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Electronic Structure and Photoemission Studies of Late Transition-Metal Oxides -- Mott Insulators and High-Temperature Superconductors

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Abstract:

Stimulated by the discovery of high-temperature superconductivity, the electronic structure of late 3d transition-metal oxides is presently one of the most extensively studied subject in condensed matter physics. In this review, we hope to summarize the progress we have made and the problems we are facing. The emphasis of the review is on the latest angle-resolved photoemission studies that have provided much insight towards the understanding of these materials. This includes the recent experiments from transition-metal mono-oxides, normal state electronic structure and Fermi surface mapping of $Bi_2Sr_2CaCu_2O_{8+\delta}$, $Bi_2Sr_2CuO_{6+\delta}$, $YBa_2Cu_3O_{7-x}$, $YBa_2Cu_4O_8$, $Nd_{2-x}Ce_xCuO_4$, and the superconducting gap of $Bi_2Sr_2CaCu_2O_{8+\delta}$.

For the transition-metal mono-oxide, we discuss the experimental manifestation of the four aspects of the electronic structure that made these Mott-Hubbard insulators so interesting. This include the large Coulomb interaction U (on the cation sites), the charge transfer as a result of strong hybridization, the energy dispersion in the crystal lattice, and the multiplet and magnetic splittings.

For the high-temperature superconductors, we concentrate on the low energy excitations, the topology of the Fermi surface in the normal state, and the superconducting gap. Angle-resolved photoemission data show that the oxide superconductors have well defined Fermi surfaces. The volume of the Fermi surface at high doping regime appear to be consistent with the results of band calculations. A striking feature of the low energy excitations is the presence of some very flat bands (due to a saddle point sigularity in the band structure) which lie near the Fermi energy in p-type compounds near their optimal doping levels for superconductivity. The corresponding flat bands are well below the Fermi energy in n-type cuprates. The energy position of these flat bands is expected to have wide ranging effects on the physical

properties of these materials, including the temperature dependence of the resistivity and the superconducting transition temperature.

High-resolution photoemission has also been successfully applied to the study of the superconducting gap in $Bi_2Sr_2CaCu_2O_{8+\delta}$. While the presently attainable energy resolution is poorer than that of many other spectroscopies, photoemission has the advantage that it is **k**-resolved as well as being very direct. This unique capability has enabled recent photoemission experiments to reveal the highly anisotropic nature of the superconducting gap in the a-b plane. This suggests the possibility of a detailed experimental determination of the superconducting order parameter.

I. Introduction

Late 3-d transition-metal oxides, in particular the copper based high-temperature superconductors, are arguably among the most intensely studied compounds in condensed matter physics today.[1-15] This is so not only because they have shown a great promise on a wide range of of important applications, but also because they have for a long time challenged our ability to construct a truly many-body theory of the solid state. First of all, they display a wide range of ground states, with their electrical and magnetic properties ranging from Mott insulating, large band gap insulating, semiconducting, metallic, ferromagnetic, ferrimagnetic and antiferromagnetic (see table I). They show dramatic changes in their physical properties as a sensitive function of temperature, pressure and stoichiometry. Secondly, they include the Mott-Hubbard insulators, in which a large on-site Coulomb repulsion suppresses charge fluctuations and prevents metallicity, even in materials with an odd number of electrons per unit cell. Finally, they comprise the high-temperature superconductors which are closely related to the antiferromagentic Mott-Hubbard insulators. The surprisingly high transition temperature and unusual normal state properties of these superconductors have rasised a real question on whether our traditional theoretical machinary of quantum liquids is an appropriate starting point for a microscopic understanding of high-temperature superconductivity.

Most of the interesting properties of these oxides appear to be related to the effects of electron correlations, induced through strong Coulomb interactions among the cation 3d electrons, in the narrow d-bands of these oxides. The most famous example of this is that of the Mott-Hubbard insulators. In these oxides insulators, the large on-site Coulomb energy prevails over the kinetic energy and thus suppress the tendency of electrons to delocalize as driven by its desire to lower the kinetic energy. Failing to consider this Coulomb interaction explicitly often leads to incorrect conclusions. The

Bloch band theory, which does not take the Coulomb interaction into account explicitly, often incorrectly predicts metallic ground states for these insulating compounds. Historically, these insulators were among the first to siganl the limitation of the one-electron band theory despite its great success. It was de Boer and Verwey's early observation from these oxides started to reveal the limitations of the one-electron band theory. They found that some of these compounds violate the Wilson rule.[16] The importance of the of the Coulomb interaction was first indicated by Peierls[17], and then emphasized by Mott, Hubbard and Anderson.[18-20] It was also in these compounds that Anderson made the connection between the Coulomb interaction and the super-exchange interactions.[20, 21]

Oxygen has also played some essential roles which make the transition-metal oxides so interesting. First, it acts like a spacer which decreases the effective bandwidth of the d-electrons and hence enhances the correlation effects. Second, it has a fortuitous chemical potential in relation to that of the transition metals, in contrast to the sulfides which are more generally metallic and fluorides which are generally strongly insulating. Iron and its oxides are good examples illustrating the role of oxygen on the electronic structure. Fe is usually regarded as an itinerent magnetic metal, while FeO is a localized antiferromagnetic insulator. With a better appreciation of the roles played by oxygen, we now understand that some of the traditional Mott insulators are actually better characterized as charge transfer insulators.[22, 23] For example, it is found that the highest hole state of CuO has most of its weight on oxygen, while the lowest electron state has most of its weight on copper.[23, 24] Hence, CuO is a charge transfer insulator with the gap energy determined by what is required to remove an electron from the oxygen and to add an electron to the copper. This understanding of the role of oxygen is essential to correctly explain the trend of super-exchange interactions in the transition-metal oxides series.[25] In this review, we will follow the historical notation and generically refer to these oxides as Mott insulators.

For the last half century, there have been continuous theoretical and experimental efforts to study these oxides. Even though the efforts during some periods have been less intensive than others, the scientific community has never lost its fondness for these compounds. The main reason for this is that we are continuously suprised by new and exciting results found in these compounds. The recent discovery of the high-temperature superconductors is a good demonstration of this fact. These new findings can generally be characterized into two categories. The first is the discovery of new compounds (such as the cuprate superconductors), and the second is the new physical insights gained in these oxides by applying new measurement techniques or theoretical approaches. Of course, in many cases, the two are intermixed.

A success story of the latter is the application of photoelectron spectroscopy to these compounds through which much insights has been gained.[14, 26-36] This technique has unique advantages in the study of the transtion-metal oxides. First, they are less sensitive to the impurities than the transport measurements. Defects such as oxygen non-stoichiometry is a notorious problem in these compounds. Second, they are direct microscopic probes of the electronic states. For example, they are sensitive to the Fermi surfaces of the metallic compounds, and are also sensitive to the nature of the energy gap for the insulating compounds.

Almost all of the early photoemission experiments were carried out in the angle-integrated mode where electrons emitted in all directions were collected. Before the discovery of the high-temperature superconductors, most of the studies concentrated on the Mott insulators.[26] The experimental data from these insulators can not be satisfactorily explained by one-electron band theory. Instead, explicit consideration of the Coulomb interaction is required to understand the photoemission data from these insulators. In addition, detailed analyses of the photoemission data revealed the important role of oxygen. For example, we now understand from spectroscopic data that CuO is not a Mott insulator in a traditional sense, but is instead a charge transfer insulator.[23, 24] This realization had a significant impact on our understanding of the super-exchange interaction in these compounds, and in establishing a basic theoretical framework for the understanding of cuprate superconductors.

After the discovery of the cuprate superconductors, much of the earlier work was performed on polycrystalline samples at room temperature. It was later found by Arko et al. that a lot of the ealier photoemission data (not including Bi2212 data) were problematic due to poor surface quality.[28] For the high-quality surfaces obtained by cleaving metallic single crystals at very low temperature, Arko et al. found that the one electron theory appears to be better than the earlier data has suggested.[28] However, it is still true that the evidence of correlation effects persists into the metallic phase. For example, the valence band satellite is observed in all the cuprate superconductors studied. The existence of the valence band satellites unambiguously reveals the importance of the Coulomb interaction on the cation site. These results from earlier angle-integrated photoemission were quite well documented before.[27-36] While it is generally agreed that the insulating compounds can not be adequately described within the framework of the one-electron theory, it remains controversial whether the metallic compounds can be treated by the one-electron theory with some self-energy corrections. In particular, it remains very controversial whether the excitations of the metallic compounds near the Fermi level can be described by the Fermi liquid theory. These issues are some of the major focal points of the recent angle-resolved photoemission studies of these oxides.

Relatively speaking, much fewer angle-resolved photoemission experiments have been carried out on the transition-metal oxides . Angle-resolved photoemission is a traditional tool for studying the energy dispersion relations of crystalline materials, and it has been extensively used to study elementary metals and semiconductors.[37-41] However, it was only extensively used in studying the transition-metal oxides after the discovery of the high-temperature superconductors. In an angle-resovled photoemission experiment, only the electrons in a small solid angle will be detected so that the direction of the electron momentum is defined. Therefore, by analyzing the kinetic energy of the photoelectrons at a known emission angle, one obtains information about both the energy and the momentum of the of the photoelectrons. Such information is directly related to the E vs **k** relationship of the occupied states. Most of the angle-resolved photoemission experiments on transtion-metal oxides were performed on the cuprate superconductors. In the normal state, angle-resolved photoemission was mainly used to study the energy dispersion near the Fermi level, and the topology of the Fermi surface. Angle-resolved photoemission data from the normal state played a key role in proving the existence of a Fermi surface in these cuprate superconductors, despite the compelling evidence of correlation effects. In the superconducting state, angle-resolved photoemission was used to probe the **k**-dependent information of the superconducting gap. Such studies became possible only because of the improved energy resolution. It is plausible that photoemission will play as an important role for the high-temperature superconductors as tunnelling has for the conventional superconductors.[42] In addition to this exciting progress, recent angle-resolved photoemission studies of the Mott insulators have also drawn considerable attention from the theoretical community.

The objective of this review is to give an updated account of the experimental efforts on these issues. Even though this field is still very fast moving, with new results constantly being discovered, we feel that a review summarizing the progress we have made and the problems we are facing is very useful at this point, especially for those readers whose speciality is not in the field of electron spectroscopy. We will try to reflect some of the excitement and information generated in this field. Instead of trying to give a general review of all the transition-metal oxides, we will concentrate on the Mott insulators and high-temperature superconductors. The primary focus of this review is on the experimental results from recent angle-resolved photoemission studies. Due to the focussed nature of the paper, it is impossible to cover many interesting areas and many interesting literatures. We refer the reader to other review articles that may be of interest.[6, 26-36]

II. Brief Review of Experimental Techniques

A. Photoemission

1. General description

Photoemission spectroscopy (PES) is today known as the common name for a variety of similar experimental techniques that all are based on photon-stimulated emission of electrons from a material.[37-41,43-47] Photoemission experiments are typically performed in ultrahigh vacuum better than 1×10^{-9} torr. A monochromatic photon beam from a discharge lamp or a monochromator at a synchrotron source is introduced into the vacuum chamber and strikes the surface of the material under investigation. If this photon is absorbed, an electron in the solid is excited to a higher energy level. This is the first step of the three-step model of photoemission (see Fig 2.1) [48]. Because the electrons were excited with a known photon energy, the energy distribution of these excited electrons will reflect the energy distribution of the initial states from which they came - in the one-electron approximation this energy distribution will reflect the density of occupied states of the material.

If the energy level of the excited electron is higher than the vacuum level of the sample, the electron has the possibility to escape the crystal and be detected by an electron energy analyzer. First it must approach the crystal surface however, which is the second, or transport step of the process. During this transport process, the electron may be scattered and lose energy, becoming what is known as a secondary electron. These secondaries will give a background to the photoemission spectrum which the primaries will ride upon. The mean free path for these scattering events determines the surface-sensitivity for photoemission, as only the primary or unscattered electrons retain the energy information that is needed. As shown in Fig. 2.2, the mean free path of an electron in a solid is a strong function of its kinetic energy, and follows what has become known as the “universal curve”[49]. As seen from the figure, photoemission experiments may have a very high surface sensitivity of 10 Å or less if their kinetic energies are in the range of 20 to 200 eV. Depending on the goal of the experiment, this inherent surface sensitivity may be either an advantage or a disadvantage. On the one hand, it makes surface preparation a critical issue for the success of any experiment. For example, some of the early photoemission data from the high-temperature superconductors were discredited due to their surface problems.[28] In addition, it also makes it a tricky issue to obtain bulk band structure information from photoemission spectroscopy. Afterall, 10Å is only a few unit cells for most materials, and is less than one unit cell for the high temperature superconductors. Fortunately, experience from materials such as Cu and Si shows that we can still learn a great deal about the bulk band structure with photoemission spectroscopy despite its surface sensitivity.[37-41, 43-47] In the case of the high-T_C superconductors, the two-dimensional nature makes it easier to interpret the data. On the other hand, the surface sensitivity of photoemission spectroscopy is used extensively to distinguish the surface electronic structure from that of the bulk. Moreover, it allows interface formations and surface chemical reactions to be studied.

The third step of the photoemission process is escape from the surface. To do this, the electron must overcome the surface workfunction, which in the simple picture will simply cause the electron to lose some energy (i.e. there will be a rigid shift of the spectrum).

The simplest mode of photoemission is the angle-integrated mode, where photoelectrons ejected into a large solid angle are collected. In reality, photoemission experiments are performed with the variation of several parameters, such as the incidence angle of the radiation, the emission angle, the azimuthal angle, and the photon energy . This leads to various specialized photoemission techniques that will be briefly outlined in the following.

2. Angle-resolved photoemission

As depicted in Fig. 2.3, since the momentum of the impinging photon (at low photon energies) is negligible compared with the crystal momentum of the electrons in the Brillouin zone, the photon-excited transitions are frequently considered as momentum-resolved, i.e. the initial and final states have the same wave vector (direct transitions as illustrated by vertical arrows). This wave vector conservation inside a single crystalline material allows individual energy bands to be mapped out for comparison with band theoretical predictions. This band mapping is often carried out in the angle-resolved mode.[37-41]

Fig. 2.4 illustrates the experimental geometry for angle-resolved photoemission studies, where both the kinetic energy and the direction of propagation of the photoelectrons are directly measurable quantities. Since the component of the wave vector that is parallel to the sample surface is approximately conserved at the solid-vacuum interface, ARPES allows the initial state energies to be mapped out as a function of the parallel component of the wave vector. However, $k_{\perp}$ is unknown in this case. For a two dimensional system where $k_{\perp}$ is not a relevant parameter , the interpretation of angle-resolved photoemission experiment is the simplest. Figure 2.5 schematically illustrates an ideal set of photoemission spectra for a metallic band. There is a spectrum for each emission angle, or value of $k_{//}$, and for each spectrum there is a peak at the band energy. When the band crosses E_F and enters the unoccupied states, the weight of the peak in the spectrum goes to zero, as photoemission only probes the occupied states. In this way, the E vs. **k** relationship and the Fermi surface may be mapped out with angle resolved photoemission.

For the cuprate superconductor, we have a fortunate situation because all these superconductors are two-dimensional. Angle-resolved photoemission experiments are often carried out along a symmetry line of the Brillouin zone. Thus, the experimental energy dispersion can be directly compared with band calculations that almost invariably are carried out along high symmetry directions.

As the measurements are carried out angle-resolved, the number of experimental parameters increases dramatically, and so does the experimental information. For example, by changing the incidence angle of the radiation and by referring to symmetry-selection rules applicable to the surface under investigation, one can determine the symmetry of the initial states for a known final state symmetry and vice versa [50-51]. Moreover, by changing the azimuthal angle, one can examine the energy versus wave vector information along various directions of the surface Brillouin zone, thus allowing anisotropic effects to be explored. Another feature of angle-resolved measurements that is frequently employed is the ability to change the effective escape depth of the photoelectrons by simply changing the emission angle of those photoelectrons that are detected. It is a simple geometrical fact that the escape depth falls as the cosine of the emission angle with respect to the surface normal. Hence, by changing the emission angle of the energy analyzed electrons, the surface sensitivity can be varied, thus making it possible to study surface reactions or surface core level shifts in more detail.

3. Resonance photoemission

Resonance photoemission usually refers to the phenomenon in which the photoemission intensity of some valence band feature exhibits a Fano-like intensity modulation as a function of photon energy near an absorption threshold of a particular element.[52-53] This phenomenon often exist in the photoemission experiments of transition-metal compounds and rare-earth compounds, and has been extensively used to identify the chemical origin of valence band features. Fig. 2.6 depicts the resonance photoemission process for 3d transition-metal compounds. It is now generally understood that the resonance photoemission involves atomic processes of the type: $3p^63d^n$ --> $3p^53d^{n+1}$ --> $3p^63d^{n-l}e_k$, where e_k labels the detected photoelectron. The first step of the process is absorption of a photon leading to a transition from 3p to 3d, and leaving an intermediate state. The second step is a two-electron Koster-Kronig decay of the intermediate state involving an Auger matrix element of the Coulomb interaction. Note that the final state can also be reached by a direct photoemission process: $3d^n \dashrightarrow 3d^{n-l}e_k$. Since the same photon can create both final states as governed by the probability wave, the two processes add coherently and thus there is a quantum interference between them, leading to the Fano-type lineshape. For a strong resonance effect, the intermediate state has to be fairly localized. This is the reason why resonance photoemission is often observed in the transition metal oxides and the rare earth compounds.[52-53] Resonance photoemission is a powerful tool for tracing the orbital origin of valence band features. It is therefore very useful in studying complicated materials such as the high-T_c superconductors.

4. Some photoemission terminologies: EDC, CIS and CFS

In a normal photoemission experiment, the intensity distribution of the photoemitted electrons is determined as a function of the kinetic energy by scanning the energy window of the analyzer for a fixed photon energy. The corresponding photoemission spectrum is commonly referred to as an Energy Distribution Curve or EDC for short. The spectrum would look something like that shown in Fig 2.1c. By recording an EDC, the photoemission intensity due to photon-stimulated excitations from various initial state energies is analyzed, thus partly reflecting the density of the occupied states. Furthermore, by recording a series of EDC's, the chemical origin of the valence band states can be predicted. For example, from a set of the EDCs taken near the threshold of a particular elements, we can distinguish the nature of the features via the resonance photoemission principle discussed above. Taking a set of EDCs at very different photon energies where the photoionization cross-section of different elements are very different is another way to learn information about the nature of the valence band features.

Because of the importance of identifying the chemical nature of various valence band states, two elegant techniques have been developed to study these resonance enhancements in more detail. In a Constant-Final-State (CFS) measurement the kinetic energy of the analyzer is kept fixed, while the photon energy is scanned over the energy range of interest (Fig 2.7a). Usually the kinetic energy of the analyzer is held a few eV above the inelastic tail of the low-energy cut-off in a photoemission spectrum, so that the CFS spectrum mimicks the absorption of radiation as a function of the photon energy. In this mode a CFS measurement basically gives the same information as absorption measurements (optical, ultraviolet, and x-ray absorption). Similarly, in a Constant-Initial-State (CIS) measurement the kinetic energy of the analyzer and the photon energy are scanned synchronously so that the photoemission intensity of a particular feature (i.e. at fixed binding energy) is determined as a function of the photon energy. Hence, a CIS measurement allows a detailed examination of photoemission resonances of the type depicted in Fig. 2.6, and consequently of the character of different valence band states.

5. Related Experimental techniques

The information obtained in photoemission is about the occupied states. To access the empty states, Inverse Photoemission Spectroscopy (IPES), Bremstrahlung Isochromat Spectroscopy (BIS) and X-ray Absorption Spectroscopy (XAS) are often used. In IPES and BIS experiments, the process of photoemission is reversed, with electron beams impinging on the sample surface and the photons emitted from the decay of the electrons analyzed. The distinction between IPES and BIS is that IPES usually refers to experimental configurations with lower energy electron beams, while BIS usually refers to experimental configurations with relatively high energy electron beams. Relatively speaking, the efficiency of inverse photoemission is much lower and the energy resolution is poorer than photoemission. In XAS experiments, electrons in the filled state (usually deep core levels) are promoted to the empty states. This way, the information of the empty state can also be probed. The combination of PES and BIS is a very effective tool to probe the energy gap of insulating materials.

6. Theoretical description of the photoemission process

We have pointed out earlier that photoemission data reflect the information about the occupied density of states. This is, of course, a very crude statement. It suggests that the spectra are completely determined by the initial state. However, in reality, one has to consider the final state relaxation effects, the photoionization cross section effect [54] and other complications.

As we have indicated earlier, an effective model for PES data analysis is the three step model proposed by Spicer.[48] In this simplified model, the photocurrent is determined by the three process as depicted in Fig. 2.1: (1) the excitation of electrons by photons; (2) the transport of the excited electrons to the surface; and (3) the escape of the photoelectrons to vacuum to be detected. The advantage of this model is its simplicity and effectiveness. This intuitive model has played a critical role in the development of photoemission spectroscopy. The best justification for this model is that it works. At a more sophisticated level, we resort to the so-called one-step model, in which the process is considered to be a single event.[55,56] While being more accurate in its treatment, the one step model is not very intuitive. It is typically used only in very specialized applications.

Without consideration of the cross section effects, we can regard photoemission as reflecting the spectral weight function, $A(\omega, k)$, which is proportional to the imaginary part of the single-particle Green's function. The photoemission spectra should therefore reflect all the well-known sum rules that exist for the Green’s functions. From the one-step model, one can do total photocurrent calculations which include the effects of both the photoelectron, the photohole left behind, and the relaxation of the system associated with the photoemission process. In such calculations, the effects of the surface and the cleavage plane, the parameters such as the photon energy, the emission angle, and the light polarization can always be explored. A draw back of it is that it often depends on band structure calculations as an input for the photocurrent calculation. For strongly correlated system, it is not clear whether this approach is very effective.

In simple materials without strong correlation effects, the spectral weight function simply reduces to the density of states. For the highly correlated materials where the correlation effects are strong, the spectral weight function could be very different from the density of states as expected from one electron theories. The difference actually is a good account of the many-body correlation effects. Of particular importance is the dramatic redistribution of the spectral weight seen in photoemission data as compared to the one electron theory. The most clear example of this spectral weight redistribution is the existence of satellite structures, as we will discuss later.

B. Sample surface preparation

Because of the inherent surface sensitivity of photoemission spectroscopy, it is evident that the quality of the sample surfaces plays a crucial role for the photoemission results. Special attention has to be paid to the surface preparation procedures in all photoemission experiments. This is particularly true for the high-temperature superconducting materials since they contain oxygen atoms that are fairly loosely bound to the lattice and therefore easily escape from the surface, especially under ultrahigh vacuum conditions. Because of the loosely bound oxygen atoms, it is obvious that many 'standard' cleaning procedures, such has high-temperature annealing or ion-beam bombardment (ion-sputtering) are in general inappropriate since they almost inevitably change the surface composition by either 'outgassing' oxygen from the surface region or preferentially sputtering the oxygen atoms so that the surface region becomes oxygen depleted.

Among the other surface preparation techniques that have been used, in-situ scraping and in-situ fracturing (cleaving) appear to be the most non-destructive. In principle, both of these preparation methods should be capable of exposing a clean surface. However, experimental caveats may easily ruin this ideal notion of obtaining a clean surface by in-situ scraping or fracturing. It is well know that grain boundaries, to which bulk contamination and impurities tend to accumulate, frequently occur in the high-temperature superconductors. Since the grain boundaries often are the weakest part of a single crystal, it is conceivable that a sample preferentially breaks at a grain boundary upon in-situ scraping or cleaving. Thus, for samples containing a non-negligible amount of impurities the chemical composition of an in-situ scraped or cleaved material may not be representative of that of the bulk. Even for single-crystals, careful examination of the surface cleanliness using standard surface sensitive probes, such as Auger Electron Spectroscopy (AES) and X-ray Photoemission Spectroscopy (XPS) is imperative prior to photoemission experiments. Unfortunately, even electron bombardment seems to deteriorate the surfaces of some of the high-temperature superconducting materials.

Besides the difficulties in preparing bulk-representative surfaces, the fragile structure of some of these materials often poses a difficult problem in ultrahigh vacuum. This is particularly true for the $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ systems, for which some reports indicate deterioration of the sample surfaces after prolonged exposure to ultrahigh vacuum.[28] The deterioration of the sample surfaces in ultrahigh vacuum has often been linked to oxygen outdiffusion from the sample, thus depleting the oxygen content at the surface. In contrast, the $Bi_2Sr_2CaCu_2O_{8+\delta}$ material, and in particular single crystals of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ material, appears to be very inert in ultrahigh vacuum. This inertness probably relates to its unigue crystal structure, as will be discussed later.

The importance of surface quality to the photoemission spectra is most amply illustrated by our early experience with $Bi_2Sr_2CaCu_2O_{8+\delta}$ superconductors. We noticed that some of the samples had much less weight at the Fermi level, and did not show a superconducting gap. We checked the Meissner transition of all of the samples, and discovered that all of the ones which did not show the gap had much broader superconducting transitions. It turns out that we had baked these samples in our vacuum chamber in order to get higher vacuum, and this baking procedure had depleted the samples of oxygen and changed their character. Since then, we have measured the Meissner transition of all of our samples before performing the photoemission experiments, and we have developed a fast-entry load-lock so that our samples can be introduced into the chamber without baking. These precautions have dramatically increased the trust-worthiness of our measurements.

III. Photoemission from Late Transition-Metal Oxides

A. Pedagogical description of the Mott insulators

As we have stated in the introduction, the theme of this article is photoemission stuies of the electronic structure of Mott insulators and the high-temperature superconductors. These two classes of materials exibit extremely different ground state properties. However, they are closely related. An example of this is the $La_{2-x}Sr_xCuO_4$ system. La_2CuO_4 is a Mott insulator while it becomes a high-temperature superconductor upon Sr doping.[57] It is the purpose of this section to provide a pedagogical tour for the reader about these materials.

The term “Mott insulator” generally refers to a particular class of materials that can not be simply described by contemporary one-electron band theory, due to the strong correlation effects induced by large on-site Coulomb interactions.[58] These insulators have some characteristic properties of that of NiO. They are typically made of transition-metal oxides, and they often have antiferromagnetic order at low temperature. Although attempts have been made, there has not been a generally accepted definition of Mott insulators.[58] Therefore, we start this section by a simple illustration which gives the essence of Mott insulators, and why the one-electron band theory fails.[59]

Suppose there are N hydrogen atoms arranged closely together in a solid chain (Fig.3.1a). Because of wave function overlapping, the energy states of each individual atom construct an energy band with a bandwidth of B that is shown in the left part of the figure. The energy band contains 2N states due to the electron spin degeneracy. If the band are filled with 2N electrons, the material would be an insulator or semiconductor and could be called a Bloch insulator - a situation we are familiar with. In the Bloch insulator, the electron wave function is an extended wavefunction filling the whole crystal. For the hydrogen chain solid, there is only one electron per atom, which means that the band is half filled. Therefore, a metallic state is expected from the band theory. Now let us examine the situation where we pull the atoms apart while keeping their positions periodic. According to Bloch's theorem, no matter how far apart the atoms are separated (as long as it is not infinity), the wavefunction overlap gives rise to a half filled band and the crystal must be a metal. In reality, we know that this picture will break down at some separation between the atoms. The key to the failure here is that the Bloch picture ignores the Coulomb interactions between the electrons competely. For the atomic chain with large enough separation, the orbitals are localized on individual atoms. Each of the N orbitals is occupied by one electron and double occupancy is energetically prohibited because the two electrons on the same orbital will repel each other by the Coulomb interaction U. This mechanism is not present in Bloch's single electron picture where it is perfectly fine to have some of the orbitals empty and some doubly occupied.

Hence, we have two competing forces here: the Coulomb energy which tends to localize the electrons, versus the kinetic energy which tends to delocalize the electrons. Electrons prefer to be in an extended state to lower the kinetic energy as required by the uncertainty principle $\Delta x \Delta p \sim h/2$. Large Δx means smaller Δp, and the kinetic energy can be lowered with a smaller energy spread. The competition between the two forces determines the properties of the material. For materials with a large band width, the Coulomb interaction is well screened and the kinetic energy prevails. In this case, the correlations can be approximated by an averaged potential and the system can be well described by the one electron theory based on Bloch's theorem. The half-filled system is a metal. For materials with narrow bands ($B<U$), the Coulomb interaction prevails and the system is an insulator at half filling. This insulator is named after Mott for his contribution to the field. In this picture of the Mott transition, the size of the Coulomb interaction is the most critical parameter. In the transtion metal oxides, the Coulomb

interaction is very strong due to the localized 3d orbitals. Therefore, the Mott insulating state is often found in the transition-metal oxides.

Magnetic properties are another important aspect of the Mott insulators. The Mott insulators are often antiferromagnetically ordered at low temperatures. The magnetic moments of the Mott insulators are formed by the unpaired d-electrons. Because of the large Coulomb interactions, the real charge fluctuations are suppressed. The spin fluctuations induced by the virtual charge fluctuations lead to the superexchange interaction and the antiferromagnetic order.[21] As we will show later, this theory is often improved by explicitly considering the role of the ligand (typically oxygen) [25].

Oxygen plays a key role in the electronic structure of the late transition metal oxides. First, the oxygen atoms act as spacers that make the d-bands even narrower due to larger transition-metal ion-ion distances. Second, their chemical potential is such that the binding energy of the oxygen 2p band is very close to the copper 3d band, leading to the interesting role of charge transfer in the electronic structure. On the basis of spectroscopic data and some theoretical analysis, Zaanan, Sawatzky and Allen (ZSA) improved the picture for transition-metal oxides by considering both the Coulomb U and the charge transfer energy Δ between the metal and ligand [22]. Figure 3.2 shows a classification scheme based on the calculations by ZSA. The main result is that if Δ is appreciable but still smaller than U, then the insulating gap will be proportional to the size of Δ instead of U (region B). This is termed a charge transfer insulator. If U is smaller than Δ, U will dominate and the material will behave as a classical Mott-Hubbard insulator [22]. As we will see later, the late 3d transition-metal oxides are all charge transfer insulators or in the intermediate regime AB of the ZSA scheme. A recent study by Park et al. further suggested that all 3d transition-metal oxides are not Mott insulators in their strict sense, but are all charge transfer insulators or insulators in the intermediate regime of the ZSA scheme [60].

B. Angle-integrated photoemission of CuO and Cu_2O

1. Experimental results and the first order explanation

Because of the cuprate superconductors, CuO and Cu_2O received special attention since they serve as model systems for the superconductors.[23, 24,61-71] CuO is usually regarded as a Mott insulator, while Cu_2O is often regarded as a Bloch semiconductor. However, it is extremely instructive to discuss these two different compounds together. As shown in figures 3.3 and 3.4, these two copper oxides have very different crystal structures. CuO has a monoclinic structure with very low symmetry [72] while Cu_2O has a simple cubic structure in which oxygen is tetrahedrally coordinated by copper atom and copper is coordinated by two oxygen atoms [73]. Based on these crystal structures, the one-electron bands of both compounds have been calculated.[62, 68, 73]

Fig. 3.5 shows a comparison between the weighted density of states from one-electron band calculations and angle-integrated photoemission data[67]. Qualitatively very similar results were reported by other groups [62,63]. Fig.3.5a shows that the agreement between experiment and theory is quite good for Cu_2O. Fig.3.5b shows that the agreement is significantly worse for CuO. In particular, there is a severe problem in the energy range of -8 to -14 eV. This problem is most evident at higher photon energies where the Cu states have larger photoionization cross-sections. Here the theory predicts no spectral weight at all, while the experimental spectrum has substantial spectral weight in this energy range. Such spectral features observed at high binding energy in photoemission spectra are often called satellite structures, and are a consequence of many-body phenomena. To first order, we can understand the origin of this satellite in the simple picture illustrated in Fig.3.6. In a very simple ionic picture, Cu has a configuration of d^9 (Cu^{2+}) and O has a configuration of p^6 (O^{2-}) in CuO. In other words, CuO has one d hole since it takes 10 d electrons to fill the Cu 3d shell. Therefore, the initial state of the system will be a linear combination of configurations with the hole either on the Cu site (d^9) or on the O site ($d^{10}\underline{L}$), where $\underline{L}$ represents a ligand hole with the appropriate symmetry of the system. Now let's look at the final state with one electron removed, and thus two holes in the system left over. The three possible final states are d^8, $d^9\underline{L}$, and $d^{10}\underline{L}^2$. For the $d^9\underline{L}$ and $d^{10}\underline{L}^2$ configurations, the two holes in the final state are well separated (either on two different orbitals or on the delocalized oxygen orbital), and so no complications arise. For the d^8 configuration, however, we now have two holes on the same localized copper orbital, and so have to overcome the strong Coulomb interaction between the two holes. Therefore, the photoelectrons leaving CuO will have lower kinetic energy, and thus will show up in the form of a satellite at higher binding energy in the photoemission spectra.

A major support for the above interpretation of the CuO photoemission data comes from the resonance photoemission data[66,68]. Fig.3.7 gives the Cu 3p to Cu 3d resonance photoemission data of CuO together with some theoretical calculations based on Fano's theory of resonance photoemission (solid lines in the right panel) [23,68]. The fact that the satellite exhibits a clear resonance at the Cu 3p threshold near 74 eV is a strong indication that the satellite is indeed due to the d^8 configuration in the final state. This interpretion of the CuO resonance photoemission data has been questioned by Brandow who suggested that the sudden approximation breaks down under such circumstances.[74] However, recent Cu 2p resonance photoemission data indicates that it is not the case, and the photoemission satellite of CuO is indeed due to the d^8 final state configuration [75]. Fig.3.8 shows the giant Cu 2p resonance photoemission data from CuO. The spectral weight of the satellite is dramatically enhanced at the Cu 2p absorption threshold near 930 eV. Tjeng et al. argued that the sudden approximation is expected to hold at such high photon energies, and thus the 2p resonance photoemission data unambiguously demonstrated that the satellite of CuO has d^8 character [75]. However, the interpretation of 2p resonance photoemission data is not without controversy. There are discussions on whether the enhancement in the spectra is due to the resonance or the Auger process [76-78].

Now let's come back to the case of Cu_2O and ask why the band theory works well in this case. The first order answer to this problem is that in the case of Cu_2O, Cu is in its d^{10} configuration (closed shell) and so the correlation effects are not an issue. This is because the initial state has no hole in the system, and so there is only one hole in the photoemission final state. Therefore, we do not have to overcome the extra Coulomb interaction between the holes as in the CuO case. In fact, it has been shown to be generally true that the one-electron band theory works well in the cases where there is only one hole in the final state (e.g., PES of Cu_2O, IPES of CuO) [67]. On the other hand, the one-electron band theory does not work in the cases where there are more than one hole in the final state of the system (e.g., Auger of Cu_2O, PES of CuO) [67].

This interpretation of the difference between CuO and Cu_2O receives further support from 2p core level photoemission data as shown in Fig.3.9 [67]. For the Cu $2p_{3/2}$ spin-orbit component, we see only one peak for Cu_2O while we see a broad peak and a strong satellite for CuO. This difference can again be explained to first order by the fact that we have no hole in the initial state of Cu_2O while we have a certain probability for a hole on the Cu site in CuO. The satellite observed in CuO is a reflection of the Coulomb interaction between the Cu 3d hole and the core hole created by photoemission.

Thus, we have to first order explained the electronic structure and the photoemission data of CuO and Cu_2O. It appears that the one-electron band theory works well for Cu_2O while it does not work well for CuO due to the strong correlation effects. Similar conclusions were drawn from a comparison of the band theory and optical data [62, 73]. We know that the reason one-electron band theory does not describe CuO well is due to the fact that it does not take the Coulomb interactions into account appropriately.

2. More Subtle Issues

As we have illustrated very clearly above, we can to first order understand the electronic structure and photoemission data of Cu_2O and CuO very well. In the former case, since the initial state is a full band (no holes) situation, no complications from correlation effects arise and the one-electron band theory works well. In the latter case, since the initial state is not a full band situation (it has one hole in the system), correlation effects are important for the photoemission data and the one-electron picture breaks down. If one looks at this problem more carefully, one finds that this picture is not completely correct [70].

The main problem comes from the fact that the above interpretation gives very unrealistic estimates for the d shell occupation number of Cu_2O in the ground state (d^{10}), which is significantly higher than the CuO case. Due to the hybridization with the oxygen states, the d shell occupation number of Cu_2O in real systems is smaller than d^{10}. Calculations show that the difference of d shell occupancy between Cu_2O and CuO is not very large ($d^{9.30}$ and $d^{9.15}$ for Cu_2O and CuO, repectively) [70]. Therefore, the above simple explanation can not be completely correct, and there have to be other reasons for the large difference seen in the satellite intensity between Cu_2O and CuO. This problem is addressed by Karlsson et al.[70]. It turns out that additional differences between Cu_2O and CuO come from the fact that the ground state couplings in Cu_2O (between 3d electrons and conduction band) and CuO (between valence electrons and 3d holes) are quite different. This was also invoked to account for the different line shapes (widths) of the main line of 2p core levels of CuO and Cu_2O. In these papers, the fact that the main line of the 2p core-level is much broader in CuO than in Cu_2O was explained along the same lines (see Fig. 3.9). On the other hand, the 2p core level broadening is attributed to strong nonlocal contributions due to the fact that the valence hole is moved away from the core hole and forms a Zhang-Rice singlet on a neighboring site [71]. The issues of the satellite intensity and the Cu chemical shift in Cu^{3+} formal valence compounds (such as $NaCuO_2$) are also discussed in these papers [70].

3. Results of cluster and impurity model calculations

The simple data analysis in the last two sections gives the essence of the photoemission data from CuO and Cu_2O. For detailed analyses of the photoemission data, usually one calculates the photoemission spectra with parameters such as the Coulomb interaction U and the charge transfer energy Δ, and then adjusts the parameters until the calculated spectra have the best fit to experimental data. In this way, the values of the important physical parameters can be extrapolated from the photoemission data. In these more realistic calculations, one also has to consider the crystal field splitting. Fig.3.10 shows a comparison between a cluster model calculation and XPS data with the following parameters: $U_{dd} \sim 8.8$ eV, $\Delta \sim 2.75$-3.50 eV, $T_{pd}(b1)/2 \sim 1.25$ eV, and $T_{pp}/2 \sim 0.50$-0.65 eV[69]. One can see that the cluster model reproduced the main features of the valence band photoemission data quite well. An important point to emphasize is that the charge-transfer energy Δ is smaller than the Coulomb interaction energy U, implying that CuO is a charge-transfer insulator [22].

So far, we have treated the system with a cluster. This appears to give a good account for the localized 3d states. However, it does not treat the oxygen states very well. There is much evidence that the band effects are important for any appropriate treatment of the oxygen states. To reconcile this problem, the Anderson impurity model is often used to calculate the spectra where the oxygen states are treated like bands. Fig.3.11 shows a comparison between an *ab intio* Anderson impurity model calculation and the XPS data for CuO [24]. This calculation treats the system as a Cu impurity embedded in the matrix of the oxygen lattice, and the parameters of the Anderson impurity model were obtained from a so-called constrained LDA calculation. The calculation is very similar to that of a supercell calculation with the supercell size going to infinity. One can see that the agreement between the experiment and the theory is very impressive. Note that the calculated satellite structure is located at higher binding energy than the experimental data: this probably implies that the U_d value obtained from the constrained LDA calculation is too large.

There are two more things that need to be pointed out in this figure. The first is the satellite near 16 eV in the experimental data. This satellite has not been observed in other Cu compounds and before its experimental confirmation was actually predicted by theoretical calculations to be a singlet with mainly Cu spectral weight. The second thing is the feature at zero energy: the calculations show that this feature is due to a singlet formed by a Cu hole together with an oxygen hole with 3d symmetry with respect to the copper site. Such singlet has never been observed in the parent insulating compounds of the high-temperature superconductors. This actually may mean that CuO and cuprate superconductors are more different than we had thought [24].

C. Angle-integrated photoemission from other Mott insulators

Fig.3.12 exhibits the common crystal and the magnetic sublattice structure of the late 3d transition-metal mon-oxides (NiO, CoO, MnO and FeO all have this structure)[79]. Below their Néel temperatures, the cation spins are ferromagnetically alligned within a {111} plane, but are antiferromagnetically alligned in two adjacent {111} planes. These oxides are customly treated in terms of ML_6 transition-metal complexes as illustrated in Fig.3.13a and Fig.3.13b [81]. This approach is justified by the localized nature of these materials. Depending on the number of d electrons in Ni, Co, Fe and Mn, the cation levels are filled differently. This simple picture is a good starting point of our discussion.

1. Experimental data of NiO and their interpretation

NiO is probably the most extensively studied and widely discussed transition-metal mono-oxide. As shown in Fig.3.13, the highest occupied states are the $2e_g^*$ antibonding orbitals (x^2-y^2, z^2) which then broaden into bands by the intra-sublattice coupling [81]. In a simple band picture, these bands were partially filled by two electrons and therefore NiO is expected by this calculation to be a metal. This result is obviously not correct since NiO is experimentally found to be an insulator with a large gap.

Historically, two fundamentally different approaches were used to explain this problem. The first initiated with Slater's antiferromagnetism approach [82]. Fig.3.14 shows the result of a recent sophisticated local-spin density functional approximation (LSDA). The calculated Fermi level lies in a 0.3 eV gap of the Ni3d bands, indicating that NiO was a small band gap semiconductor (0.3 eV) [79,80]. Fig.3.15 schematically illustrates this result [79,80]. According to the band calculation, the magnitudes of the exchange splitting, ligand-field splitting and d band-width are all comparable. As shown in the left panel of the figure, it just happens that the exchange splitting is slightly larger than the d-band width. The eight Ni electrons fill the triplet t_{2g} states and one of the doublet e_{2g} states. The e_g orbital with the (local) majority spin is filled while the e_g orbital with (local) minority spin is empty. This calculation gives a semiconducting ground state for NiO, which was certainly better than the metallic ground state from the simple analysis. However, the size of the calculated energy gap is an order of magnitude smaller than the 4 eV value measured experimentally.[83,84] Furthermore, the LSDA calculation gives a magnetic moment for NiO which is much smaller than the experimental result [79]. These are the key reasons to question the applicability of one-electron theories to understand the electronic structure of NiO. It should be noted here that the LSDA is designed to calculate the ground state energy only, and is not designed to understand the excitation spectra. However, for many simple materials, the LDA turns out to give a good account of the band structure by virtue of Koopman’s theorem. The above problems suggest that it is not the case for NiO.

The other approach to explain the problem of NiO and related materials is that of Mott and Hubbard.[18, 19] This approach views NiO a as highly correlated material due to the strong Coulomb interaction among the 3d electrons. The key to this approach is that occupied electrons see the potential due to d^{n-1} electrons on the metal-site while the unoccupied d electrons see the potential due to the d^{n} electrons on the site. Hence, there is an energy difference U (controlling the size of the insulating gap) between these two sets of states which can not be appropriately approximated by an average potential as in the case of band calculations. Therefore, this approach views the one-electron theory as having a fundamental difficulty in explaining the electronic structure of NiO.

In light of the controversy over NiO, many photoemission experiments were carried out aimed at understanding its electronic structure [84-89]. Fig.3.16 reproduces earlier angle-integrated photoemission spectra from single crystal NiO by Eastman and Freeoff at various photon energies [85]. These spectra can not be explained within the context of the one-electron band theory, in particular the multi-electron satellite 8 eV below the main valence band, similar to the Cu satellite discussed in Sec. III.b. From the photoionization cross section behavior of the satellite, Eastman and Freeoff concluded that the satellite has predominantly 3d character [85]. This assigment of the satellite character was confirmed later in resonance photoemission experiments by Oh et al. as shown in figures 3.17a and 3.17b [86]. Fig.3.17a plots angle-integrated EDCs from single crystaline NiO at photon energies near the Ni 3p threshould of 66 eV. It is very obvious that the multi-electron satellite shows a clear enhancement at the resonance photon energy near 66 eV. The Fano lineshape of resonance is more clearly revealed in the CIS spectra of Fig.3.17b. The satellite exhibits a clear resonance while the main band exhibits a clear anti-resonance at the threshold. The resonance behavior of the oxygen feature is clearly weaker. The authors suggested that this weak resonance is due to the inseparable satellite structure and the oxygen states [86]. The other possible reason for the weak resonance of the oxygen feature is the hybridization of oxygen states and the Ni states.

The photoemission data of NiO was traditionally interpreted by the ligand field (LF) theory, as illustrated in Fig.3.13. Here NiO was regarded as a classical Mott insulator with Δ larger than U. The highest occupied states have mainly Ni 3d character separated by the ligand field splittings. In this case, the insulating gap is mainly determined by the large Coulomb interaction - the classical case of a Mott insulator. This interpretation of the data is difficult to reconcile with the resonance photoemission result. According to this interpretation, the multi-electron satellite is due to the emission from $d^8\underline{L}$ final state configuration. This configuration is mainly an oxygen related state, and is not expected to show a strong resonance according to the standard resonance photoemission picture.

Facing this problem, Fujimori and Minami proposed a revised interpretation for NiO photoemission data based on a cluster model calculation [88]. Their calculation has included many of the higher order corrections, such as for examplethe crystal field splitting. Fig.3.18 reproduces the result of their CI model calculation in comparison with the experimental photoemission data. The key parameters used in the calculation here is U ~ 8 eV and Δ ~ 3.5 eV [88]. For a comparison, the result of ligand field theory is also presented. It is quite obvious that the CI model did a better job explaining the photoemission data than the LF theory. The key to this reinterpretation of NiO data is the realization that Δ is actually smaller than U, and NiO is a charge transfer insulator instead of the Mott insulator in the traditional sense. As we have pointed out earlier, we regard Δ as an effective U here. In this picture, the satellite is due to the emission of the d^7 final state configuration while the main band is due to the $d^8\underline{L}$ configuration. Since d^7 will clearly resonate at the Ni 3p threshold, this new interpretation can easily explain the resonance photoemission data of NiO. A similar interpretation of the photoemission data of NiO was also proposed by Sawatzky and Allen who use the CI (configuration interaction) model to reinterpret the photoemission and BIS data of NiO [84]. They found that the first photoemission peak and the first BIS peak have an energy separation of about 4 eV, which unambiguously proved that the intrinsic gap of NiO is 4 eV. This is an important point since the earlier optical data might not give the intrinsic gap due to complications arisng from the selection rules in optical absorption experiments. The first photoemission peak and the first BIS peak are interpreted as due to emission from $d^8\underline{L}$ and d^9 final state configurations, respectively. The energy difference between these two configurations determines the insulating gap.

As we will discuss later, more recent studies suggest that the first photoemission peak is actually a bound state pushed out of the continuous oxygen band. The actual difference between Δ and U appears to be smaller than the number quoted here [88]. Hence it is closer to the intermediate regime AB of the Zanaan-Sawatzky-Allen scheme [22]. Another complication comes from the fact that the above discussion did not include the exchange interactions. To fully understand the spectroscopic data of NiO, the exchange interaction has to be included because it is of a similar magnitude with Δ. Recently, a LDA+U potential correction approach was also used to calculate the photoemission spectra of NiO [90]. For this scheme to work, it is necessary to renormalize the Ni3d-O2p hopping parameters.

2. Results from CoO, FeO and MnO

Photoemission and resonance photoemission experiments were also performed on CoO, Fe_xO and MnO [91-101]. Figures 3.19a and 3.19b show the EDC stack and CIS spectra near the Co resonance threshold of 60 eV, taken on single crystal CoO by Shen et al.[91]. The satellite about 10 eV from the valence band maximum shows a resonance while the main valence band shows an anti-resonance. Figures 3.20a and 3.20b give the EDC stacks and CIS spectra from an MnO single crystal near the Mn 3p resonance threshold of 50 eV [93]. It is seen that the resonance effect of the main band in MnO is much stronger than in NiO and CoO (note the difference in the lineshape between the 49 and 50 eV spectra). Resonance photoemission experiments have also been performed on polycrystaline FexO samples.[89] The experimental data also show a satellite structure which resonates at the Fe 3p threshold.

Since the resonance photoemission data of the later 3d transition metal mono-oxides are very similar, it is natural to expect the electronic structure of these compounds to be similar. It is believed that CuO is in the charge-transfer-insulator regime ($U>\Delta$), while NiO, CoO, FeO, and MnO are in the intermediate regime ($U\sim\Delta$). This point is a little bit controversial in the literature. Fujimori et al. suggest that FeO (and presumably CoO) is a charge transfer insulator, while only MnO and CrO are in the intermediate regime [93,94]. On the other hand, van Elp et al. suggest that both MnO and CoO are in the intermediate regime [92,95]. The fact that the main band of MnO shows a strong resonance is consistent with the fact that MnO is farther away from the charge transfer insulator regime. More recently, on the basis of resonance photoemission data at the O 1s and TM 2p edges, Park et al. suggested that NiO, CoO, FeO, MnO, V_2O_3 and Ti_2O_3 are all in the intermediate regime [60]. The main point of this paper is to give a reinterpretation of V_2O_3 and Ti_2O_3, which are usually regarded as in the $U > \Delta$ regime. From the overall picture, these are small differences within the same global framework, consistent with the results from a theoretical analysis of the electronic structure of transition metal oxides by Zanaan, Sawatzky and Allen [22].

3. Role of the magnetic interactions

In the last two sections, we discussed and classified the electronic structure of late transtion-metal mono-oxides by two physical parameters, namely the Coulomb interaction energy U and the charge transfer energy Δ. This approach is sufficient if the energy scales of these two parameters dominates the system. The other interactions with smaller energy scales can be treated as higher order corrections. In reality, the exchange interactions in these oxides are sometimes quite large. Under such conditions, the exchange interaction has to be included to fully understand the spectroscopic data.

The Ni 3s core level data from NiO provides a good example demonstrating the role of magentic interactions in the system. Fig.3.21 shows the high-resolution (0.3 eV)

Ni 3s core level XPS data by Bagus et al. [97]. Five features can be distinguished as marked by A-E. The existence of five features can not be explained by the simple charge transfer model alone which can only give a main line and a satellite. This spectrum can be understood by considering several effects at the same time: ligand to metal 3d charge transfer screening(Δ), the near degeneracy correlation among 3s, 3p, and 3d shells (U), the exchange coupling of the ionized core level with the open d shell (multiplet splitting), and the extra-atomic covalent bonding in the final state [97]. Analysis shows that the exchange coupling here is of the same order of magnitude as Δ, suggesting it can not be regarded as a higher order correction. The effects of exchange coupling are most clearly seen in the 3s core level data because it the simplest case. However, one would also anticipate that the exchange coupling (or multiplet splitting) is important for understanding the valence band data. The more realistic cluster model calculations included such effects [88,92].

A trend in these mono-oxides is that as one moves from CuO to MnO, the influence of charge transfer on the electronic structure is getting smaller, but the exchange interaction becomes larger. This trend manifests itself in the cation 3s core level spectra. In CuO, the 3s core level splitting is mainly determined by the large Coulomb interaction between the core hole and a 3d valence hole U_{cd} as a consequence of charge transfer. In MnO, on the other hand, the 3s core level splitting is basically determined by the exchange interaction of the ionized core level and the open d shell [98, 100]. In NiO, CoO and FeO, we have a mixture of the two extreme situations.

The above discussion also explains an earlier question why the splitting of 3s core levels do not track with the size of the magnetic moment. In the earlier literature, the magnetic exchange interaction of the ionized core level and the open d shell was regarded as the sole reason for the 3s core level to split. Now we also know that the charge transfer also plays a role in the 3s core level splitting so that the splitting does not track linearly with the size of the magnetic moment. It is also appropriate to point out here that the calculation of the superexchange interaction using $J \sim t^4/U^2 * (1/\Delta+1/U)$ after considering the role of charge transfer improves the agreement with experimental data as compared with the calculation using $J \sim t^4/U^3$.[25] This is the reason for us to earlier state that the consideration of the charge transfer degree of freedom improves our understanding of the magnetic properties of the Mott insulators.

The role of exchange coupling in Mn compounds is also discussed by Oh et al. in a recent paper [100]. The anslysis shows that there are many factors involved in determining the electronic structure of transition-metal oxides: the correlation interaction, the charge transfer, the exchange interaction, and others. This is probably the reason why the electronic structure of transtition-metal oxides has been a difficult problem for such a long time. In the following chapters, we will see yet another factor - namely the energy dispersion.

D. Angle-resolved photoemission from Mott insulators

As we have indicated in the introduction, angle-resolved photoemission has only very recently been used to study the Mott insulators. This is the case partially because the evidence of correlation effects in these compounds is so compelling that one’s first impression is that we might not be able to learn very much from angle-resolved studies. However, stimulated by the renewed interest in these oxides as a consequence of the discovery of the high-temperature superconductors, angle-resolved photoemission has been applied to the classical Mott insulators such as NiO, CoO and MnO.

1. Results from NiO

There are several recent reports of angle-resolved photoemission studies of NiO performed on {100} surfaces cleaved in ultra-high vacuum [102-106]. In addition to confirming the strongly correlated nature of this compound as found by angle-integrated photoemission, these studies also have revealed remarkable dispersion of the valence band features, suggesting the importance of the lattice effects to the electronic structure [102,103]. The angular dependence of the photoemission spectra is particularly strong for the higher binding energy bands, which are mainly oxygen derived. However, this effect also exists for the Ni 3d derived features, including the valence band satellite of d^7 local configuration. So far, experiments have been performed along the three high symmetry directions of (100), (110) and (111). In this review, we concentrate our discussion on data along (100).

Figures 3.22, 3.23, and 3.24 reproduce the complementary normal and off-normal emission data along the NiO (100) direction by Shen et al.[103]. Figure 3.22 show the normal emission data with photon energies ranging from 13 to 35 eV, while figures 3.23 and 3.24 give the off-normal emission spectra along NiO (100) direction with different incident photon polarizations. In the case of off-normal emission, the authors changed the photon energy and the emission angle to keep $\mathbf{k}_{\perp}$ fixed at 2ΓKX while changing $\mathbf{k}_{//}$ along one of the (100) direction in the NiO (100) plane. Here the pinning position of the experimental Fermi level is determined by a Au reference spectrum. The data in these figures unambiguously demonstrate the importance of the lattice aspects of the photoemission spectra from NiO, in spite of the compelling correlation effects. We can see that the spectra are remarkably different with different photon energies and emission angles corresponding to different **k** values in the Brillouin zone. Crudely speaking, the top curves in these data sets correspond to the spectra taken near the X point while the lower curves represent the spectra taken near Γ point. Some of the valence band features show very strong energy dispersions up to about 4 eV. Comparing figures 3.25 and 3.26, we can also see the dramatic changes in photoemission spectra due to the optical selection rules. For example, the relative intensity of feature E is much stronger in the spectra taken with the photon polarization out of plane (Fig.3.25), indicating an out-of-plane symmetry for these features. There are five cleary distinguishable features in the main valence band, A, B,C, D and E. Features C, D, and E are believed to be oxygen related states, while features A and C are mainly nickel derived. The oxygen features, in particular E, show very strong photon energy and emission angle dependence. Moderate changes of Ni 3d states as a function of emission angles and photon energies were also observed.

Based on the experimental data in figures 3.22-3.24, the authors deduced the experimental E vs **k** dispersion relation. In order to achieve this deduction, they assumed a free-electron final state, which is a standard practice in angle-resolved photoemission experiments [37-41]. With the adjustable parameters of the inner potential set at 8 eV and the effective mass set at 0.95 m_e , the experimental E vs **k** relation is deduced and plotted in figures 3.25 and 3.26. These panels correspond to the data in figures 3.22 and 3.24, respectively, although soem additional normal emission data not shown here was used. The experimental E vs **k** relations were compared with the results from an LSDA calculation. This way, the authors were able to learn information about to what extend the one-electron band theory can describe the electronic structure of NiO. Another reason for the authors to compare their data with band calculations was that band calculations are presently the only theoretical calculations with detailed E vs **k** dispersion relations, allowing a direct comparison with experiment. The lines in the upper and the lower panels are results of band calculations without and with antiferromagnetic order, respectively. Since the antiferromagnetic order of the Ni sublattice is along the (111) direction, the unit cell of the crystal is doubled and the Brillouin zone is reduced to half. The bands along $\pi/a(111)$ and $\pi/a(311)$ are folded back to (000) and $\pi/a(200)$, and are then modified slightly near the crossing points after incorporating the magnetic interactions.

Comparing the data with the non-magnetic bands, they found that the energy dispersion relation for the lowest oxygen band (feature E(•)) agrees remarkably well with the calculated result. The agreement is better for the normal emission data than the off-normal emission data, which is probably due to the fact that $\mathbf{k}_\perp$ is not exactly fixed at

2ΓKX in the off-normal emission data [103]. The fact that this feature is stronger with the incident photon polarization along the surface normal is also consistent with the Δ1 symmetry in the calculation. The situation about the other oxygen derived features is more complicated. This is particularly clear for the three bands between -3 to -5 eV in the upper panel of Fig.3.26. One can see that there are three experimental bands (one of them actually is nickel derived), while there are only two theoretical bands. Therefore, the experimental data and non-magnetic bands clearly disagree on this issue. Similarly, sporadic data points were also observed in the normal emission data. Furthermore, the agreement between the experiment and the calculated non-magnetic nickel 3d band is also poor. The authors then compared the data with the AF bands (lower panel). Even though the agreement was not perfect, it clearly improved. This explains why there are three experimental bands in the intermediate band positions in Fig.3.26. The (+) band energy is off, as we will discuss later, mainly due to the fact that LDA underestimates the d band-width.

The situation of the Ni 3d bands is more complicated. First of all, the lineshape of feature A changes distinctly as a function of photon energy and emission angle, indicating that it has several components. This is most clearly revealed in Fig.3.27 where some selected spectra with an energy window around feature A are presented (from Fig.3.24). This indicates that feature A contains at least three components. The authors also noted that the features are much broader than one would expect from the intrumental resolution. From Fig.3.26, one can also see that the experimental E vs **k** relation agrees with the AF bands better than the non-magnetic bands. However, even with the magnetic bands, the experimental band C is still flatter than the theoretical band, indicating that the LDA calculation overestimates the 3d band width. This fact is actually related with our earlier observation that the + band is higher than its theoretical counterpart. It turns out that this particular oxygen band has more d character then the other oxygen bands, and that the theoretical curves are therefore pushed downwards too much as a consequence of overestimating the p-d matrix element. As we have emphasized earlier, some information about the 3d bands is contained in the $3d^7$ satellite. Shen et al. reported interesting emission angle and photon energy dependences of the d^7 valence band satellite, as reproduced in Fig.3.28 [103]. The strong enhancement of the satellite at the photon energies of 66 and 68 eV is due to the resonance effect at the Ni 3p to 3d absorption threshold. For photon energies far away from the resonance, one can still see clear changes of the spectra as a function of emission angle and photon energy. The authors discuss several possible explanations for this observation, suggesting that energy dispersion is the most likely scenario.

A related issue that should be discussed here is the number of Ni3d bands, as stressed by Shih et al.[104]. In the angle-resolved photoemission data, there are five distinct features within the first 3.5 eV with the band edge, as shown in Fig.3.29. Here feature C is not very visible, but can be clearly seen in other emission angles [104]. This is very different from the result of angle-integrated photoemission that show only two distinct peaks within the first 3.5 eV from the band edge, as shown in section III.c.1. According to the cluster calculation by Fujimori and Minami, these spectra should exhibit only three features corresponding to final state configurations with $^4T_1$, ^2E and $^2T_1$ local symmetry [88]. The existence of at least five bands within the first 3.5 eV clearly shows that the cluster model which considers only the local symmetry is too simplified: the addition of intercluster hopping further splits the degenerate states.

Hence, the angle-resolved photoemission data from NiO helps us to better understand the following issues. First of all, we can see that it is essential to include the antiferromagnetic order in the theoretical calculations. This effect is most clearly seen for the Ni 3d bands. The antiferromagnetic 3d bands are much narrower than the non-magnetic bands, thus improving the agreement with the experimental data. This is consistent with our earlier assertion from core level data analysis that the exchange splitting has to be considered to fully understand the experimental spectra. There are three experimental bands in the energy range where the antiferromagnetic bands are heavily populated (e.g. from -1 to -2.5 eV in Fig.3.28), and these bands spread out in an energy range which is very similar to the theoretical prediction. Even though the importance of the antiferromagnetic order to the band structure has been theoretically recognized for a long time[82], this problem has only recently been explicitly addressed experimentally. For the oxygen 2p bands, the effect of the antiferromagnetic order exists, but is not as evident as for the Ni 3d bands. This is not unexpected since the antiferromagnetic order is formed on the moments sitting on the Ni sites. In the off-normal-emission data along (100), there is an extra oxygen band in the energy range of the Δ5 band if the antiferromagnetic order is not considered (Fig.3.28). This extra band is believed to be due to the folded-back band from the π/a (111) to π/a (311) symmetry directions as a result of the antiferromagnetic order. However, the energy position of this band is somewhat off, a fact probably related with the fact that LDA overestimates the overlap matrix elements of the 3d bands.

The second issue deserving attention is the energy separation between the Ni3d and O2p bands. This turns out to be a tricky issue. An earlier comparison of an LDA calculation with angle-integrated photoemission data suggests that the LDA calculation gives an energy separation which is about 2 eV too large [107]. The comparison of the LDA calculation and angle-resolved photoemission data gives a more complicated picture[103]. If we match the energy positions of the theoretical and the experimental oxygen bands, we find the data points fall in the energy range where there are theoretical Ni 3d bands. However, the relative intensity of various 3d bands is still an open question. This result is different from the 2 eV shift scenario proposed earlier. Shen et al. suggested three possible explanations for this discrepancy: (a) When Kübler et al. compared the LDA result with the angle-integrated data, they also tried to give the best intensity match. Hence the matching criteria in the two cases are different [107]. (b) If one looks at the analysis of Kübler et al. (see Fig.3 of reference 107), one finds that the energy separation between the Ni3d and O2p bands is about 1 eV too small after they shift the Ni3d bands down by about 2 eV (check the O2p band noted by σ, for example). (c) Previous angle-integrated photoemission data taken with a CMA (cylindrical mirror analyzer) could be quite different from the total density of states. After all, the data taken with a CMA is not truly angle-integrated. Furthermore, the experimental spectrum was the coherent summation of the partial density of states weighted by the photoionization cross-sections.

Third, we discuss the discrepancies between the data and the LDA calculation. The first one is the absence of the theoretical bands just below E_F in the experimental data. As shown in figures 3.25 and 3.26, there are always theoretical bands in the energy range between E_F (pinned position of the Fermi level) and the first observed Ni 3d band (usually near -1 eV). These are the theoretical bands that should be empty if we count the number of electrons. Obviously, since their predicted energy positions are wrong, they are below the experimental Fermi level. Therefore, this discrepancy is related to the fact that the LDA calculations can not reproduce the experimental gap value of NiO. The second major discrepancy is the observation of the photoemission satellite which can not be predicted by the LDA calculation, as we have discussed in Section III.c.1. In addition to the two major discrepancies, we have also observed disagreement between the details of the angle-resolved photoemission data and the band theory. For example, even though the general energy spread of the Ni 3d bands is very similar for the theory and the experiment, the details of the energy dispersion of the individual bands in the experiment may be different (usually narrower) than that of the theory.

Finally, we examine to what extent the angle-resolved photoemission data can be explained by the cluster model. The main advantage of this model is that it can explain the satellite structure very nicely. With appropriate fitting parameters, this model is expected to reproduce the gap information, the general energy spread of the 3d band, as well as the energy separation between the 2p and 3d bands. However, this model can not provide the E vs **k** information which is so evident in the angle-resolved photoemission data. Furthermore, the cluster model can not explain the fact that we can see five 3d like features in the main valence band. Thus, we see that one has to go beyond the cluster model to explain the angle-resolved photoemission data. It may be possible to start out with a cluster model and then incorporate the effects of energy dispersion.

It is also appropriate here to point out an often misunderstood point about the cluster model for NiO. In the cluster model, without considering the p-d hybridization, the Ni 3d band is split into upper and lower Hubbard bands with the lower Hubbard band completely filled. The oxygen bands are located between the two Hubbard bands and are filled, thus forming the charge transfer gap with the upper Hubbard band. If we take this picture naively, then we will find this is inconsistent with our angle-resolved photoemission data which show that the Ni bands are above the O bands (closer to E_F). In this picture, the occupied oxygen bands are located at lower binding energy than the occupied nickel bands. This paradox can be easily explained if one considers the hybridization between the O 2p and the Ni 3d states. Due to the hybridization, the oxygen states that are very strongly hybridized with the nickel states are pushed up. The cluster calculations actually show that bound states with mixed $d^8\underline{L}$, $d^9\underline{L}^2$ and d^7 characters are pushed out. Therefore, for the oxygen bands, the upper part has more Ni 3d character so that these bands are localized. The lower part has less 3d character so that these bands are more dispersive. The lower Hubbard band is located at even higher binding energy in the form of the satellite. In the same context, we want to emphasize that the bands which we called "d-bands" in the comparison with the LDA calculation are actually the bound states in the cluster picture. These bands in our data can either be interpreted as the "d-bands" of the LDA calculation or the bound states of the cluster calculation. We called those bands "d-bands" in most parts of this section only because we were comparing our data with the LDA calculation. It is easier for the comparison if we use the LDA language. Δ is reflected by the energy difference between the top of the oxygen band and the bottom of the upper Hubbard band (d^9). Without including the "bound state", the top of the oxygen band is lower than the experimental valence band maximum of NiO.

2. Results from CoO and MnO

Besides NiO, some angle-resolved photoemission experiments were also performed on other transition metal mono-oxides [91,99,108]. Fig.3.30 reproduces the data and the deduced E vs **k** relation from CoO by Brooks et al [108]. Again we can see clear energy dispersion and intensity modulations as a function of photon energy. However, the interpretation of angle-resolved photoemission from CoO is less unambiguous than that from NiO. This is mainly due to the fact that the CoO features are much broader and less distinct than NiO features. As a matter of fact, Brooks et al. and Shen et al. drew somewhat different conclusions based on very similar data. By comparing with an earlier and very crude band calculation, Brooks et al. concluded that CoO is a band insulator even though the experimental E vs **k** relation for the 3d bands is just the opposite of the band calculation [108]. Influenced by the NiO data and the belief that there should be some similarity between NiO and CoO, Shen et al. interpreted the CoO differently [91].

An angle resolved photoemission study of MnO was reported by Lad et al.[99]. However, the authors later pointed out that their sample surface was contaminated by Mn_2O_3, as evidenced by the 4 eV magnetic splitting of the Mn 3s core level. 109] . The correct value for the magnetic splitting of the Mn 3s core level in MnO is approximately 6 eV[98,109]. Fig.3.31 reproduces normal emission angle-resolved photoemission data by Shen et al., which is actually quite similar to the results reported by Lad et al. [109]. Shen et al. verified the Mn 3s core level magnetic splitting to be 6 eV for the sample from which they took the data in Fig.3.31. The oxygen states at higher binding energies are more dispersive while the Mn 3d states are less dispersive. Like CoO, however, the

ARPES data of MnO is less distinctive than NiO, making the data more difficult to interpret. Therefore, we can see that the qualitative picture of angle-resolved photoemission data from NiO, CoO and MnO is very similar, even though the data quality of NiO is the best. The detailed information obtained from NiO is apparently not limited to that one particular compound, but is representive of this class of highly correlated materials.

E Closing remarks

From the discussion of this chapter, we can see that there are at least four effects which determine the electronic structure and photoemission data from transition metal mono-oxides: the charge transfer screening process, the Coulomb correlation of the 3d electrons, the exchange and multiplet splitting, and the energy dispersion (especially for the oxygen bands). These effects are all quite important for an overall understanding of the electronic structure. This is probably the reason why the electronic structure and properties of these oxides and their derivatives are so complicated and hard to understand. It is fair to say that we have made much progress towards a more satisfactory theoretical description of these materials, at least in the sense that the problems are better identified and laid out.

There have been some recent theoretical efforts which have tackled the issue of the electronic structure of these oxides. Theoretical efforts based on the impurity and cluster model calculations as we have discussed in this chapter are summarized by Zanaan and Sawatzky [110]. In addition, there are several other efforts. The first is the so-called self-interaction correction (SIC) approach. This approach goes beyond the local density calculation by excluding the self-interaction of electrons which is unphysically included in the local density calculations. Using this method, Svane and Gunnarsson have obtained results for the insulating transition-metal mono-oxides that are in much better agreement with experimental data [111]. The magnetic moment is in good agreement with the experimental data and the energy gap size agrees with the experimental data much better than the local density calculation. Furthermore, they have uncovered an antiferromagnetic, insulating solution for La_2CuO_4 which the local density calculation incorrectly predicted to be a metal. They have also correctly found the metallic ground state for VO. It is also very interesting to note that they can only get good results with extended oxygen 2p states, and they can not minimize the total system energy if they use localized oxygen states. It is presently unclear how to compare the SIC results with the spectroscopic data. If one simply compares the theory and experiment and take the "renormalized many body bands" as the 3d bands, one finds that the calculated energy separation between the 3d bands and the oxygen 2p bands does not agree with the experiment. We note that no spectral weight calculation was carried out with SIC.

The second approach for these oxides is the orbital polarization correction method. By taking the orbital polarization correction to the spherical orbitals of the density functional calculation, Norman obtained a semiconducting ground state for CoO [112]. However, the gap size obtained is much smaller than the experimental data. In a separate paper, Norman and Freeman suggested that the problem of the gap size is associated with the fact that the empty states and the filled states see different potentials [113]. Their supercell calculation based on this idea gives a gap size that is very close to the experimental data. The third recent theoretical development on the electronic structure of the transition metal oxides is using the Hubbard U to replace the stoner parameter I in the LSDA calculation [114]. As discussed earlier, this approach was also applied to calculate the PES spectra for NiO. Even though it is still a mean field approach, it gives the insulating nature for all the transition-metal mono-oxides.

Before leaving this section, let us point out that several interesting experiments have been carried out to study the doping behavior of these oxides. For details of these works, we refer to the two following references [92,115].

IV. Photoemission Studies of the Normal State of Cuprate Superconductors

A. Ground state properties and issues to be addressed

In this section, we give a brief survey of some relevant ground state properties and the theoretical issues on which the electron spectroscopic experiments can shine some lights. It is usually true that the information one obtains from spectroscopic and ground state measurements (such as transport) are complementary to each other.

The cuprate superconductors are highly anisotropic materials, with most of their important properties determined by the two dimensional CuO_2 planes. This is evident from the strikingly similar $\rho(T)$ curves for optimized compositions in very different crystal structures with CuO_2 layers as the electrically active building blocks. This property of the cuprate superconductors is determined by the crystal structures, as depicted in figures 4.1 and 4.2 for the two most extensively studied compounds: $YBa_2Cu_3O_7$ and $Bi_2Sr_2CaCu_2O_8$ [116]. Soon after the discovery of the cuprate superconductors, it was recognized that these compounds have unusual normal state properties, and the understanding of these normal state properties is a key to understanding the mechanism of high- temperature superconductivity [4,5,8,9,117,118]. For example, the charge dynamics and magnetic properties of these superconductors all exhibit some unusual aspects that are widely thought to be an indication of a peculiar electronic state. All of the optimized p-type cuprate superconductors show a linear temperature dependence for the normal state resistivity over a remarkably large temperature window. The optical conductivity data suggests a peculiar temperature dependent charge carrier scattering rate. The Hall coefficient from $YBa_2Cu_3O_{7-x}$ exhibits a strong temperature dependence, in contrast to that of ordinary Fermi liquid metals. The Raman data reveal a broad electronic excitation. The understanding of these peculiar normal state properties appears to be a key to the understanding of the high-temperature superconductivity. Another important property of these superconductors is that they are related to the antiferromagnetic Mott insulators [57]. Fig. 4.3 depicts a phase diagram of the electronic properties of the cuprate superconductors [117]. Near half filling (0 holes per CuO_2 layer), the materials are acturally antiferromagnetic charge transfer insulators. (See Section III) With the increase of hole doping, the long range magnetic order fades away and superconductivity begins to prevail at low temperature at appropriate doping levels. The superconducting transition temperature increases with doping until it reaches a maximum at $x \sim 0.15$, it then drops down with further doping and the material eventually becomes a paramagnetic metal. However, short range antiferromagnetic order persists into the doping region where the superconducting ground state prevails at low temperature.

These unusual normal state properties of the cuprate superconductors raise the question whether the normal state of the cuprate superconductors can be described by the Fermi liquid picture [2, 8, 119]. If they are, then much of the traditional theoretical tools developed over the last forty years can be readily used to develop a microscopic theory of high-temperature superconductivity. On the other hand, if they are not, then we probably would have to develope new theoretical tools to address the issues of both the normal states and the superconducting states of the cuprate superconductors. This issue is very important because the Fermi liquid picture is the underlying foundation of the traditional BCS theory of superconductivity. Without the quasiparticle concept introduced in the Fermi liquid theory, it is hard to imagine the stability of the Cooper pair bound state against the fluctuations of the electron-electron and electron-lattice interactions that are several orders of magnitude larger.

The concept of a Fermi liquid has been developed following the landmark work of Landau in 1956, [120] and has been the central piece of our modern theory of a quantum liquid. The issue here is the appropriate description of degenerate Fermions with interactions. For non-interacting degenerate Fermions, the system can be well described by Fermi statistics as shown in classical textbook examples. In this limit, the Fermions move independently, and we can define quantities such as the Fermi momentum, Fermi energy, and Fermi surface. Many physical properties of the system can be described very elegantly with this approach. For interacting degenerate Fermions, the situation is not so simple anymore. At first sight, this seems to be an impossible problem. However, for the low energy physics (which in most cases are the things we care about), it turns out that the system can be reasonably well described by the so-called "elementary excitations". At low temperatures, there are only a few such "elementary excitations", and they have long life times. In this limit, much of the interesting physics of the system can be described by these elementary excitations only.

Based on this observation, the basic concept of the Fermi liquid was introduced: A normal Fermi liquid is a system of fermion particles in which the properties of the system are not dramatically modified by the particle interactions, no matter how strong the interaction may be. This concept assumes a one to one mapping between "quasi-particles" of an interacting fermion system and free particles of a non-interacting fermion system. Such a mapping was thought (and proven to be the case) to be possible if the interaction was turned on slowly and adiabatically. This way, we will still have a Fermi surface, a corresponding Fermi momentum, and Fermi energy. However, as illustrated in Fig. 4.4, the discontinuity in the momentum distribution function is reduced from 1 in the non-interacting system to a value z (often called the renormalization factor). From the conservation of particle number arguments, we find that the volume enclosed by the Fermi surface of the quasi-particles should be conserved (Luttinger's counting theorem) [121]. This concept of the Fermi liquid has provided a foundation for the modern theory of quantum liquids on which much of the modern many-body physics concepts and theoretical machineries are based. Even though liquid He_3 is the only know example of a

Fermi liquid in real life, the concept of a Fermi liquid can be extended to include neutron stars, and conduction electrons in solid where the band effects are relatively small. As a matter of fact, this concept is so robust that almost all metals (even the strongly interacting ones such as the heavy fermions) are typically regarded as Fermi liquids.

Much of the controversy regarding the applicability of the Fermi liquid concept in the high-temperature superconductors arises from the fact that the conducting carriers in these superconductors are composed of oxygen 2p electrons (holes) and strongly interacting copper 3d electrons (holes). It has been argued that the on-site Coulomb interaction between the copper 3d electrons is so strong that the Fermi liquid concept can not survive. This perception received support from some unusual properties of the superconductors. Most importantly, this viewpoint is reinforced by the fact that these superconductors are evolved by doping from antiferromagnetic Mott insulators where it is generally accepted that the Fermi liquid concept has broken down. On the other hand, it is argued that while the undoped parent compounds of the high-T_c superconductors are not Fermi liquids, the Fermi liquid concept will recover at doping levels where superconductivity prevails at low temperature [11,28]. It is fair to say that the theoretical community is divided over this issue.

Given this controversy, much experimental and theoretical work has been carried out to test the validity of the Fermi liquid concept in the high-temperature superconductors. A very impressive body of ground state (such as transport) and spectroscopic data is available now, and they have been extensively analyzed and discussed. Since photoemission data reveals very direct information about the electronic state at the microscopic level, recent high-resolution photoemission data has attracted much attention from the theoretical physics community [6,7,11,42,122]. A better understanding of the electronic structure clearly supports the efforts to resolve this important question. For the past several years, the electronic structure information as obtained by photoemission experiments has played a crucial role in shaping up our current view of this issue.

Photoemission studies of the normal state properties can be divided into two classes. The first is the class of studies performed by angle-integrated photoemission (and x-ray absorption or x-ray emission) over the whole valence band. These experiments can often be directly related to the work of the Mott insulators which have been briefly described in Sec.III.b and Sec. III.c. The theme of many of these experiments was: what is the most appropriate starting point to describe the electronic structure of these superconductors? Specifically, what kind of simplified model will be sufficient to account for the essential physics? For the simplified model, what are reasonable values of the model parameters? These spectroscopic experiments were often carried out in parallel with many theoretical studies of many-body model calculations. The second is those experiments mainly performed in the angle-resolved mode in the vicinity of the Fermi level. These experiments were the first to positively identify the existence of a Fermi surface [123-124] - a crucial point that is now well accepted by the community. Later experiments covered a very wide range of topics, from the detailed shape of the Fermi surfaces and the bands near the Fermi surfaces, the symmetry and origin of the states making up these bands, and the energy-dependence of the lifetimes of the near-E_F quasiparticle states.

The information one obtains from these two classes of experiments is complimentary. The most common starting point of interpretation for the two classes of experiments is diametrically opposed. The first class of experiments was most often interpreted within the theory of localized models that is very appropriate for insulators as we have discussed earlier in Seciton III.b. One distinct advantage of this approach is that the physical picture of the problem is very clear. The second class of experiments was more often interpreted in connection with an extended approach such as band theory. The advantage for this is that the calculation of the Fermi surface by band theory includes many of the long-range interactions which are important for the symmetry and the shape of the Fermi surfaces. Therefore, a direct comparison with the experiment is possible. The experiments have indicated that Luttinger's theorom seems to hold for the cuprates, implying that a one-electron theory such as band theory can still tell us important information such as the volume of the Fermi surface [121]. On the other hand, the band calculations have the problem of dealing with the electron correlation effects. Since the cuprate superconductors are correlated metals, the two classes of experiments provide complementary information. In this section, we summarize these two classes of experiments with emphasis on the latter since a number of review articles already exist for the former [27-36].

B. Samples and Sample quality issues

Since photoemission is a very surface sensitive experimental technique, it is crucial to have a good sample surface. For the high-temperature superconductors, it turns out that the preparation of a good sample surface is a very tricky issue. Many of the earlier photoemission works have been subjected to question because of the sample quality [28]. The samples studied involved both single crystals and polycrystalline materials. It is now clear that only those experimental data that have been confirmed on single crystals should be trusted. Often, even data obtained from single crystals is problematic. The problem arises from complications such as surface contamination, oxygen loss or disorder, cleavage damage, surface flatness, surface reconstruction and others. The sample surface quality is compound dependent, with some of the compounds (such as $Bi_2Sr_2CaCu_2O_{8+\delta}$) being much more stable than the other compounds (such as $YBa_2Cu_3O_{7-\delta}$). We will point out the problems related with samples as we pursue with the discussion of results from various compounds in the following sections.

C. Basic framework of the electronic structure

The electronic structure of these cuprate superconductors are determined by the conducting CuO_2 planes. Again, as shown in Fig. 4.5, the basic electronic structure of these cuprates have two characteristic properties: strong Cu-O covalency due to the proximity of the Cu 3d and O 2p energy levels and the strong Coulomb interaction among the Cu 3d electrons [125]. Due to crystal field interactions, the Cu 3d orbital are split into e_g and t_{2g} levels, which then further split into four levels. The highest orbital is the antibonding σ^* x^2-y^2 orbital. This general picture is true both from the quantum chemistry cluster calculation and band structure calculation, and this picture provides a foundation for the rest of the section.

D. Angle-integrated photoemission data from the whole valence band.

Most of the early photoemission studies of the cuprates were performed in the angle-averaged mode. The experimental data were usually analyzed by simple cluster model calculations in analogy to those developed for the insulating transtion-metal oxides. The results of angle-integrated photoemission studies were reviewed by several authors [27-36]. Here we only give a brief account of the major results of this class of experiments. Furthermore, we focus ourself on valence band data only, the core level photoemission data will not be discussed. The readers can find relevant core level photoemission data in earlier publications.

1. Evidence for strong correlation effects

The first experiment to point out the importance of strong correlation effect as a consequence of the large Coulomb interaction was performed by Fujimori et al. Fig.4.6 reproduces the valence band data and a simple cluster model calculated result by Fujimori et al.[126]. As we have indicated in Sec.III, the key here is the presence of the valence band satellite structure. This satellite structure can not be explained within the context of one-electron band theory, and is a consequence of the large Coulomb interaction among the 3d electrons. Even though Fujimori et al. had plausibly predicted the existence of the valence band satellite, the satellite structure can not be clearly distinguished in Fig. 4.6. (Note, they have shown in their paper clear evidence for the core level satellite.). The existence of the valence band d^8 satellite was later confirmed by resonance photoemission experiments carried out by several groups. Fig. 4.7 gives the resonance photoemission data from $La_{2-x}Sr_xCuO_4$ by Shen et al.[127]. As the photon energy is sweep through the Cu3p absorption threshold of 75 eV, the intensity of feature D increases and then decreases again, suggesting a resonance behavior. The Fano lineshape of the resonance profile is shown in panel b as a function of initial energy in a series of CIS curves. Figures 4.8, 4.9 and 4.10 reproduce the resonance photoemission data of $YBa_2Cu_3O_7$, $Bi_2Sr_2CaCu_2O_8$, and Nd_2CuO_4, respectively [128-130].

These resonance photoemission data reveal the compelling evidence for the strong correlation effects in all the superconducting compounds studied. These experimental data were often analyzed and compared with cluster or impurity model calculations based on the Anderson hamiltonian [127, 130]. The two solid curves of Fig. 4.10a are theoretical calculations based on the Anderson impurity model, with the model parameter derived from an ab-initio calculation [130]. We can see that the Anderson impurity model correctly describes many of the essential features of the spectral weight function, just like the case of CuO with one possible difference of significance. The theoretical calculation for Nd_2CuO_4 shows a distinct peak at lower binding energy than the main valence band. This peak is due to the spectral weight from the singlet state formed by a Cu spin coupled with the spin of an oxygen ligand surrounding the Cu. However, no such peak is present in the experimental data, in contrast to the CuO case where a peak is observed at lower binding energy than the main peak.(See Sec. III.b) This difference between CuO and Nd_2CuO_4 on the issue of the singlet indicates that they might be more different than we originally had thought, especially for the low energy excitations. This difference can not be understood within the framework of the Anderson hamiltonian.[24] Gunnarsson et al. noted that the bond angle of CuO and CuO_2 planes are not the same, and this might be a reason for the observed difference.[24]

Fig. 4.11 gives the basic energy level schematic of these cuprates in the cluster model language as summarized by Fuggle et al.[131]. The essential parameter values have been estimated using a variety of high energy spectroscopies (PES, core level XPS, Auger, and X-ray absorption), and range between $0 \leq \Delta \leq 3$ eV and $5 \leq U_{dd} \leq 13$ eV [10,127,131,132] More recent analysis of the experimental situation tends to give higher values of Δ [133]. These parameters suggest that the basic electronic structure can be fairly well described by a two band Hubbard model. These experimental data and their analysis provided empirical support for a large body of theoretical calculations where the model parameters were deduced from first principle calculations [134-137]. Most of the calculations involve the so-called constrained LDA calculation. In these calculation, the basic electronic structure is obtained first by band calculations, then the Coulomb interaction is determined by counting the total energy difference while varying the 3d orbtal occupation number by integer numbers. Both the spectral weight function and the model parameters from these first principle calculation were very consistent with the experimental results [137].

2. Low energy excitation state

A key issue is to determine the simplest theoretical model for the CuO_2 planes which can account for the main physics in these materials. The question to be addressed is: Is it possible to reduce from the practical two band Hubbard model to a simpler one band Hubbard model or even t-J model?

The first theoretical effort was made by Zhang and Rice who suggested that one need only consider the dynamics of a spin singlet formed by Cu and its oxygen ligand[138]. A recent summary of the theoretical efforts along this line is given by

Hybertsen et al.[137]. It is generally agreed that we can reduce the two band model to a simple one band t-J model which can be used as a starting point for microscopical models of high temperature superconductivity.

The experimental effort has already been addressed in the last section. In a simple picture, if one could reduce the Hamiltonian to a t-J type of model, one would expect to see a peak in the spectral weight function at the lowest energy corresponding to the singlet. For example, the theoretical calculation of Nd_2CuO_4 shows such a distinct singlet peak at the lowest binding energy well separated from the rest of the states . However, no such peak is present in the experimental data of Nd_2CuO_4 [130], athough a peak in this energy is seen in CuO [24]. It is not clear what the significance of this experimental observation is at this point. It could mean that the lowest energy excitation state is more complicated than we have anticipated, or it could simply mean that the singlet state is near degenerate with other low energy states with basically no coupling.

3. Important experimental issues regarding the earlier data

An important experimental issue worth emphasizing is that the surfaces of the cuprate superconductors are often unstable in the ultra-high vacuum. This point was most clearly established in the important experiments by Arko and his coworkers [28, 128]. Arko et al. found that for single crystal $EuBa_2Cu_3O_7$ cleaved at very low temperature (20K) in UHV, the photoemission spectra changed dramatically and irreversibly when the samples were warmed up to liquid nitrogen temperature. They attributed this change of the spectra as a consequence of oxygen loss near the sample surface. For the spectra taken at 20K, Arko et al. found a well defined Fermi edge that was absent in all the previous experimental data [28, 128]. This actually is the first indication of the existence of a Fermi surface in this family of superconductors, a fact that is widely accepted now but was not so then. The well defined Fermi edge disappeared immediately if the sample temperature was raised up to 50K or so [28]. Later work on presumably higher quality samples showed that the surface could be robust to temperature cycling [139]. Due to the surface sensitive nature of the photoemission experiments, such surface problems have forced us to examine the experimental data very critically. Experimental data from ceramic materials are highly suspect and should be interpreted with caution. In the field of photoemission studies of high-temperature superconductors, only those experimental results that are verified by low temperature single crystal works should be trusted, and then even in that case, one must be cautious.

There are a few empirical indications for us to enforce the quality of the experimental data. These, of course, are necessary but not sufficient conditions. One indication of good data is the absence of the notorious -9 eV peak and multicomponents (with energy separations of several eV) in the oxygen 1s core level data. The importance of this is primarily based upon empirical evidence [14]. For instance, the -9 eV peak is observed to grow in intensity as the samples age, with a corresponding decrease in the intensity of the near-E_F peaks. Of course, some aspects of data sets that contain the -9 eV peak may still be good. Other empirical indications for good data are the spectral stability vs. time, the sharpness of the features, a low background, and consistent, repeatable results. For metallic or superconducting samples, the spectral weight at E_F is also often a good indicator, with better samples having more weight. For angle-resolved measurements, a large amount of dispersion as well as very sharp clear Fermi surface crossings (in metals) are indications of good quality data. Even then, the story is not so straightforward. For instance, the sharpest features observed in a normal state angle-reolved photoemission study of a cuprate are those observed in single-crystals of YBCO (see section E 4). However, it is known that the YBCO surface has non-idealities, and there is not yet a consensus as to whether these features are intrinsic.

Certainly the data from many of the earlier studies should be reexamined, with the possible exception of those from $Bi_2Sr_2CaCu_2O_8$. The information obtained near the Fermi level was clearly questionable. However, the important finding outlined in the last section, namely the existence of a correlated satellite structure in the valence band photoemission data, withheld the test of later more careful experiments carried out on better prepared single crystals. Fig. 4.8 shows the spectra taken from $YBa_2Cu_3O_7$ cleaved and kept at 20K [128]. It is quite clear that there is a Cu satellite at -12 eV which shows a strong enhancement at 74 eV. As a matter of fact, this is the strongest valence band satellite seen in the cuprates at the Cu 3p threshold. As a side remark, we also notice a small peak at -9 eV in the 74 eV spectrum but not present in the 70 eV spectrum. As we have pointed out before, usually the -9 eV peak found in the cuprate superconductors is due to the extrinsic emission caused by (most likely) oxygen disorder. However, this data shows that there is a small intrinsic Cu satellite peak at -9 eV also. This peak is visible at the Cu resonance but not visible otherwise. This peak is most likely due to one of the multiple components of the d^8 final state.

Despite the compelling evidence of correlation effects, Arko et al. also found that, except for the satellite region, the photoemission spectra taken at low temperature agree with the band calculation much better than previous experiments[128]. Fig.4.12 shows photoemission data in comparison with results from band calculations by Arko et al.. We can see that the calculation gives quite useful result. The agreement at both 70 eV and 20 eV is very decent. This result naturally brings us to the next section in which angle-resolved photoemission data are directly compared with the results of band calculations.

E. Angle-resolved photoemission data from near the Fermi level

1. Overview

The focus of most of these angle-resolved photoemission experiments was on the Fermi surface and very low energy excitations of the cuprates, as these low energy excitations are the most important for the physical properties of the system. These are technically very difficult experiments because very high energy resolution is necessary in order to observe the relevant energy scales, and because high count rates are needed in order to get the necessary statistics. In addition, the samples used for these studies are very complicated and fragile. For this reason, progress in these studies for a large part followed the developement of the state-of-the-art ARPES instrumentation as well as improvements in sample quality.

The primary significance of the earlier experiments were that "bands" were observed to disperse towards and then cross the Fermi surface as expected for a metal. And, although there are significant differences between the experimental data and band caclculations, the majority of the experimental data indicated that the Fermi surface crossing points were similar to those predicted by band theory calculations. This was widely accepted as indicative of the fact that Luttinger's counting theorom was obeyed in the cuprate superconductors - that the volume of the Fermi surface was unchanged by the correlations [121]. This is a very strong constraint on theory, and is for instance a necessary ingredient for a Fermi liquid [120]. Since these early studies, many experiments have been carried out to map out the details of the Fermi surfaces and near-E_F band structure of a wide variety of the cuprate superconductors, including single crystals of the Bi2212 system [123,124,140-152], Y123 and Y124 [139,153-160], the n-type superconductors NdCeCuO [161-163], the Bi2201 system [164,165], as well as some "model" systems such as the two-dimensional metals $TiTe_2$ and $NbSe_2$[166,167]. Samples with a variety of doping levels have also been studied in the Bi2212 system [147,168,169], the Y123 system [153,157,158], and in the NdCeCuO system[161, 170].

While in general the measured Fermi surfaces agree with the band calculations to first order, the differences are significant enough that any real need of Fermi surface information should be accomodated by experimental data (as opposed to a band theory calculation). The large amount of available data has brought out a number of trends in the data, and it is starting to enable us to make strong statements about the relationship of the electronic structure to the physical properties of the system. For instance, one of the most striking aspects of the experimental data is the presence of some flat bands (little energy dispersion over a significant **k**-space region) which lie very near E_F in the p-type cuprates[142,143,139,156,158,165]. While the details of these flat bands vary from sample type to sample type, and confusions such as a possible origin from the chains in Y123 [139,156,158] or the BiO pocket in Bi2212 exist [142,150], the fact that data exists on a wide variety of samples lends credence to the observation. Flat bands are also observed in the n-type cuprate NdCeCuO, but in this case they are ~ 300 meV below E_F, and so they will be electrically inactive [161]. Dessau et al.[142,143] and King et al. [161, 165] suggested that this striking difference in the band structures of the p- and n-type superconductors may be related to the fact that many of the physical properties of the p-types are "anomalous" while thse same physical properties are much more "normal" in the n-type cuprates.

a. Notation of the high symmetry points of the Brillouin zones of the cuprate supercondutors

Before we begin any of our discussions, it is important to straighten out the notation used to denote the high symmetry points in **k**-space. Due to slight differences in their crystal structures, the Brillouin zones of each family of the cuprates is labeled differently, and these differences can lend to a great deal of confusion in the interpretation of the data. The simplest way to understand the notation is to reference everything to the Cu-O planes. Figure 4.13a shows the Brillouin zone of a single Cu-O plane, with the plane oriented as shown in the right panel (the Cu-O bond directions are parallel to the edges of the paper). The Γ point is at the middle of the Brillouin zone, the M point is at the corner (π/a, π/a), and the X(Y) points are midway along the edges (π/a, 0) or (0, π/a). The Γ-X(Y) direction is along the Cu-O bonds and the Γ-M direction is 45° to the bonds, as shown in the figure.

Figure 4.13b shows the Brillouin zones for the real (but still relatively simple) materials LaSrCuO and NdCeCuO. Again, the orientation is such that the Cu-O bonds are parallel to the edges of the paper, but we find that the notation has changed so that the X and Y points are at the corner and the G_1 point is midway along the edge. In essence we can consider the changes as a one-to-one mapping, with Γ-->Γ, M-->X(Y), and X(Y)-->G_1. Due to their finite amount of three dimensionality, the Brillouin zones of these materials are also three dimensional. The Z point can be reached by moving normal to the planes from the Γ point, or by moving from Γ past G_1, as shown in the figure. Due to their near two-dimensionality, it is often a good approximation to consider the Γ and Z points to be equivalent. The most common notations used to describe the high symmetry points of Bi2212 and Y123 are shown in figures 4.13c and 4.13d, respectively (more complicated versions which account for the slight three dimensionality and orthorombicity have also been used). Again, the alignment is such that the Cu-O bonds are parallel to the bottom of the page. The mapping for Bi2212 is Γ-->Γ, M-->X(Y), and X(Y)-->$\overline{M}$, and for Y123 it is Γ-->Γ, M-->S, and X(Y)-->X(Y).

b. Results of model calculations of the electronic structure of the cuprates

This section briefly discusses the results of calculations that have been carried out on the cuprates, including both first-principles band theory calculations and simpler tight-binding calculations. We principally concentrate on the information needed to understand the data - much more complete reviews of these topics have been published elsewhere [10].

We begin by considering a tight-binding analysis of the CuO_2 planes. This is one of the simplest possible **k**-dependent approximations for the cuprates we can make. The predominant coupling is the nearest-neighbor sigma-bonded coupling between Cu d-states and O p-states. As shown by Harrison, the highest energy band has x^2-y^2 symmetry and, as shown in figure 4.14, reaches its maximum at M and has a saddle point at X [171]. This saddle point gives a singularity in the density of states (a van-Hove singularity) that is observed in figure 4.14d. At zero doping the x^2-y^2 band is half filled and the Fermi energy lies at the van Hove singularity. A square Fermi surface forms, denoted by the dashed line of figure 4.14a.

This model, as well as the band theory calculations, predicts a metallic ground state for the undoped parent compounds, which are in reality antiferromagnetic insulators of the Mott-Hubbard type, with the insulating nature due to the strong on-site Coulomb interactions. This failure of the simple models has been discussed in chapter III. The high T_c's are formed by doping the parent compound with either electrons (as in the n-type superconductor $Nd_{2-x}Ce_xCuO_4$) or holes (as in the p-types $La_{2-x}Sr_xCuO_4$, YBCO, Bi2212, etc.). As we will see, the Fermi surfaces for the optimally doped materials calculated by these simple methods do a surprisingly good job at predicting the measured Fermi surfaces, even though the models fail completely in the half-filled or undoped case.

To first order, we can envision the doping process as either raising or lowering the Fermi energy, respectively. This will cause the Fermi surface to expand so that it is centered around the M point (electron-doping) or contract so that it is centered around the Γ point (hole doping). In reality, the inclusion of O-O coupling terms buckles the Fermi surface slightly, as shown in figure 4.15 from Dickinson et al. [172] The main significance of this is that it moves the van-Hove singularity off of the Fermi surface at half-filling, with moderate p-type doping required to bring it back.

Fig. 4.16 reproduces the Fermi surface and the band structure of $Nd_{2-x}Ce_xCuO_4$ as calculated by Massidda et al.[173]. The calculated Fermi surface of this compound is the simplest with a hole pocket arount the X point. In this sense, this is a good system to perform experimental studies.

A large "spaghetti" of bands is observed to exist from approximately -0.5 eV to -6.5 eV. These are primarily Cu 3d and O 2p derived and correspond very roughly to the main valence band observed in the figures of the previous section. The great number of bands is due to the fact that the unit cells are very large, and so the Brillouin zone is very small with many bands folded back in. It will be difficult to do more than compare the calculated and measured (in an angle-integrated measurement) density of states in this region because we don't expect to be able to track the dispersion of individual bands.

A number of bands are observed to split off from the main spaghetti of bands and cross through the Fermi level. These bands are of the greatest interest, for they will be responsible for most of the physics. It is therefore fortunate that they are split off from the "spaghetti" of bands so that they will be individually resolvable.

Results from an LDA calculation of the band structure of stoichiometric $Bi_2Sr_2CaCu_2O_{8+\delta}$ by Massida et al. are shown in figure 4.17 [174]. This band structure is much more complicated than that of NdCeCuO. First of all, there are two Cu-O planes per unit cell, instead of just one. In the absence of coupling, there will be two degenerate x^2-y^2 bands, and the Fermi surface will be the same as in the single layer case. While it has been hypothesized that these couplings would in fact be absent in the normal state [175], other theories predict non-zero coupling which will split these two bands. The matrix element for this coupling is very small along the Γ-X(Y) symmetry direction (45° to the Cu-O bonds) and so the bands will remain near degenerate there. Off of Γ-X(Y) the coupling is finite and so the bands and the Fermi surface will split, creating a more complicated Fermi surface. A calculated Fermi surface for Bi2212 is shown in figure 4.18, along with the band structure along the Γ-$\overline{\text{M}}$-Z direction [174]. As we will discuss next, the inclusion of the Bi-O planes alters this band structure and Fermi surface. The results of figure 4.18 were obtained by Massidda et al. by ignoring the interaction between the Cu-O and Bi-O bands[174].

In the calculation of figure 4.17, a set of bands corresponding to Bi $p_{x,y}$ -O $2p_{x,y}$ ($pp\sigma$) states dip below the Fermi level forming an electron pocket around the $\overline{\text{M}}$ (and L) point. Due to the interaction (anti-crossing) of the Bi-O and Cu-O bands, only one Bi-O band crosses E_F, and the Cu-O band coming up from Γ towards $\overline{\text{M}}$ is repelled and does not cross the Fermi level, as it would in the non-interacting case. We note that this interaction implies a degree of hybridization between the Bi-O and Cu-O planes, and so it is not strictly fair to keep calling them a Bi-O or Cu-O band. For simplicity however, we will keep calling them by those names. A schematic drawing of the calculated Fermi surface and band structure near $\overline{\text{M}}$ for this scenario is shown in figure 4.19 [174]. The important differences between the Fermi surface in this scenario and that shown in figure 4.18 are the existence of the Bi-O based electron "pocket" centered at $\overline{\text{M}}$, and the fact that the Cu-O derived Fermi surface is very different from that in figure 4.18; in the full calculation both of the Cu-O bands are centered around the X(Y) points, while in the calculation which ignores the BiO-CuO$_2$ coupling one of the CuO$_2$ bands is centered around the Γ point.

Fig. 4.20 gives the band structure and the Fermi surface of $YBa_2Cu_3O_7$ as calculated by Pickett et al.[176]. This calculation takes into accout the smearing that incured from the dispersion along the third dimension. There have beeen several band calculations for $YBa_2Cu_3O_7$ [176-178]. In general, these calculations are quite similar with the Fermi surface mainly determined by the x^2-y^2 antibonding bands. They all show three bands that cross the Fermi level along Γ-S and X-S directions with more or less the same topology. The main area of difference lies in the chain derived band along the Γ-Y direction. Two of the calculations suggest that there is a Fermi surface crossing going from Γ-Y [177-178], while the other calculation does not have this crossing [176]. (As we will show later on, whether this crossing exists or not is still controversial).

There has been no state-of-the-art band calculation done for the $Bi_2Sr_2CuO_6$ yet. The only available band calculation was performed by the simple tight-binding method [179]. For experimental purposes, the data can be compared with the band structure of $Bi_2Sr_2CaCu_2O_8$ since one would expect some similarity of their band structures.

c. Two-dimensionality

The cuprate superconductors are highly two-dimensional, and this two-dimensionality is reflected in their electronic as well as their physical properties. The effect on their band structures is that there is little or no dispersion along the k_z direction (see for example the Γ-Z cuts in figures 4.16, 4.17, and 4.20). This property plays a simplifying role for the successful application of angle-resolved photoemission on these materials. As discussed in Sec.II, in an angle-resolved photoemission process, only the momentum component parallel to the crystal ($k_\parallel$) surface is conserved when the electron escapes from the sample, and thus can be fully determined experimentally. The perpendicular component of the crystal momentum ($k_\perp$) is not conserved at the sample/vacuum interface and thus can not be fully determined. This problem often causes confusion in the analysis of three dimensional materials. However, for two dimensional material such as the high-temperature superconductors, this is not a problem since the effects caused by the uncertainty in $k_\perp$ are not very severe. Hence, experiments on 2-d materials are relatively straight-forward, and for most purposes we can ignore the third dimension. One instance where this may not be so is in the case of the detailed study of the photoemission lineshapes, where the dispersion of the final state band along the k_z direction will add some additional broadening terms. These issues will be disussed in more detail in section 10.

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2. Rules and methods to determine the Fermi surface from photoemission

Since the main thrust of this chapter is to determine the Fermi surface using photoemission spectroscopy, it is intructive to state the methods and the rules to make such a determination. Ideally, the Fermi surface is the topological surface in **k**-space where the energy bands cross the Fermi energy. If the quasi-particle is a well-defined peak and if there are no extra complications due to effects such as the elastic and inelastic scattering, then the procedure of determining the Fermi surface is well defined as illustrated in Fig. 2.5. For simplicity, here we do not consider the incoherent part of the quasi-particles. As one changes the emission angle and hence varies the **k** value, the quasi-particle peak disperses in energy. Due to increased lifetimes, the quasi-particle peak sharpens up as it approaches the Fermi level, until it is a true delta function peak (infinite lifetime) when $\mathbf{k}=k_F$. The quasi-particle peak disappears from the photoemission spectrum after it passes E_F, as photoemission only measures the occupied density of states (electron removal spectrum). From the emission angle at which the the peak in the photoemission spectrum crosses Fermi level, we can in principle determine k_F and thus the Fermi surface information.

In reality, the determination of the crossing point may be much more difficult than illustrated in the ideal case above. On top of the obvious problems of finite energy and momentum resolution and statistics (signal/noise), effects such as thermal broadening, elastic and/or inelastic scattering of the photoelectron, and the possibility of a non-flat sample surface may contribute. These mechanisms will add to the uncertainty in the crossing position. In addition, there may be multiple bands, each of which contributes a peak, and there will be effects due to the incoherent part of the spectrum. The situation is further complicated by the fact that we do not yet have a real theoretical understanding of the lineshape of the excitations (see section 10), and so a fitting effort to try to remove some of these broadening effects is severely hampered. For these reasons, the determination of the Fermi surface crossing points from the experimental data is not always straight-forward and is sometimes quite subjective. On the other hand, if the data is very good, the crossing may be extremely clear and obvious, and qualitative rules can be used very effectively to determine the crossing.

The qualitative rules that we have found most reliable in determining the Fermi surface crossing follow. First, a quasiparticle peak must be clearly distinguishable from the background. When the peak gets very close to E_F, it will begin to be cut off by the Fermi function. When the quasiparticle energy is at E_F, the peak will have approximately half its original weight and the leading edge of the spectrum will be intercepted midway or higher by the Fermi energy. Note that this implies that the most intense part of the spectrum will no longer correspond to the quasiparticle energy, a fact that adds to the complications of picking a Fermi surface crossing. For this reason we also recommend that the peak be tracked over a wide range of angles, and an extrapolation of its dispersion relationship made to E_F. This extrapolation should agree with the intensity modulation and and leading edge energy position. Finally, it is exceptionally valuable to have many cuts through the Brillouin zone, and/or to use multiple photon energies and polarizations. Only in this way can the real trends and consistencies in the data be uncovered.

These cautions aside, we should say that the Fermi surface determination by angle-resolved photoemission is not an arbitrary process. In fact, most of experimental results are remarkably consistent with each other, particularly once the sample quality and statistics improved. The fact that there is no hard rule in the data interpretation merely implies that one should be aware of the errors that might be involved in the interpretation of the photoemission data. We will pay attention to such issues as we pursue our discussions ofphotoemission data taken on the various compounds.

3. Results from $Bi_2Sr_2CaCu_2O_{8+\delta}$

The first and most extensive angle-resolved photoemission studies of cuprate superconductors have been performed on the $Bi_2Sr_2CaCu_2O_8$ system. This is mainly due to the high quality of the cleaved surface as well as its great stability in vacuum. The reason that the $Bi_2Sr_2CaCu_2O_8$ surface is so ideal is probably related with the fact the crystal cleaves between the two adjacent Bi-O planes connected by the weak Van der Walls bond. (See figure 4.2 for the $Bi_2Sr_2CaCu_2O_8$ crystal structure.) A very strong indication of the superiority of the $Bi_2Sr_2CaCu_2O_8$ surface is the fact that photoemission studies of the superconducting state of $Bi_2Sr_2CaCu_2O_8$ have given very beautiful and valuable results, while there have as yet been no clear successes in the observation of the superconducting gap in any of the other cuprate superconductors (see section V). In addition, the Bi2212 surface has been carefully characterized by surface-structural spectroscopies such as LEED and STM.

The first reported angle-resolved photoemission study of $Bi_2Sr_2CaCu_2O_8$ was by T. Takahashi et al.. This study was done with relatively poor energy resolution and statistics; nevertheless it was able to provide the first experimental evidence for a dispersive feature crossing the Fermi level [140]. The first state of the art high-resolution high-statistics photoemission experiments were performed by Olson et al [123,124]. This work represented a real breakthrough in the field, in the sense that it really opened up the field of studies of the near-E_F states (low energy excitations) of the cuprate superconductors. Since these low energy excitations are the most important for a physical understanding, we will mainly concentrate on high-resolution photoemission studies near the Fermi level, even though some angle-resolved photoemission studies on the whole valence band have been carried out [140,141,180].

Fig. 4.21 shows the now famous data by Olson et al. along a line parallel to the Γ-Y high-symmetry direction [124]. The experimental data were collected from a single crystal cleaved at very low temperature and kept slightly above its superconducting transition temperature. The energy and momentum resolution of the experimental set up were about 32 meV and two degrees (corresponding to about ten percent of the Γ-Y length), repectively. From the bottom curve up, one moves from near the Γ point towards larger **k** value along the line parallel to Γ-Y. We can see that there is a very broad feature centered at approximately -350 meV near the Γ point, and it disperses to lower binding energy as we move towards the Y point. As the feature approaches E_F, it sharpens up and grows in magnitude, reflecting an increased quasiparticle lifetime. Between the θ emission angles 12° and 14°, the peak dissappears, indicating a Fermi surface crossing. The inset at the lower left corner compares the experimentally determined E vs **k** relation with that from a band calculation [174]. We can see that the experimental and the theoretical bands cross the Fermi level at approximately the same position, reflecting very similar Fermi surface topologies at this area of **k**-space. However, the dispersion rate of the experimental band is about half of that from the theoretical calculation, implying that the experimentally determined effective mass is twice the band mass.

While the above data was very convincing, it should be noted that there were other reports that gave different interpretations. Takahashi et al. suggested that there were two bands crossing the Fermi level along the Γ-Y high symmetry direction, one approximately 25-30% of the way from Γ-Y and one much later at 50% [141]. A complimentary angle-resolved inverse photoemission study by the same group claimed to see band crossings from what were possibly these same two bands [181]. Manzke et al. reported one band crossing the Fermi surface with similar effective mass but with a crossing position quite different from that of Olson et al.[151]. Mante al al. also reported experimental data recorded at room temperature that gave somewhat different crossing positions and a high effective mass near 4 [144]. Hwu et al. reported data off of the high symmetry directions, but which was very inconsistent with the band calculation that Olson's data agreed with [152]. The most likely explanation for these differences appears to be sample quality, particularly surface uniformity and flatness. This is somewhat of a unique problem to Bi2212 and other very soft materials, because even though they cleave easily and always give a nice looking valence band, all but the most carefully prepared samples will buckle slightly during the cleave, or be left with some small flakes standing up. These of course will add to angular averaging, and may give peaks or crossings at anomalous locations. In addition, the cuprates are sensitive to oxygen loss, and the standard process of baking an experimental chamber to get ultra-high vacuum may severely alter a sample if the sample is also baked. For this reason, a number of groups have implemented schemes where a sample can be load-locked without baking into a pre-baked vacuum chamber.

The question then, is how to decide which (if any) represent the “true” results. First, one should look for reproduction by other groups. Recently, Dessau et al. has presented a very detailed study of Bi2212 which agrees well with the Olson data of figure 4.21, but not with the other data [142,143]. Secondly, the sharpness of the features, the peak/background ratios, and the sharpness of the crossings can be used as an indication of which data is “better”, as a higher quality and more uniform surface will give less angular averaging, and hence sharper features and crossings. The Olson/Dessau data had sharper features, crossings, and a higher peak/background ratio than the other data. They also had higher statistics, making real features easier to see and making noise less likely to be attributed to be a real feature.

Olson et al. took a number of other cuts through the Brillouin zone, in particular aimed at determining whether the band theory prediction of a BiO pocket centered at $\overline{\mathrm{M}}$ was correct. Their data is shown in figure 4.22 [124]. This is a very difficult issue, for there are predicted to be a number of bands in very close proximity to each other, as shown in the inset to the figure or in Fig. 4.17 [174]. While they could not give a definitive answer, Olson et al. felt that their data suggested that the BiO pocket did in fact exist.

Wells et al. addressed the issue of the BiO pocket in a very different way, by performing what is known as a “crud” test in an oxygen annealed sample which has lower transition temperature[147]. This test took advantage of the facts that 1) the outermost surface of cleaved $Bi_2Sr_2CaCu_2O_8$ is a BiO plane, and 2) photoemission is a surface sensitive probe with probing depths of the order of 10 Å or less, implying that essentially all of the BiO signal came from the outermost BiO plane (this fact was dependent upon the particular photon energy used for the experiment). Fig. 4.23 shows the photoemission spectra taken near the Fermi level crossing along the Γ-X and the Γ-$\overline{M}$ directions before (thin lines) and after (thick lines) a submonolayer of Au was deposited on the surface (Au was chosen to avoid any dramatic chemical reactions upon deposition. See references 14 and 33 for details of the chemistry of the metal/superconductor interface.). We can see that the feature near the Fermi level along the Γ-$\overline{M}$ direction is dramatically modified by the Au deposition while the feature near the Fermi level along the Γ-X direction is basically unaffected. Wells et al. took this to imply that the states along Γ-$\overline{M}$ had much more surface or BiO character than the states along Γ-X. While this conclusion is consistent with the band theory prediction of a BiO pocket centered at $\overline{M}$, it is not a proof, for a separate BiO band was not observed in the experiment. In the same paper, Wells et al. also noted that the band near Γ-$\overline{M}$ is very sensitive to the oxygen content. They found in a sample with lower oxygen content, the band along Γ-$\overline{M}$ is not at the Fermi level.

The next study of the Fermi surface and near-E_F electronic structure of Bi2212 was the very detailed study by Dessau et al. [142,143]. This study took advantage of the high counting rates and high resolution available from an undulator source at SSRL, as well as some high quality single crystals of Bi2212 which survived a solid week of data taking with no detectable deterioration. This enabled them to map out the Brillouin zone in great detail and uncover some intriguing results. A photon energy of 20.5 eV was used, and the sample was maintained at a temperature of 100K, comforatably above the superconducting tramnsition of 85K. A selection of the cuts taken by Dessau et al. is shown in figure 4.24 [142]. Panel a shows a cut along the Γ-X high symmetry direction which is very similar to Olson’s famous data of figure 4.21. As in Olson’s data, we observe a dispersive quasiparticle peak sitting on top of a non-dispersive “background” which extends up to E_F. The main emphasis in this section is on the quasiparticle peak, which is observed to cross E_F near the emission angle 10/10. This is indicated in figure 4.25a by the dark shading of the circle. The non-dispersive “background” will be discussed in sections 9 and 10. Panels b through e of Fig. 4.24 show a number of cuts along other directions through the Brillouin zone, with the general directions as indicated in the inset of each panel. The cut of panel b, taken along the Γ-$\overline{M}$ zone diagonal, shows a peak dispersing towards and then skimming very near E_F for emission angles beyond θ/ϕ = 15/0. Since the peak does not show a strong intensity modulation as it remains near E_F, a FS crossing can not be distinguished. All one can infer is that a band is very near E_F (probably within ± 30 - 50 meV) throughout this region. This is indicated in figure 4.25a by the diagonally striped circles. The cut of panel c shows the behavior of these states as one moves from near $\overline{M}$ towards X. The near-E_F peak at 20/0 remains essentially unchanged until near 20/8, where the intensity begins to dramatically decrease, signalling a FS crossing. As we can see from figure 4.25a, there is a peak near E_F for a very large portion of the BZ.

Panel d shows a cut along Γ-$\overline{M}$ taken by varying the ϕ emission angle. Surprisingly, this cut shows a clear FS crossing, even though panel b (taken along a crystalographically equivalent direction) did not show the crossing. To determine the cause of this, Dessau et al. rotated the sample by 90° (leaving the direction of polarization of the incident light fixed) and retook some of the cuts [142]. A comparison with the unrotated spectra indicated that the lack of symmetry is due to matrix element differences associated with the photon polarization direction relative to the electron emission direction, and not a result of any broken symmetry of the crystal itself. These polarization effects proved to be an especially valuable tool in the deconvolution of the band structure (see section 9). They also are important in helping us understand the detailed lineshape of the quasiparticle excitations, as will be discussed in section 10.

Figure 4.25b shows the experimentally determined FS of Bi2212 obtained by reflecting the crossing points of 4.25a around the high symmetry axes. This figure dramatically highlights the strong propensity for Fermi surface nesting in this material. In particular, Dessau et al. showed that there is a nesting vector **Q** near (π,π) which may help explain why the measured dynamical susceptibility $\chi(q,\omega)$ is so strongly peaked near the wavevector (π,π) [182]. We also note that there is another nesting vector that is not at (π,π) but is rotated by 45°. A comparison of the nesting as well as other Fermi surface properties with the other cuprates will be given in section 7.

The full band calculation of Bi2212 depicted in figures 4.17 and 4.19 does not agree well with Dessau's experimental Fermi surface of figure 4.25b. In addition to the absence of the BiO pocket, which could be hard to observe, the main difference is the fact that one of the two CuO_2 pieces of Fermi surface encloses the Γ point in the experiment, while the theory shows both pieces enclosing the X(Y) points. However, Massida et al.'s calculation which artificially ignores the interaction between the BiO states and the CuO_2 states agrees relatively well with the experimental Fermi surface (see Fig 4.18) [174]. Of course, if the BiO band did exist as calculated, there would be no reason to expect that it would not interact with the CuO_2 bands. The most likely scenario is that the BiO bands remain entirely above E_F for all **k**, and therefore would not disrupt the observed CuO_2 band structure. This scenario is consistent with that from tunneling experiments, which have found the Bi-O plane to be non-metallic [183.184], and with quantum chemical calculations which have found that the BiO potential may be raised due to the non-stoichiometry of the compound as well as the superstructure in the BiO planes [185,186]. Of course, this does not rule out a degree of hybridization between the BiO and CuO_2 bands.

This result of the absence of a BiO pocket appears to be in contradiction with Wells et al.'s study presented in Fig. 4.23 [147]. While Dessau et al.'s study is more complete, it is nevertheless important to try to understand the apparent inconsistency. First of all, we note that the samples used for the two studies were slightly different. Extra oxygen had been incorporated into Wells et al.'s sample through an annealing procedure, and it is believed that the extra oxygen goes near the BiO planes. STM[187] as well as photoemission studies have reported that this makes the BiO planes more metallic. Secondly, the results of measurements of the size of the superconducting gap vs. **k** have shown that the largest gap occurs near the $\overline{\mathrm{M}}$ point (see chapter V). While it is conceivable that a gap could be induced in the BiO planes through the proximity effect, it is very unlikely that the gap in those planes would be larger than that observed in the CuO_2 planes. Aside from the sample issue, a possible reason for the results observed by Wells et al. is that the gold adatoms doped the surface in such a way that the Fermi surface crossing (CuO_2-derived in this scenario) shifted from between the Γ and $\overline{\mathrm{M}}$ points to between the $\overline{\mathrm{M}}$ and X(Y) points, making the feature along Γ-$\overline{\mathrm{M}}$ disappear. Further studies of the effect of gold or other adsorbates on the surface of Bi2212 would be quite worthwhile.

The experimental E vs. **k** relationship from Dessau et al's data is shown in Fig. 4.26 [142]. The circles represent the experimental data points along the high symmetry directions, while the lines represent an interpretation of the dispersion relationships. On this scale, the data points near $\overline{\mathrm{M}}$ all appear to be right at E_F. Because two distinct pieces of FS are observed in Fig. 4.25, two bands are shown, one each from the even and odd combinations of the two CuO_2 planes per unit cell. One of these bands crosses E_F between Γ and $\overline{\mathrm{M}}$ and one crosses between $\overline{\mathrm{M}}$ and X(Y), as in Fig. 4.25. The bands are in general non-degenerate, except along Γ-X(Y) where the splitting appears to be small or zero, in agreement with the predictions of LDA calculations [174].

Fig. 4.26 illustrates a saddle-point behavior for the bands near the $\overline{\mathrm{M}}$ point: the bands exhibit a maximum when traversing Γ - $\overline{\mathrm{M}}$ - Γ, and a minimum upon traversing X-$\overline{\mathrm{M}}$ - Y. As shown in Fig. 4.14, a saddle-point is expected at this location of the Brillouin zone, and ignoring broadening effects, will lead to a singular behavior in the density of states. This behavior is typically referred to as a saddle-point-singularity of van Hove singularity. As we will detail later, this feature is expected to have wide ranging effects on the physical properties of the system.

Dessau et al.'s interpretation of the data is not unique; P.W. Anderson has proposed an explanation of the data that doesn't require intra-cellular coupling but instead relies on both real and "ghost" pieces of FS [188]. In his theory, the electronic excitations are a composite of charge bosons (holons) and spin bosons (spinons). In one dimension, an electron operator at $\mathbf{k}_F$ will create a holon of momentum $2\mathbf{k}_F$ and a spinon of $-\mathbf{k}_F$. In two dimensions, the momentum of the holon and spinon need not be colinear, and so an electron can create holon-spinon pairs at a momentum which differs from the "real" Fermi surface. This is what Anderson terms a "ghost" Fermi surface. The construction for obtaining the ghost Fermi surfaces is illustrated in Fig. 4.27. A Fermi surface for the spinons at $\mathbf{k}_F$ and for the holons at $2\mathbf{k}_F$ is drawn. Next, the $-\mathbf{k}_{F(2)}$ portion of the spinon Fermi surface at each point $2\mathbf{k}_{F(1)}$ of the holon Fermi surface is scribed in. The difficulty in performing the calculation is estimating the weighting factors for the non-colinear holon-spinon pairs. A preliminary random dot picture of the Bi2212 Fermi surface using this construction and a severe weighting factor favoring colinearity is shown in Fig. 4.28. In this picture the "true" Fermi surface is that which surrounds the Γ point. Due to the strong curvature at the $\overline{\mathrm{M}}$ point, this region shows pronounced "ghosting". This explains the flat bands observed near the $\overline{\mathrm{M}}$ point by Dessau et al. [142]. The sharp drop in intensity between $\overline{\mathrm{M}}$ and X(Y) that Dessau has attributed to a crossing is in this picture a result of a "quasi-van-Hove singularity" in the holon spectrum which exists at the X(Y) point of the Brillouin zone [188].

More work needs to be done to distinguish between the different interpretations. One important experimental finding would be the clear presence of each of the two CuO_2 bands in one spectrum. Anderson feels that the absence of this in the present data is a strong support for his two-dimensional "confinement" idea central to his theories [188]. Dessau et al. feel that the fact that they have not definitively observed these two separate bands in any one spectrum may also be due to the strong selection rules as a function of polarization that is detailed in Fig. 4.24 and 4.25, as well as discussed in section 9 [142,143]. In addition, they have pointed out that the rapid broadening and weakening of the quasiparticle peaks as a function of energy is responsible for making the two peaks appear as one [142]. More studies of the near-E_F band structure and Fermi surfaces, possibly done with a variety of polarizations and photon energies, will be important for answering this very fundamental question.

The experimental electronic structure near E_F shown in figure 4.26 diverges even more from the band theory than does the Fermi surface. The calculation of figure 4.17 shows what appears to be these same two bands, yet they show much greater dispersion near the $\overline{M}$ point and a much greater energy splitting. These differences may imply that the correlation effects which are responsible for the renormalization are much greater near $\overline{M}$ than along Γ-X(Y) where a mass enhancement (relevant to the LDA result) of a factor of two is observed [124,142]. In fact, it has been suggested that the correlations are so strong that the concept of a quasiparticle may no longer be relevant, and the flat band at E_F in such an extended **k**-space region is a signature of non-Fermi liquid behavior in a confined CuO_2 plane [188].

Another piece of information obtainable from Dessau et al's data is $N(E_F)$, the density of states at the Fermi level. This information is obtainable because clear dispersion relationships existed over the entire Brillouin zone. Dessau made the $N(E_F)$ estimate from the dispersion relationships of the quasiparticle peaks (and ignoring the "background") in the following way: the striped circles of Fig. 4.25a occupy approximately 20% of the Brillouin zone, and represent bands which lie within approximately ±40 meV of E_F. This gives an average $N(E_F)$ for that region of (2 states per band * .20%)/80 meV-Cu site, or 5 states/eV-Cu site.

This value of $N(E_F)$ is rather large, particularly in comparison to the LDA results of between 1 and 2 states/eV-Cu site [174]. However, it is in the neighborhood of other experimental measurements such as Pauli susceptibilty performed on very similar samples which gave an $N(E_F)$ of 7.0 states/eV-Cu site[189] and thermodynamic measurements (specific heat discontinuity and zero temperature critical field) of $YBCO_7$ which gave an $N(E_F)$ of approximately 5.8 states/eV-Cu site [190]. In contrast to this, one usually expects low carrier concentrations as inferred from the high resistivities, the Hall effect data, and chemical arguments. Many of the discrepancies can be accounted for by the fact that the flat bands will have low electron mobilities, and so will not contribute significantly to the resistivity or Hall effect data. (Note that the two pieces of FS will also cause a cancellation of the Hall coefficient, and the temperature dependence may be related to the curvature of the FS orbits [191]).

4. Results from $Bi_2Sr_{1.9}Pr_{.1}CuO_{6+\delta}$

Very recently, Ratner et al. [164] and King et al.[165] have taken high resolution angle-resolved photoemission data on single crystals of the T_c = 10K cuprate superconductor $Bi_2Sr_{1.9}Pr_{0.1}CuO_{6+\delta}$ (Bi2201). This is the single layer analog to the T_c = 85K Bi2212 system, and so retains many of th eadvantages of the Bi2212 system, including the very high quality cleavage plane between the weakly bound BiO planes. In this material, Pr is added to help stabilize the crystal structure. Resonance photoemission experiments show that the Pr 4f states do not extend all the way up to E_F, and so presumably are not electrically important [164]. This is consistent with the location of the Pr within the unit cell.

Fig 4.29 shows a near-E_F cut along Γ-X and a cut along Γ-$\overline{M}$ by King et al.[165]. The basic behavior is similar to that taken by Dessau et al.[142] on the Bi2212 system, with a clear crossing along Γ-X(Y) and a band which is very flat and near E_F around the $\overline{M}$ point of the Brillouin zone. King et al. have taken cuts throughout the Brillouin zone, and determined Fermi surface crossing points as indicated in Fig 4.30. Only one piece of Fermi surface is seen, consistent with the fact that there is only one CuO_2 plane per unit cell. The Fermi surface approaches very close to the $\overline{M}$ point of the Brillouin zone (π/a,0), consistent with the slice of Fig 4.29b which shows the states at $\overline{M}$ very close to E_F. The result is also very consistent with the results from Bi2212 in that no sign of a separate BiO electron pocket at $\overline{M}$ is seen. Finally, the very flat pieces of Fermi surface may give a strong tendency for Fermi surface nesting. However, as will be discussed in section 7, the Bragg condition is not met as well as it is in Bi2212, so the effects on the electronic structure are not likely to be as significant as they are in Bi2212.

An E vs. **k** diagram along the high symmetry directions of King's data is shown in Fig 4.31 [165]. The flat bands near E_F at $\overline{M}$ are clearly seen. Due to the lower T_c of these samples, this data should imply that the simple presence of flat bands in the general vicinity of E_F will imply a high T_c.

5. Results from $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_4O_8$

The results from $YBa_2Cu_3O_{7-\delta}$ (Y123) and $YBa_2Cu_4O_8$ (Y124) have historically been more confusing than those from Bi2212, even though a great deal of effort has gone into photoemission studies of these compounds. The reason for this confusion is probably in large part due to the fact that there is no natural cleavage plane in Y123 or Y124, and so the surface vs. bulk issue is much more of a problem. As shown in Fig 4.32. three different cleavage planes are possible for Y123, leaving six possible surfaces, since each of the cleavage planes are asymmetrical [160]. The possibility of some sort of surface reconstruction on each face as well as a cleave leaving a combination of faces is quite large.

Many studies have been performed to try to determine the cleavage plane[157,160,192-199], although the conclusions have varied a great deal. One possibility arises from the realization that the structure is composed of alternating (CuO_2-Y-CuO_2) and (BaO-CuO-BaO) units or blocks that are separated by a long 2.3Å bond (the longest Cu-O bond in the structure, with most others being ~ 1.9 Å) [192]. Since charge is reasonably well balanced within these blocks, cleaving the crystal at their interface may not cause severe charge redistribution. This observation has received some confirmation from tight-binding model calculations by Calandra et al. [193], who concluded that cleavage most likely occurs at this long bond. Zandbergen et al., using high resolution electron microscopy data [194], and Ogawa et al., using Auger spectroscopy [195] both concluded that the cleave occurs at the BaO-CuO_2 interface. Photoemission measurements of the Ba [196] and Gd core levels (in Gd-Ba-Cu-O) [157] also appear most consistent with this termination.

Both theoretical and experimental studies have also argued that cleavege predominantly occurs at the BaO-CuO interface. Lindroos et al. have calculated momentum and polarization dependent photoemission spectra for a variety of different cleavage planes, using the single-step photoemission model within a band theory framework [197]. By comparing with ARPES measurements, they conclude that cleavage occurs at this interface. This view is supported by STM studies on YBCO crystals cleaved in vacuum at 20K [198], and by low energy ion scattering spectroscopy studies of film surfaces, which showed surfaces stabilized by Cu(1)-O(1) chains [199].

Finally, Schroeder et al. have argued that cleavage occasionally occurs at the Y-CuO_2 interface, with Y atoms distributed approximately equally between the two cleavage faces and forming a c(2x2) superstructure [160].

The above issues are of crucial importance because photoemission is a very surface sensitive technique. If the surface is reconstructed in some way or has dangling bonds, then the photoemission spectra may not in fact be telling us anything about the bulk electronic structure. This concern is compounded by the fact that the superconducting gap has not been successfully observed in YBCO, with the one possible exception of two samples studied by Schroeder et al. which may have had a very unusual but favorable cleave[160]. While the gap issue will be discussed in more detail in section V, it is important to keep in mind, for it is an indication that the surfaces may be problematic.

The first angle-resolved photoemission attempt on cuprate superconductors was actually made on Y123 by Stoffel et al. on single crystals cleaved at room temperature [200]. They found no distinct features near the Fermi level which can now be understood in terms of sample surface problems [28]. Campuzano et al. performed some early angle-resolved photoemission studies on twinned single crystals of Y123 cleaved at very low temperature, and they have plausibly concluded from their preliminary data that the experimental Fermi surface has the essence of the Fermi suface from the band calculations.[201]

One of the first detailed angle-resolved photoemission studies of Y123 was performed by Tobin et al. [139]. A unique aspect of the study was that untwinned crystals were used. The as-grown Y123 single crystals usually have 90^{o} twins that make the a and b directions indistinguishable. These crystals could be made twin-free by preferencially adding pressure along one direction while annealing the crystal in flowing oxygen. The advantage of using untwinned single crystals is that one might distinguish the contributions from the planes and the chains. However, useful information can also be obtained from twinned crystals, in particular for the information as a function of doping as we will show later.

We start out our discussion with a broad view of the valence band features. Fig. 4.33 reproduces angle-resolved photoemission spectra taken at different parts of the Brillouin zone by Tobin et al.[139]. We can clearly see that the experimental spectra vary dramatically at different locations in **k** space. Furthermore, they are also very sensitive to the polarization of the incident photon, and as Fig 4.34 shows, to the photon energy. Tobin et al. attributed this dramatic photon energy dependence to photoemission final state effects, and pointed out the interesting aspect that the intensity modulation as a function of photon energy for the states near the Fermi level and -1 eV feature is not in phase. The -1 eV feature reaches it maximum at 24 and 74 eV photon energies, while the feature near the Fermi level reaches it maximum at 17 and 28 eV photon energies.

One of the most striking and controversial aspects of the data is the very intense and sharp feature at approximately -1 eV. Fig. 4.35 reproduces the experimental data by Tobin et al. detailing the behavior of this feature near the S and the X points, respectively [139]. From Fig. 4.35a, we can see that the band dispersion of the -1 eV feature is symmetric with respect to the S point, reflecting a typical critical-point behavior. Furthermore, we can see that there are at least two features which collapse into a single feature at the S point and these features are quite dispersive. However, this behavior is not observed near the X point as shown in Fig. 4.35b. From the lower curves up in Fig.4.35b, we can see that a sharp feature grows up from a large background, and it disperses towards lower binding energies. The amount of dispersion is very small near the X point, and hence the sharpness of the feature is not compromised by the finite angular resolution of the spectrometer. Fig. 4.36 gives the experimentally determined E vs **k** relation near the X (Y) point. This sharp feature was also observed in the twinned single crystals, and was used to determine the surface normal [153-158].

The origin of this sharp feature in the main valence band is presently unclear. Tobin et al. argued that this feature is associated with states derived from the CuO_2 planes [139]. The fact that the peak exhibited comparable strength at the X and the Y points in spectra taken from untwinned single crystals indicated that it was probably not chain-related. They also found that this feature showed a sizable Cu resonance near the X(Y) point but not away from these high symmetry points, indicating that this feature has an appreciable Cu character near the X(Y) points. Liu et al. also argued that the -1 eV peak was intrinsic, and that the strength of this peak was indicative of the sample quality, as oxygen-deficient samples as well as samples which have “aged” in vacuum show the peak to be dramatically attenuated [158].

On the other hand, Claessen et al. argued that the -1 eV peak was a surface state, based upon the sensitivity of it to surface contamination test and the fact that it shows basically no k_z dispersion [154]. Schroeder et al. found that the strength of the -1 eV peak was diminished or even absent for some of their cleaves, and noted an anti-correlation between the intensity of the -1 eVpeak and the intensity of the near-E_F peak [160]. Fig 4.37 shows this behavior for two different YBCO samples. Sample 1 is very unusual (this was the only cleave of this type that they obtained, after at least 12 tries) in that it does not have the strong -1 eV peak. This sample had more strength in the near-E_F peak, than Schroeder’s typical samples, and, as will be discussed in chapter V, showed indications of a superconducting gap. This is clearly a very difficult and complicated issue, and more studies need to be done, in particular to characterize the nature of the surface that is left behind by a cleave.

As shown in Fig. 4.38 the -1 eV peak is also observed to exist in Y124 [155]. In light of the fact that Y124 has a slightly different crystal structure than Y123, this fact may be important for understanding the nature of the cleave in each of these materials.

Fig.4.39 shows five cuts through the Brillouin zone that Tobin et al. used for determining the Fermi surface of untwinned crystals of $YBCO_{6.9}$ [139]. The location of each cut is indicated by the lines in figure 4.40a which shows the Brillouin zone of YBCO in the extended zone scheme. Cut i corresponds to the data of 4.39a and cut v corresponds to the data of 4.39e, respectively. The locations where Tobin et al. felt there was a Fermi surface crossing is indicated in figure 4.40a by an open circle, with the size of the circle indicating the system resolution, and sometimes also by an asterisk in figure 4.39. Some of the crossings are fairly ambiguous and are open to interpretation - see for example the crossings in panel 4.39b and 4.39c indicated by the asterisks.

The most remarkable aspect of the data presented by Tobin et al. is probably the very sharp peaks that are seen near the Y point at hν=17 eV (figure 4.39e). The data exhibit a very sharp structure very close to the Fermi level and a more broad feature near -0.1 eV. The sharp feature near the Fermi level has a full width at half maximum of 40 meV, mainly determined by the instrumentational width of 30 meV. A partial reason for the sharpness of this feature is the lack of energy dispersion so that the finite angular resolution does not contribute to the broadening of the peak. The data near the X point shown in Fig. 4.39d is very different in that we do not see the sharp peak.. Tobin et al. attributed this assymetry to the crystallographic differences between the two directions, namely one of them is parallel to the chain layers and one is perpendicular. From a combined analysis of valence band and Ba 4d core level data, Tobin et al. contend that the sharp peak near the Fermi level at Y is associated with the chain layer [139]. As we will see, other papers contended that these sharp near-E_F peaks were CuO_2 plane derived, or were possibly due to a surface state. This issue is still very much unsettled.

Fig.4.40B shows the comparison of experimental crossings in the reduced zone scheme together with the Fermi surface calculated by Pickett et al. with the smearing due to the k_z dispersion [139,176]. It is quite clear from this data that, similar to results from the $Bi_2Sr_2CaCu_2O_{8+\delta}$ system, the experimental data has the essence of the calculated Fermi surface from band theory. However, Tobin et al. have cautioned that one should not take the agreement or disagreement of crossing points with the band calculation too literally. There was only a limited amount of data, and the uncertainties of the crossing points were rather large.

More information about the Fermi surface was obtained from experiments on twinned single crystals by several other groups. Recently, Liu et al. have performed a very detailed Fermi surface mapping of $YBa_2Cu_3O_{6.9}$ [158]. Fig 4.41 shows data taken with a photon energy of 21.2 eV along two of the high symmetry directions. These measurements were taken in the superconducting state at a temperature of 20K, as were

Tobin et al.'s measurements. Because no clear superconducting gap was ever observed, Liu et al. felt that this data could tell us Fermi surface information. Cut a, along Γ-S, shows a peak with very clear dispersion and a nice crossing. To first order, this data is very similar to Olson et al.'s and Dessau et al.'s Bi2212 data taken along the equivalent direction in **k**-space (Γ-X) [124, 142]. However, Liu et al. felt that two crossings could be observed in the data; one near the angle 7/7 and one near the angle 9/9. Liu indicated these crossings by the dark shading of the circles in the inset to the figure. While the second crossing is very clear, the first one is more controversial. This is because it is not clear if the "shoulder" observed closer to the Fermi level is due to an additional band, as Liu argued, or if it is simply due to the Fermi function cutting off a very broad feature. As a matter of fact, based on very similar data, Mante et al. only reported a single crossing along the Γ-S direction [159]. Along the Γ-X(Y) direction, a peak appears starting near 9 degrees. It shows a small amount of dispersion and then appears to cross the Fermi level near 15 degrees. Note however that the photoemission spectra taken near this portion of the Brillouin zone are very strongly photon energy dependent, and measurements taken with different photon energies have given qualitatively different results. This point will be addressed later.

In addition to the spectra along the high symmetry directions shown in Fig. 4.41, Liu et al. have taken spectra throughout almost the entire Brillouin zone, as shown in Fig. 4.42. Using the criterion that a Fermi surface crossing occurs everywhere that a spectrum has a) a peak near the Fermi level and b) a sharp Fermi-edge cutoff, Liu et al. determined an experimental Fermi surface as shown in Fig. 4.43. The circles are the experimental data points, which are plotted together with the band theory Fermi surface calculated by Pickett et al. [176]. There is a partial agreement between the experiment and the theory. On the one hand, one can see that there is a remarkable agreement between the experimental data and the theoretical Fermi surface from the CuO_2 planes. (Fermi surfaces marked as #2 and #3) On the other hand, the authors noted that they could not see the chain derived Fermi surface well, especially band #4 for which they have specifically searched. This is very different from an earlier report by Campuzano et al. where they claimed to have seen the chain Fermi surface #4 [201]. From a study of $YBa_2Cu_3O_{6.8}$, Mante et al. also reported the absence of the chain derived band #4 [159]. Liu et al. have also found that the effective mass of the experimental band #3 is about a factor of 2 heavier than the calculated band mass, which is consistent with the results from $Bi_2Sr_2CaCu_2O_{8+\delta}$.

Although the agreement between the experiment and theory (for bands #2 and #3) looks very impressive, we caution that the criterion Liu et al. used for determining the crossings is different from the typical criterion used. In the case where the band is dispersing very rapidly through the Fermi level, the criterions are essentially identical. On the other hand, if the band is very flat, the criterions are very different. For the sake of consistency, we redid the Fermi surface crossing points using Liu et al.'s and Gofron et al.'s data and our own criterion, which we previously outlined in section IV-E-2 [156, 158]. The results of this are shown in Fig 4.44, where the error bars correspond to the locations of crossings, and the shaded region enclosing these error bars show the location where a Fermi surface crossing may possibly exist. The reason why the shaded region is so large near the Y point is because the bands are very flat (non-dispersive), and so an exact crossing is difficult to pinpoint. Also, as we will point out shortly, the photon energy dependence of these features is very complex, making precise determinations of the crossing difficult. Although the result of Fig 4.44 is very consistent with that shown in Fig 4.43, the agreement between the theory and experiment no longer appears as robust. In addition, this figure appears to imply a "generic" shape for the Fermi surface of the p-type superconductors: a Fermi surface centered around S (π,π) and an extended region of flat bands very near E_F centered around the Y point $(\pi,0)$.

High resolution studies of the near-E_F feature near the Y point at a variety of photon energies were done by Gofron et al.[156]. Fig. 4.45 shows data from Y124 taken at a photon energy of 28 eV, which accentuates the peak near E_F. Panel a) shows the behavior of the peak between Γ and Y, and b) shows the behavior between Y and S. Fig. 4.46 shows the E vs. **k** relationships for the peaks along those same high symmetry directions. The diamonds correspond to Y124 data taken at a photon energy of 28 eV, and the squares correspond to Y123 data taken with a photon energy of 17 eV. It is observed that the peaks have a "saddle point" behavior, with the saddle point at the Y point. Gofron et al. pointed out that this is not a conventional saddle point, but is much more extended, due to the fact that there is so little dispersion along the Γ-Y direction. The "extended" nature of the saddle point is expected to qualitatively change the nature of the divergence in the density of states [202]. According to Gofron, the main difference between the Y123 and Y124 data is that the saddle point is slightly closer to E_F in Y123 (~ 10 meV below E_F) than in Y124 (19 meV below E_F) [156].

Before leaving the subject of the flat bands, it is important to make a few cautionary remarks. The saddle point near E_F at the X(Y) points in Y123 and Y124 are most clearly observed at the photon energies of 17 eV and 28 eV. However, there is other evidence from data taken with 21.2 eV suggesting a band at the X(Y) point is chain related. First of all, Tobin et al. revealed that the bands at the X and Y points are very different in untwinned single crystals. Secondly, as we will discuss later in section 4.8, the bands at the X(Y) point recorded at 21.2 eV is much more sensitive to the oxygen content as compared with bands along the Γ-S line. Since the chain states in Y123 are most sensitive to the oxygen content, this implies that the bands at X(Y) recorded at 21.2 eV may be chain related. The data recorded at 28 eV appear to behave differently. First of all, it is much less sensitive to oxygen content. Similar features are observed with $YBCO_{6.5}$ and $YBCO_{6.9}$. Secondly, the data from 28 eV suggest that the band is always below the Fermi level along the Γ-Y line (Fig 4.45a), while the data from 21.2 eV clearly suggest a crossing (Fig 4.41b). This raises the possibility that there are two bands near

E_F at X(Y) in twinned crystals. Why there should be two bands, and whether one of them is actually a surface state remain an interesting problem for further studies.

From the above discussions of the Fermi surface mapping of Y123 and Y124, we can see that the experimental Fermi surfaces have some of the essence of the band Fermi surface. They have the generic shape of a rounded square centered at the S point (π,π). However, there are significant differences between the data and the band calculation regarding the chain bands. It is presently unclear why these chain bands have not been observed by photoemission. This picture is very consistent with the result we get from $Bi_2Sr_2CaCu_2O_{8+\delta}$. Actually, the level of agreement found between the experimental data and the band calculation for the Fermi surfaces is quite surprising. For Y123, the experiments were usually performed on crystals with oxygen content of 6.9 or lower, while the calculations were usually carried out on the idealized crystal with oxygen content of 7. There should be some differences because oxygen content is very important to the electronic structure in this system. Secondly, unlike the case of $Bi_2Sr_2CaCu_2O_{8+\delta}$ where the crystal cleaves between the two adjacent Bi-O planes connected by weak van der Waals bonds, the cleavage plane of $YBa_2Cu_3O_{7-\delta}$ is very uncertain. Actually, very strong bonds were broken here so that one would expect surface reconstruction and other surface phenomena to happen in this case. In fact, it is plausible that some features in YBCO data are surface-state related. Such activities are expected to cause distortions to the electronic structure. Finally, a large puzzle in the experimental data from Y123 and Y124 in general is that it misses a logical link. The data were usually collected at 20K. However, the sample surface area as probed by photoemission is not superconducting with an upper bound of 5 meV for the superconducting gap (which we will discuss in the next chapter). Based on this, one would attempt to say that the surface area of the sample as probed by photoemission is likely not $YBa_2Cu_3O_{7-\delta}$ (with small δ) as one would hope it to be. Judging from the relation between T_c and oxygen content in Y123, it is not unreasonable to say that the fact that one does not see a superconducting gap probably means that one is either studying a reconstructed surface or a surface with much less oxygen content. Because a gap is also not observed in Y124 and this system is much or more more stable to oxygen loss, the possibility of a reconstructed surface in both these systems should be taken most seriously. The question then is why do we obtain a Fermi surface that has so many similarities to the calculated Fermi surface of these materials? This is presently still an open issue.

6. Results from n-type superconductors

Relative to the p-type superconductors such as $YBa_2Cu_3O_{7-\delta}$ and $Bi_2Sr_2CaCu_2O_{8+\delta}$, much fewer angle-resolved photoemission studies have been carried out on n-type superconductors. Only very recently have there been reports of success in observing dispersive bands near the Fermi level in $Nd_{2-x}Ce_xCuO_{4-\delta}$ (NCCO) [161-163]. These studies have opened a new window into the physics of the cuprates because they have very different doping levels than the p-types, have a simple structure and only one CuO_2 plane per unit cell, making them ideal candidates for the study of the plane, and have in many cases much more “normal” physical properties than the p-types. For instance, in NCCO the T_c’s are relatively low, the resistivity has a T^2 temperature dependence instead of the linear -in-T dependence of the p-types [203-205] and the superconducting gap appears much more likely to be isotropic [206], while emerging data indicates that the gap in the p-types is strongly anisotropic and maybe even d-wave (see chapter V). The combination of data on the n- and p-type cuprates is especially useful in understanding the relationship between the electronic structure and the physical properties.

Fig. 4.47 presents ARPES data near E_F from NCCO from King et al. [161] and Anderson et al. [162]. King et al. presented data from two different doping levels : as a superconductor, x=0.15, and over-doped as a metal, x=0.22. A relatively high photon energy of 70 eV was used for these studies, as King et al. found an enhancement of the weight of the near-E_F states near this energy. However, this had the negative effect of decreasing the attainable energy and momentum resolution. The grid in Fig. 4.48 displays the relationship between θ/ϕ and locations in the 2D Brillouin zone for King's studies. As seen in Fig. 4.47a, the constant ϕ and constant θ scans are always taken with both positive and negative angles, and the spectra properly exhibit the crystal symmetry about the Γ-G_1-Z line. This observed symmetry with respect to the Γ-G_1-Z line is an excellent internal check of the sample orientation and data reproducibility and generates increased confidence in the data. The intensity of the photoemission peak, however, does not reflect the symmetry. This is most likely caused by a matrix element effect arising from the different photoelectron emission angles relative to the sample surface and incident photon direction. The ARPES peak is much broader near E_F than observed in YBCO and Bi2212 (note that the experimental energy resolution is not the limiting factor here since the observed peak FWHM's are at least twice as broad as the instrumental resolution). The width of the peak was not found to be photon energy dependent.

Fig. 4.48 presents the experimentally determined Fermi surface from the superconducting and over-doped metallic samples, together with the corresponding LDA calculated Fermi surface [173]. The solid line represents the calculated Fermi surface with k_z smearing included in the line width. The experimental Fermi surface is marked with error bars with the orientation of each error bar along the direction of the slice in the Brillouin zone where the peak is observed to cross E_F. The empty circles indicate **k**-space locations wherethe ARPES measurements were performed, and their diameter represents the angular resolution of the spectrometer (±1°). The experimentally determined Fermi surface for both doping levels agrees very well with results from the LDA calculations. The Fermi surface that Anderson et al. measured on x=.15 samples with a photon energy of 17 eV agreed very well with King et al.'s measured Fermi surface [162].

Many theoretical models of the cuprates are based on the hypothesis that the essential physics are included in the nearest-neighbor interactions in the CuO_2 plane. A tight-binding calculation of a half-filled CuO_2 band with only nearest-neighbors generates a square FS with perfect nesting along the [110] direction (Γ-X). By including the next-nearest-neighbor interactions, the FS is rotated by 45° and the corners of the square are rounded[207]. The measured FS agrees with the latter scenario, suggesting that the next-nearest-neighbor interactions are very important to the electronic structure near E_F and model Hamiltonians including only nearest-neighbor interactions are not sufficient.

Also very interesting is the fact that the measured FS consists of a hole pocket centered at X, which according to semiclassical theory contains hole charge carriers. In disagreement with this prediction, the superconducting samples ($x = 0.15$) have a negative Hall coefficient, revealing electron charge carriers [205, 208]. The Hall sign becomes positive for over-doped metallic samples ($x \geq 0.20$); however, King et al.'s data does not show a large change in the shape of the Fermi surface to reflect the transition from hole to electron carriers. In addition, they find that for increased Ce doping, the Fermi surface shrinks (see section 8). Therefore, we should expect the free carrier concentration to diminish. This is in contrast to both the resistivity and Hall coefficient measurements which decrease with increased Ce doping, consistent with a direct enhancement of the carrier density [205, 208].

Despite the LDA calculation's remarkable success in predicting the Fermi surface of NCCO, King et al. found that it had difficulty describing the electronic structure below E_F [161]. This is similar to the case in Bi2212, where the calculated Fermi surface matched experiment much better than the near-E_F band structure. Fig. 4.49 compares the measured and LDA calculated band structure along the X-G_1-X high symmetry direction. In disagreement with one-electron band theory, they find that for both samples the band is narrower than calculated along the X-G_1-X direction, a factor of two narrower for the metallic sample (x=0.22) [161]. However, along the Γ-X direction, Anderson et al. found that the dispersion relation matched the band theory prediction very well, as shown in the inset to Fig 4.47b [162]. This is analogous to the case of Bi2212, where the discrepancy between the experimental and theoretical band dispersion is greater near (π,0) (the $\overline{M}$ and G_1 points) than along the Γ-X direction.

7. Comparison of band and Fermi surface mappings from the different families of the cuprate superconductors

The recent availability of detailed and reliable data on a wide range of cuprate superconductors gives us the unique opportunity to make a comparative analysis of the electronic structure and the physical properties of the different classes of the cuprate superconductors. We pay particular attention to those aspects of the near-E_F electronic structure and Fermi surface that appear to be derived from the CuO_2 planes, as these are the most important and common aspects of all the cuprates. Such an analysis shows many trends and commonalities in the data, and also reveals some striking contrasts, especially between the n- and p-type superconductors. A very self-consistent picture emerges, which appears relevant to our understanding of many of the “anomalous” physical properties of the p-type superconductors, as well as the more “normal” physical properties of the n-types.

In figure 4.50 we replot the experimental E vs. **k** relationships from Bi2212 [142], Bi2201 [165], Y123 [156,158], Y124 [156] and NCCO [161]. To allow a better comparison of the data between the different materials, we overlay the data (points) with a simple E vs. **k** relationship which is consistent with the Bi2212 data from Dessau et al. [142]. It is immediately obvious from the figure that there are many commonalities in the electronic structure of these materials. In particular, they all have a) highly dispersive bands which cross the Fermi level near the mid-point of [0,0] to [π/a,π/a] , and b) flat bands at the points [π/a,0] and [0,π/a]. In NCCO, these flat bands are approximately 300 meV below E_F, while in the p-types they are very near E_F. As we will discuss later, this presence/absence of the flat bands at E_F may have a significant impact on many of the physical properties of these materials.

To first order, we can understand the location of these flat bands from a tight binding analysis of the CuO_2 plane electronic structure. As shown in Fig. 4.14, inclusion of the nearest-neighbor Cu-O coupling leads to a van Hove singularity at E_F for half filling (zero doping). Inclusion of higher order terms buckles the Fermi surface and moves the saddle point below E_F, as shown by a number of authors [137, 172, 211]. Electron doping will move the Fermi level farther away from the saddle point, while hole doping will move it closer. This is consistent with Fig. 4.44, and with the notion that the amount of hole doping in p-types doped near the optimal level for superconductivity will place the Fermi level very near the saddle point.

However, the behavior of the bands between [0,0] and [π/a,π/a] is not consistent with this simple picture, for in this picture one would expect the crossing points between between the n- and p-type superconductors to be very different along this line. More work needs to be done to understand these intriguing similarities and differences.

We now return to the issue of the saddle-point, often termed a van Hove singularity or vHs. In the ideal two-dimensional system, it leads to a logarithmic singularity in the density of states, as shown in figure 4.14. While it has long been realized that a vHs in the DOS may lead to very unusual physics if it lies near E_F, the existence of a vHs in the DOS of the cuprates [209-212] was controversial. There were theoretical concerns that the vHs would not lie near E_F for the optimal doping levels for superconductivity, as well as the fact that the vHs may be significantly smeared out in the real material due to three dimensional effects, inhomogeneities, or finite temperatures.

A key contribution of the ARPES measurements is that the saddle point or vHs does exist, and it is at or very near E_F for the p-type cuprates . The fact that it is near E_F for the p-types and not the n-types can be understood on the basis of a simple tight-binding model of the electronic structure of the CuO_2 plane. As shown in figure 4.14 the simple tight binding model which includes only the nearest neighbor Cu-O bonds gives a square Fermi surface at half filling with the vHs at E_F due to the saddle point at [π/a,0]. However, theoretical studies have shown that the inclusion of long range interactions (such as O-O hopping) buckles the Fermi surface and moves the saddle point below E_F. Moderate p-type doping is then necessary to bring the saddle point or vHs back to E_F [172, 211, 212].

Due to their energy position with respect to E_F, the flat bands would be expected to play a significant role in the physical properties (transport, superconductivity, etc.) of the p-type cuprates but not in the physical properties of the n-types. We will next try to make connections between the spectroscopic evidence of the flat bands and other physical properties of the cuprates, with particular attention paid to those properties which are found to be different in the n- and p-type cuprates. Much of this discussion assumes we can borrow the quasiparticle concept. It should be pointed out however, that due to uncertainties regarding the photoemission lineshape and background, it is still a question whether photoemission data can be interpreted using the quasi-particle concept as defined by Fermi liquid theory.

A number of physical properties are found to be different in the p- and n-type cuprates. These include the T_c, which may be significantly higher in the p-types than in the n-types, and the temperature dependence of the resistivity, which is linear over a very wide temperature range in optimally doped p-types [117, 213], but which is quadratic for NCCO [203-205]. The possibility that these and other anomalous properties may be related to flat bands at E_F has been theoretically discussed in the literature, primarily within the context of a vHs in the density of states [214, 215]. While the relationship between the flat bands near E_F and the linear T dependence of the resistivity appears to be fairly robust, the relationship between the flat bands and T_c is not yet so clear, particularly in light of the fact that Bi2201 has the flat bands yet has a very low T_c. Of course, the possibility does exist that minor differences in the location or curvature of these bands will have a profound effect on the T_c. It should also be pointed out here the existing data at 28 eV as a function of doping also cast doubts about the simple connection between the van Hove singularity and physical properties.

Finally, there is the issue of the symmetry of the superconducting order parameter. As we will discuss in section V, there is evidence from nmr [216], ARPES [149, 217, 218], penetration depth [219,220], Josephson Junction measurements[221], tunneling spectroscopy [222], electronic Raman background[223], and infrared transmission [224] that the gap in the p-type cuprates is strongly anisotropic and possibly even d-wave. On the other hand, penetration depth measurements indicate an isotropic s-wave gap in the n-type superconductor NCCO [172]. The ARPES results, in combination with some theoretical work by Dickinson and Doniach, raise the question whether the differences in the gap symmetry may also be a function of the differences in the electronic structure, in particular, the energy position of the flat bands. The idea is that a d-wave or generally anisotropic gap may be stabilized by a **k**-space anisotropy in the contribution to $N(E_F)$, with a larger gap in the region of high state density due to the energy gain from gapping many states. This is precisely what has been observed in Shen’s ARPES measurements of the SC state of Bi2212 - $\Delta(\mathbf{k})$ is maximum near $\overline{M}$ and minimum near the crossing along Γ-X(Y) (see section V) [218]. In NCCO, a strongly anisotropic or d-wave gap may not be favored since the flat bands are well below E_F.

A comparison of the experimental Fermi surfaces of Bi2212, Bi2201 and NCCO is also very interesting, and is shown in figure 4.51. Due to the larger error bars, the Fermi surface of YBCO shown in Fig 4.44 is not included. We observe that the Fermi surfaces of both Bi2201 and NCCO are closed around the X(Y) points, although they have different sizes. The difference in the doping level can very naturally explain this difference - the extra electrons raise the Fermi level in NCCO, causing the Fermi surface to shrink around the X(Y) points.

For Bi2212 and Bi2201, the Fermi surface is strongly nested. As discussed in section 3, this implies that the quasiparticle scattering will be strongly centered near the nesting vectors, which is expected to affect the susceptibility as well as other physical properties. However, as can be seen in the figure, the magnitude of the nesting vector is slightly smaller in Bi2201 than in Bi2212. An important point to note is that the nesting vector in Bi2212 is nearly commensurate with the antiferromagnetic wave vector (π,π), while the nesting vector in Bi2201 is less commensurate. Therefore, this subtle difference in the Fermi surface may be very important, particularly for mechanisms of superconductivity based on antiferromagnetic spin fluctuations [182, 225-227]. A fraction of the Fermi surface of YBCO also appears to be nested along the (π,π) direction (see Fig 4.44).

8. Doping behavior of the cuprates as studied by angle-resolved photoemission

As we have pointed out in the introduction, among the most interesting physical properties of the high temperature superconductors is their doping mechanism: the superconductors are made by doping antiferromagnetic insulating materials. Many experiments have been carried out to understand this issue[168-170]. These include an earlier angle-integrated photoemission study by Allen et al. where they did not observed a large Fermi level shift as a simple doping picture would suggest when one goes from p-type($La_{2-x}Sr_xCuO_4$) to n-type($Nd_{2-x}Ce_xCuO_4$) superconductors [170]. This led to the scenario that the doping of Mott insulators creates new states inside the Mott gap and the Fermi level is pinned by these states, in contrast to a theoretical investigation which suggest that the chemical potential shifts across the gap when a compound is doped from p-type to n-type.[172b] This view point has been challenged by Hybertsen et al. who suggested that the potentials of the $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$ system are large enough so that the first ionization state could be very different [137]. They suggested that one can not simply compare the results from $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$. Furthermore, Chen et al. have successfully explained the doping of $La_{2-x}Sr_xCuO_4$ system by a model involving the chemical potential shift [227]. Since then, some angle-resolved photoemission experiments have been carried out to study this problem. We summarize the experimental data from angle-resolved photoemission on the doping issue in this section.

Fig. 4.52 reproduces photoemission spectra recorded from $Bi_2Sr_2CaCu_2O_{8+\delta}$ single crystals by Shen et al.[168]. The four panels represent angle-resolved photoemission spectra for as-grown (thin line) and 12 atm O_2 annealed (thick line) samples at different parts of the Brillouin zone: normal emission, near where the first band (with the lowest binding energy) crosses E_F along Γ-Y, Γ-X and Γ-$\overline{M}$ directions. The oxygen annealling dopes more holes into the system and resulted in a reduction of Tc from 89K to 78K. This is because the $Bi_2Sr_2CaCu_2O_{8+\delta}$ samples used for this study lie in the over doped region of the doping phase diagram where T_c drops with the increase of carrier concentration.(see Fig. 4.3) Besides some small line-shape changes, the main valence-band features of the 12 atm oxygen annealed sample shift about 0.2 eV towards the Fermi level. Shen et al. suggested that this shift is actually a consequence of the chemical potential shift as a function of doping [168]. The amount of shift is consistent with the amount of oxygen content change (and thus the carrier number change) in the samples. This result suggested that the Fermi level shift is a direct consequence of doping for $Bi_2Sr_2CaCu_2O_{8+\delta}$ in its highly metallic regime. Shen et al. have also attempted to study the associated change of the Fermi surface with doping but have failed to find a conclusive result [168]. Takahashi et al. have also observed similar chemical shifts from valence band photoemission data on the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ system [169].

Recently, van Veenendaal et al. have performed a valence band and core level study of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ system with a large doping range covering both the metallic and the semiconducting regime [229]. The experiment were performed on polycrystalline materials scraped in situ. Fig 4.53 shows XPS valence band data (angle-integrated) obtained on samples with a variety of different doping levels x. Fig 4.53b shows a blowup of the region near the Fermi level, indicating that there is a shift in the emission onset of the spectra, similar to what Shen et al. have observed for oxygen doped Bi2212 samples [168]. While van Veenendaal’s data had much less structure, making a definitive determination of the shift more difficult, they took data covering a much wider range of doping, as well as taking core level data. Fig. 4.54 summarizes the results of their study. The horizontal axis gives the number of holes per CuO_2 unit and the vertical axis gives the shifts required to align the leading edges of the various core levels and the valence band. Itti et al. [230] and Shichi et al.[231] obtained similar results on core level data. Van veenendaal argued that a chemical potential shift was the only way to fully explain the fact that all of the core levels and the valence band moved in the same direction in a consistent way. They speculated that the rapid shift at small hole concentrations (large Y content) was due to the movement of the chemical potential within the band gap, and the slower shift at higher hole concentrations occurred after the chemical potential reached the top of the valence band. Finally, they speculated that the increase in the spectral weight with increased doping was likely to do the incoherent part of the one-electron Green's function, as opposed to moving new states into the gap.

A very powerful technique to studying the doping effects is with angle-resolved photoemission. The most extensive of these studies was carried out by Liu et al. on $YBa_2Cu_3O_x$.[153]. Fig. 4.55 shows angle-resolved photoemission spectra taken along the Γ-S direction for samples with an oxygen content of x=6.9, 6.7, 6.5, 6.4 and 6.35. The results from the 6.9 sample are very consistent with those discussed in the previous section. Liu et al. identified these states as the Cu-O plane derived bands #2 and #3. The experimental data from samples of x=6.7, 6.5, 6.4 were very similar to the x=6.9 data, indicating that the Fermi surface crossings of these plane bands along this direction do not change appreciably. This result may be related with the fact that the change of oxygen in $YBa_2Cu_3O_{7-\delta}$ is mainly affecting the oxygen atoms in the chains, not the planes. The spectra taken from the x=6.35 sample show much less dispersive weight, although there is a remnant of a feature which still appears to “cross” the Fermi level, even though the material at this doping level is an insulator. This is a very unusual behavior which definitely deserves more attention. Liu et al. speculated that the correlation effects suddenly became important at this doping level [153]. They did not, however, give justification for this argument. From a theoretical point of view, it is easier to see a continuous increase of importance for correlation effects as fewer and fewer carriers become available to screen the Coulomb interaction.

Fig. 4.56 shows Liu et al.'s angle-resolved photoemission data along the Γ-X(Y) direction for differently doped samples [153]. We can clearly see the systematic weakening of the sharp narrow band near the Fermi level as x decreases, although again the “crossing” point is basically unaltered. As we have discussed earlier, this is the general region of **k**-space where the Cu-O chain bands are predicted to occur. If this interpretation is correct, then this result is consistent with the fact that doping of oxygen most directly affects the oxygen chains. However, as we have discussed earlier, there has not yet been a study which has been able to definitively prove the nature and origin of the states in this general region of **k**-space. Very complete studies of the effect of doping on untwinned single crystals may be able to answer these questions.

Gu et al. studied the effects of cation doping YBCO crystals with Co and with Zn, which substitute for Cu at the chain and plane sites, respectively [157]. The valence states near E_F along Γ-S were virtually unaffected by the substitutions for the samples that were superconducting. However, the spectral weight near E_F disappears for a higher Co-doped, non-superconducting crystal.

An angle-resolved doping study of the $Nd_{2-x}Ce_xCuO_4$ system was carried out by King et al., for x=0.15 and x=0.22 [161]. The experimental Fermi surfaces from this study are shown in figures 4.48a and 4.48b, respectively. Figure 4.57 shows a comparison of the two experimental Fermi surfaces. We observe that the increase in electron doping in going from x=0.15 to x=0.22 causes the Fermi surface to get marginally smaller. While the change is only slightly greater than the error bars, it does appear to be a real effect, and is in the direction expected by the band-filling model.

To summarize, two primary effects have been observed as the cuprates are doped. (1) There is a chemical potential shift consistent with band filling for some p-type systems and the n-type compound in its metallic regime.. This effect has been observed by core level shifts [229-231], valence band shifts from both angle integrated [229] and angle-resolved photoemission [168, 169], and changes in the volume of the Fermi surface [161]. (2) There is an increase in the weight of the states near the Fermi level as the material is doped away from an insulator. This is observed in absorption edge studies [232], angle-integrated photoemission [170] and angle-resolved photoemission studies

[153, 233]. Interestingly, these effects are not observed consistently in all samples and they sometime appear exclusive with respect to each other. The differences may be due to sample quality, with one of the two effects explainable on the basis of poor quality samples. More studies clearly need to be done to resolve this important and complicated issue.

9. Symmetry information obtained from the polarization of the incident photon beam.

As we have seen throughout this chapter, there are very strong matrix element effects due to the direction of the polarization of the incident light. These polarization effects can be a very powerful tool for revealing some basic information about the electronic structure. First, these polarization effects can help us to deconvolute some features from others by selectively enhancing or diminishing the strength of one feature relative to another. For example, this has been very helpful in the analysis by Dessau et al . centering around the data of Fig. 4.24 - 4.26 [142-143]. Second, a careful analysis of the polarization effects may shed some insight into the symmetry of the states being studied. This section will concentrate on the latter.

While these effects can be most precisely studied using the one-step model and a real calculation such as LDA band theory,[234] a simple analysis can very effectively describe the situation, as well as lend much intuition into the physics of the problem. This approach has been used to understand the polarization effects in ARPES for a variety of materials systems, and has been found to work quite well [235-237]. The matrix element M for absorption is given by $M=(e/mc)\langle\psi_f(\mathbf{k})|\mathbf{A}\cdot\mathbf{p}|\psi_i(\mathbf{k})\rangle$ where $\mathbf{A}$ is the vector potential of the light (colinear with the E vector), $\psi_i(\mathbf{k})$ is the initial (hole) state, and $\psi_f(\mathbf{k})$ is the final (electron) state. The basic point is that since $|M|^2$ is an observable quantity, it must always be invariant under symmetry operations, and so only those combinations of initial state, final state, and vector potential that leave $|M|^2$ invariant contribute to the photoemission process.

The simplest experimental situation for discussing and understanding the polarization effects is illustrated in figure 4.58. The sample is assumed to be Bi2212, although the analysis of course works for all the cuprates, with the requirement that the labeling of high symmetry points is mapped correctly as discussed in section 1.a. We are assuming (for now) that the a-axis of the sample is vertical or horizontal. This will put the lobes of the Cu $d_{x^2-y^2}$ orbital at a 45° angle to the horizontal and vertical directions, as illustrated in the figure. We then consider normal incidence photons with the E vector parallel to the floor (as it will be from a synchrotron), and electron emission from this $d_{x^2-y^2}$ orbital in the Γ-Y plane, as shown. Relative to this Γ-Y mirror plane, the initial state (considering just a $d_{x^2-y^2}$ orbital here) has odd symmetry, for positive (negative) lobes reflect into negative (positive) lobes. The final state can to first order be thought of as a plane wave, with spherical wave fronts. These wave fronts are symmetric about the mirror plane, and so the final state has even symmetry relative to this plane. We can get away without having to take the effect of the momentum operator $\mathbf{A}\cdot\mathbf{p}$ by realizing that it is just the dipole operator, and the symmetry of it will be the same as $\mathbf{A}\cdot\mathbf{r}$ (or else we can expand the initial and final states as a series of spherical harmonics, operate on the final state with the momentum operator, and integrate over the spherical harmonics).

From figure 4.58 we see the dipole operator is even with respect to the mirror plane, and so the matrix element M = even$*$even$*$odd=odd, or emission in the Γ-Y mirror plane is not allowed. Keeping everything else the same and considering emission in the Γ-X mirror plane, we see that the initial state is still odd, the final state is still even (with respect to the Γ-X plane now) and the dipole operator now odd. The matrix element is now even and so emission is allowed.

Figure 4.59 shows some normal state data of Bi2212 from Dessau et al. taken in a geometry similar to that shown in Fig. 4.58 [143]. Because of the superstructure in this material arising from a slight lattice mismatch between the BiO and CuO_2 planes, the Γ-X and Γ-Y directions are not necessarily equivalent, and so data was taken along both the Γ-X and Γ-Y for both polarizations. This was achieved by taking the Γ-X and Γ-Y cuts and then rotating the sample by 90° and retaking the cuts but with the different polarizations. For both Γ-X and Γ-Y, there is less intensity if the electron emission is in the mirror plane defined by the surface normal and the polarization direction, in agreement with the simple discussion based upon the symmetry of the states. This indicates that the initial state has odd symmetry with respect to the Γ-X and Γ-Y planes, i.e. this result to first order confirms that the orbital which makes up the band crossing E_F along Γ-X(Y) has significant $d_{x^2-y^2}$ symmetry, in agreement with the predictions of tight-binding or band theory models of the electronic structure of the cuprates. The fact that one does not see strict selection rules indicates that states with a variety of symmetries may be present, and/or that the simple arguments used here are not sufficient. The fact that there is in general less intensity along Γ-Ythan Γ-X is consistent with the fact that the superstructure is along the b-axis, as determined by LEED, Laue, and STM. The superstructure appears to be a sizable perturbation to the electronic structure near E_F.

An in-depth look at the polarization dependences of the near-E_F features of the Y123 system was carried out by Lindroos et al. using a combination of photoemission data and theory based on the one-step photoemission model and LDA-based wave functions [234]. Lindroos et al. also considered the simple geometry indicated in Fig. 4.58, and thus took spectra along the Γ-S line (remember that Γ-X(Y) for Bi2212 maps to Γ-S for Y123). Calculations were carried out for each of the six possible surface terminations in Y123 (see Fig. 4.32) and then compared to the experiment. The BaO layer followed by the CuO_2 plane was found to agree best with the experiment, and so was presented in the paper (of course if there is only one termination on a surface, then at most only half of the surfaces could have this termination). The data and theory are shown in Fig. 4.60. As in the case of Bi2212, the feature is much stronger when the emission direction is normal to the polarization direction.

Before closing this section, we return to the question of the nondispersive spectra of figure 4.59d. These spectra look identical to the spectra that we always see when the (dispersive peak) is far enough below or above E_F that it is no longer visible, and so it is very tempting to consider these spectra to be just a background that the dispersive peak sits upon. Note that this is a very different type of background than we usually see in photoemission. Typically this background is a result of electrons inelastically scattered on their way out of the sample, and so these electrons show up at a lower kinetic energy (higher binding energy) than the primary photoelectron peak. The number of these secondary electrons is then proportional to the number of electrons (primaries or primaries plus secondaries, depending primarily upon the kinetic energy) at higher kinetic energies. These spectra do not look like that, for there are no primary electrons at higher energies. One possible explanation for this background is that it is due to *elastically* scattered electrons, that is, the weight came from the dispersive peak at a different **k** value. Other more exotic types of explanations center around the possibility that the nondispersive "background" is in fact intrinsic to the spectrum. Regardless of the origin of this feature, the polarization results are still very important for they tell us that we can in effect deconvolute the dispersive peak from the nondispersive "background", simply by subtracting the spectra of the two polarizations, or by subtracting a spectrum which does not have the dispersive peak present. This type of background subtraction will be important for the discussion of the photoemission lineshape in the next section.

10. Analysis of the quasi-particle line shape

Another very controversial aspect of the angle-resolved photoemission spectra is the lineshape of the low energy excitations [118, 124, 166, 167, 238-243]. The lineshape of photoemission spectra has long been a good source of information. For example, the well-known Doniach-Sunjic lineshape of core level photoemission spectra gives us the information about the particle-hole excitations in a metallic system[244]; the lineshape of valence band photoemission spectra of transition-metal compounds (in particular the satellite lineshape) lead to a better understanding of these materials as illustrated in the Zanaan-Sawatzky-Allen (ZSA) scheme discussed earlier in Chapter III.

The lineshape issue in the cuprate superconductors first surfaced when Olson et al. presented their beautiful high resolution angle-resolved photoemission spectra from $Bi_2Sr_2CaCu_2O_{8+\delta}$ shown in Fig. 4.21. The data was analyzed by Olson et al. with an ansatz as shown in Fig. 4.61 [124]. Within the framework of this ansatz, the lineshape of the experimental spectra is modeled with a series of Lorentians cut off by the Fermi distribution function on top of a large background. With this hypothesis, Olson et al. concluded that the width of the lorentzians, and hence the quasi-particle lifetime, is proportional to its energy referenced to the Fermi level [124]. This is in contrast to what one would expect from a canonical Fermi liquid picture where the lifetime is expected to be proportional to the square of the energy referenced to the Fermi level [120]. This result is often quoted as a piece of supporting evidence for the marginal Fermi liquid hypothesis, which predicts lifetimes which vary linearly with energy [118]. More or less the same conclusion has been reached by Campuzano et al. for data from $YBa_2Cu_3O_{7-\delta}$ using the same ansatz (see Fig. 4.62) [241].

The above interpretation of the lineshape of the photoemission data has been questioned by a number of authors and has sparked a lively debate. There are concerns of the energy scale over which the fits were carried out, the background subtraction used in the fits, the simple ansatz of using lorentzians to model the spectra, as well as many others. We will briefly review these issues issues here and point out some alternative interpretations and fits that have been carried out. Finally, we will discuss some experiments done on model systems aimed at giving us an understanding of these low energy excitations in simpler systems that we understand well.

The first issue, that of the energy scale of the features that have been fit, is of crucial importance if one is trying to use this data to address whether the cuprates are Fermi liquids or not. This is because the imaginary part of the self-energy of a classical Fermi liquid only needs to vary quadratically over a small energy range near E_F. The magnitude of the energy range is to first order expected to be similar to the energy scale of the relevant physics. The centroids of the features fit by Olson et al. range in energy from approximately -.3 eV to -.05 eV, or between 3600K and 600K [124]. Relative to the energy scale of most of the processes that we are concerned with, this is very high.

Next there is the issue of the background subtraction. There are a number of possible mechanisms for a background to exist, and it has been argued that the background was not properly removed by Olson et al. Olson et al. assumed that all of the background was due to inelastically scattered secondary electrons, which were subtracted in the standard way by assuming that the number of secondary electrons at any energy is proportional to the number of primaries at higher (kinetic) energies. A signal that the background subtraction used was not entirely self-consistent is evidenced by the fact that the amount of background subtraction required to do this appears to be unusually large. This is because to first order we would expect that in a given spectrum the ratio of the inelastically scattered electrons to the primary electrons at higher kinetic energies would be roughly constant. Liu et al estimated this constant from the full valence band scans (figure 4.63a), and arrived at a value almost two orders of magnitude smaller than that used in the fits to the near Fermi level states, that is, to first order it would appear that the background subtracted to obtain the spectra shown in figure 4.61 is approximately two orders of magnitude larger than would be expected as a result of inelastic scattering of the primary electrons [240].

Liu et al. fit Olson et al's data of Fig. 4.61 but used a more realistic lineshape than a lorentzian cut by a Fermi function [240]. They modelled the spectra as the spectral weight function $A(k,\omega) = \frac{1}{\pi}\mathrm{Im}\, G(k,\omega)$ where $G(k,\omega)$ is the single particle Greens function. The expression for the Green's function is $G(k,\omega) = [\omega - \varepsilon_k - \Sigma(k,\omega)]^{-1}$ where ε_k is the free-particle excitation energy and Σ is the self energy. The self energy for Fermi liquid theory was assumed to be momentum independent and so was taken to be $\Sigma(k,\omega) = \alpha\omega + i\beta\omega^2$. The imaginary part of the self energy gives the damping and so for the Fermi liquid case goes as ω^2 (assuming a spherical Fermi surface). For an imaginary part going as ω^2, the real part goes as ω as can be seen by doing a Kramers-Kronig analysis. Plugging in, we find that the spectral weight function is $A(k,\omega) = \frac{1}{1-\alpha}\left(\frac{\beta'\omega^2}{(\omega-\varepsilon_k')^2 + (\beta'\omega^2)^2}\right)$ where we have made the scaling $\varepsilon_k' = \frac{\varepsilon_k}{1-\alpha}$ and $\beta' = \frac{\beta}{1-\alpha}$. Essentially this is a lorentzian which goes to zero at E_F due to the ω^2 term in the numerator. Only for $\varepsilon_k=0$ (at E_F) is $A(k,\omega)$ a true lorentzian. Figure 4.63b shows theoretical spectra for one **k**-value for both the Fermi liquid (FL) and marginal Fermi liquid (MFL) [118] self energies. Both of these give photoemission spectra (negative energies) which are asymmetric, with the MFL spectra having more weight away from the Fermi level. This asymmetric lineshape in general, and the weight at higher binding energies in particular, were some of the key points of Liu et al's paper, for they ascribed as intrinsic much of the high binding energy weight that Olson et al. had subtracted from his spectra. Results of Liu et al's fits to Olson's data of Fig. 4.61 are shown in Fig. 4.63c for both the FL and MFL cases. The quality of the fits for both the FL and MFL case were roughly equivalent, with the main problems being excessive weight near the Fermi level which could not be accounted for by the theory. Additionally, the amount of background subtraction needed to make these fits was still way too large. Using the full valence band as a guide to the subtraction (figure 4.63a), the background coefficients were approximtely 60 times and 15 times too large for the FL and MFL cases, respectively. Liu et al. thus felt that neither lineshape fell off slowly enough [240].

By doing some studies of the effect of the polarization of the incident light, Dessau et al. argued that there was an additional part of the background that should be subtracted before such a fitting is done [143, 149]. The key results of the study were shown in Fig 4.59, which shows data along Γ-X(Y), as in Fig. 4.61, but this time with variable polarizations. We observe that the dispersive peak is very sensitive to the polarization of the incident light, while there is a “background” which extends up to E_F which is essentially independent of the polarization of the light. This indicates that the dispersive peak and this background are distinct, and so this flat background should be removed from the spectra before the lineshape of the quasiparticle or dispersive peak is fit. This will clearly improve the fits that Olson and Liu have attempted, as their major problem was in fitting the region near E_F (particularly when the quasiparticle was far from E_F so that the background contributed more strongly).

It should be noted that the origin of this flat background which extends up to E_F is not yet known. It may be an extrinsic effect due to a poor quality sample: for instance, it may be due to elestically scattered electrons. Arguments against this fact are that the Bi2212/Bi2201 surface is generally regarded as being the highest quality of the cuprates, yet this background is larger in Bi2212/Bi2201 than in the other cuprates (the high quality surface is generally attributed to the fact that the crystal cleaves so nicely between the pair of BiO planes, and is evidenced by the fact that the superconducting gap has so far been convincingly observed only in Bi2212). If this background is intrinsic, it is likely due to an incoherent part of the spectrum.

Anderson also argued that too much background was cut off by Olson’s ansatz, although he was principally concerned with the background at higher binding energies. He suggested an alternative interpretation of the experimental data which can be best illustrated by replotting Olson's data as shown in Fig. 4.64 [239]. He felt that the data could be regarded as a changing of the peak position within a fixed envelope. This way, he concluded that the data actually supported the novel theoretical concept of charge and spin separation.

Due to the above desire to obtain lifetime information from the photoemission lineshapes, a fundamental question was raised: do we really know what the photoemission line shape should look like in systems usually regarded as good examples of a Fermi liquid? Without this knowledge, the above discussion is premature. Fig. 4.65 illustrates what the idealized photoemission spectra should look like if the canonical Fermi liquid picture is valid. Without the complications of finite angular resolution and the inelastic background, the quasiparticle spectra of a Fermi liquid should be a delta function at the Fermi level and then a finite peak which broadens as it moves away from the Fermi level [238]. In addition to the quasiparticle part of the spectra, experimental data should also have a contribution from the incoherent background.

The photoemission spectra obtained in reality is often quite different from the idealized result. Fig. 4.66 shows angle-resolved photoemission data of the Cu (111) surface state by Kevan et al.[245]. In contrast to what one would expect from a Fermi liquid (Cu metal is usually regarded as a Fermi liquid), we can see that the peak actually becomes sharper as it disperses away from the Fermi level. Contributing factors for this are likely to be the combination of the parabolic band structure and the finite angular resolution of the experiment. Even after these are taken into account however, the high binding energy features are still sharper. Tersoff and Kevan interpreted this in terms of the surface scattering (Umklapp) of electrons, which artificially broadens the states nearer E_F [246]. This example shows that we have to be very careful in drawing conclusions from the lineshape of photoemission spectra. Therefore, the focus of the lineshape discussion has currently switched to the question of what is the ideal photoemission lineshape near the Fermi level for the known Fermi liquids. The questions that should be asked are the following: What is the photoemission spectrum of a Fermi liquid? (this includes the influence of the periodic potential which in a way is different from the canonical behavior of the original Fermi liquid picture which assumes that the periodic potential is weak enough to be ignored). What are the roles of other parameters such as phonons and temperature? What is the appropriate way to handle the background issue?

What is the role of the spectrometer (non-perfect transmission function, finite angular resolution and other practical problems)?

Prior to these discussions, there were actually some nice studies touching the issue of the photoemission lineshape in the simple metallic system such as Al, Mg, and Be [247-249]. Even though these works were performed at room temperature, and with clearly worse energy resolution than what one could achieve with a state of the art spectrometer, some fundamental theoretical issues have been discussed [247-249]. For example, the simplest version of the final state effect on the line width has been incorporated by considering the convolution of the photoelectron and photohole lifetimes. This was modeled in a simple expression: $\Gamma = \sqrt{\Gamma_{hole}^2 + (2R\Gamma_{electron})^2}$. Here R is ratio of the slope (dE/dk) of the initial and the final state bands, and the first and the second term in the squre root representing the contribution to the total life time from hole and electron lifetimes [242, 247-249]. Only in the case where R is very small (the initial state is very flat as compare to the final state) can one simply interpret the photoemission line width as the quasiparticle lifetime. For ideal two dimensional material, R is zero so that Γ reflects only the hole lifetime, a feature we want to measure. For the cuprate superconductors, Smith argued that the electron lifetime term limits our ability to measure the lifetime down to energy low enough for the problem here [242]. This is so because even though the cuprate superconductors are highly two dimensional, they are not perfectly two dimensional.

Overall, much more needs to be done about the issue of the quasi-particle lineshape for cuprates as well as ordinary simple metallic systems. One side benefit of the studies on high-temperature superconductors has been to focus our attention on this important issue more sharply than ever before. To address the issue of what photoemission can really show, the most important step now is to perform careful high-resolution (both angular and energy resolution) photoemission studies on some model

Fermi liquid system such as simple metals. Some preliminary efforts have been made to carry out such experiments.

A recent study by Claessen et al. shows that one obtains a picture similar to what one would expect from a Fermi liquid picture from highly two dimensional $TiTe_2$ [166]. Fig. 4.67 shows a data set along the Γ-M direction, where the intensities are normalized to the photon flux. Claesson et al. fit the data near $\theta=14.75^o$ using a method essentially identical to that used by Liu et al on Bi2212 [240]. The advantage here was that the background in the spectra was very low, and the system is presumably a known Fermi liquid. The results of the fits are shown in Fig. 4.68, and are very good for the spectra near 14.75^o. Fits based upon a marginal Fermi liquid lineshape did not agree as well. Claessen et al. took this to imply that the ARPES lineshape, if interpreted properly, does reflect the nature of the interacting electron system. A different study on two dimensional $NbSe_2$ gave a different result from what is expected in a Fermi liquid [167].

A few simple arguments by Smith indicated, however, that one may have to consider other effects before concluding that the ARPES lineshape is reflecting the nature of the interactions [242]. First, he pointed out that the magnitude of the parameter β' extracted from the fits was unphysically large, implying that the broadening from the theory would be greater than ω for $\omega \geq 25$ meV. Smith felt that this was a problem since the measured peak width was 45 meV. Second, he pointed out that the peak width will reflect the lifetime width of the photoelectron in addition to the lifetime of the photohole. The measured linewidth Γ_{meas} in this case is expected to be related to the photoelectron lifetime width Γ_e and the hole lifetime width Γ_h through the band derivatives normal to the surface,[242]

$$\Gamma_{meas} = \Gamma_h + \Gamma_e (v_{h\perp}/v_{e\perp})$$

where $hv_{h\perp} = \partial E_h/\partial k_\perp$ and $hv_{e\perp} = \partial E_e/\partial k_\perp$. In the limit of a two dimensional material, $\partial E_h/\partial k_\perp$ will go to zero, and the measured linewidth will be a reflection of the hole width. From the published band structure of $TiTe_2$, however, Smith argued that $\partial E_h/\partial k_\perp$ was not in fact small enough, and the measured linewidth would be dominated by the photoelectron instead of the photohole, and no definitive conclusion regarding the validity or non-validity of Fermi-liquid theory can be drawn from the present data. This concern of smith is compounded by the fact that α and β value obtained from photoemission will imply transport properties that are very different from what know about $TiTe_2$. Clearly, this is a very active research area, both experimentally and theoretically, and much more work needs to be done. There are other discussions regarding the analysis of data from $TiTe_2$ [243]. These discussions concentrate on accuracy of keeping only the first term in the Taylor expansion of the self-energy. More detailed experiments and data analysis are underway to address these issues.

11. Information of Fermi surface from other techniques

Besides photoemission, there are other experimental techniques that have been used to investigate the Fermi surface of the cuprate superconductors. Among these techniques are positron annihilation and de Hass van Alfen experiments. Although they have not appeared to be able to provide as much detail as the photoemission measurements, these experiments are important additions because they are complementary to the photoemission measurements. For example, these experiments do not suffer from the surface sensitivity problems that photoemission does. The reader can get some idea about these experiments from the proceedings of a recent workshop on the Fermi surface of the high-temperature superconductors.[6] Most of the positron annihilation experiments were performed on untwinned single crystals of $YBa_2Cu_3O_{7-\delta}$. These studies are most sensitive to the chain Fermi surface of the material, and these Fermi surfaces are quite consistent with those from band calculations. By comparing data from Bi2212 with band theory calculations, an experiment suggested that there is a Bi-O Fermi surface, as the band calculation has indicated [250]. This is different from other results which indicated that the BiO band was above E_F for all $\mathbf{k}$

[142,143,183,184]. More studies need to be done to resolve this apparent discrepancy, including studies of samples with different doping levels and a more careful gold overlayer experiment such as that done by Wells et al. [147].

The de Hass van Alfen experiments were carried out in two different modes. The first uses a very high pulsed magnetic field generated by an explosive device, and the second uses a relatively lower static magnetic field [251,252]. The general result of these experiments is that in YBCO they have observed a Fermi surface piece which is consistent with the small chain derived piece of Fermi surface centered around the S(R) point (see Fig.4.20). This is important complementary information to the ARPES studies, as the ARPES studies have shown other pieces of Fermi surface but not this one (with the exception of one very preliminary study.[201]).

12. State of affairs and implications

A number of key experimental results have been obtained by angle-resolved photoemission measurements of the normal state of the cuprate superconductors. Selected results and their implications are briefly listed below.

1) Fermi surfaces exist for highly doped metallic systems.

    Certain aspects are similar to the results from band theory.

    Luttinger's theorom generally accepted.

2) Flat bands due to saddle point in band structure.

    Near or at E_F for p-types - may be related to the anomalous physical properties.

    Well below E_F for n-types - may explain more normal properties.

3) Fermi surface nesting.

    Nesting along the (π,π) direction is seen in Bi2212, Bi2201 and may be in YBCO. Appears strongest for Bi2212. Neutron data from $La_{2-x}Sr_xCuO_4$ implies a Fermi surface nesting also.

4) Unusual line shapes near E_F.

Presently inconclusive, but opened up new area of active study.

V. Photoemission Studies of the Superconducting State

The successful detection and subsequent study of the superconducting energy gap by high resolution photoemission was one of the most important highlights in the history of the application of photoelectron spectroscopy. This success was made possible by the development of high energy-resolution electron spectrometers, the relatively large size of the superconducting gap in the cuprates, and the relatively high superconducting transition temperatures. The angle-resolved capabilities of photoemission meant that **k**-dependent effects of the superconducting gap could be mapped out - a currently unique capability. This capablity was especially useful in that it allowed the study of the symmetry of the superconducting gap - one of the most fundamental issues related to the mechanism of the superconductivity.

A further important aspect of the study of the superconducting gap in Bi2212 was that it gave us greatly increased confidence that the information obtained from photoemission experiments on the cuprates were representative of the bulk electronic structure. This concern was related to the surface sensitivity of the technique as well as the known fragility of the cuprate superconductors. In addition, there were theoretical papers suggesting that the surface of the cuprate superconductors would not be superconducting due to their short coherence lengths [253]. The successful detection of the superconducting gap in Bi2212 by high-resolution photoemission effectively addressed this concern, and indicated that for Bi2212 at least, the photoemission experiments are truly probing the bulk electronic structure.

So far, the detection of the superconducting gap in $Bi_2Sr_2CaCu_2O_{8+\delta}$ has been verified by several groups [123,124,147-152, 217, 218, 254-261]. However, the situation regarding the superconducting gap in $YBa_2Cu_3O_{7-\delta}$ is still controversial, with most studies reporting a small or nonexistent gap [139,158-160]. In this chapter, we will summarize these results and discuss their implications on the mechanism of superconductivity in the cuprate superconductors.

A. Background: conventional theory and the superconducting gap of conventional superconductors

We start out this section with some background information about superconductivity based on the traditional BCS theory. Even though it is presently unclear how relevant BCS theory is to the cuprate superconductors, it serves as an important reference point for which to compare experimental results. Much of this discussion will be familiar to those familiar with tunneling spectroscopy of conventional superconductors, as the experiments are both measuring very similar things (they both measure the one-electron removal (or addition) spectrum, or spectral weight function $A(\mathbf{k},\omega)$). Important differences come when we consider the angle-resolved photoemission case, in which we need to explicitly include the effects of the coherence factors.

In the BCS theory, a Fermi sea of quasi-particles is unstable against the phonon-mediated attractive interactions among the quasi-particles. As a consequence, the Fermi sea collapses and the quasi-particles form singlet pairs. The singlet pairs are energetically favored since their spatial wavefunctions are symmetric and wavefunction overlapping of the two particles is relatively large, preferred by the attractive pairing interaction. A minimum amount of energy is required to create any excitations of the system, a crucial factor for the stability of these cooper pairs. The energy required to break one of these pairs is twice the gap energy, or 2Δ. Simple weak-coupling BCS theory predicts a simple relation between the size of the gap (at zero temperature) and the T_c of the sample, of $2\Delta(0)/k_BT_c = 3.52$. However, some of the strongly coupled superconductors such as Pb or Hg are found to have ratios $2\Delta/k_BT_c = 4.6$ and 4.3, respectively.

Figure 5.1a shows the expected effect of a BCS gap on a flat normal-state density of states as measured by tunneling spectroscopy or the combination of angle-integrated photoemission and inverse photoemission. Due to the opening of the gap there is a depletion of weight over a distance of 2Δ around the Fermi level (with the Fermi level exactly in the center of the gap), and due to the sum rule on the spectral weight, the missing intensity piles up at energies beyond the gap in the form of a square-root singularity. (The total density of states gained in the singularity peak region is equal to that lost in the energy gap region.) This behavior in conventional superconductors has been extensively studied by tunneling spectroscopy [262-264], infrared reflectivity [265] and other more indirect measurements, and in most cases was found to fit the predictions of BCS theory very well. The disagreements with BCS theory of the tunneling spectra of the strongly-coupled superconducors will be discussed in more detail in section C.

The angle-resolved photoemission case is more complicated, as we need to consider the normal-state quasiparticle energy and the effect of the coherence factors. First, we consider the normal-state quasiparticle energy (or band energy), which we will denote ε_k. We then have the relation $E_k = \sqrt{\Delta^2+\varepsilon_k^2}$ where E_k is the energy of the quasiparticle in the superconducting state and Δ is the superconducting gap. From this expression, we can see that only the states near the Fermi surface ($\varepsilon_k \leq \Delta$) have their excitation energy dramatically modified by the superconducting transition. This is the reason why we usually say that only the states near the Fermi level are important for superconductivity.

The coherence factors enter in because the superconducting state quasiparticle can be thought of as having mixed electron-like and hole-like character, with the coherence factor $u_k{}^2$ descibing the amount of electron character and $v_k{}^2$ the amount of hole character. The magnitude of the coherence factors is determined by the relations

$u_k^2=0.5(1+\varepsilon_k/E_k)$.and $v_k^2=0.5(1-\varepsilon_k/E_k)$. The effects are illustrated in figure 5.1b, which shows a series of ideal (no broadening of any sort) angle-resolved photoemission and inverse photoemission spectra of the normal and superconducting state. Keeping in line with the flat density of states of figure 5.1a, the normal state peak ε_k disperses linearly across the Fermi level, and since there is no broadening considered, it is illustrated as a delta function peak of weight one. For $\varepsilon_k >> \Delta$, $E_k = \varepsilon_k$ and $u_k^2 = 1$, so the normal and superconducting states are indistinguishable. As ε_k approaches E_F the superconducting quasparticle energy E_k deviates more and more from ε_k, u_k decreases and v_k grows (i.e. the inverse photoemission spectrum picks up weight). When $\varepsilon_k = 0$ (the normal state peak is at E_F), $E_k = \Delta$ and $u_k^2 = v_k^2 = 1/2$. The behavior at further **k** values is obviously symmetric to that at earlier **k** values. It is clear that a summation (integration) of the angle-resolved spectra of figure 5.1b will yield the angle-integrated spectra of figure 5.1a, with the BCS equation for the density of states $\frac{N_s(E)}{N(0)} = \frac{E}{(E^2-\Delta^2)^{1/2}}$; the high density of states in the superconducting pileup is a result of the fact that the dispersion relation of the superconducting state guasiparticle peak has zero slope for $E_k = \Delta$ (infinite slope in the figure). In addition, integrating over all **k**'s cancels the effects of the coherence factors, since the effect on the states with **k** > **k**$_F$ will offset the effect on the states with **k** < **k**$_F$. The existence of the coherence factors has never been directly observed, though its existence is well accepted due to its manifestations in a wide variety of experimental data such as acoustic attenuation, nuclear-spin relaxation rates and electromagnetic absorption [266].

Gap-like features have been observed in the cuprate superconductors by a number of experimental techniques besides photoemission, including the relatively direct techniques of tunneling, IR reflectivity and Raman scattering (see for example the many articles published in refs 1-7). However, a consensus has not yet been reached as to the nature of the gap, including the lineshape, magnitude, symmetry, doping dependences, etc.. Much of the reason for this confusion has been due to materials problems, for as discussed in section IV-B, the crystal structure of the cuprate superconductors is very fragile, particularly with regard to the formation of defects or of oxygen loss/diffusion. Indeed, reported values for the ratio $2\Delta/k_BT_c$ range from 0 to as high as 18, with most clustered between 3 and 8. The widespread use of high quality single-crystalline materials has improved the situation somewhat, although difficulties still exist. Tunneling measurements must still make use of a contact electrode, which introduces many new uncertainties, and IR reflectivity is hindered by the large anisotropy in the dielectric constant. Due to its short probing depth, photoemission also has potential problems. If the surface is unreconstructed and has no additional defects or oxygen loss, this should not be a problem. As we will discuss shortly this appears to be the case for Bi2212, and indeed photoemission measurements on Bi2212 have contributed greatly to our understood of the nature of the superconducting excitations of the cuprate superconductors [42, 267]. Surface problems are the most likely explanation as to why efforts to consistently observe a gap in YBCO have failed. (studies have not yet been reported on any of the other cuprates).

Photoemission has the further disadvantage that the maximum attainable energy-resolution at present is only on the order of the size(s) of the gap. However, this relatively poor energy resolution is more than made up for by the fact that we may obtain the additional **k**-resolved information by doing measurements in the angle-resolved mode. As we will show, this has enabled photoemission to obtain a wealth of information in a very unique and direct way, which is complementary to that obtained by the other, more traditional probes of superconductivity.

B. Angle-integrated photoemission from $Bi_2Sr_2CaCu_2O_{8+\delta}$

The first unambiguous demonstration of the detection of the superconducting gap by high-energy resolution photoemission from a high-temperature superconductors (or any other superconductor) was the experiment performed by Imer et al. on single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$. The experiments were performed with an angle-integrated spectrometer and 21.2 eV photons produced by a helium discharge lamp. The total energy resolution was about 20 meV as determined by the Fermi edge of a Cu sample placed in good electrical and thermal contact with the superconductor. During the course of one scan (approximately 3 hours), the samples were repeatedly recleaved every 20 minutes to keep the surface clean [254].

Fig. 5.2 reproduces results from two different samples S1 and S2 above (105K) and below (15K) the superconducting transition temperature of the samples (88K). As the samples are cooled down below their transtion temperature, the leading edges of the photoemission spectra are pulled back to higher binding energy, signalling the loss of spectral weight near the Fermi level and the opening of the superconducting gap. In addition, a peak appeared just below (at higher binding energies) the leading edges in the superconducting spectra. This peak was interpreted as the singularity peak in the BCS function. Of course, the singularity is smeared out due to (among other things) the finite energy-resolution and the finite temperature. The lower panel depicts a model fitting of results expected from the BCS theory by first modeling the normal-state density of states as a linearly increasing function which is then multiplied by a 105 K Fermi function and convoluted with the experimental energy-resolution. The superconducting state density of states was determined by multiplying the as-determined normal-state density of states with the usual BCS function and a 15 K Fermi function, and then convoluting with the experimental energy resolution. The best agreement between the theoretical and experimental curves was obtained for values of the gap parameter $\Delta = 30 \pm 5$ meV, corresponding to a ratio $2\Delta/k_BT_c = 8 \pm 1.4$.

There are two additional aspects to the data by Imer et al. that deserve attention. First is the linear background of the density of states below the superconducting gap. This linear background has been seen in many tunneling experiments,[268,269] and has also been discussed theoretically [118, 269, 270]. The second issue is that a finite intensity of spectral weight remains in the gap, and cannot be attributed to experimental energy resolution. As we will see in the next section, angle-resolved measurements on this same compound show that certain regions of the Brillouin zone have a very small or zero gap, while others have a large gap. This will cause an angle-integrated measurement to have a finite intensity up to very low energies, as observed by Imer et al.

C. Angle-resolved photoemission from $Bi_2Sr_2CaCu_2O_{8+\delta}$

Soon after Imer's work, Olson et al. reported the first angle-resolved photoemission study of the superconducting state of $Bi_2Sr_2CaCu_2O_{8+\delta}$ [123]. The major results of his study are reproduced in figure 5.3. The total energy resolution and angular resolution of Olson's experiment was about 32 meV and $\pm$ 1^o, respectively. As the sample was cooled below the superconducting transition temperature, the photoemission spectra showed clear and dramatic changes, particularly when the normal state quasiparticle peak was very near E_F. As shown in Fig 5.1a for the angle-resolved case, the superconducting state spectrum taken at $\mathbf{k} = \mathbf{k}_F$ is the most relevant for determining the magnitude of the gap. For this reason, Olson et al. chose the spectra at 18° to determine the magnitude of the superconducting gap in Bi2212 [123].

Olson et al. determined the magnitude of the gap at 18° by the following fitting procedure. First, the normal state spectrum was modeled as a lorentzian on a linear background cut by a Fermi function and convolved with the instrument response functino. The fit shown in Fig 5.4 resulted. Following that, the lorentzian and the linear function were multiplied by a BCS density of states and a 20 K Fermi function, and then convolved with the instrument function (the lorentzian peak was not shifted). Olson et al. found that they could fit the edge well for a small range of values of the gap Δ, but the calculated spectrum did not peak as high as the measured one. However, by reducing the value of the lorentzian width (argued to be physically reasonable procedure because there will be less electron-electron scattering with a gap present), a good fit to the data could be obtained for Δ betwen the values of 22-26 meV. Results of the fit for Δ=24 meV ($2\Delta/k_BT_c = 7.0$) are shown in Fig 5.4. Although the fit is quite good, one should keep in mind that an angle-integrated formalism was used for this fit, even though the measurement was angle-resolved. This may be justified if the effective **k**-resolution (including sample flatness and electron scattering effects) is poor enough so that over the region of interest (centered around $\mathbf{k}_F$) there will be enough **k**-integration to put us in scenario 5.1a instead of 5.1b. Almost at the same time, Manzke et al. also performed an angle-resolved photoemission study of the superconducting gap in the $Bi_2Sr_2CaCu_2O_{8+\delta}$ compound with high angular resolution and modest energy resolution. Based on empirical anguments, they concluded their data is consistent with a superconducting gap of 30 meV with a large error bar [151].

At the time these experiments were being reported on, the magnitude of the gap in the cuprates was a very controversial issue, with reported values of $2\Delta/k_BT_c$ ranging from 0 to 11. The values reported from the photoemission experiments were consistent with more recent values from other experiments and were taken very seriously. Thus this data was very important in helping build a consensus within the community that the gap in the cuprates was somewhere near $2\Delta/k_BT_c = 5 - 8$ for optimally doped samples.

Olson et al. has also performed temperature dependent studies of the superconducting gap. Fig.5.5 gives shows the 15° degree spectrum of Fig 5.3a at different temperatures [123]. The temperature dependence of the data is a piece of very convincing evidence that the effect we see in the photoemission data (the appearance of the "pile up" peak at -40 meV and the shift of the leading edge) is really due to the opening of the superconducting gap. In the 90K spectra, we do not see the "pile up" peak. However, it begins to show in the 80K spectra and is very visible in the 70 K spectra. Furthermore, Olson et al. have performed temperature cycling of their experiment and found that their results were reproduceable. It appears that Olson et al.'s samples were more stable in vacuum than those of Imer et al. Olson et al. reported that they can measure the sample for a long time while Imer et al. indicated that their sample showed signs of deterioration after 20 minutes[254].

1. Anomalous spectral weight transfer

The next important experimental work in the field was the observation of an anomalous spectral weight transfer in the superconducting state by Dessau et al. [257]. This observation was made possible by a more detailed study of the experimental data. The experiments were again performed on $Bi_2Sr_2CaCu_2O_{8+\delta}$ with a relatively high energy resolution of 35 meV and angular resolution of±1° and ±4°.

Fig. 5.6 reproduces the experimental results by Dessau et al. [257] The inset shows the Brillouin zone locations where the measurements depicted in the figure were taken, with the size of the circles indicating the angular resolution. Note that in this case the angular resolution is poor enough that the spectra may essentially be interpreted in the angle-integrated framework of Fig 5.1a. Each set contains three spectra taken at temperatures above (100K), just below (80K) and well below (10K) the superconducting transition temperature of the sample (91K). The experimental data show the general features involved in the opening of a superconducting gap from the BCS theory. The spectral weight near the Fermi level is depleted and the pile up peak (which corresponds to the singularity in the BCS density of states) is observed. In addition to these general features, the data from the superconducting state show a number of features that are not predicted by the simple weak coupling BCS theory. First of all, there was a clear depletion of the spectral weight near -90 meV (a dip structure) which opened up at the superconducting transition for the spectra taken along the Γ-$\overline{M}$ direction. [257] Along Γ-X the dip is small or nonexistent. Secondly, there are some interesting changes in the overall occupied spectral weight which occur as the sample is lowered through the transition temperature. Along Γ-X there appears to be more weight transferred into the pileup than has been depleted from the gap region. Along Γ-$\overline{M}$ the situation is reversed: there appears to be less weight transferred into the pileup than has been depleted from the gap plus dip regions. Finally, the magnitude of the superconducting energy gap as inferred from this data is larger along the Γ-$\overline{M}$ direction than along the Γ-X direction, i.e. the gap is anisotropic in the $\mathbf{k}_{xy}$ plane. The first two points will be discussed in this section, beginning with the high binding energy dip. The gap anisotropy will be discussed in the next section.

We first concentrate our attention on the implication of the dip structure. As a matter of fact, the dip structure is also apparent in some of the earlier data of Olson et al. from $Bi_2Sr_2CaCu_2O_{8+\delta}$, even though that data did not have enough statistics to positively identify it [150]. The results have also been reproduced to some degree by Hwu et al. [152], as shown in Fig. 5.7. However, they have observed much less **k**-space dependence, and have hence observed the condensate peak and dip at rather unusual locations in the Brillouin zone (see Fig 5.7). In addition, their normal state data shows much less **k**-space dependence than the earlier measurements of Dessau et al. and Olson et al., and drastically disagrees with the predictions of band theory [152]. Hence, although the detailed **k**-space dependences from this data should be questioned, the data is still a very good verification of the existence of the dip in the superconducting state spectra.

There is also strong evidence that this dip structure also exists in the tunneling spectra of the cuprates,[268, 271] as it must if the dip is intrinsic to the excitation spectra of the superconducting state. Since its initial observation by Dessau et al., the dip has also been extensively addressed by the theoretical community [272-275]. The ideas behind a number of these works will also be addressed in this section. Before we do that however, it is important to go over the studies that have been carried out to try to determine if the dip is really intrinsic to the superconducting state excitation spectra, or if it is simply a reflection of the detailed band structure of Bi2212.

A paper by Dessau et al. presented two simple interpretations of the dip structure in the experimental data [148]. Panels (b) and (c) of Fig. 5.8 show these two simple scenarios for the dip structure reproduced in panel (a). However, as explained in that paper, these simple explanations of the dip are not consistent with the overall body of experimental data. Panel (b) suggests the possibility that the dip is due to a unique normal state band position. There is a quite broad feature peaking below E_F, and this feature still has appreciable spectral strength at E_F. As the sample goes through the superconducting transition, the spectral weight near the Fermi level is pushed away to form the pile-up peak, and the dip is formed as a valley between the pileup peak and the broad normal state peak. Even though such an explanation is quite plausible, it is not consistent with the experimental data. In this scenario, the intensity at the lowest point of the dip will always be greater than the intensity of the normal state curve at that corresponding energy. The experimental data clearly shows that the lowest point of the dip is lower than the normal state spectra, that is, weight is being depleted from the normal state at that energy. Therefore, this scenario is unlikely to be able account for the dip structure in the experimental data. As depicted in panel (c) of Fig. 5.8, the second scenario considers the possibility that there may be two bands in close proximity to each other along the Γ-$\overline{\mathrm{M}}$ high-symmetry direction. In the normal state, these bands would superimpose (by coincidence) to form one resolvable feature. Below T_c, one or both of these bands may sharpen up (due for instance to reduced electron-electron scattering and hence increased lifetimes) and so the dip would appear between them. This explanation appears not consistent with experimental observation [148].

Since that time, Dessau et al.'s detailed study of the near-E_F band structure and Fermi surface of Bi2212 discussed in section IV-E-3 was carried out [142,143]. As discussed in that section, the general picture of the band-structure in the region of the $\overline{M}$ point is that there are two CuO_2-derived bands, one just below E_F and one just above E_F. Therefore, one should perhaps add a panel (d) to figure 5.8, where the effect of a band which is slightly <u>above</u> E_F in the normal state contributes to the superconducting condensate peak through its coherence factor, while the band just below E_F in the normal state contributes strongly to the spectral weight at binding energies greater than the dip. Experimental data relating to this possibility will be shown in Fig. 5.10 [258].

Before we show that data, we point out an experimental difficulty in obtaining this information due to the time-dependence of the spectra as reported by Shen et al. and reproduced in Fig. 5.9 [218]. This figure shows data taken at the $\overline{M}$ point of a T_c = 88K Bi2212 sample at a measurement temperature of 35K. Spectra are shown as a function of time since the cleave, with the freshest spectra on the bottom. Gap magnitudes Δ are also reported for each spectrum, which were determined by the energy position of the midpoint of the leading edge relative to E_F. The reason for choosing this simple technique for determining the gap will be discussed more in section 2, but essentially come down to the fact there is as yet no established theory of the lineshape with which to fit to, particularly for the spectra which show the dip.

Figure 5.9 clearly shows that both the size of the gap and the magnitude of the dip are strong functions of the time since the sample was cleaved. The lower four spectra were taken within 1 hour and 40 minutes and nineteen hours and thirty five minutes after the cleave. Both the size of the gap and the strength of the dip were found to decay during this time period. The sample was then warmed up to room temperature and allowed to sit in the vacuum chamber for almost two weeks, at which point the sample was cooled back to 35K and the top two spectra were measured. The size of the gap and the strength of the dip were found to have recovered to a large degree, implying that the ageing was predominantly caused by the cryo-condensation (physisorption) of residual gases onto the sample surface. This necessitates that experiments be carried out as quickly as possible, and in as good a vacuum as possible. Also, the fact that the dip and the size of the gap are simultaneously affected by the physisorption is an indication that the dip is intimately related to the superconducting state. Interestingly, Dessau et al did not find very dramatic changes in the normal state measurements depicted in Fig. 4.24-4.26, even though these measurements took an entire week to complete [142]. This may indicate that the nomal state spectra are much less sensitive to physisorption of gases and/or that much less gas freezes out onto the sample surface at the higher temperatures used for the normal state studies.

Fig 5.10 shows some recent superconducting state data of Bi2212 taken by Dessau et al. [258]. This data was taken with the very good angular resolution of ±1° over the first few hours on two freshly cleaved Bi2212 samples. Cut a shows some data from $\overline{M}$ to X, cut b shows some data parallel to this line but closer to the Γ point, and cut c shows data from Γ to $\overline{M}$. Note that the sample t4, used for cuts b and c, appears to have slightly different Fermi surface crossings than the sample dx4 used for the mapping of the normal state Fermi surface (see Fig. 4.24-4.26). The data of Fig. 5.10 shows that the dip is strongest very near $\overline{M}$, and it gets weaker or dissappears away from $\overline{M}$, consistent with the earlier observation in reference 257. In Fig. 5.10a, the dip exists for a range of angles near $\overline{M}$, but then disappears rather suddenly at the emission angle 22/5. At this time the condensate peak gets more intense and maybe even a little wider, after which time intensity is rapidly lost due to the band crossing. The same type of behavior is seen in Fig. 5.10b, and has been reproduced on a number of samples. By taking the different spectra in a different order on different samples, we have confirmed that the effects are not due to the ageing of the sample surface.

One possibility which is generally consistent with the present data is that the dip occurs near $\overline{M}$ due to the fact that there are two CuO_2-derived bands, one just below E_F and one just above E_F. The band which is slightly above E_F in the normal state contributes to the superconducting “pileup” peak through its coherence factor, while the band just below E_F in the normal state contributes strongly to the spectral weight at binding energies greater than the dip. For example, near 22/5, the lower band begins to move very close to E_F, and so contributes to the pileup instead of the weight beyond the dip. This would also explain why the dip is stronger and broader. Well beyond 22/6, both bands move far away from E_F and so don't contribute any weight to the pileup.

In addition to these effects, we should consider the possibility that the lifetime of the excitations may be strongly energy dependent. For instance, theoretical studies have shown on onset to scattering that starts at 3Δ, and so the linewidths at energies below 3Δ may be very much narrower than those above 3Δ (the situation is more complicated when we consider an anisotropic or d-wave gap) [274, 275]. It is clear that more data of this type and more theoretical input is needed for a detailed understanding of the dip.

Tunneling measurements on a wide variety of the cuprates clearly show a high binding-energy dip very reminiscent of that seen in the photoemission data [268, 271, 276]. Selected results from these studies are shown in Fig. 5.11.. It should be noted that due to difficulties in preparing the tunneling barriers, reported results from tunneling studies of the cuprate superconductors have varied tremendously. However, tunneling spectra generally regarded to be of high quality, including those presented in Fig. 5.11, typically show the dip structure. Among the key features that make these data stand out are very low zero-bias conductance, a strong pileup of intensity above the gap, and relatively symmetric behavior around zero bias.

If it is indeed true that the dip structure seen in the photoemission and tunneling is an intrinsic feature of the superconducting excitations of the material, then this result is clearly different from the weak coupling BCS theory. The understanding of such experimental data might be a key to the understanding of high-temperature superconductivity. However, since the mechanism of high-temperature superconductivity is still unclear at this point, and the interpretation of the dip data is still controversial,[272-275] it is very instructive to review a very similar situation in the conventional superconductors before we get down to specific interpretations of the dip data.

As we have stated earlier, in the conventional weak coupling BCS theory, one does not expect such a dip structure in the superconducting density of states. However, for some "bad actors" in the low T_c superconductors such as Pb and Hg, modulation structures were observed in the density of states at energies beyond the pileup peak. Fig. 5.12 reproduces the tunnelling data from Pb which have high energy features as shown in panel (a) [263, 277]. Panel (b) of the figure gives a closer look at the region of interest. The dashed line is what one expects from a weak coupling BCS theory and the solid line is the normalized experimental data. The deviation of the experimental data from the BCS theory was explained by the strong coupling formulism of Nambu and Eliashberg, usually regarded as an extended version of the BCS theory [278, 279]. It turns out that there are two important hidden assumptions made in the weak coupling BCS theory. First, it regards the quasiparticles that form the cooper pairs as having an infinite lifetime. In a real system, of course, the quasiparticles have finite lifetimes. Second, the weak coupling theory is not retarded. In other words, it assumes that the attractive interaction between the two quasiparticles mediated by the phonons is instantaneous. This again is only an approximation because the phonon-mediated electron-electron attraction in a real system is retarded. Here is how the physics works: the first electron (or quasiparticle) polarizes the lattice, whose dynamic reponse to the electron is such that it tries to overscreen it. A second electron is then attracted to the net positive charge left behind by the polarized lattice. This is how the two electrons involved experience the attractive interaction. It is obvious from the above discussion that this interaction is retarded, instead of instantaneous, for it takes time for the lattice to respond. It is this time delay which gives rise to the energy structure in the tunnneling spectra.

Recognizing the importance of these two approximations in the weak coupling BCS theory, Nambu and Eliashberg improved the weak coupling theory by including the effects of the quasiparticle lifetime and retardation in the pairing interaction in the self energy calculation [278, 279]. McMillan and Rowell realized that one could invert the tunneling data using the Eliashburg equations and obtain the electron-phonon interaction spectrum $\alpha^2F(\omega)$ from the high energy oscillations in the tunneling spectra [263]. Panel

(c) of Fig. 5.12 shows the $\alpha^2F(\omega)$ deduced from the tunnelling data, which compares very favorably to the Pb phonon spectrum $F(\omega)$ as measured directly by neutron scattering experiments. This data is shown in panel (d) of Fig. 5.12. This truly impressive agreement was historically one of the key experiments which solidified earlier speculations that the electron-phonon interaction is the pairing mechanism responsible for superconductivity in conventional materials [277].

Now we turn back to the interpretation of the data in Fig.5.6 which have attracted much attention in the theoretical community [272-275]. There are several interpretations of the experimental data that heve been proposed. The first explanation, proposed by Arnold, Mueller and Swihart [273], is a more or less conventional approach which is analogous to the strong-coupling theory discussed in the last two paragraphs, although they did not make any assumptions on the exact nature (i.e. electron-phonon) of the interaction. In analyzing the data, Arnold et al. assumed that the experimental data near $\overline{\mathrm{M}}$ is representative of all locations in **k**-space. Hence, they treated the experimental data as if it was **k-**space averaged. Based on this assumption, they obtained a bosonic density of states that was dominated by a strong feature at a low energy of 10 meV and a suprisingly high coupling constant λ of 8.67. This analysis is certainly an interesting approach. However, it is not clear whether the starting point of such an approach is justified. There is clear experimental evidence that the photoemission spectra taken at different locations in **k-**space are very different, and thus the angle-resolved photoemission data may not simply be taken to be the same as the tunneling data. Furthermore, one also has to justify the meaning of the large coupling constant and its compatibility with other normal and superconducting state properties of the cuprates.

The second and third scenarios to explain the dip differ significantly from the conventional line of thinking. The second scenario was suggested by P.W. Anderson [272]. He views the appearance of the dip structure in the photoemission data of the superconducting state as a consequence of interlayer tunnelling. In the normal state, there is a doubling of the calculated energy bands at general points in the 2-dimensional zone due to the hopping matrix element connecting the two close CuO_2 layers in BSCCO. Within his 2-dimensionally correlated non-Fermi liquid theory in which the charge and spin of the electrons are seperated, this splitting should not be observable in the normal state. (See Figs. 4.24-4.26 from which Dessau et al. have argued that the band splitting does exist in the normal state [142].) However, in the superconducting state, the charge and the spin recombine, the interlayer coupling becomes possible, and so the degeneracy of the two bands is lifted. Anderson thus ascribes the two features (the pole at -45 meV and the region beyond the dip) to quasiparticle poles belonging to odd and even linear combinations of states at the same transverse **k**. The absence of the dip along Γ-X is in this theory due to the fact that the band splitting is much smaller along this direction by symmetry. This scenario is very nice in that it can explain the observed anisotropy, although questions about the presence or absence of the coupling in the normal state still need to be answered. In addition, the SIS tunneling data by Zasadzinski et al. shows the existence a dip in the single Cu-O layer cuprate superconductor $Bi_2Sr_2CuO_6$, as shown in Fig. 5.11b [276]. If one believes that the dip seen in photoemission and tunneling are the same, it would seem to rule out Anderson's hypothesis of interlayer tunneling as the origin of the dip.

The third scenario is based on the Marginal Fermi liquid hypothesis [274]. Within the framework of the marginal Fermi liquid hypothesis, the spectral weight function in the superconducting state consists of two peaks located at Δ and 3Δ. The valley between the two peaks resembles the dip structure observed in the experimental data along the $\Gamma\text{-}\overline{M}$ direction. According to their theory, the dip is not observed along Γ-X because of increased smearing due to the much more rapid dispersion rate of the bands along that direction [274]. Only more experimental work and more detailed analysis of these experimental data may distinguish the correct interpretation of the experimental data from the others.

Finally, Coffey and Coffey have postulated that the dip arises due to quasiparticle decay which acts as a correction to the weak coupling mean field treatment of the quasiparticle states [275]. According to this theory, an isotropic s-wave gap would produce a dip starting at $4\Delta_o$, while a d-wave order parameter would produce a dip starting at $3\Delta_o$. Based upon the dip observed in the photoemission and tunneling data, Coffey and Coffey propose that the cuprates are d-wave superconductors [275].

Now let's turn back and discuss another interesting aspect of the data, namely the non-conservation of the occupied spectral weight as the sample passes through the superconducting transition temperature. Along Γ-X, Dessau et al. found that the amount of weight transferred into the pileup peak is greater than the amount of weight transferred from the gap region (see Fig 5.6) [257]. Olson et al. found similar results [123]. Along Γ-$\overline{M}$, Dessau et al. found the opposite behavior: less spectral weight was transferred into the pileup than was depleted from the gap plus dip regions. These are very interesting results, though experimental complications may play a roll in these effects and so must be considered. The most obvious of these complications is that the spectral weight in the normal as well as the superconducting state is a sensitive function of the normalization procedure. For example, the normalization of the data used by Olson et al.in Fig. 5.3 is very different from Dessau et al.'s normalization in Fig. 5.6. The experimental data in Fig. 5.3 were normalized by the photon beam intensity, while the experimental data in Fig. 5.6 were normalized so that the spectral intensity far away from the superconducting gap is the same. In principle, the procedure of Fig. 5.3 should be an accurate one. However, because the samples are so small, and they are mounted on a long cryostat, any temperature changes will result in sample position changes so that the absolute intensity calibration is lost. Other possible complications are final state or matrix element effects and the possibility that spectral weight has been transferred to the unoccupied states. This last point is especially important since the sum rule that one expects to hold for a **k**-resolved experiment such as angle resolved photoemission extends over both the occupied and the unoccupied states. Thus any mechanism which transfers weight to or from the unoccupied states will have the effect of altering the weight in the photoemission spectrum. One mechanism that may have an effect on the data is the act of the Fermi function cutting off a broadened (by for instance lifetime effects) peak. It is clear from the normal state dispersion studies discussed in chapter IV that as the "band" approaches and then crosses the Fermi level, the intensity of the feature weakens as if being cut off by a Fermi function. The amount of weight cut off by the Fermi function could clearly be quite different in the normal and superconducting states. As discussed in subsection a of this chapter, the "coherence factors" that describe the amount of electron-like and hole-like character of the quasiparticle excitations of a BCS-like theory may also transfer weight between the occupied and unoccupied states.

Dessau et al. argued that because their normal and superconducting state spectra overlay on top of each other so well, their normalization procedure was reasonable [257]. However, Anderson suggested that the spectra should be normalized so that the integrated area under the spectra should be the same in the normal and superconducting states. [272] For the spectra along Γ-X, this would imply that weight has been transferred from a wide region of states at high energies (out to a few J, or a few tenths of an eV) into the superconducting pileup. This would suggest that the system energy in the superconducting state is lower by the electronic energy, indicating an electronic mechanism of superconductivity. Although this suggestion is very interesting, it is clear that many details need to be understood before we can positively arrive at such a conclusion.

Hwu et al. also studied the amount of spectral weight transferred between the normal and superconducting states [152]. They stated that the nonconservation of the spectral weight cannot be generalized to all spectra, as the area under their spectra in Fig. 5.7 is conserved to within 2%. Two points should be made regarding this comment. First, it is expected that if there is a positive weight transfer at some angles and a negative weight transfer at others, then it is expected that there will be zero net weight transfer at others. Secondly, the fact that they have observed much less **k**-space dependences argues for a general smearing of the **k**-space dependences in their data, so near-zero net weight transfer would be expected for many more angles.

2. k-dependence and symmetry of the superconducting gap

In this section we report the results of detailed studies of the variation of the gap size throughout the two dimensional Brillouin zone of Bi2212. This ability of ARPES to directly measure the gap as a function of crystal momentum is currently unique. This has allowed ARPES experiments to obtain some breakthrough information beyond what can be learnt from other experimental techniques. The data allows us to make very important inferences about such things as the **k**-dependence of the coupling matrix elements and the symmetry of the superconducting order parameter. This is crucial information that should help direct the development of a theory of the mechanism of the superconductivity.

The conventional BCS theory has an s-wave order parameter, reflecting the spherically symmetric nature of the pair wave function. For the high-T_c cuprates, theoretical analysis on the crucial CuO_2 plane with consideration of the strong on-site Coulomb interaction leads to other possible symmetries of the order parameter [172, 225, 226, 280-285]. In particular, pairing theories based on the Hubbard model or its derivatives lead to a d-wave order parameter or a mixed symmetry order parameter with a strong d-wave component. Very recently, motivated by the NMR data, this issue of the order parameter has been brought to the forefront of high-T_c research again [284, 226]. The ability to measure the gap as a function of **k** is a particularly attractive and perhaps unique capability of ARPES, making it an exceptionally powerful tool for the study of the symmetry of the order parameter.

The first experimental effort to address this issue was carried out by Olson et al. [150]. Fig. 5.13 shows the **k**-space locations where the experimental data was taken. From their curve fitting studies, they determined that the magnitude of the gap was a constant throughout the Brillouin zone, with a magnitude of approximately 18 meV. This would imply that the superconducting order parameter was of the isotropic s-wave type. More recently, Wells et al. [217] and Dessau et al. [256, 257] presented experimental data that showed that the gap was larger near the $\overline{\mathrm{M}}$ point than near the band crossing along along Γ-X(Y). Fig. 5.14 from Wells et al. shows superconducting state spectra taken at two different angles along Γ-$\overline{\mathrm{M}}$ and at three angles along Γ-X(Y) [217]. This data is the first explicit demonstration of gap anisotropy in the a-b plane. The normalization of the curves in this case is such that the leading edge or emission onset of the spectra can be most readily compared. From this data we can see that the leading edge postion for the spectra taken along Γ-$\overline{\mathrm{M}}$ is located at higher binding energy than the leading edge position for spectra taken along Γ-X, suggesting that the superconducting gap is larger along Γ-$\overline{\mathrm{M}}$ than along Γ-X.

This information was put on a more quantitative and firm footing by Shen et al. [218]. Normal and superconducting state data taken near the band crossings (A) along Γ-$\overline{\mathrm{M}}$ and (B) along Γ-X are shown in Fig 5.15. These **k**-space locations were chosen such that the normal state peak is at the Fermi level, and so the midpoint of the leading edge in the normal state coincides with the Fermi level both at A and at B. These data were taken with the very high angular resolution of ±1° and an energy resolution of approximately 30 meV. Very clear spectral changes are observed at A as the sample is cooled below T_C. The leading edge of the superconducting spectrum is pulled back to higher binding energy reflecting the opening of the superconducting energy gap. At the same time, a "pile-up" peak and a "dip" near -90 meV appear in the data. At B, only very minor changes with temperature are observed, the shift of the leading edge is undetectable within experimental uncertainty. The striking difference in data at the two **k** space locations is indicative of the highly anisotropic nature of the superconducting gap.

Before moving on to a discussion of the details of Shen's study, it is important to address the possible reasons why these results are so different from the earlier results of Olson et al. Perhaps the most likely explanation for the differences is that the quality of the sample used in Olson et al.'s experiment was much poorer. The samples studied by Wells, Shen and Dessau had very sharp superconducting transition widths of less than 2K, while the samples studied by Olson et al. had broader superconducting transition of around 20K. Also, the possibility of multiple domains or twinning exists for any one sample. Since the Wells-Shen-Dessau result of a large anisotropy has been reproduced on a very large number (> 20) of samples, this seems to be a robust result. On top of this, the general trend that a greater amount of anisotropy has been observed with the movement of time and sample quality implies that the anisotropic result is correct. A very recent result from the group at Argonne National Laboratory reproduces the large gap anisotropy on two Bi2212 samples that showed a good amount of dispersion in the normal state [261]. Another sample which was of such poor quality that it did not show normal state dispersion showed an isotropic gap very similar to that reported by Olson et al. [261].

Shen et al. discussed four aspects of experimental difficulties in quantifying the gap anisotropy [218]. (i) Finite energy resolution. This limits the precision of the measurements. (ii) Energy calibration of the spectrometer. This is spectrometer dependent and it limits the accuracy of the gap value. For the data they reported, the uncertainty is about ±1 meV for sample #1, and ~ ±2-3 meV for samples #2 and #3. (iii) Sample surface flatness and finite angular resolution. This limits the momentum resolution of the experiment, and is probably a major factor preventing the experiment from determining whether a d-wave node exists. Furthermore, the surface flatness is sample dependent, causing a scatter in the experimental data. The method used by Shen et al. to characterize the surface flatness is to measure the divergence of a laser reflection from the cleaved surface. This method shows that the surfaces of samples #1 and #3 are flatter than sample #2. (iv) Time dependence of the data, as was illustrated in Fig. 5.9. ARPES is a surface sensitive technique so that its spectra may change as the sample surface ages.

The theoretical diffculties mainly center about the fact that we do not have an adequate theory to describe the photoemission lineshape of either the normal or superconducting states. In BCS theory, the difference between the normal and the superconducting state ARPES spectrum is a shift of peak position from ε_k to $\sqrt{(\varepsilon_k^2+\Delta^2)}$ and a change of spectral weight by the coherence factor u_k^2. Obviously, this can not account for the -80 to -90 meV dip seen in the data near $\overline{M}$. Furthermore, due to finite momentum resolution, the data exhibit aspects resembling angle-integrated photoemission (AIPES) spectra that reflect the BCS density of states $E/(E^2-\Delta^2)$. This is why previous ARPES data were fitted by a BCS function to extract the superconducting gap size [123, 124, 150, 217]. Such a fit should be viewed as a crude approximation.

For these reasons, and for greatly increased simplicity in carrying out and understanding the method of gap extraction, Shen et al. have chosen to call the gap the energy position of the midpoint of the leading edge of the superconducting state spectrum [218]. With this criterion, the spectrum at point A in figure 5.15 gives a gap of 12 meV ($2\Delta/k_BT_c = 3.6$) and the spectrum at point B gives a gap of 0 to 0.5 meV. Of course the edge position will only reflect the gap size if the normal state peak is at the Fermi level (see Fig. 5.1).

The measured **k**-dependence of the gap from three Bi2212 samples is displayed in figure 5.16, after Shen et al. [218]. Each spectrum is labeled with a letter, with the order of the measurements corresponding to the alphabetic progression. The location of the measurement relative to that of the measured Fermi surface is displayed in panel (a), and the magnitude of the gap for each measurement is displayed on the vertical axes of the graphs of panel (b). The horizontal axis of panel b is the **k**-space function $0.5 * |\cos k_x a - \cos k_y a|$. On this scale, the simplest $d_{x^2-y^2}$ gap function would be linear with a zero intercept. This allowed Shen et al. to highlight not only the very large gap anisotropy observed in the Bi2212 samples but also to make a comparison of the <u>magnitude and direction of the anisotropy</u> with what is predicted by simple theories.

As shown in Fig 5.16, all samples showed a very large gap anisotropy with the maximum gap near the $\overline{M}$ point and the minimum near Γ-X(Y). This is independent of the measuring sequence and so is not caused by the time dependence of the spectra. The magnitude of the measured anisotropy is very large, ranging between a factor of roughly 2 and 10, depending upon the sample. This is one to two orders of magnitude larger than what is observed in conventional superconductors [286].

In addition, the basic trend of the data is very similar to that expected by a $d_{x^2-y^2}$ order parameter. The most relevant aspect of the data for answering this question is whether the gap actually goes to zero along Γ-Y (a node exists), or whether the gap just gets small there. The importance of this distinction is illustrated in Fig 5.17, which schematically illustrates the expected **k**-dependence of the order parameter and gap magnitude for a d-wave superconductor and an s-wave superconductor with large gap anisotropy. The important distinction is that the d-wave order parameter changes sign as a function of **k** while the s-wave order parameter does not. For this reason, the d-wave gap, which is proportional to the square of the order parameter, must go exactly to zero at specific **k**-space locations. The s-wave gap has no such requirements, although it of course is not excluded from going to zero at specific **k**-space locations.

The data of Fig 5.16 shows that the gap minimum is very near zero for samples 1 and 3, while it is significantly greater than zero for sample 2. Shen et al. argued that samples 1 and 3 were higher quality and more representative than sample 2, particularly in regard to sample flatness (determined by the sharpness of a laser beam reflected off of the cleaved sample surface) [218]. The idea was that the greater **k**-averaging imposed by the non-flat surface could hide the region with a zero gap by averaging in other regions nearby which have a finite gap.

Later experiments by Dessau et al.[258] on flatter Bi2212 crystals and by Marshall et al.[287] on cleaved MBE-grown thin films of Bi2212 showed that indeed the gap along the Γ-X(Y) directions in Bi2212 samples is indeed very small, confirming the guess that Shen's sample #2 was not representative. The data is shown in Fig 5.18, which is a compilation of 14 different Bi2212 samples by Dessau et al.[288]. The first three samples are from Shen's original paper (only the freshest data is retained) [218]. Normalized gaps (with the maximum gap for each sample equal to 1) are plotted against the d_{x2-y2} order parameter $0.5|\cos k_x a-\cos k_y a|$. This data implies that the gap near the Γ-X(Y) direction is, within the experimental error bar, essentially zero. Higher resolution and better sample preparation methods will certainly be important in determining whether there is in fact a node in the gap function, but even then, we will never really know if the gap goes exactly to zero, as it must for a d-wave superconductor. A final determination of whether the gap is d-wave or anisotropic s-wave therefore must wait for experimental evidence which is sensitive to the phase of the order parameter. This is very crucial and fundamental information, because the d-wave and anisotropic s-wave order parameters will arise from a very different class of interactions.

The interpretation of the anisotropic gap data with the d-wave theory is not unique. A recent study by Chakravarty et al. associates the gap anisotropy to the anisotropy of the interlayer tunneling matrix element. Fig. 5.19 reproduces their fit of the data within the framework of the interlayer tunneling mechanism [297].

At this point we would like to comment on a few of the details which may have sppeared to have been glossed over in the discussion of the gap symmetry from Shen's experiment [218]. The first is about the possibility that the measurements may have been affected by the BiO bands, with perhaps a different gap being associated with a different band or layer. This is not an issue for two reasons. First, because the normal state Fermi surface mapping done by Dessau et al on similar samples indicated that the BiO bands do not approach very near the Fermi level, as discussed in section IV-E-3 [142]. Second, even if the BiO bands were to contribute, they would contribute near the $\overline{\mathrm{M}}$ point. From this we would expect a smaller gap near $\overline{\mathrm{M}}$ instead of the experimentally observed larger gap.

The second issue is why there is such a large variation reported in the gap size at $\overline{\mathrm{M}}$. The answer is that the variation is not random, but that it is observed to depend sensitively on the sample type. As discussed in section IV-E-9, the Bi2212 samples may be annealed so as to give a range of oxygen content, and hence a different T_c. The samples annealed in an excess of oxygen have a lower T_c of near 78K, and are experimentally found to have a relatively small gap of 12 meV near $\overline{\mathrm{M}}$. Reduced samples may have a T_c as high as 90K, and have a larger gap of approximately 22 meV at $\overline{\mathrm{M}}$. As depicted in Fig 5.16 and 5.18, both the higher and lower T_c samples are found to have a minimum gap near 0 along the Γ-X(Y) direction.

Recently, Kelley et al. have reported that they were able to determine the symmetry of the order parameter in Bi2212 based upon the symmetry rules in angle-resolved photoemission [260]. They measured angle-resolved data for two different photon polarizations along both the Γ-X and the Γ-Y direction in Bi2212, and in both the normal and superconducting states. The data from the superconducting state are shown in Fig 5.20. The key experimental point that Kelley et al. were trying to make is that a "condensate peak" was visible for orientations a,b, and d, but not c, and this effect must be related to the symmetry of the order parameter.

Kelley et al. used the standard argument that the matrix element $M=(e/mc)<\psi_f(\mathbf{k})|\mathbf{A}\cdot\mathbf{p}|\psi_i(\mathbf{k})>$ must be invariant under symmetry operations and hence can tell one symmetry information about the initial state wavefunction $|\psi_i(\mathbf{k})>$ (see section IV-E-9). They compiled a table listing possible symmetries and whether an initial state of such symmetry would be observable for each of the four experimental geometries. They then compared the results of their experimental observations to this table. The superconducting state matched the $d_{xz}+d_{yz}$ and p_x+p_y symmetry states. Based on the differences between the normal and superconducting states, Kelley et al. inferred that their observations in the superconducting state reflected the symmetry of the superconducting order parameter, i.e. the order parameter must have either $d_{xz}+d_{yz}$ or p_x+p_y symmetry.

As pointed out in a comment by Dessau et al.[], the type of analysis that Kelley et al. tried to use is flawed and leads to a result which is not even self-consistent. Further, Dessau et al. showed that Kelley et al.'s experimental observations can be explained in a simple and consistent way without provoking these unusual order parameters.and cannot be used to determine the symmetry of the order parameter.

Dessau et al.'s argument centered around the point that Kelley et al. attempted to determine the symmetry of the pair state using a technique which can only determine the symmetry of a single-particle state. This error lead Kelley et al. to a conclusion which was not even self-consistent. Dessau et al. proposed an alternative explanation for their data based upon two points. (1) All of the data comes from along the Γ-X(Y) directions where measurements indicate that the gap has its smallest value and may even vanish. (see the beginning of this section) This explains why the effects of the superconductivity in the spectra of Fig 5.20 are so weak, with the result that the uncertainty in the data is large. (2) An analysis based upon the strength of the "condensate peak" must take account for the strength of the normal state quasiparticle peak, as the strength of the former will track that of the latter. However, the weight above the background of the dispersive quasiparticle peak for orientation c is significantly weaker than that for all of the other orientations. This implies that the lack of a "condensate peak" for orientation c is expected and so is irrelevant to the symmetry issue.

D. Results from $YBa_2Cu_3O_7$

In addition to the $Bi_2Sr_2CaCu_2O_{8+\delta}$ studies, much effort has been directed to study the superconducting gap of $YBa_2Cu_3O_{7-\delta}$. The situation here is much more complicated than in YBCO, and there is not yet an agreement within the community whether the gap actually exists, let alone what are the details of its lineshape or **k**-dependance. As discussed in chapter IV-E-5, most of the confusion centers around the issue of different possible surface terminations of YBCO and which of these, if any, are representative of the bulk. The possibility of surface reconstruction leaving a non-superconducting phase near the surface goes a long way to explaining the lack of a clear gap.

Most of the studies have reported the absence of a gap in YBCO, although a few have reported some prelimary evidence that a gap may exist in a few rare cleaves [160, 300]. Fig. 5.21 shows the data taken by Tobin et al. from an untwinned single crystal of $YBa_2Cu_3O_{7-\delta}$ [139]. It is clear that the leading edge of the spectrum from the superconducting state does not pull away from the Fermi level as determined by the Pt reference spectra, in contrast to the case found for $Bi_2Sr_2CaCu_2O_{8+\delta}$. This suggests that the sample surface studied either has no superconducting gap or a gap smaller than 5 meV [139]. Recently, very detailed work by Liu et al. also reported a null result for the superconducting gap [158]. The most likely reason for the lack of a gap in these measurements is that the surface of $YBa_2Cu_3O_{7-\delta}$ could reconstruct after breaking the strong bonds fom cleaving, leaving a non-superconducting phase near the surface.

Schroeder et al. measured the low temperature (10K) photoemission spectra of a variety of YBCO samples, and suggested that some samples, which had a very weak or nonexistent -1 eV peak, exhibited a superconducting gap [160]. Fig 5.21 shows temperature dependent data on their second “best” sample, and Fig 4.37 shows low temperature data of their best sample (#1) in comparison to a “poorer” sample (data at $T>T_c$ was not available for their best sample). These spectra were taken at various locations along the $\Gamma-X(Y)$ direction. Based upon the results of fitting to a BCS density of states, Schroeder et al. argued that their results supported a gap of near 20 meV. Unfortunately, the statistics as well as the energy resolution of these experiments was not very good, and so these results are not as convincing as they might be.

It should be noted that there is another, entirely different explanation which may explain the lack of a consistent gap in YBCO. This is the possibility that the chain states may not go superconducting, and the spectral weight from the chains may superimpose over the gap from the planes. Along the Γ-S direction, where there should be no chain contribution to the near-E_F states, the gap is likely to be small or even zero, in analogy to the situation of an anisotropic gap observed in Bi2212 (note that the Γ-S direction in YBCO is equivalent to the Γ-X(Y) direction in Bi2212). Perhaps careful studies done away from the high symmetry directions would be able to detect a gap in YBCO.

E. Comparison to superconducting state measurements by other techniques

For the conventional superconductors, the BCS theory was developed and accepted on the basis of many experimental facts: the isotope effect, tunnelling experiments, IR reflectivity, the Meissner effect, the NMR relaxation rate and Knight shift, the penetration of the electromagnetic wave, ultrasonic attenuation, magnetic flux quantization and others [266, 289]. For the high-temperature superconductors, due to the more complex nature of the materials, it is even more important to look at the overall picture from many experiments.

No measurement technique can be expected to convey all the information needed to understand the exciting and complex phenomena displayed by the high temperature superconductors. However, by a combination of experimental techniques, the strengths and weaknesses of each technique can be offset, and the true physical behavior can be more readily uncovered. We have shown how tunneling and photoemission have combined to prove the existence of the high binding energy dip as intrinsic to the superconducting excitations, and how they can be used to steer theories of the mechanism of the superconductivity.

The finding of the anisotropic nature of the superconducting gap may help to account for the excitations observed by a variety of experimental techniques which are smaller than the "BCS gap", as well as the spread of the gap size obtained by different measurement techniques. There is strong evidence from many experiments that the superconducting gap of YBCO and Bi2212 is very anisotropic. First, we have the microwave penetration depth measurements from YBCO by several groups 219,220,290. All these measurements suggested that the London penetration depth of the superconductor has a power law behavior at energies well below the "BCS gap". In particular, the earlier work by Anlage et al. was interpreted to have two gaps, with the smaller gap well below the BCS value [290]. The details of the experiment are still controversial at present. Ma et al. reported that the temperature dependence of the penetration depth is T^2 [220] while Hardy et al. reported that the temperature dependence of the penetration depth is T [219]. The linear temperature dependence of the penetration depth is required if the superconductor is to have line nodes in the gap. Second, we have the angle-resolved photoemission data as discussed above. Although the photoemission data has relatively poor energy resolution, it’s unique contribution to the understanding of the gap anisotropy lies in the fact that it provides direct and specific **k** information of the gap anisotropy. Third, we have the electronic Raman experiments [291]. These experiments show low energy electronic excitations well below the BCS gap value. With different polarizations of the laser light, the on-set of the low energy excitation is very different, suggesting a very anisotropic superconducting gap. A recent paper reported that the polarization dependence of the superconducting gap is consistent with the $d_{x^2-y^2}$ order parameter [223].

In addition to these experiments that reveal direct information about the superconducting gap, there are several important experiments that are indirectly related with the gap anisotropy issue. Historically, one of the most important experiments indicating the gap anisotropy is NMR. Both the knight shift and anisotropy of the nuclear relaxation rate between copper and oxygen have been interpreted to be consistent with a d-wave order parameter [284]. If this interpretation is true, then the superconducting gap of YBCO will be very anisotropic. In addition, we have the IR reflectivity measurements. Recent data from that field is that these superconductors have a p-wave pairing state [292]. While this interpretation is controversial, the data nevertheless strongly points towards an anisotropic gap.

Finally, we have the recent YBCO-Pb dc SQUID experiment conducted by Wollman et al. [221]. SNS Josephson Junctions were fabricated on the a and b faces of a single crystal of YBCO. A $d_{x^2-y^2}$ order parameter would be expected to give an additional phase shift of π, while an s-wave order parameter should not give an additional phase shift. Although not conclusive, the authors stated that the data as a whole strongly points to a d-wave picture. The beauty of this experiment is that because it is sensitive to the phase of the order parameter, a d-wave gap is in principle distinguishable from a very anisotropic s-wave gap.

In contrast to the above experiments, there are several experiments which imply an isotropic gap. The first is a neutron scattering experiment by Mason et al. [293]. This experiment suggested that while there are excitations well below the BCS gap, the q-dependence of the excitations are not consistent with the $d_{x^2-y^2}$ proposal if the material is clean. In the presence of impurities (which is very likely in the neutron experiments because of the large crystals required), the authors indicated that they could not make a strong statement. This interpretation of the neutron data was challenged by Scalapino et al. who claimed that the q-dependence of the data is actually consistent with the d-wave scenario [294]. Secondly, there are the tunnelling experiments. The tunnelling community is divided in this field. On the one hand, some STM tunnelling data from the Tokyo group showed a very clean gap in both YBCO and Bi2212 [295, 296]. Fig. 5.22 reproduces some of their data on the 001 surface of an epitaxially grown film of YBCO. These results were interpreted by the experimentalists as support for a clean s-wave gap. The key argument here is that since the STM tip is so localized, the momentum resolution is lost due to the uncertainty principle. The counter argument here is that the **k**-space average could be strongly weighted in a certain direction away from the gap node. On the other hand, there are both junction and STM experiments from Bi2212 [222, 271] and YBCO [198] revealing excitations inside the BCS gap. What is even more confusing is the fact that many of these experiments which do not see the clean gap were carried out on what appear to be better characterized and more carefully prepared surfaces. For instance, while the STM measuremants of Edwards et al. were performed on single crystals cleaved in UHV at low temperature[198], Nantoh et al. studied films which were transported in air and received no further treatment [295].

VI. Summary and Concluding Remarks

Photoelectron spectroscopy has played a crucial role in helping us to understand the electronic structure of transition-metal oxides. In this review, we have concentrated on the Mott insulators and high-temperature superconductors. Even though these classes of compounds have extremely different ground state properties (large gap insulator versus superconductors!), they are clearly related since the high temperature superconductors have sister compounds that are Mott insulators.

For the Mott insulators, (Section III) photoemission is sensitive to the four important aspects of the electronic structure, namely the large Coulomb interaction energy U involved in the polar type of charge fluctuation $d_i^n d_j^n \leftrightarrow d_i^{n+1} d_j^{n-1}$, the charge transfer energy Δ in the transfer type of charge fluctuation $d^n \leftrightarrow d^n\underline{L}$, the energy dispersion due to the wave function overlap, and the magnetic exchange splittings.

The large U is the main reason why these compounds are large gap insulators at half filling rather than metals or small gap semiconductors as predicted by band theory. It apparently is also responsible for the band theory to predict a much smaller magnetic moment than the experimental data. The large U is the prime reason why these compounds have attracted so much attention over the last half century. The charge transfer is a direct consequence of the fact that these oxides are not purily ionic, but that there is large hybridization involved. The consideration of charge transfer is crucial for interpreting the photoemission data from copper and nickel compounds.

Resonance photoemission shows that only the satellite exhibits a strong resonance at the cation absorption edge, while the main band near the valence band maximum shows an anti-resonance. This suggests that the satellite has the d^{n-1} configuration while the main band near the valence band maximum has the $d^n\underline{L}$ configuration. Hence, the insulating gap is more directly influenced by the charge transfer energy Δ. Therefore, the copper and nickel compounds are often called charge transfer insulators. (In most of the paper, we simply called them Mott insulators for historical reasons) The charge transfer insulator picture also helps to explain the trend of magnetic interactions in these mono-oxides [25].

The relative role of U and Δ is summarized by ZSA [22]. When $\Delta<U$, charge transfer fluctuations dominate the low energy excitations. Where $\Delta> U$, the material is a traditional Mott insulator with polar charge fluctuations dominating the low energy excitations. The general trend is that the charge transfer energy is most important in the copper compounds, and its role decrease as one goes to compounds with less d electrons. CuO and NiO are charge transfer insulators ($\Delta<U$) , while V_2O_3 (and thus presumably Ti_2O_3) and ScO are Mott insulators ($\Delta>U$). CoO, FeO, MnO and CrO (hypothetical) are in the intermedia regime (Δ~U). We note that for the earlier TMO's this simple picture has been recently challenged by Park et al. [60]. They stressed the importance of the metal-oxygen hybridization energy T, and estimated that U, Δ, and T are all of comparable magnitude for the early TMO's. If they are correct in this, then there are really no "true" Mott-Hubbard insulators.

The energy dispersion is a direct consequence of the wavefunction overlapping, and is particularly important for the ligand bands. We can see that the energy dispersion for an oxygen band is about 4 eV, which is the same scale as the charge transfer energy. Since these oxides are not purily ionic, it is essential to consider the energy dispersion. The importance of the energy dispersion is recognized in some recent theoretical effects also. For example, the energy dispersion of the oxygen bands are essential to the convergence of the so-called self-interaction-correction (SIC) calculations [111]. The energy dispersion is particularly important for the charge transfer insulators. In these insulators, the low energy excitations are dominated by the charge transfer fluctuations involving not only the less dispersive d bands but also the very dispersive oxygen bands. For example, the recent angle-resolved photoemission studies from insulating $YBCO_{6.35}$ clearly showed that it is essential to consider the energy dispersion in order to have a complete understanding of this compound [153].

The magnetic interactions are also important for a complete understanding of the electronic structure. We see that the Ni3s core level splits into at least four features. One has to provoke the magnetic exchange multiplet splitting in order to understand this data. The size of the splitting suggests that the exchange splitting in NiO could be of the order of several electron volts. In addition, we also see that the consideration of the antiferromagnetic order is essential to understand the angle-resolved valence band photoemission data. Here one should note that there were two types of definition of Δ, with one including and the other excluding the exchange contribution. One should be careful about the two different definitions and this issue is explicitly discussed recently. [301, 302]

The four aspects of the electronic structure discussed above are all important for a complete understanding of the electronic structure of these oxides. It is not clear whether one can use the perturbation approach to this problem because they each could be of the same order of magnitude (perhaps with the exception of U). For example, in the case of NiO, we have U~8 eV, Δ~4 eV, the energy dispersion for the oxygen band could be about 4 eV, and the magnetic multiplet splitting is about 2 to 3 eV. These aspects make a full theoretical calculation of the electronic structure of these compounds a very difficult task.

For the high-temperature superconductors, we surveyed both angle-integrated and angle-resolved measurements. The angle-integrated data were most often compared with cluster or impurity model calculations. This approach has many similarities to that of the Mott insulators discussed in the last section. These experiments showed that the strong correlation features such as the high energy satellite persist into the superconducting state. This shows that the large Coulomb interaction U is not significantly screened, and must be important for a complete understanding of the electronic structure of the high-temperature superconductors.

We have also spent some time discussing the tricky issues in the preparation of good sample surfaces for photoemission experiments. There is now a general consensus that only the results that have been reproduced in single crystalline samples should be trusted. However, this is not a sufficent condition. Many of the results from single crystals (such as the early angle-resolved photoemission data from $YBCO_{6.9}$ at room temperature) could be problematic. Therefore, one has to judge the photoemission data very critically. It appears that the best angle-resolved photoemission data are those obtained from high quality single crystals for which a known high quality cleavage plane exists. The samples should be characterized by as many other means as possible, such as the sharpness of the superconducting transition, LEED, the width of the x-ray lines, and the flatness of the cleaved surface.

For the most part, we concentrated on the recent angle-resolved photoemission results (Sec. IV.E and Sec V). In the normal state, these experiments addressed the issue of the Fermi surfaces and the excitations near the Fermi level. Despite the compelling evidence of correlation effects, angle-resolved photoemission clearly demonstrated the existence of the Fermi surfaces. Furthermore, the measured Fermi surfaces have similarities to theoretical Fermi surfaces calculated by band theory. In particular, it appears that the highly metallic cuprates probably obey Luttinger's counting theorem, which requires that the Fermi surface of the interacting electron system encloses the same volume as the Fermi surface of the non-interacting system. This was a very significant contribution to the understanding of the electronic structure of the cuprate superconductors.

Also very significant are the connections between the electronic structure and the other physical properties of the cuprates, including the superconductivity. These connections arose out of a wide range of very careful and detailed measurements on a variety of the cuprate superconductors. Key features in the electronic structure which existed for a wide range of the cuprates were uncovered, and the details of these features were compared and contrasted. These key features are (1) very flat bands in CuO_2 band structure which have saddle point behavior. These flat bands are very near E_F for the p-type cuprates studied so far (Bi2212, Bi2201, Y123 and Y124) and so will have a significant effect on the physical properties, including possibly the temperature dependence of the resistivity, the isotope effect, the Hall effect, and the symmetry of the superconducting gap. On the other hand, these flat bands appear significantly below (~ 300 meV) E_F for the n-type cuprates, and so will not be electrically active. (2) Significant Fermi surface nesting has been observed for most of the cuprates. In particular, a very strong nesting vector near (π,π) has been observed in Bi2212. The effects of this nesting on the electron scattering, susceptibility, and symmetry of the order parameter have been discussed.

The contribution photoemission has made to our understanding of the superconducting state of the high-T_c superconductors has been equally valuable. The superconducting gap has been observed in Bi2212 in both the angle-integrated and angle-resolved modes, and has been studied by quite a few groups. The superconducting gap sizes obtained by various photoemission groups are remarkably consistent with each other, and are consistent with those obtained by most other methods (typically 20-25 meV for T_c= 85K-90K samples). The gap has not been reproducibly observed in YBCO, presumably due to surface problems. There have not as yet been any reported attempts at measurements on other samples. This has to do with both the availability of high quality samples and the available instrumentation; the gap in many of the lower-T_c cuprates is so small that not very much could be learned from them with the presently attainable energy resolution.

Although photoemission was only very recently applied to the study of the superconducting gaps, its power has become immediately obvious, particularly because of its unique ability to directly measure the momentum dependence of the gap. While other classical measurements of measurement such as tunneling and infrared reflectivity have better energy resolution, they do not have the capability of measuring the momentum dependence, and have in addition been hindered by many practical problems such as the difficulty in making a good contact for tunneling and by the large anisotropy of the dielectric constant for the IR reflectivity measurements.

While early measurements indicated that the superconducting gap was essentially isotropic in k-space, favoring an s-wave pairing state[150], later measurements showed significant anisotropy, with the gap a maximum near the $\overline{M}$ point of the Brillouin zone and minimum along the Γ-X(Y) zone diagonal [217, 257]. Shen et al.'s study showed that the gap minimum in some samples (those independently determined to be of the highest quality) was, within the experimental uncertainty (a few meV), essentially zero [218]. Because the location of the gap minimum (along the Γ-X(Y) diagonal) was exactly where the node in a d_{x2-y2}-wave gap (the most likely symmetry of a d-wave gap) should be, a tremendous amount of excitement was generated. Since that time, experiments of many different types were carried out aimed at probing the symmetry of the gap, including tunneling [222, 276, 295, 296], Raman spectroscopy [223], microwave penetration [206, 219, 220], infrared transmission [224] and Josephson Junction measurements [221], among others. The majority of these concluded that the gap was indeed very anisotropic, and that the anisotropy matched that of the d_{x2-y2} gap. However, it must be realized that with the exception of the Josephson Junction experiment[221], none of the measurements are sensitive to the <u>phase</u> of the order parameter, and so it is not possible to distinguish between a very anisotropic s-wave gap [297-299] and a d-wave gap. More experiments which are sensitive to the phase are definitely necessary, as the difference between a d-wave and a very anisotropic s-wave gap is very fundamental; an s-wave gap requires that the electron-electron interaction is attractive, while a d-wave gap can take advantage of a repulsive interaction.

In addtion to measurements of the symmetry of the gap, photoemission has revealed some anomalous spectral weight transfer which occurs at the superconducting transition in Bi2212 [257]. For the spectra near $\overline{M}$ (where the gap is large), a dip structure appears near -90 meV in the spectra recorded in the superconducting state. This is a very high energy scale when compared to the gap energy (near 20-25 meV), and is not expected to occur in a simple BCS type of pairing theory, where spectral weight is only depleted from states with an energy lower than the gap. Spectra taken just above T_c do not show any sign of the dip. This effect has also been observed in tunneling spectroscopy for a wide range of the cuprates, and the energy of the dip is observed to scale with T_c [276]. This dip has generated quite a bit of theoretical interest [272-275], although there is as yet no consensus on its origin. Much of the reason for the excitement over this feature was historical, as analogous high energy oscillations in the tunneling spectra of some of the strong coupling superconductors proved to be critical information in determining that the electron-phonon coupling was the driving force behind the superconductivity in conventional superconductors. It is possible that the dip in the cuprates may also hold an imporant clue to our understanding of the mechanism of superconductivity.

Finally, we point out that there are very interesting connections between the different measurements and the results on different sample types. Much of the interest in pairing mechanisms of d-wave symmetry stems from the realization that there is a large on-site Coulomb energy U between the electrons in transition metal oxides in general (see section III). The observation that the high binding energy satellite persists into the superconducting state implies that this Coulomb U will have to be overcome if the electrons are to be paired in a classical way. Going to higher momentum channels such as in the d-wave case is a very effective way of overcoming this U, as there is a node at the origin and so there will be less wave-function overlap.

The superconducting state properties (as well as many other properties) of the p- and n-type cuprates are very different. In particular, the maximum T_c presently observed for an n-type cuprate is ~25K, and most indications are that the gap in the n-types is quite isotropic [206]. We point out that the electronic structure of the p- and n-type cuprates is very different, particularly in regards to the presence/absence of the flat bands at E_F, and suggest that this may be responsible for the differences in gap symmetry. Some theoretical work by Dickinson and Doniach supports this proposition [172]. They showed that a d-wave gap may be stabilized by a $\mathbf{k}$-space anisotropy in the contribution to $N(E_F)$, with a larger gap in the region of high state density due to the energy gain from gapping many states. This is precisely what has been observed in the ARPES measurements of the SC state of Bi2212 - $\Delta(\mathbf{k})$ is maximum near $\overline{M}$ and minimum near the crossing along

Γ-X(Y) [218, 288]. In NCCO, a strongly anisotropic or d-wave gap may not be favored since the flat bands are well below E_F.

Looking towards the future, we believe that ARPES will continue to play a key role in ths study of high-T_c superconductivity. The energy and momentum resolution of the experiments will certainly improve. In Fig 6.1 we show a gas phase spectrum taken in our lab from a Xe $5p_{3/2}$ core level taken with a new very high energy resolution spectrometer built by Scienta Instruments AB. As shown in the figure, the line has a FWHM of 6.1 meV. Similar equipment using a higher resolution Helium lamp have produced spectra with a FWHM of 4.3 meV [303]. This is better than a factor of five improvement over most of the high resolution studies reviewed here. We are very optimistic about the impacts this new generation of instrumentation will have on the photoemission community.

VII. Addendum:

In the process of reviewing this paper, we noticed several recent developments which we summarize in the following paragraphs.

The superconducting gap anisotropy in the a-b plane is now confirmed by several groups.[304, 305, 306] The superconducting gap is smallest in the vicinity of the (π/a, π/a) direction, and it reaches a maximum as one moves away from it. Whether the gap reaches zero along (π/a, π/a) is still an unsettled issue, due to reasons similar to those discussed earlier. At this time, much more work is need to sort out more detailed issues such as whether the node line is slightly off the (π/a, π/a) direction,[304] the temperature dependence of the gap anisotropy,[305] and impurity scattering effects on the gap anisotropy.[306, 307]

There is a detailed Fermi surface mapping by Aebi et al. of Bi2212.[309] The experiment was carried out in a different way than those discussed in this paper. In their measurement, Aebi et al. fixed the energy window at energies near the Fermi level and scanned the detector angle. This approach allows them to survey the Brillouin zone in more detail than those measurements discussed earler, although with a loss of som energy information. Their results confirmed the flat bands near Fermi level in an extended k-space region. However, the Fermi surface obtained in this way is slightly different from those by Dessau et al. Aebi et al. interpreted their data as evidence of seeing the short range antiferromagnetic spin fluctuations. This interpretation is controversial and has been challenged by Chakravarty who pointed out that one should not see folded back bands in materials with extremely short spin-spin correlation lengths and without a staggered magnetization.[310]

There are active theoretical works simulating angle resolved photoemission data using Monte Carlo methods, as well as calculating the dispersion relationship using the t-J model.[311-316] These simulations are carried out on clusters with intermediate

Coulomb interaction U strength. (e.g. U = 8t) These theoretical calculations reproduced many aspects of the experimental data from both the metallic and insulating regime. In the insulating regime, recent experimental data by Wells et al. serves as a good test case for theoretical calculations.[317] Wells et al. found that the spectral behavior along the (0, 0) to (π/a, π/a) line predicted by the Monte Carlo as well as t-J model calculation is very similar to those found experimentally, while the spectral behavior along (0, 0) to (π/a, 0) line does not agree with the experiment. A potentially very siginficant finding is that these simulations give very flat bands near the Fermi level in the vicinity of (π/a, 0). This finding is very consistent with the flat bands observed in angle-resolved photoemission experiments, and is very suggestive that the flat bands observed in the experiments are manefestations of many-body effects in these materials.

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Table I: Selected examples of transition-metal oxides with various ground state electric and magnetic properties.

Mott-Hubbard insulators:	Cr_2O_3, α-Fe_2O_3, NiO, CoO, MnO, La_2CuO_4, $YBa_2Cu_3O_6$
Large band gap insulators:	Cr_2O_3, α-Fe_2O_3
Semiconductors:	V_2O_5, Cu_2O, VO_2*, V_2O_3*, Fe_3O_4*, Ti_2O_3*
Metal	CrO_2
High-Tc Superconductors:	$La_{2-x}Sr_xCuO_4$, $YBa_2Cu_3O_7$
Antiferromagnetic:	NiO, CoO, La_2CuO_4, α-Fe_2O_3, Cr_2O_3, $YBa_2Cu_3O_6$
Ferrimagnetic:	γ-Fe_2O_3, Natural Fe_3O_4
Ferromagnetic:	CrO_2, K_2CuF_4

* Semiconductors via Mott transition

Figure captions (contact author for figures)

Fig. 2.1 The three-step model of photoemission spectroscopy, from ref 48.

Fig. 2.2 The “universal curve” of electron escape depth vs. kinetic energy, from ref 49.

Fig. 2.3 A vertical transition in photoemission, due to the fact that the photon carries negligible momentum.

Fig. 2.4 The experimental geometry for an angle-resolved photoemission experiment.

Fig. 2.5 Schematic of an ideal angle-resolved photoemission experiment. A peak is observed at the band energy in each spectrum, but disappears when the band crosses throgh the Fermi level to the unoccupied states.

Fig. 2.6 Schematic for the resonance photoemission process for 3d transition metal compounds.

Fig. 2.7 Illustration of two additional modes of photoemission spectroscopy. a) CFS or Constant Final State, and b) CIS or Constant Initial State.

Fig.3.1 Schematic model of N hydrogen atoms arranged closely together in a solid chain, from ref 59.

Fig. 3.2 A classification scheme based upon calculations by Zaanen, Sawatzky and Allen (ZSA) (ref 22). The diagram is calculated for W=3 and V=1 eV. Region A is the classical Mott-Hubbard regime, where the gap is proportional to the Coulomb U. Region B is the charge transfer insulator regime.

Fig.3.3 Monoclinic crystal structure of CuO, from ref 72.

Fig.3.4 Cubic crystal structure of Cu_2O, from ref 73.

Fig.3.5 Comparison between the weighted density of states from one-electron band calculations and that angle-integrated photoemission data The agreement for Cu_2O (panel A) is much better than the agreement for CuO (panel B), from ref 67.

Fig.3.6 Cluster picture for the photoemission process of CuO. The initial state is a linear combination of configurations with the hole either on the Cu site (d^9) or on the O site ($d^{10}\underline{L}$). The three possible final states are d^8, $d^9\underline{L}$, and $d^{10}\underline{L}^2$.

Fig.3.7 Cu 3p to Cu 3d resonance photoemission data of CuO together with the theoretical calculations based on Fano's theory of resonance photoemission (solid lines panel B), from ref 68.

Fig.3.8 Giant Cu 2p resonance photoemission data from CuO, from ref 75.

Fig.3.9 Cu 2p core level photoemission data of Cu_2O and CuO, from ref 67.

Fig.3.10 Valence bands of CuO a) Cu 3d partial DOS, from LDA band structure calculations; (b) experimental valence band data; (c) Cu 3d spectral weight using

Fig 4.18 LDA calculation of band structure and Fermi surface of Bi2212 along the Γ-$\overline{M}$-Z direction, by Massida et al. [174]. The interaction of the BiO states with the CuO_2 states was ignored for this calculation.

Fig 4.19 The full LDA calculation of the band structure and Fermi surface of Bi2212 along the Γ-$\overline{M}$-Z direction, by Massida et al., including the interactions of the BiO states with the CuO_2 states [174].

Fig. 4.20 An LDA calculation of a) the band structure at $k_z = 0$ and b) at $k_z = \pi/c$, and b) the Fermi surface of YBCO by Pickett et al. [176]. The k_z smearing of the Fermi surface is indicated by shading of the crossings.

Fig. 4.21 a) Normal state ARPES data of Bi2212 parallel to the Γ-Y high symmetry direction (cut “a” of panel b) by Olson et al [124]. b) Location of cuts through the Brillouin zone of Bi2212, shown relative to the Fermi surface calculated by Massidda et al. [174].

Fig 4.22 Cuts through the Bi2212 Brillouin zone, by Olson et al. [124]. Locations are as indicated by cuts “b” and “c” in Fig. 4.21b.

Fig 4.23 A “crud” test by Wells et al. to determine whether any of the states had surface, or BiO character [147].

Fig 4.24 A selection of cuts taken at 100K on a Bi2212 sample by Dessau et al. [142]. Exact **k**-space locations of the spectra taken are shown in Fig. 4.25a.

Fig 4.25 a) A summary of the results of Dessau et al.’s study of Bi2212 [142]. Each circle indicates the location of a spectrum, with the size of the circle indicating the **k**-resolution. Filled circles correspond to Fermi surface crossings and striped circles to locations where the band energy is indistinguishable from E_F. b) The experimental Fermi surface obtained by reflecting the crossing points (dark circles) of a) around the high symmetry directions. A nesting vector **Q** near (π,π) is shown.

Fig 4.26 Experimental E vs. **k** relationship along various high symmetry directions of Bi2212, after Dessau et al.(points) [142]. The lines illustrate a simple scenario compatible with the data.

Fig. 4.27 The construction for producing both the "real" and "ghost" Fermi surfaces within Anderson's RVB theory [188].

Fig. 4.28 A random dot picture of the Fermi surface of Bi2212 using a strong weighting factor which favors colinearity of the spinon and holon, after Anderson [189]. The "real" Fermi surface in this case is the one which encloses the Γ point.

Fig 4.29 A cut a) along Γ-X and b) along Γ-$\overline{M}$ from a Bi2201 single crystal by King et al.[165]. The photon energy was 21.2 eV.

shaded region shows the general **k**-space location where Fermi surface crossings may exist.

Fig 4.45 The near-E_F feature in Y124 along the Γ-Y high symmetry direction, taken with a photon energy of 28 eV, after Gofron et al. [156].

Fig 4.46 The experimental E vs. **k** relationship for Y124 along the Γ-Y high symmetry direction, after Gofron et al. [156]

Fig 4.47 a) ARPES data near E_F from NCCO for x=0.15 (superconductor) and x=0.22 (over-doped metal), after King et al. [161]. b) ARPES data from NCCO for x=0.15 from Anderson et al. [162].

Fig 4.48 Experimental Fermi surface of NCCO compared with results from LDA calculations for (a) x=0.15 and (b) x=0.22, after King et al. [161].

Fig 4.49 Comparison of experimental and theoretical E vs. **k** relations for (a) x=0.15 and (b) x=0.22 NCCO samples, after King et al. [161].

Fig 4.50 E vs. **k** relationship (points) for (a) Bi2212 from Dessau et al. [142], (b) Bi2201 from King et al. [165] and (c) Y123 from Liu et al. [158] and Gofron et. al. [156] (d) Y124 from Gofron et al. [156] and (e) NdCeCuO from King et al. [161]. Dashed lines are a simple E vs. **k** relationship which are consistent with the Bi2212 data, after Dessau et al. [142].

Fig 4.51 Comparison of the experimental Fermi surfaces of Bi2212 from Dessau et al. [142], Bi2201 from King et al. [165], and NdCeCuO from King et al. [161], as compiled by King et al. [165]. Note that the nesting vector in Bi2212 is closer to the Bragg condition than in Bi2201.

Fig. 4.52 Angle resolved photoemission data from two different oxygen concentrations of Bi2212, taken at four distinct Brillouin zone locations, after Shen et al. [168]. The 12atm O_2 annealed spectra are semi-ridgidly shifted to lower binding energy because of the increase in hole concentration.

Fig 4.53 XPS valence band data from a series of $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ samples, after van Veenendaal et al. [229]. The full valence band is shown in (a), and a blowup of the near-E_F region is shown in (b).

Fig 4.54 A summary of a doping study of the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_{8+\delta}$ system, after van Veenendaal et al. [229]. The shifts needed to match the leading edges of the major core lines and the valence band are plotted.

Fig 4.55 Angle-resolved photoemission data from $YBa_2Cu_3O_x$ taken along the Γ-S direction for samples with an oxygen content of x=6.9, 6.7, 6.5, 6.4 and 6.35, after Liu et al. [153].

obtained by an inversion of the tunneling data using Eliashburg theory. (d) The phonon spectrum F(ω) as determined by neutron scattering. All compiled by Bardeen [277].

Fig 5.13 **k**-space locations where Olson et al. measured the magnitude of the gap in Bi2212 [150]. Fitting studies implied that all points led to a gap of magnitude approximately 18 meV.

Fig 5.14 Superconducting state spectra from Bi2212 taken at two different angles along Γ-$\overline{\mathrm{M}}$ and at three angles along Γ-X(Y), after Wells et al. [217].

Fig 5.15 Normal and superconducting state spectra from Bi2212 taken near the Fermi surface crossings (A) along Γ-$\overline{\mathrm{M}}$ and (B) along Γ-X(Y), after Shen et al. [218]. The effect of the gap is very clear at (A) and is very weak or nonexistent at (B).

Fig 5.16 (a) The Brillouin zone locations where the gap was measured by Shen et al. for three different Bi2212 samples [218]. The shaded area corresponds to **k**-space locations where the bands are very close to E_F. (b) Gap size vs. $0.5|\cos k_x a - \cos k_y a|$ for the three samples. The straight lines are predictions of the d_{x2-y2} order parameter.

Fig 5.17 An illustration of the expected **k**-dependence of the order parameter and gap magnitude for a d-wave superconductor and an s-wave superconductor with large gap anisotropy, plotted in one dimension for simplicity. The d-wave gap, which is proportional to the square of the order parameter, must go exactly to zero at specific **k**-space locations.

Fig 5.18 Data from Dessau et al. showing the normalized gap magnitude (maximum = 1) plotted vs. the d_{x2-y2} order parameter $0.5|\cos k_x a - \cos k_y a|$ for 14 different Bi2212 samples [288]. The first three samples are identical to those published by Shen et al. [218] and reproduced in Fig. 5.16. The vast majority of the samples show a very small gap along the Γ-X(Y) direction of less than 15% of the maximum gap.

Fig 5.19 Anisotropic s-wave gap Δ_k in eV as a functino of $k_x a$ and $k_y a$, after Chakravarty et al. [297].

Fig 5.20 Data from Kelley et al. showing low temperature spectra of Bi2212 along the Γ-X and Γ-Y directions for a variety of polarizations, as indicated in the figure [260].

Fig 5.21 Temperature dependent data from Tobin et al. searching for the existence of a superconducting gap in an untwinned single crystal of YBCO [139].

Fig 5.22 Temperature dependant measurements on a YBCO sample with a very small amount of weight in the -1 eV peak, after Schroeder et al. [160] The solid line is