with previous observations.[74]

Along $(0,0)$ to (π, π) an increasingly more common feature in ARPES data on cuprates was found, namely, a peak-dip-hump structure. We now address the possible origins for such a feature. Pure macroscopic phase separation can be ruled out, since the insulating feature would not have shifted to the chemical potential in this case. Furthermore, unless a specific doping level were energetically favorable one would expect that a distribution of doping levels would prevent any sharp features. The spin density wave picture presented by Kampf and Schrieffer suggests an appealing candidate. They find a sharp, coherent peak growing with doping, while the incoherent features at half filling slowly vanish.[45] This result is similar to the recent phase string calculations done by Muthukumar, Weng, and Sheng.[151] In this sense, the two components would hint at a balance between the antiferromagnetic insulator and the drive for the system to become metallic. An alternative scenario is that the peak-dip-hump structure is the result of coupling to a collective mode, which would also naturally explain the presence of the kink. A kink in the nodal direction

is now seen almost universally in the cuprates,[140] and is surprisingly robust in Na-doped CCOC given the spectral variation as a function of photon energy. Although still controversial, Lanzara *et al.* propose that the kink is due to electron-phonon coupling.[140] In this regard, it is interesting to note that the phonon breathing mode is expected to be roughly 10meV less for CCOC on the basis of its a-axis lattice constant than in the case of insulating Bi2212 or LSCO as determined by optics,[152] while the kink energy determined by ARPES is less by roughly the same amount.

Distinguishing between these two scenarios will be difficult. The problem with the picture from Kampf and Schrieffer would be that the kink would have to be explained as an artifact of the MDC analysis due to the multiple electronic features which are not individually resolved. The main problem with the coupling scenario, is that it can not easily explain why the shadow band is not observed at E_F . The coherence factors predominantly responsible for the intensity of the shadow band should get stronger, not weaker, as the Fermi energy is approached. It is possible that the matrix elements have masked the low energy portion of the shadow band, which will be revealed if the proper photon energy is used, but this is yet to be found. Finally, there is a possibility to combine these two pictures, which would resolve both of these issues. Namely the fact that only a single coherent band crosses the Fermi energy explains why the shadow band is absent at E_F , while the coupling to a collective mode creates the observed kink. Unfortunately, the present data can not distinguish between these three possibilities, and we must leave this as an opportunity for future experiments to investigate.

Independent of the origin of the electronic structure observed in the Na-doped CCOC data, the implications for the electronic evolution across the metal to insulator transition differ markedly from those found in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ (LSCO) system. Most notably, the doping dependence of LSCO suggests that the chemical potential remains fixed, while states are created inside the gap upon doping.[42] Here the fingerprints of the antiferromagnetic insulator in the Na-doped samples can naturally be explained by a shift of the chemical potential to the top of the valence band. However, as Na-doped CCOC samples between $x=0$ and $x=0.1$ are not yet available, we can not discern whether the chemical potential shifts continuously, in a single

discontinuous jump, or by a manner which lies between these two extremes.

Aside from the difference in doping dependence, LSCO and Na-doped CCOC superconducting samples have another dramatic difference in their electronic structure. The predominance of low energy spectral weight in LSCO occurs near $(\pi, 0)$. [42, 47] This situation is similar in Bi2212 crystals. [153] The low energy spectral weight in Na-doped CCOC is strikingly different, as shown in figures 6.8 and 6.17, where the predominance of weight occurs near $(\pi/2, \pi/2)$. This is partially due to the large pseudogap seen in this material about $(\pi, 0)$. In LSCO the one dimensional structure of the intensity maps near $(\pi, 0)$, are attributed to dynamical stripes, a form of spin and charge ordering. [42, 47] These are the states which have been created inside the charge transfer gap. However, in Na-doped CCOC, the fingerprints of the insulator which reveal the chemical potential shift indicate that the low energy excitations should be found near $(\pi/2, \pi/2)$. We note that there may be some ambiguity in the exact doping level used in this study, but regardless, a difference between LSCO and Na-doped CCOC will remain. For instance, if the doping is less than $x=0.10$, then one would expect to clearly see the two components in the electronic structure separated by a large energy as is the case in LSCO which indicated that states are created inside the gap [42]. On the other hand, if the doping level is as we believe or larger then the pseudogap is extremely large compared with similar doping levels of LSCO and Bi2212.

Why is the oxychloride system so strikingly different compared to other cuprates such as LSCO and Bi2212? Structurally, the main difference lies in the apical site (chlorine versus oxygen). Na-doped CCOC also retains its tetragonal nature much better than LSCO² or Bi2212, implying larger hopping integrals. [155] Perhaps these slight structural differences help stabilize various different phases with respect to one another. Such a dependence, particularly on the apical site, would be surprising considering that it is generally accepted that the physics of the cuprates is dominated

²Although the LTT phase of LSCO is tetragonal at low temperature, it differs from the high temperature tetragonal phase which is observed in Na-doped CCOC down to 10K. The later has a space group of $I4/mmm$, while the former has a space group of $P42_1ncm$ which results from additional tilting of the CuO_6 octahedra causing a four-fold increase of the unit cell in the a-b plane. [154]

by the CuO_2 planes. Such high sensitivity to seemingly insignificant details could necessitate the explanation that these systems lie in close proximity to a quantum critical point. This would naturally explain how stripes could be favored in one system and not another system which is almost identical.

As the electronic evolution apparently differs from LSCO, we comment briefly here on a few alternative theories for the Fermi surface evolution which are illustrated in figure 6.21. The LDA Fermi surface gives a hole-like Fermi surface centered at (π, π) which is destroyed as electron correlations are turned on. In a theory where umklapp scattering is believed to create gaps in both the spin and charge channels when the umklapp surface (equivalent to the antiferromagnetic zone boundary in this case) intersects with the underlying Fermi surface, Fermi arcs have been predicted for the underdoped cuprates which appear consistent with the Na-doped CCOC data presented in figure 6.8.[46] However, the shadow bands demonstrated in figure 6.3 seem to escape this formalism. Alternatively, the RVB flux phase,[156] or the more general arguments made by Chakravarty *et al.* [157] naturally contain shadow bands. In this case the Fermi surface is predicted to appear as four hole pockets centered about $(\pm\pi/2, \pm\pi/2)$, which would continuously transform into the large hole-like Fermi surface in heavily overdoped samples. It is possible that the coherence factor for the shadow band prevents the identification of a second Fermi crossing, but then it is surprising that we observe this feature at higher binding energy. The Na-doped CCOC system provides a new playground for these other theories, which previously seemed less compatible with the cuprates.

Finally, here we speculate on a few ways to reconcile the outstanding differences in the LSCO and Na-doped CCOC systems. As mentioned above, the path of the chemical potential shift in Na-doped CCOC is unknown. The only way to reconcile the chemical potential shift with the lack thereof in the data from LSCO,[41] is to claim that the chemical potential jumps to the top of the valence band the moment a few holes are doped into the system, and that the LSCO which has been studied at “ $x=0$ ” actually has a few holes already doped into it. The latter claim is reasonable considering that LSCO is relatively easy to dope, while the oxy-halides have only been doped with extremely high pressure synthesis techniques, and may therefore be truly

Figure 6.21: Theoretical Fermi surfaces obtained for a CuO_2 plane from a) LDA[113], b) truncation of a 2D Fermi surface due to umklapp scattering[46], c) RVB/flux phase approach[156], and d) stripe models from vertical and horizontal domains of disordered stripes[158]. (Figure from ref. [159])

regarded as half-filled. In a band insulator, the addition of a single hole indeed causes the chemical potential to jump to the top of the valence band. Similar behavior in the case of the cuprates is initially counterintuitive based on the fact that the Mott gap is created by electron correlations which are not easily destroyed. However, naive expectations of a Hubbard model would also expect a jump in the chemical potential. Similarly, Quantum Monte Carlo calculations of a projected $\text{SO}(5)$ also predict such a behavior while reproducing the chemical potential vs doping curve for LSCO [160]. Note that in these cases, the system could still be insulating as the doped holes would remain localized by the strong antiferromagnetic correlations. The problem associated with the picture presented here, is that the top of the valence band, refers in Na-doped CCOC to the centroid of the feature at $(\pi/2, \pi/2)$ which has shifted to the Fermi energy. Meanwhile, in LSCO at $x=0$, a structure similar to that seen in CCOC, lies roughly 0.5eV below E_F . If the chemical potential has already shifted to the top of the valence band in this LSCO sample, then why is this feature, identified with the insulator, at such high binding energy? In the case of undoped CCOC

multiple electronic components were identified with strong matrix element variations, opening the possibility that the features in LSCO may not be identical to those seen in the oxy-halides (See chapter 5). This, however, requires more investigation. Interestingly, the tail of the -0.5eV feature in LSCO only vanishes once it reaches the chemical potential. The origin of this spectral weight is unknown, but may explain why the chemical potential is unable to shift any further in the LSCO system. Lastly, it is interesting to note that in both LSCO and Na-doped CCOC it appears that states are created at the chemical potential with doping. The difference is that in LSCO the states are created near $(\pi, 0)$ while in the oxy-chloride they appear near $(\pi/2, \pi/2)$. Hopefully, the improving spectral quality of LSCO and the increase of available doping levels for Na-doped CCOC will resolve these issues.

6.10 Conclusions

This has been the first ARPES measurement on a doped single crystal oxychloride cuprate. The chemical potential is observed to shift to the top of the valence band upon doping. This results in the observed shadow band and a large pseudogap characterized by a 130meV leading edge midpoint at $(\pi, 0)$. Remarkably the shadow bands have little weight at the Fermi energy, and thus the low energy excitations are more well described as a Fermi arc than as hole pockets. Surprisingly, the results in this chapter appear to present a different evolution across the metal to insulator transition than what was found in LSCO where the chemical potential remained fixed with doping. Furthermore, a two component structure near $(\pi/2, \pi/2)$ is also observed. While coupling to a collective excitation could give such a structure, and explain the observed kink in dispersion at 50meV attained by an MDC analysis, this does not immediately explain why the shadow band loses intensity as it approaches the Fermi level. Alternatively, the two components may be the result of coherent states being created on top of the incoherent background of the insulator, but this does not have a satisfactory explanation for the observed kink. Unexpectedly, we have found that the Na-doped CCOC system casts a new paradigm in the experimentally observed electronic structure evolution of the cuprates. As more doping levels become available

many of the open questions left in this chapter should be resolved.

Chapter 7

Conclusions and Future Prospects

7.1 Half-filling

We are now at a point where we can assess all the photoemission data on the half-filled cuprates, and decide which models are valid descriptions of the physics. Certainly, the photon energy dependence has shown that $A_2CuO_2Cl_2$ ($A=Sr,Ca$) can indeed be treated as a two dimensional CuO_2 plane. In this regard, we have found that the t - t' - t'' - J model calculations accurately describe the overall dispersion including the flattened dispersion about $(\pi/2, \pi/2)$, the bandwidth of $2.2J$, and the d -wave-like modulation along the antiferromagnetic zone diagonal.[36] We note that all the aspects of the dispersion described above have also been correctly described in a diagrammatic expansion of the Hubbard model when second and third nearest neighbor hopping terms are included[134]. The t - t' - t'' - J calculations also found that t' and t'' cause spin charge separation in the momentum region about $(\pi, 0)$ [105, 106]. This suggests that RVB and flux-phase models may be an appropriate way to think of the excited states even though the ground state at $x=0$ is clearly a Néel antiferromagnet [108, 109]. However, the t - J calculations fail to produce the asymmetry in $n(\mathbf{k})$ about the diagonal from $(\pi, 0)$ to $(0, \pi)$. Meanwhile, this is captured in exact diagonalization[37, 38] and Monte Carlo[39] results of the one band Hubbard model, from which the t - J model can be derived by projecting out doubly occupied states. The biggest failure however, of the t - J numerical calculations, is the sharp lineshapes

which they predict. The broadness of the photoemission spectra can not be understated. The half width at half maximum of the sharpest spectra found at $(\pi/2, \pi/2)$ is still 300meV, which is roughly equal to the total bandwidth. It is certainly wrong to think of the dispersive features in terms of quasiparticles in the usual sense. Instead the spectra are perhaps more properly described as revealing structure in the incoherent part of the spectral function. Certainly, the correlation which created an insulator out of a metal must also be responsible for the broad lineshapes. In fact, in some scenarios it is believed that the insulator is better described as a continuum of excitations. Along this reasoning, Laughlin suggested that the dispersion of the insulator actually represented the edge of a spinon branch.[44]. This is in analogy with results from one dimension where spinons are well defined theoretically, and this type of behavior has also been observed experimentally by ARPES.[161] This is also similar to the phase string results of Weng *et al.*[122] With this knowledge we are now ready to tackle the doped case.

7.2 $x \neq 0$

The study of the insulator is of course motivated by the hope of learning about the true origins of the superconducting state. The high energy pseudogap of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ is believed to originate from the features of the insulator. This claim hinged on the fact that we can treat the features of $\text{A}_2\text{CuO}_2\text{Cl}_2$ as being truly representative of the spectral function from CuO_2 plane, which we have shown to be true. Furthermore, a high energy pseudogap is also seen in Na-doped $\text{Ca}_2\text{CuO}_2\text{Cl}_2$. When put together with the observed chemical potential shift in this system, it leaves no doubt, that the high energy pseudogap seen in angle resolved photoemission is a remnant property of the electronic structure of the insulator. Although, the connection between the high energy pseudogap and the low energy pseudogap, which appear correlated[74], is still an open question.

The chemical potential shift we observe in Na-doped $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ is very informative on the nature of the metal to insulator transition in the cuprates. From the shift of the chemical potential to the top of the insulating valence band, one would

expect that the Fermi surface would consist of small hole pockets centered about $(\pm\pi/2, \pm\pi/2)$. In fact, the broad, low energy features of the insulator are observed to approach the chemical potential in the doped samples, and pull back while losing weight rapidly after crossing the antiferromagnetic zone boundary. This is the shadow band behavior expected from short range antiferromagnetic correlations.[45] However, a small integration window about E_F and a sharp peak along the nodal direction which becomes more pronounced with increased doping, suggest that the low energy excitations are more properly defined as a Fermi arc as opposed to a hole pocket about $(\pm\pi/2, \pm\pi/2)$. Whether the shadow Fermi surface has been missed by the present set of experiments or is a theoretical shortcoming for describing the cuprates will need to be answered by future experiments.

A rigid chemical potential shift is perhaps expected when leaning on the familiarity of band theory, but is particularly surprising when considering the lack of chemical potential shift in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. [41] In the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ it is believed that states are created inside the gap upon doping. It is remarkable that there appear to be two different paths for the electronic structure evolution across the insulator to metal transition. Although it is possible to construct a single electronic structure evolution across the metal/insulator boundary given the existing data, this will require further investigation.

7.3 What Remains

Clearly, as more doping levels become available for Na-doped $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ we will be able to answer many questions. With low dopings, particularly those very near half-filling, we will be able to address precisely how radically different the chemical potential as a function of doping is compared to the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system. At higher dopings we will hopefully be able to observe the vanishing of the high energy pseudogap, and whether or not the low energy pseudogap still persists. Also, one will be able to determine whether the broadness of the features in the underdoped regime relative to the overdoped regime, as observed in Bi2212, is intrinsic or simply due to sample preparation. Furthermore, if with higher dopings the low energy

excitations become more well defined, then one can further examine the low energy electronic structure with regards to the “kink” in the dispersion; presently a subject of significant controversy. Finally, the technique of using high pressure synthesis to produce single crystals provides hope for being able to study the bi-layer compound, $(\text{Ca,Na})_2\text{CaCu}_2\text{O}_4\text{Cl}_2$ (powders of which have been synthesized under pressure) [162]. Presumably, this system would also be tetragonal and free from superstructure as the single layer compound. This system could then be used to further elucidate the fascinating yet controversial nature of the electronic excitations near $(\pi, 0)$.

Expanding our discussion to consider the unoccupied states, inelastic X-Ray scattering on $\text{A}_2\text{CuO}_2\text{Cl}_2$ indicates that the Mott-Hubbard gap is indirect.[163] By performing angle resolved inverse photoemission one will hopefully be able to present a unified picture of the electronic structure. Due to the poor quantum efficiency of inverse photoemission relative to photoemission such a study necessitates slightly doped samples, which could overcome the charging problems experienced when measuring the insulator. Finally, the doping dependent study using inverse photoemission is necessary to have complete information on the evolution of the insulator to metal.

Theoretically, there are many open questions regarding photoemission and high T_c in general. Meanwhile, the Na-doped $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ system has opened up a new testing ground for many theories previously believed to be incompatible with the cuprates. A comprehensive theory will have to sort through the system dependent details, but certainly can not neglect the broad spectral functions observed. Although it sometimes feels like an exhaustive search has already been performed, new experimental results appear almost daily, and our theoretical understanding is continually improving. Certainly one can conclude that contrary to popular myth: high T_c is *not* dead.

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