Electronic structure of iron arsenic high temperature superconductors studied by angle resolved photoemission spectroscopy (ARPES)

Chang Liu
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Electronic structure of iron arsenic high temperature superconductors studied by angle resolved photoemission spectroscopy (ARPES)

by

Chang Liu

A dissertation submitted to the graduate faculty in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Condensed Matter Physics

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Iowa State University
Ames, Iowa
2011
DEDICATION

To my father Zhiwei Liu and my mother Wanqiong Li.
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CHAPTER 1. Introduction

The discovery of superconductivity marks one of the greatest scientific and technical breakthroughs experienced by mankind in the twentieth century. With the promise of absolute zero resistance, perfect diamagnetism and hence unlimited potential applications, superconductors with increasing transition temperatures ($T_c$) are expected to reform our world to a magnificent wonderland where the floating Hallelujah Mountains in the movie Avatar can in principle be brought to reality. The first step towards such future glory happened in 1986 when the copper oxide (cuprate) high temperature superconductors were discovered. Their highest $T_c$ is 135 K at ambient pressure [See Ref. (1) for bibliography arrangement; (2; 3; 4)], compared with less than 40 K for the “traditional” BCS-type superconductors. While the MgB$_2$ superconductor discovered in 2001 (5) attracted considerable attention, its transition temperature of 39 K is surpassed by the iron based superconductors discovered in 2008 by Prof. Hosono and collaborators (6), in which superconductivity is observed up to 56 K (7; 8). Scientists believe that a detail study on the physical properties of the iron based superconductors would shed light on the unknown mechanism of high temperature superconductivity, and provide a more complete recipe for production of higher $T_c$ materials. The entire solid state community focused immediately on this project, making it one of the most rapid-growing frontiers in modern physics, with thousands of research articles published in the last three years.

In terms of crystallographic properties, all families of the Fe-based compounds contain planelike Fe layers sandwiched between As or Se, forming a quasi two dimensional structure. Most undoped parent compounds of the Fe-based superconductors are well-defined semimetals showing no sign of superconductivity. They become superconducting at intermediate carrier doping levels or external pressure. A low temperature phase with long range antiferromag-
Netism is found in close vicinity to the superconducting region. The antiferromagnetic and superconducting order parameters are found competing with each other, although in some cases they are allowed to coexist. For different carrier dopants, the superconducting region extends to different doping levels. In selected systems, a universal scaling of this domelike region occurs only when the horizontal axis of the phase diagram changes to number of extra carriers (9; 10; 11). This behavior, along with other evidences, implies that their electronic structures are closely linked to the observed high temperature superconductivity.

To gain a comprehensive understanding of novel materials, the knowledge of their electronic structure is of essential importance, as it is the beginning point of understanding the low energy excitation spectra from which important transport, magnetic and superconducting properties are derived. In the case of some of the Fe-based superconductors, the Fermi sheets are holelike at the Brillouin zone center, and electronlike at the zone corners, forming typical Fermi surfaces with central hole pockets and corner electron pockets (10; 11). It is believed that superconductivity arises due to inter-orbital interactions between these two sets of Fermi pockets [See Ref. (11) and references therein]. Angle resolved photoemission spectroscopy (ARPES) is one of the leading experimental techniques to probe the electronic structure of single crystalline samples. Utilizing the well-known photoelectric effect, ARPES measures the intensity of the outgoing photoelectrons as a function of their momenta \( k \) and kinetic energies \( E_k \), with the assumption that the \( (k, E_k) \) values can be related to their initial states inside the crystal (12). With the capability to probe the band structure directly, the ARPES technique is proven to be extremely helpful in unveiling the mystery of high temperature superconductivity.

The main purpose of the present thesis is to present our ARPES results on the iron arsenic superconductors. As revealed by a series of ARPES measurements on both the \( \text{AEFe}_2\text{As}_2 \) and the \( \text{RFeAs(O,F)} \) families (parent compound and carrier-doped systems), the electronic structures of the pnictides are complicated, three dimensional, and closely linked to their superconducting behavior (13; 14; 15; 16; 17; 18; 19). Parent compounds of these materials exhibit the basic hole-electron pocket dual plus an apparent Fermi surface reconstruction caused by long range antiferromagnetism (13; 15). When carriers are introduced, the chemical potential shifts
in accordance with the Luttinger theorem and the rigid band shifting picture \(^{(13)}\). Importantly, both the appearance and disappearance of the superconducting dome at low and high doping levels have intimate relation with topological changes at the Fermi surfaces, resulting in a specific Fermi topology being favored by superconductivity \(^{(15, 16)}\). On the low doping side, superconductivity emerges in the phase diagram once the antiferromagnetic reconstruction disappears below the Fermi level, returning the Fermi surface to its paramagnetic-like appearance. On the high doping side, superconductivity disappears around a doping level at which the central hole pocket vanishes due to increasing electron concentration. Such phenomena are evidence for the governing role the electronic structure plays in their superconducting behavior.

The present thesis is arranged in the following way. Chapter 2 discusses the basic textbook knowledge in condensed matter physics necessary for understanding the thesis. This includes the definition of the reciprocal space and reciprocal lattice, the concept of electronic structure and ways to calculate it, and a brief introduction of superconductivity along with important BCS theory predictions. Chapter 3 discusses the technique of ARPES, focusing on components of the state-of-the-art ARPES facilities. Chapter 4 reviews the physical and electronic properties of the iron pnictide superconductors. Summary of transport, magnetic and neutron scattering measurements is followed by typical phase diagrams summarizing the temperatures for various phase transitions. Chapter 5 presents our ARPES measurements on the \( AEF_{2}A_{2}S_{2} \) (122) systems. This chapter contains the central information of the present thesis, since systematic studies on the Fermi surface for both hole and electron doped 122 systems reveal an intimate link between their underlying Fermiology and high temperature superconductivity, as discussed above. Chapter 6 presents ARPES results on the \( RFeAs(O,F) \) (1111) systems. The most important finding of this chapter is that the measured electronic structure in those materials is dominated by surface reconstruction effects. Chapter 7 presents summary and concluding remarks.
CHAPTER 2. Background knowledge

This chapter introduces the background knowledge in condensed matter physics relevant to the main topic of the thesis. It begins by introducing reciprocal space and the concept of a Fermi surface, which derives naturally from Pauli’s exclusion principle and the finite number of total electrons in a given system. When the periodicity of an ideal crystal is added to the picture, the $k$-space is divided into Brillouin zones, whose electronic properties mirror one another. Electrons in an ideal crystal experience the periodicity of the crystal and corresponding periodic boundary conditions. As a result, the $k$-points become discrete, and electrons can not reside in every position of the $k$-space. The allowed $k$-space positions - eigenvalues of the Schrödinger equation - then form the electronic structure or “energy bands” of the specific crystal. Using angle resolved photoemission spectroscopy (ARPES) one can directly observe the electronic structure. The ARPES technique, however, is particularly sensitive to the crystal surface. For this reason, the chapter includes a brief introduction on surface physics, describing how such surface effects can change the observed band structure. In Section 2.6 we introduce the basic knowledge of magnetic ordering and magnetic structure in a crystal, since the superconducting state in the iron pnictides, like in the cuprates, is in close vicinity to an antiferromagnetic order. Finally, this chapter concludes with an introduction to superconductivity, discussing the theoretical and experimental aspects of conventional and high temperature superconductors.

The main reference books for this chapter are Refs. (12; 20; 21; 22).
2.1 Free electron Fermi gas

The model of free electron Fermi gas describes an ensemble of non-interacting electrons confined in a $d$-dimensional spatial region with length scale $L^d$. Each electron in this ensemble satisfies the Schrödinger equation

$$\frac{\hbar^2}{2m} \nabla^2 \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r}).$$  \hspace{1cm} (2.1)

With the periodic boundary condition $\psi(x_1 + L, x_2, \ldots) = \psi(x_1, x_2, \ldots)$, the solution to Eqn. 2.1 is the standing wave

$$\psi_k(\mathbf{r}) = \exp(i \mathbf{k} \cdot \mathbf{r}),$$ \hspace{1cm} (2.2)

where the wavevector $\mathbf{k}$ takes discrete values

$$\mathbf{k} = \left(\frac{2n_1 \pi}{L}, \frac{2n_2 \pi}{L}, \ldots\right); \quad n_1, n_2, \ldots \in \mathbb{Z}.$$ \hspace{1cm} (2.3)

This form of solution hints at the introduction of a space with length units “reciprocal” to the real space: $x \to k_x, y \to k_y, \ldots$. Such a reciprocal space ($k$-space) can be viewed as the Fourier transformation of the real space. In the $k$-space, each electron occupies a distinct lattice point (disregarding spin), since Pauli’s exclusion principle states that no Fermions with completely the same quantum numbers can coexist. Now imagine the free electron gas containing a single electron. In the ground state, this electron occupies the origin of the $k$-space: $k_1 = k_2 = \ldots = 0$. As the number of electron increases, electrons are forced to occupy the $k$-points farther and farther away from the origin, thus they have higher and higher kinetic energies. Since the total number of electrons is finite, there must exist a highest energy for the occupied states, corresponding to the largest radius in the $k$-space from the origin. This highest energy is called the Fermi energy (or Fermi level) $E_F$ with the corresponding Fermi wavevector $k_F$. The $d$-dimensional spherical surface with radius $k_F$ is the Fermi surface of the free electron gas. The number of possible electron states at a given infinitesimal energy range is called the density of states, defined as $D(\epsilon) = dN/d\epsilon$. If non-zero temperature $T$ drives the electron gas away from the ground state, the electrons within $\sim k_B T$ of the Fermi level will increase some of their kinetic degrees of freedom, smoothing out the sharp Fermi cut-off of electron occupancy (Figure
2.1). In this case, the energy that is occupied by one half the number of electrons compared to the ground state value is called the chemical potential $\mu$. This definition is incorporated in the Fermi-Dirac distribution function for fermions

$$f(\varepsilon) = \frac{1}{\exp[(\varepsilon - \mu) / k_B T] + 1}. \quad (2.4)$$

In the ARPES field, the concept of Fermi energy and the chemical potential is often used interchangeably, because the energy scale of the temperature used in the experiment (below or close to room temperature) is usually much less than the Fermi energy.

### 2.2 Reciprocal lattice and Brillouin zone

Now we add an infinite array of atoms to the real space, resembling the crystal. From now on we focus on the three dimensional case. In the real space, the locations of atoms are defined by three unit vectors $\mathbf{a}_1, \mathbf{a}_2$ and $\mathbf{a}_3$ and a set of basis. Correspondingly, the reciprocal space is also quantized, with unit vectors

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{\mathbf{a}_i \cdot (\mathbf{a}_j \times \mathbf{a}_k)}; \quad i, j, k = 1, 2, 3. \quad (2.5)$$

The primitive vectors $\mathbf{b}_i$ thereby construct the *reciprocal lattice*, a Fourier transformation of the real lattice.

It is crucially important to study the response of a crystal to an incident radiation in both the real and reciprocal space. In the real space, constructive interference occurs if the adjacent
plane distance $d$ and the incoming wavelength $\lambda$ satisfies the Bragg law

$$2d \sin \theta = n\lambda; \quad n \in N.$$  \hspace{1cm} (2.6)

The interference pattern repeats for consecutive $n$. The $k$-space counterpart to Eqn. 2.6 can be written as

$$2k \cdot G = G^2,$$  \hspace{1cm} (2.7)

where $G = \nu_1 b_1 + \nu_2 b_2 + \nu_3 b_3$ ($\nu_i \in Z$) is a reciprocal lattice vector. This form of the Bragg diffraction condition leads to a central concept of condensed matter physics: the Brillouin zone.

If we divide Eqn. 2.7 by 4 we have $k \cdot G/2 = (G/2)^2$, which describes $k$-space planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from the origin. The smallest volume entirely enclosed by these planes defines the first Brillouin zone. Like the same diffraction pattern between consecutive $n$’s in Eqn. 2.6, other Brillouin zones are replicates to the first one. The first Brillouin zone thus contains all electronic information about the crystal.

Below we try to give an intuitive, non-scientific description of what a Brillouin zone really is. Consider a “fan” with only one propeller rotating against its central axis. A nearby camera takes one picture of the fan per second. Our job here is to judge the angular velocity of the fan propeller only from the camera pictures (with time information). It is not difficult to realize that we cannot distinguish the velocity difference between, say, zero and one round per second (rps). In other words, we can conveniently define a velocity range such that any velocities outside that range can be mapped uniquely to a velocity within that range; these two velocities appear to be exactly the same in the camera pictures. For example, the velocity of 3.4 rps looks the same as 0.4 rps in the camera pictures. With the present setup, both the ranges of $-0.5 \leq f < 0.5$ rps and $0.5 \leq f < 1.5$ rps satisfy the above requirement. We call such a velocity range a “Brillouin zone” of the fan. Specially, the first Brillouin zone is the Brillouin zone that contains zero velocity. It is important to point out two necessary conditions for the existence of a Brillouin zone: (1) the repeated rotation of the fan or the satisfaction of the periodic boundary condition, and (2) the discrete picture taking of the camera or the discrete nature of the crystal lattice.
2.3 Band theory and Fermi surface of crystals

When electrons reside within a periodic array of atoms, they are arranged in energy bands separated by regions in energy within which no wavelike electron orbitals exist (energy gaps). The simplest model capturing the bandlike nature of crystal electrons is the one dimensional Kronig-Penney model in which electrons experience a periodic potential energy,

\[- \frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} + U(x) \psi = \varepsilon \psi, \quad (2.8)\]

where

\[U(x) = \begin{cases} 
0, & nb \leq x < nb + a \\
U_0, & nb + a \leq x < (n + 1)b 
\end{cases} \quad (2.9)\]

with \(a < b\) and \(n \in \mathbb{Z}\). We seek for a solution with the Bloch-like form

\[\psi = \begin{cases} 
A e^{iKx} + B e^{-iKx}, & nb \leq x < nb + a \\
C e^{Qx} + D e^{-Qx}, & nb + a \leq x < (n + 1)b 
\end{cases}. \quad (2.10)\]

Taking the limit of \(a \to b\) while maintaining \(Q^2 ba/2 = P < \infty\), we obtain a condition for Eqn. 2.8 to have a solution:

\[(P/Ka) \sin Ka + \cos Ka = \cos ka. \quad (2.11)\]

It is important to notice that Eqn. 2.11 is not satisfied by all \(k\)'s. If \(|(P/Ka) \sin Ka + \cos Ka| > 1\), no Bloch-like solutions can exist, and band gaps are formed. This idea can be generalized (although non-trivially) to three dimensional systems where energy bands form four dimensional surfaces \(C(k_x, k_y, k_z, E)\). In Section 2.2 we showed that it suffices to discuss only the electronic structure within the first Brillouin zone. Figure 2.2 shows the standard way of visualizing such a four dimensional band structure. We note that the vertical axis of Figure 2.2 is energy \(E\), while the horizontal axis represents a spatial broken line in \(k\)-space that runs through all high symmetry points of the corresponding Brillouin zone, reducing the three dimensional \(k\)-space to one dimension. Such a band structure map contains a lot of physical information. For example, the metallic nature of copper can be realized by the existence of energy band(s) that cross the Fermi level.
Figure 2.2 Calculated band structure of copper. The horizontal axis represents a line that runs through all high symmetry points of the Brillouin zone. The vertical axis is energy. From Ref. (23).

Figure 2.3 Fermi surface of copper within the first Brillouin zone - intersection of the four dimensional band structure at energy $E = E_F$. From Ref. (24).

Figure 2.3 shows the Fermi surface of copper within the first Brillouin zone. The Brillouin zone of copper, a face-center-cubic (fcc) crystal, has a highly non-trivial shape. Within this zone, the Fermi surface closer to the zone center (often denoted as the $\Gamma$ point) maintains a spherical shape, depicting the similarity in electronic structure between metal and the free electron gas. The zone boundary distorts the simple sphere, creating the “linking bones” between different zones. One of the basic applications of ARPES is to map the three dimensional Fermi surface as well as the entire four dimensional electronic structure of a given compound. The experimental procedure is discussed in Section 3.7.

2.4 Methods for calculating band structure

Though the Kronig-Penney model describes the principle and origin of energy bands, it is of little use for calculating the band structure of real three dimensional crystals in which each atom contains multiple electron orbitals. A relatively simple method for calculating bands in a solid with nearly-isolated atoms is the tight-binding model. By definition, the tight-binding approximation deals only with the case in which the distance between nearest atoms is short.
enough to require corrections to the picture of isolated atoms, but not so short as to render
the atomic description completely irrelevant (Figure 2.4). To begin this approach, we write the
crystal Schrödinger equation as [derivation in this section taken from Ref. (21)]

$$
\mathcal{H}\psi(r) = (\mathcal{H}_{\text{at}} + \Delta U(r)) \psi(r) = \mathcal{E}(k)\psi(r),
$$

(2.12)

where $\mathcal{H}_{\text{at}}$ represent the Hamiltonian for an isolated atom, satisfying $\mathcal{H}_{\text{at}}\psi_n = E_n\psi_n$ where $\psi_n$ is the $n^{\text{th}}$ atomic bound level with eigenvalue $E_n$; $\Delta U(r)$ contains all corrections to the atomic potential; the crystal wave function satisfies the periodic boundary condition

$$
\psi(r + R) = e^{ikR}\psi(r).
$$

(2.13)

Now if we assume that the eigenfunction components of the crystal wave function are not very
different from that of the atomic ones, we can expand $\psi(r)$ as

$$
\psi(r) = \sum_R e^{ikR}\phi(r - R),
$$

(2.14)

respecting

$$
\phi(r) = \sum_R b_n\psi_n(r)
$$

(2.15)

with limited number of sufficiently large $b$’s. At this point, we arrived the eigenvalue equation
for the tight binding model by multiplying Eqn. 2.12 with $\psi^*_m(r)$ and integrate over all $r$,

$$
(\mathcal{E}(k) - E_m) b_m = - (\mathcal{E}(k) - E_m) \sum_n \left( \sum_{R \neq 0} \int \psi^*_m(r) \psi_n(r - R) e^{ikR} dr \right) b_n
+ \sum_n \left( \int \psi^*_m(r) \Delta U(r) \psi_n(r) dr \right) b_n
+ \sum_n \left( \sum_{R \neq 0} \int \psi^*_m(r) \Delta U(r) \psi_n(r - R) e^{ikR} dr \right) b_n
$$

(2.16)
As an example we solve Eqn. 2.16 for a single s-atomic level. The solution for the band structure $\mathcal{E}(\mathbf{k})$ is

$$
\mathcal{E}(\mathbf{k}) = E_s - \beta - \sum_{n.n.} \gamma(\mathbf{R}) \cos \mathbf{k} \cdot \mathbf{R}
$$

(2.17)

where

$$
\beta = - \int \mathrm{d}\mathbf{r} \Delta U(\mathbf{r}) |\phi(\mathbf{r})|^2
$$

$$
\gamma(\mathbf{R}) = \int \mathrm{d}\mathbf{r} \phi^*(\mathbf{r}) \Delta U(\mathbf{r}) \phi(\mathbf{r} - \mathbf{R}).
$$

(2.18)

From Eqn. 2.17 we notice that the tight binding bands always disperse in a trigonometric fashion. This process can be easily applied to other atomic levels or even mixing between different atomic levels. In most cases, however, the tight binding approximation is suitable only for the representation of bands arising from the ion core levels, while the free electron approximation cannot be directly applied to any real solid.

Besides the fulfillment of the Schrödinger equation 2.12 and the periodic boundary condition 2.13, any serious attempt to calculate the band structure should endorse the continuousness of the first space derivative of the wave function $\psi$ at the boundaries of the Brillouin zone, i.e.,

$$
\hat{\mathbf{n}}(\mathbf{r} + \mathbf{R}) \cdot \nabla \psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \hat{\mathbf{n}}(\mathbf{r}) \cdot \nabla \psi(\mathbf{r}),
$$

(2.19)

where $\hat{\mathbf{n}}$ points to the outward direction of the Brillouin zone boundaries, and $\mathbf{r}$ locates at the zone boundary. This condition is not emphasized in the tight binding process since both $\psi$ and $\nabla \psi$ is assumed to be small at the zone boundaries. A common beginning point for solving Eqn. 2.12 with boundary conditions 2.13 and 2.19 is the assumption of the muffin-tin potential, defined as

$$
\Delta U(\mathbf{r}) = \begin{cases} 
V(|\mathbf{r} - \mathbf{R}|), & |\mathbf{r} - \mathbf{R}| < R_{\text{MT}}; \\
0, & |\mathbf{r} - \mathbf{R}| > R_{\text{MT}},
\end{cases}
$$

(2.20)

where $V(r)$ is the spherical potential of an isolated ion, $R_{\text{MT}}$ is the muffin-tin radius at which $V(R_{\text{MT}}) = 0$. The shape of such a potential looks like an array of upside-down muffin tins, hence the name. Based on the muffin-tin potential we discuss below the augmented plane-wave method for calculating band structure.

The augmented plane-wave (APW) method begins with the assumption that the correct solution of the crystal Schrödinger equation 2.12 takes the form of a superposition of augmented
plane-waves $\phi_{k,E}(r)$:

$$\psi_k(r) = \sum_K c_K \phi_{k+K,E}(r).$$  \hspace{1cm} (2.21)

Each of the $\phi_{k,E}(r)$’s satisfy the atomic Schrödinger equation in the atomic region ($|r - R| < R_M$), while takes the form of a plane wave $\phi_{k,E}(r) = e^{ik \cdot r}$ at the interstitial region ($|r - R| > R_M$). In the boundaries between these two regions, $\phi_{k,E}(r)$ is continuous, while $\nabla \phi_{k,E}(r)$ does not have to be continuous. For this reason we exploit the functional principle to obtain the convergent bands $E(k)$ instead of solving the Schrödinger equations directly. Define the energy functional

$$E[\psi] = \int \left( \frac{\hbar^2}{2m} |\nabla \psi(r)|^2 + \Delta U(r) |\psi(r)|^2 \right) dr / \int |\psi(r)|^2 dr,$$

it can consequently be shown that the band locations $E(k)$ are stationary points for this functional with respect to $\psi(r)$. Thus the coefficients $c_K$ can be obtained via numerically solving a set of homogeneous equations $\partial E/\partial c_K = 0$.

2.5 Effect of crystal surface

ARPES is an experimental technique sensitive to the sample surface, because of the small escape depth of the photoelectrons in a solid (See Section 3.1). Electronic states of the crystal surface are in principle different than the ones in the bulk since the atomic arrangement of the surface is affected by the vacuum. For example, the shrinking of the interlayer distance between the first and the second atomic layer with respect to bulk layers is a common phenomenon. Surface chemical bonding is also expected to differ from the bulk.

As a first example of the surface electronic structure, a work function $\phi$ - potential energy difference of an electron between the vacuum level and the Fermi level - is ubiquitous on any surface. Typical values of the work function range from 2 to 5 eV. The famous Einstein equation of photoelectric effect states that the work function is equal to the threshold energy for photoelectric emission at zero temperature,

$$h\nu = \phi + E_{k_{\text{max}}}. \hspace{1cm} (2.23)$$
From this we define the binding energy of the outgoing electron in a photoemission process to be the incident photon energy subtracted by the work function and the kinetic energy of the electron,

$$|E_b| = h\nu - \phi - E_k.$$  \hspace{1cm} (2.24)

Apparently electrons with Fermi energy has zero binding energy. This definition is widely used in the field of photoemission spectroscopy (Section 3.1).

The existence of a semi-infinite vacuum region will introduce additional states that occur in the conduction or valence bands, or even in band gaps. These are called the surface states since they are localized at the surface atomic layers. As one of the most modern examples, the fascinating physics of “topological insulators” occurs solely at the sample surface (25; 26). Below we briefly discuss the experimental results elucidating these surface states without going into theoretical details.

A typical calculation result of a surface state is shown in Fig. 2.5. In this figure we see three extra bands in the Cu(111) surface apart from the bulk continuum. Apparently, one prerequisite for the confirmation of such a surface state is the lack of band dispersion along the direction perpendicular to the surface (See also Section 3.7), because the sample surface...
surface is always two dimensional. On the other hand, the lack of perpendicular dispersion is not a sufficient condition for the surface state, because several important systems exist whose *bulk* electronic structure is intrinsically two dimensional. The cuprate high temperature superconductors are good examples of this; the iron pnictide superconductors also have close relation to a two dimensional system. The ARPES technique alone cannot easily distinguish between bulk and surface two dimensionality.

There are a number of theoretical methods to calculate a surface state. For example, one may first construct the bulk crystal structure and add by hand an increased distance between two adjacent layers, resulting in a “crystal + vacuum” structure as the new unit cell for calculation. For a more accurate description of the surface, customization of the lattice constant for the first layer of atoms is usually performed such that the atomic force (including surface bonds) between atoms is minimized. Using the above method we calculated the surface electronic structure for iron arsenic superconducting parent compound NdFeAsO (Section 6.2) with remarkable similarity between calculation and ARPES data.

### 2.6 Magnetic order

This section gives a brief introduction on the definition and occurrence of basic magnetic orders. First we define the *low field magnetic susceptibility*

\[
\chi = \frac{M}{B}igg|_{B=0}
\]  

(2.25)

where \(M\) is the magnetization (magnetic moment per unit volume), and \(B\) is the macroscopic magnetic field intensity. Along with this we define a material with \(\chi > 0\) to be *paramagnetic*, and a material with \(\chi < 0\) to be *diamagnetic*.

Examples of long range magnetic order are seen in Fig. 2.6. *Ferromagnetism* describes a substance in which spontaneous magnetic moments arrange parallel to each other, whereas *antiferromagnetism* describes a substance in which these moments arrange in an antiparallel fashion. The temperature below which magnetic order takes place is usually called the Curie temperature \(T_C\) in the ferromagnetic case (not to be confused with the critical temperature of
superconducting transitions, $T_c$), and the Néel temperature $T_N$ in the antiferromagnetic case. Above the transition temperatures, all magnetic substance show Curie-Weiss-like behavior, namely,

$$\chi = \begin{cases} 
\frac{C}{T}, & \text{paramagnetic;} \\
\frac{C}{T - \theta}, & \text{ferromagnetic, } T > T_C; \\
\frac{C}{T + \theta}, & \text{antiferromagnetic, } T > T_N.
\end{cases} \quad (2.26)$$

where $C$ is the Curie constant and $\theta$ is some positive temperature.

The magnetic structure of a crystal can be determined experimentally by e.g. magnetic X-ray diffraction and neutron diffraction. In these experiments the incoming X-ray or the magnetic moment of the neutron interact with the magnetic moment of the electron. This allows the determination of the distribution, direction and order of the magnetic moments.

Electronic structure (observed by ARPES) can also be affected by the magnetic order. Antiferromagnetism and stripe-typed ferromagnetism create additional symmetry to the electronic structure by increasing the size of the unit cell (in the case of antiferromagnetism, for example, one new unit cell contains an atomic unit cell with “up” moment and another one with “down” moment). Consequently, the Brillouin zone size is shrunk by the corresponding ratio. One important implication for this is that the energy bands for the disordered state will “fold back” with respect to the new zone boundaries (e.g. antiferromagnetic zone boundary or AFZB). These new-formed bands will further hybridize to form a more complicated electronic structure. The iron pnictides serve as perfect examples for this effect (Section 5.2).
2.7 Superconductivity

2.7.1 Historic and experimental overview

This section gives a brief overview on the rich experimental and theoretical aspects of superconductivity - the main research subject of the present thesis. The phenomenon of superconductivity was discovered in 1911 by Kamerlingh Onnes, who observed that the resistivity of mercury suddenly drops to zero at 4.2 K. Instead of some finite residual resistivity, the resistivity of a superconductor below the critical temperature $T_c$ is a true zero. Besides this, a superconductor deep in its superconducting state is always incompatible with magnetic induction: $B = 0$. This is called the Meissner effect. Zero resistivity and Meissner effect (or perfect diamagnetism, $\chi = M/B = -1/4\pi$) define the superconducting state for low fields.

Onnes' discovery marked the beginning of an ongoing scientific search for superconductors with higher $T_c$ values, with the dream (for some) of finding room temperature superconductivity some day. Figure 2.7 summarizes the progress of $T_c$ as a function of time for the last 100 years. In this figure, the blue trend represents the rise of $T_c$ in “conventional” superconductors - materials that obeys the BCS predictions and exhibit s-wave superconductivity (see following paragraphs). The two upturn arrows mark the discoveries for two classes of high temperature (high-$T_c$) superconductors. The discovery of copper-oxide superconductors (the cuprates) happened in 1986 when Bednorz and Müller observed a $T_c$ of $\sim 30$ K in the layered Ba-La-Cu-O system (2). Within a few years the $T_c$ of cuprates rose to an astonishing 135 K under ambient pressure (3; 4), much higher than the liquid nitrogen temperature (77 K). The other class of high-$T_c$ superconductors, the iron-based superconductors (the pnictides), were discovered by Hosono and collaborators in 2008 (6). The current record of $T_c$ is around 55 K (7; 8). The present thesis focuses on the electronic structure of the iron pnictide superconductors.

One of the most important experimental characteristics of superconductors is the existence of a superconducting energy gap $\Delta(T)$ (20; 21; 22). Experimentally, this gap always occurs at the chemical potential, occupying the same energy range below and above $\mu$. The quantity $2\Delta(0)/k_BT_c$ usually lies between $\sim 2$-5 for different elemental superconductors, hinting at
a universal superconducting mechanism among them. Furthermore, the discovery of the isotope effect (the relation between $T_c$ and the atomic mass) helped identify the superconducting mechanism to be phonon (lattice vibration) mediated.

### 2.7.2 Results of BCS theory

Based on the above experimental evidences, a milestone paper by Bardeen, Cooper and Schrieffer in 1957 described the theory for conventional superconductivity (BCS theory). The BCS theory begins with assuming a electronic ground state Hamiltonian in which electrons have a small attractive interaction [derivation in this section taken from Ref. (22)]:

$$
\mathcal{H}' = \mathcal{H}_0 + \sum_{k,s,k',s',q} W_{k k' q} c_{k+q,s}^\dagger c_{k-q,s} c_{k,s'}^\dagger c_{k',s'},
$$

(2.27)

Here $\mathcal{H}_0$ is the Hamiltonian of the noninteracting system of electrons and phonons, and $W_{k k' q}$ is a matrix element of the form

$$
W_{k k' q} = \frac{|M_q|^2 \hbar \omega_q}{(\varepsilon_k - \varepsilon_{k-q})^2 - (\hbar \omega_q)^2}.
$$

(2.28)

In light of the Bogoliubov theory that applies to liquid $^4$He, BCS made a brilliant guess that in the superconducting problem the scattering unit was a pair of electrons with equal but
opposite momenta. These are called the Cooper pairs. In this way the Hamiltonian 2.27 is reduced to

$$\mathcal{H}_{\text{BCS}} = \sum_k \mathcal{E}_k \left( c_k^\dagger c_k + c_{-k}^\dagger c_{-k} \right) - \sum_{k,k'} V_{kk'} c_{k'}^\dagger c_{-k'}^\dagger c_{k} c_{-k},$$

where

$$V_{kk'} = -2W_{-k,k',-k} - U_{kk'}$$

with $U_{kk'}$ a screened Coulomb repulsion term.

The BCS Hamiltonian 2.29 can be solved analytically by introducing a set of quasiparticle operators $\gamma, \gamma^\dagger$ via the Bogoliubov transformation

$$c_k = u_k \gamma_k + v_k \gamma_{-k}^\dagger, \quad c_{-k} = u_k \gamma_{-k} - v_k \gamma_{k}^\dagger,$$

with the requirement that the occupation number of these quasiparticles $m_k = \gamma_k^\dagger \gamma_k, m_{-k} = \gamma_{-k}^\dagger \gamma_{-k}$ being zero at the ground state. Instead of presenting the rather complicated solving process, we list here the central results of the BCS theory. First, the superconducting gap $\Delta_k$ is found to be

$$\Delta_k \equiv \sum_{k'} V_{kk'} u_k u_{k'} v_{k'}, \quad \Delta = \frac{1}{2} V D(\mu) \int_{-\hbar \omega_D}^{\hbar \omega_D} \frac{\Delta}{(\hat{\mathcal{E}}^2 + \Delta^2)^{1/2}} d\hat{\mathcal{E}},$$

where $D(\mu)$ is the energy density of states at the chemical potential, $\omega_D$ is the Debye frequency, $\hat{\mathcal{E}}_k = \mathcal{E}_k - \mu$, and we assume $V_{kk'} = V$ if $|\hat{\mathcal{E}}| < \omega_D$, $V_{kk'} = 0$ otherwise. From this we further obtain

$$\Delta = \frac{\hbar \omega_D}{\sinh \frac{1}{V D(\mu)}} \simeq 2\hbar \omega D e^{-1/V D(\mu)}.$$  

The second semi-equal mark in Eqn. 2.33 is valid only in weak coupling superconductors where the rapid damping of the quasiparticle states is negligible.

Next we examine how the presence of such a gap affects the energy dispersion of a band. Rewriting the BCS Hamiltonian 2.29 as

$$\mathcal{H}_{\text{BCS}} = \mathcal{E}_S + \sum_k \left( \hat{\mathcal{E}}_k^2 + \Delta^2 \right)^{1/2} (m_k + m_{-k}) + \cdots$$

with $\mathcal{E}_S$ the ground state energy of the superconducting system, we find the energy for the elementary excitations to be $E_k = \left( \hat{\mathcal{E}}_k^2 + \Delta^2 \right)^{1/2}$. Now assuming a linear band crossing the
Figure 2.8  Energy dispersion of an electron-hole pair in a normal metal, compared with that of the elementary excitation in a superconductor. Note the presence of superconducting gap and the “back-bending” of the linear band. From Ref. (22).

chemical potential with density of states $D(\mathcal{E}) = \text{const.}$ (Left of Figure 2.8). In the superconducting state, this band splits equally on both sides of $\mu$, forming an energy gap of magnitude $2\Delta$. Near this gap the two half-bands bend back from the normal state position (Right of Figure 2.8). The bending-back effect is present for both weak and strong coupling materials, and is a unique feature for the superconducting gap. The corresponding quasiparticle density of states near the gap is

$$D(E) = 2D(\mathcal{E}) \frac{d\hat{\mathcal{E}}}{d\hat{E}} \approx \begin{cases} 
2D(\mu) \frac{|E|}{(E^2 - \Delta^2)^{1/2}}, & \text{if } |E| > \Delta; \\
0, & \text{if } |E| < \Delta. 
\end{cases} \quad (2.35)$$

Note that $D(E) \to \infty$ as $|E| \to \Delta^+$, meaning the quasiparticles form some kind of condensate. This can be understood if one realizes the fact that the Cooper pairs are intrinsically bosons instead of fermions like a single electron. At low temperatures, bosons tend to condense at the ground state energy. The superconducting state is nothing but a macroscopic Bose-Einstein condensate formed by the bosonic Cooper pairs.

While the above discussion applies only to zero temperature, we now examine a superconducting system at finite temperature. Our propose is to find an expression of the transition temperature $T_c$. After considerable derivation effort one would find that Eqn. 2.32 changes to

$$\Delta(T) = \frac{1}{2} V D(\mu) \int_{-h\omega_D}^{h\omega_D} \Delta(T) \tanh \left[ \frac{(\hat{\mathcal{E}}^2 + \Delta(T)^2)^{1/2}}{2k_B T} \right] \frac{d\hat{\mathcal{E}}}{\left( \hat{\mathcal{E}}^2 + \Delta(T)^2 \right)^{1/2}}, \quad (2.36)$$
the only difference being a temperature-dependent term: \( \tanh \left[ \left( \hat{\mathcal{E}}^2 + \Delta^2 \right)^{1/2} / 2k_B T \right] \). Now \( T_c \) is evaluated by putting \( \Delta(T_c) = 0 \),

\[
VD(\mu) \int_0^{\hbar\omega_D/2k_B T_c} \frac{\tanh x}{x} dx = 1. 
\tag{2.37}
\]

For weak-coupling superconductors the upper limit of the integral can be extended to infinity, yielding

\[
k_B T_c = 1.14 \hbar \omega_D e^{-1/VD(\mu)} 
\tag{2.38}
\]

or

\[
\frac{2\Delta(0)}{k_B T_c} = 3.53. 
\tag{2.39}
\]

Eqn. 2.39 gives a classic measure for the coupling strength of a superconductor. Elemental superconductors usually have a value of 2-5, indicating relatively weak coupling. In cuprate high-\( T_c \) superconductors, this value can be as large as \( \sim 10 \). There have been evidences that the coupling strength of the iron pnictide superconductors lies between the weak and strong limit.

ARPES is one of a few experimental techniques that can directly measure the magnitude of the superconducting gap. In Chapter 3 we will see that the presence of the superconducting gap results in a peak structure in the measured energy distribution curves. The value of the gap is often determined by the energy difference between the peak and the chemical potential.

### 2.7.3 High temperature and non-s-wave superconductors

The high temperature superconductors triggered explosive scientific efforts not only because of their incredible transition temperatures, but also the fact that they contain a lot of new physics that goes beyond the phonon-mediated BCS theory. For example, the high-\( T_c \) cuprates are quasi two dimensional electronic systems, since they contain planar CuO\(_2\) layers [note that not all low dimensional electronic systems have high-\( T_c \), see e.g. NbSe\(_2\), Ref. (27)]. One aspect of low effective dimensionality is that the screening of the Coulomb interaction is reduced, which is argued to be helpful for higher transition temperatures. Another important experimental observation in high-\( T_c \) materials is the non-s-wave superconducting gap. In Section 2.7.2 we
see that the gap $\Delta(T)$ for elemental superconductors is independent of momentum $k$. This is called the s-wave superconductivity. In the high-$T_c$ cuprates, the gap is anisotropic in the $k$-space: in the $(1,0)$ or $(\pi,0)$ direction of the two dimensional electronic structure, the gap gets the largest value; in the $(1,1)$ or $(\pi,\pi)$ direction, the gap vanishes, i.e., having a node. We thus called the cuprates “d-wave” superconductors, respecting the four-propeller shape of a $d$-wave atomic orbital. Another interesting superconductor, MgB$_2$, has a two gap s-wave symmetry, because the two sets of Fermi contours there show different gap values. These three examples are depicted in Figure 2.9. The momentum dependence of superconducting gap in iron pnictides will be discussed later in greater detail.

Momentum dependence of the superconducting gap is now of central interest for any newly discovered superconductors. So far, ARPES is the only experimental technique that can directly probe this property. Thanks to its unique ability of scanning the $k$-space, one can obtain energy distribution curves at in principle every $k$-space location. Spectral peak positions thus give us the absolute values of the gap at different $k$-points.

In this section we see that superconductivity is a phenomenon that can appear in a number of forms. A complete explanation requires a correspondingly wide range of theoretical and experimental approaches.
CHAPTER 3. Angle resolved photoemission spectroscopy (ARPES)

This chapter presents a comprehensive description of the angle resolved photoemission spectroscopy (ARPES) technique. We begin by introducing basic concepts of photoemission spectroscopy (PES): the historical development, and the typical shape of the PES spectrum. This is followed by the discussion of theoretical concepts of the ARPES technique, focusing on the spectral function as a theoretical equivalence of the observed spectrum. Next we discuss in detail the ARPES equipment. A typical ARPES machine contains of three major parts: the photon source, the ultra-high vacuum chamber, and the electron analyzer. Photons created by either a gas discharge lamp, a laser, or a synchrotron source hit a sample prepared with clean surface inside the vacuum chamber. The properly grounded sample then emits photoelectrons. These electrons escape the sample surface at different energies and directions according to the underlying band structure. Some of them enter the hemispheric electron analyzer; their trajectories are bent inside the analyzer due to a set of electrostatic lenses and a hemispherical capacitor. Electrons with different momenta and energies will be deflected differently, resulting in a two dimensional intensity map with $E$ and $k$ along the two axes. In the last part of this chapter we discuss some basic techniques of data processing and analysis: how we perform a typical ARPES experiment, what a certain shape of bands usually means, etc. With this basic knowledge we will be well equipped for the APRES studies of high temperature superconductors.

The main references of this chapter are Refs. (12) and (29).
3.1 Photoemission spectroscopy

First detected by Hertz in 1887 (30; 31), the term *photoemission* describes a process in which electrons are emitted from matter (metals and non-metallic solids, liquids or gases) as a consequence of their absorption of energy from electromagnetic radiation. It was observed that the maximum kinetic energy of the photoelectrons is proportional to the frequency of the incoming light instead of the intensity, and that there is a material-dependent threshold light frequency below which no photoelectron can be emitted. These early puzzles were resolved by the famous 1905 formula of Einstein, invoking the quantum nature of light:

$$ h\nu = \phi + E_{k_{\text{max}}}, $$

(3.1)

where $h\nu$ is the energy of the incoming photon, $\phi$ is the work function, and $E_{k_{\text{max}}}$ is the maximum kinetic energy of the photoelectrons. From this we can obtain the relation between the momentum - kinetic energy ($p, E_k$) of the photoelectron and the energy of the incoming photon,

$$ E_k = h\nu - \phi - |E_b|, $$

$$ |p| = \sqrt{2mE_k}. $$

(3.2)

Figures 3.1 and 3.2 show the basic concepts of the photoemission process. As in Figure 3.1, a beam of monochromatic radiation impinges on the sample, and photoelectrons are emitted with different momentum $p$ and energy $E_k$, obeying Eqns. 3.2. The blue hemisphere denotes the possible energies and directions of all outgoing electrons. No electron with kinetic energy larger then $E_{k_{\text{max}}}$ can be emitted. Figure 3.2 shows schematically how the energy level diagram of the sample and the energy distribution of the photoelectrons relate to each other. A typical solid sample (usually metal) has core levels and valence bands. The Fermi energy $E_F$ is separated by $\phi$ from the vacuum level $E_{\text{vac}}$. When an electron with binding energy $E_b$ in the sample is excited by an incoming photon $h\nu$, it can be detected with a kinetic energy $E_k = h\nu - \phi - |E_b|$ in the vacuum. As a result, the detected energy distribution of photoelectron gives an approximate replica of the electron energy distribution of the solid, the difference being that all bands are “smeared out” according to the spectral function. By definition, photoemission cannot detect
energy levels that are not occupied by electrons in the solid. The resulting spectrum thus experiences an intensity cut-off at the chemical potential. Unoccupied levels can usually be detected by inverse photoemission spectroscopy.

Figure 3.3 shows a photoemission spectrum of single crystal Pb_{1-x}TlxTe (x = 1.39 at.%) for 0 ≤ E_b ≤ 45 eV. Note that this spectrum is angle integrated, i.e., does not contain any angle resolved information. At the ARPES facility, this is usually done by utilizing the so-called “transmission mode” of the electron analyzer (Section 3.5). In Figure 3.3, the Pb 5d and Te 4d core levels are the best visible. Their binding energies are 40.8 eV (Te 4d_{5/2}), 39.3 eV (Te 4d_{3/2}), 20.9 eV (Pb 5d_{3/2}) and 18.2 eV (Pb 5d_{5/2}). By enlarging the region marked by a purple box we can also recognize the 5d levels of thallium at binding energies ~ 15 and ~ 12.5 eV (fine energy splitting possibly due to a splitting of Tl valences). At still lower binding energies
Figure 3.3  Photoemission spectrum of single crystal Pb\textsubscript{1-x}Tl\textsubscript{x}Te (x = 1.39 at.%) for 0 ≤ E\textsubscript{b} ≤ 45 eV. The incident photon energy is h\nu = 70 eV. Data is taken at the PGM beamline of the Synchrotron Radiation Center, Wisconsin, with a Scienta SES2002 electron analyzer.

(E\textsubscript{b} < 5 eV) there is a slight increase of intensity (marked by a purple ellipse in Figure 3.3). This is due to the existence of delocalized valence electrons from which energy bands are formed. At high binding energies (E\textsubscript{b} approaching h\nu) the background intensity shows an exponential upturn. This reflects the existence of secondary electrons created by photoelectrons that are inelastically scattered during the emission process - an effect that is directly related to the finite escape depth.

In the following paragraph we explain the reason why ARPES is a surface technique, while X-ray photoemission spectroscopy (XPS) detects bulk electronic properties. The reason is very simple. As is shown in Figure 3.4, in the kinetic energy region of interest, between about 10 ∼ 2000 eV, the electron escape depth is about a few Å, which means the electrons that are able to escape to the vacuum come from no more than several atomic layers deep in the crystal. Especially for the region of ARPES (h\nu = 10 ∼ 200 eV), the escape depth is less than 10 Å, i.e., less than three atomic layers for most crystals. This also explains why atomically clean surfaces and ultra-high vacuum conditions are required in the ARPES experiments - if
the surface is covered by an oxidation layer, very few electrons from the real sample can escape. In the region of XPS ($h\nu > 1000$ eV), electrons can escape from as deep as 50 Å beneath the surface. Usually such electrons provide information about the bulk state of the sample. It is also noticeable that a large escape depth is available in the extra-low energy side. Since in ARPES the incident photon energy is inversely proportional to the momentum resolution (See following paragraphs), low energy light source has an unique advantage compared with the usual ones. This is the basis for the development of xenon lamp ($h\nu \sim 8$ eV) and laser-based ARPES ($h\nu \sim 6 - 10$ eV).

With the above discussion, one might wonder why ARPES is still an important technique for the study of bulk electronic structure, such as the superconducting gap. The success of ARPES is based on a remarkable similarity between the measured band structure and the theoretically predicted ones (and often results from other bulk sensitive measurements). This indicates that, in a lot of samples of interest, surface reconstruction and/or relaxation is minimized, and the surface electronic structure is very similar to the bulk ones. Only in this case can we use ARPES to examine bulk electronic properties.
3.2 The concept of ARPES

In this section we discuss the basic concepts of ARPES. The derivation shown in this section comes mainly from Ref. (29). Rigorously speaking, each data point in the ARPES spectrum is proportional to the transition possibility for an optical excitation between the \( N \)-electron ground state and one of the possible \( N \)-electron final states. The bulk, surface and evanescent states have to be included in the Hamiltonian describing the crystal. This is the so-called one-step model. Due to the complexity of this description, the photoemission process is often discussed within the context of the phenomenological three-step model, in which the whole process is subdivided to three subsequent steps: (1) The incoming radiation excites the electron in the bulk; (2) The electron travels from the bulk to the surface; and (3) The electron escapes into vacuum. The total photoemission intensity is then given by the product of three independent terms: the total probability for the optical excitation, the probability that an electron travel to the surface without scattering, and the transmission probability through the surface potential barrier. The second and the third term can be described in the language of a mean free path and the material work function \( \phi \), respectively. The first term contains all information about the intrinsic electronic structure of the material.

We begin to examine step (1) by writing down the ARPES intensity via Born approximation and Fermi’s golden rule,

\[
I(k, E_k) = \sum_{f,i} w_{f,i} \sum_{f,i} \frac{2\pi}{\hbar} \left| \langle \Psi_f^N | \mathcal{H}_{int} | \Psi_i^N \rangle \right|^2 \delta \left( E_f^N - E_i^N - h\nu \right),
\]

where \( E_i^N = E_i^{N-1} - E_b(k) \) and \( E_f^N = E_f^{N-1} + E_k \) are the initial and final state energies of the electronic system, \( E_b(k) \) is the binding energy of the photoelectron with kinetic energy \( E_k \) and momentum \( k \). The electron-photon interaction Hamiltonian has the form

\[
\mathcal{H}_{int} = -\frac{e}{2mc} (\mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A})
\]

when choosing the gauge \( \Phi = 0 \) and dropping higher order terms. Assuming the validity of the three-step model and the sudden approximation, i.e., the system does not relax before the
escape of the photoelectron, we can factorize the initial and final state wave function to be
\[ \Psi_f^N = \mathcal{A} \phi_f(k) \Psi_f^{N-1}, \]
\[ \Psi_i^N = \mathcal{A} \phi_i(k) \Psi_i^{N-1}, \] (3.5)
where \( \mathcal{A} \) is a Fermionic antisymmetric operator, \( \phi(k) \) is the wave function of the photoelectron, and \( \Psi_f^{N-1} (\Psi_i^{N-1}) \) is the final (initial) state wavefunction of the \((N-1)\)-electron system left behind. If we express \( \Psi_f^{N-1} \) as a sum of the excited eigenstates \( \Psi_m^{N-1} \), the matrix element in Eqn. 3.3 can be factorized as
\[ \langle \Psi_f^N | \mathcal{H}_{int} | \Psi_i^N \rangle = \langle \phi_f(k) | \mathcal{H}_{int} | \phi_i(k) \rangle \langle \Psi_m^{N-1} \ | \Psi_i^{N-1} \rangle \equiv M_{f,i}(k)c_{m,i}. \] (3.6)
The total photoemission intensity is then
\[ I(k, E_k) = \sum_{f,i} |M_{f,i}(k)|^2 \sum_m |c_{m,i}|^2 \delta \left( E_k + E_m^{N-1} - E_i^{N} - E_k \right). \] (3.7)

If the system contains only non-interacting particles, the coefficients \( c_{m,i} \) will be unity for one particular state, and zero otherwise. This is equivalent of saying that all bands in the observed ARPES spectrum have zero width (\( \delta \)-function like). In reality, particles inevitably interact with each other and with the crystal lattice, resulting in finite values for several nearby \( c_{m,i} \)'s. Along with experimental finite temperature, the ARPES bands always have finite widths, even if the facility has unlimited resolution. We utilize the Green’s function approach to investigate this effect. In general, a Green’s function describes the time retarded (or advanced) output of a system due to a \( \delta \)-function input at time zero. In the case of photoemission, we define two quantities \( G^+(k,\omega) \) and \( G^-(k,\omega) \) as the one-electron addition and removal Green’s function \((\hbar = 1)\),
\[ G^\pm(k,\omega) = \sum_m \frac{|\langle \Psi_m^{N\pm1} | c_k^\pm | \Psi_i^{N} \rangle|^2}{\omega - E_m^{N\pm1} + E_i^{N} \pm i\eta}, \] (3.8)
where the operators \( c_k^+ = c_k^\dagger_\sigma \) \( (c_k^- = c_k^\dagger_\sigma) \) creates (annihilates) an electron with energy \( \omega = \mu - E_k \), momentum \( k \), and spin \( \sigma \) in the \( N \)-particle initial state \( \Psi_i^{N} \), and \( \eta \) is a positive infinitesimal. In the limit of \( \eta \to 0^+ \) the mathematical identity \( (x \pm i\eta)^{-1} = \mathcal{P} (1/x) \mp i\pi \delta(x) \) transforms Eqn. 3.8 into the expression of the one-particle spectral function \( A(k,\omega) = A^+(k,\omega) + A^-(k,\omega) = \)
\[-(1/\pi)\text{Im} G(k, \omega), \] with
\[
A^{\pm}(k, \omega) = \sum_{m} \left| \langle \Psi_{m}^{N \pm 1} | c_{k}^{\pm} \Psi_{i}^{N} \rangle \right|^2 \delta \left( \omega - E_{m}^{N \pm 1} + E_{i}^{N} \right). \tag{3.9}
\]

Note that $A^{-}(k, \omega)$ define the one electron removal spectra, which is exactly what photoemission probes. This can be seen by comparing Eqn. 3.9 with Eqn. 3.7, noting that $\Psi_{i}^{-1} = c_{k} \Psi_{i}^{N}$ and thus $|c_{m,i}|^2 = \left| \langle \Psi_{m}^{N-1} | c_{k}^{-} \Psi_{i}^{N} \rangle \right|^2$. The photoemission intensity can now be written as
\[
I(k, \omega) = \sum_{f,i} |M_{f,i}(k)|^2 A^{-}(k, \omega).
\]

Adding the effect of finite temperature is again non-trivial. by applying the sudden approximation one rewrites the ARPES intensity as
\[
I(k, \omega) = I_0(k, \nu, A) f(\omega) A(k, \omega), \tag{3.10}
\]
where $I_0(k, \nu, A) \propto |M_{f,i}(k)|^2$ is the so-called matrix element which depends on the electron momentum, and on the energy and polarization of the incoming photon. $f(\omega) = \left( e^{\omega/k_B T} + 1 \right)^{-1}$ is the Fermi function for finite temperature $T$, $A(k, \omega) = A^{-}(k, \omega)$ is the spectral function containing all information of the intrinsic electronic structure. In Eqn. 3.10 we neglect all effects due to finite experimental resolution for energy and momentum. Eqn. 3.10 usually serves as a beginning point for the physical interpretation of the ARPES spectrum.

Now we examine how electron-electron correlations affect the spectral function. We introduce the electron proper self-energy $\Sigma(k, \omega) = \Sigma'(k, \omega) + i \Sigma''(k, \omega)$, its real and imaginary part containing all the information on the energy renormalization and lifetime, respectively. The Green’s function and spectral function are then given by
\[
G(k, \omega) = \frac{1}{\omega - \varepsilon_{k} - \Sigma(k, \omega)}, \tag{3.11}
\]
\[
A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma''(k, \omega)}{[\omega - \varepsilon_{k} - \Sigma'(k, \omega)]^2 + [\Sigma''(k, \omega)]^2}. \tag{3.12}
\]
These two quantities are related by Kramers-Kronig relations. The form of $A(k, \omega)$ also indicates that, in simple cases ($\Sigma = \text{const.}$), the ARPES spectral lines have a Lorentz shape.

Next we give a brief description of the effects the matrix element term $I_0(k, \nu, A) \propto |M_{f,i}(k)|^2$ has on the observed ARPES signal. We will see in later chapters that this term
affects the ARPES spectra on iron pnictides greatly, resulting in apparent photon polarization dependence of the observed bands. According to Eqn. 3.4 and the commutation relation

\[ \hbar \mathbf{p} / m = -i [\mathbf{x}, \mathcal{H}] \]

we write

\[ |M_{f,i}(\mathbf{k})|^2 \propto |\langle \phi_f(\mathbf{k})| \mathbf{e}_r \cdot \mathbf{x} |\phi_i(\mathbf{k}) \rangle|^2, \]  

(3.13)

where \( \mathbf{e}_r \) is a unit vector along the polarization direction of the vector potential \( \mathbf{A} \). Let us consider photoemission of an electron from a \( d \)-orbital (as for the case of the iron pnictides), whose shapes are depicted in Figure 3.5. Assume that the photon comes along the \( y-z \) plane and the detector also locates at this plane (mirror plane). In order to have nonvanishing photoemission intensity, \( \langle \phi_f(\mathbf{k})| \mathbf{e}_r \cdot \mathbf{x} |\phi_i(\mathbf{k}) \rangle \) has to be an even function under reflection with respect to the mirror plane. In our approximation, electron final states are plane waves, i.e., \( \langle \phi_f(\mathbf{k}) \rangle \) is always an even function. Therefore there are two possibilities. (1) Electrons are emitted from an odd orbital, e.g. \( d_{xz} \) or \( d_{yz} \). In this case, \( \mathbf{e}_r \) has to be an odd function with respect to the mirror plane, i.e., perpendicular to the mirror plane. (2) Electrons are emitted from an even orbital, e.g. \( d_{yz}, d_{x^2-y^2} \) or \( d_{z^2} \). In this case, \( \mathbf{e}_r \) has to be along the mirror plane.

Finally we intend to discuss the effects from finite energy and momentum resolution. As we know, no machine is perfect. ARPES spectrum is always convoluted with energy and momentum resolution functions \( R_E \) and \( R_k \), plus an extrinsic continuous background,

\[
I(\mathbf{k}, \omega) = \tilde{I}(\mathbf{k}, \omega) \otimes R_E(\omega) \otimes R_k(\mathbf{k}) + B \\
= B + \int d\mathbf{k'} d\omega' I_0(\mathbf{k}, \nu, \mathbf{A}) f(\omega') A(\mathbf{k'}, \omega') R_E(\omega - \omega') R_k(\mathbf{k} - \mathbf{k'}). 
\]

(3.14)

It is both a technical and theoretical challenge to develop facilities with better resolution and to deconvolute the ARPES spectrum in order to obtain a pure \( \tilde{I}(\mathbf{k}, \omega) \).
3.3 Photon source

In the following three sections we investigate the experimental ARPES setup in detail. A typical ARPES equipment contains three major parts: the photon source (Section 3.3), the vacuum chamber and sample stage (Section 3.4) and the electron analyzer (Section 3.5). Extreme ultraviolet photons (with energies larger than 6 eV) are generated by the photon source, hits the sample with atomically clean surface in the ultra-high vacuum chamber, then the photoelectrons emitted by the sample enters the electron analyzer. We begin our investigation with the photon source. The two most commonly used types of photon source for ARPES studies are the gas discharge lamps and the synchrotron radiation sources. Below we discuss them separately.

3.3.1 Gas discharge lamp

Gas-discharge lamps are a family of artificial light sources that generate light by sending an electrical discharge through an ionized gas, i.e. a plasma. In operation, the gas atoms are first ionized (excited to a quantum state with higher energy) by external means like high voltage electro-sparks or collision with existing gas ions. In the subsequent relaxation process to the ground state, a photon with frequency characterized by the gas atom is emitted. In ARPES, these photons must have an energy higher than the work function ($\phi = 2 \sim 5$ eV) to be able to generate photoelectrons, i.e., they are ultraviolet (UV) photons. The most commonly used lamps are the helium lamp, the xenon lamp and so on. Below we use the helium lamp (routinely used in the present thesis) as an example to explain the principle and typical composition of a gas discharge lamp.

Figure 3.6 shows the components of a typical helium lamp used in ARPES experiments. All data in this paragraph comes from Ref. (35). In this setup, the helium plasma is generated by electron cyclotron resonance due to external microwave radiation. When helium gas is imported into the plasma discharge area (marked by a bulb symbol in Figure 3.6), gas discharge is initiated by high voltage electric sparks generated at the UV source head (the area beneath the UV lamp). The released electrons are then motivated by 10.0 GHz microwave generated in
Figure 3.6  The VG Scienta VUV5k helium lamp package. Helium gas is injected into the UV lamp in which it is ionized by initial high voltage electric sparks and collision with existing ions due to microwave electron cyclotron resonance. From Ref. (34).

...the microwave generator, making cyclotron movements inside the plasma cavity. More helium atoms are subsequently ionized due to collisions with existing seed ions. Using this electron cyclotron resonance technique, a total UV flux as high as $2 \times 10^{16}$ photons/(sr s) can be obtained. The helium emission spectrum contains three major photon wavelengths functional for photoemission: the He Iα line (584 Å or 21.218 eV, $\sim 82\%$), the He Iβ line (537 Å or 23.08 eV, $\sim 8\%$) and the He IIα line (304 Å or 40.814 eV, $> 10\%$). Since the He Iβ line is shadowed by the intense He Iα line, we normally use the He Iα and He IIα lines for experiment. After leaving the plasma cavity photons enter a monochromator chamber in which different wavelengths are selected. In the case of helium lamp, this monochromating process is optional, since it will greatly reduce the photon intensity, and the He Iα line is separated sufficiently in energy from the He IIα line, that the spectra from those lines will not substantially overlap in most cases even without the monochromator. On the other hand, one obtains higher signal-to-background ratio, reduces the photon spot-size and prevents helium gas from leaking to the main chamber by using the monochromator. After the monochromator, the photons exit the photon source...
package via an exit capillary. The resulting beam has a typical dimension of a millimeter or so. In the experimental setup at Ames Laboratory, the monochromator is not used; the exit capillary is replaced by a toroidal reflection mirror in which photons from different angles are refocused at the sample stage. The beam dimension is about 1 mm along the long axis of the elliptical bright spot.

One of the most important advantages for using a gas discharge lamp as photon source is the availability of large photon flux at $\sim 1$ meV bandwidth and unlimited machine time. With the help of automatic controlling procedure of the sample stage, we succeeded in unmanned week-long measurements for a single sample at Ames Laboratory, resulting in some of the best quality data available in the ARPES literature (36; 37). Moreover, the gas discharge lamp is financially favorable. The cost of a helium lamp ($\sim$ $100,000) is well within the budget of a typical research group. Besides, the lamp is not at all space consuming and will last for tens of years if taken proper care of. As we will see in Section 3.3.2, the experiment time at a synchrotron light source is very competitive and limited. The entire synchrotron facility (typical for condensed matter physics research) can be as large as hundreds of meters in diameter, its operating cost being an astronomical number. It is still widely used today because it has unique scientific advantages that can not be reached by a fix wavelength lab-based system.

3.3.2 Synchrotron light source

The other type of photon source that are widely used in the ARPES field is the synchrotron light source. Figure 3.7 gives a first glance of a typical synchrotron facility - the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory. While the facility gives a simple and enjoyable view at a distance, it is a landmark for the perfect match of scientific and technological complexity that have contributed to the deepest understanding of Nature - the origin of the universe, the forming of life, and, of course, the mechanism of high-temperature superconductivity. Basic electrodynamics tells us that when electrons accelerate, they emit light. When relativistic electrons accelerate centripically, they generate narrow beams of photons that travel along the forward tangent of the trajectory. In a synchrotron storage ring, several
“bunches” (packets) of electrons travel close to the speed of light. Their trajectories are stabilized by synchronized electromagnetic field applied to the bending magnets. Using insertion devices like undulators and wigglers, these electrons emit collimated radiation from microwave to hard X-ray, polarized within the plane of the storage ring or perpendicular to the line between the two poles of a dipole magnet inside an undulator (Figures 3.8, 3.10). The photons are then selectively collected by beam lines specially designed for a certain range of wavelengths (energies). For example, the energy range of Beamline 10.0.1 of the ALS is $17 \sim 350$ eV. This range is further separated with three monochromator gratings (380, 925, 2100 lines/mm). The
final destinations of the synchrotron photons are the end-stations in which scientific experiments are held. In the ALS, there are several end-stations for ARPES experiments, among which two facilities are used in the present thesis. They are the Electronic Structure Factory (ESF) of Beamline 7.0.1, and the High Energy Resolution Spectrometer (HERS) of Beamline 10.0.1.

In a synchrotron facility, electrons are injected into the main ring at substantial energies by either a linear accelerator or by an intermediate synchrotron (booster ring, Figure 3.7). There are at least two modes of injection. One older-fashioned procedure is to inject all bunches of electrons at the same time. The short coming is that electrons will scatter and fall out of the
ring, resulting in an exponential time decay of ring current. It is therefore necessary for an electron refill 3 or 4 times per day (Left of Figure 3.9). Higher level of radiation is emitted during the refill process, so a lot of facilities (e.g. the early days of the ALS and the Synchrotron Radiation Center, Wisconsin, USA) evacuate the experimental hall at the time of refill. To avoid such inconvenience and obtain a constant current for all times, facilities like the ALS now use a “top-off” injection mode. This operation scenario “requires full energy injection from the booster ring into the storage ring and constant operation of the injector” (42). The difference of photon current between these two modes are clearly shown in Figure 3.9.

Means of acquiring higher photon intensity include the usage of insertion devices like the undulators (Figure 3.10). An undulator consists of a periodic structure of dipole magnets. The static magnetic field is alternating along the length of the undulator with a certain wavelength. Electrons traversing the periodic magnet structure are forced to undergo oscillations and thus to radiate energy (light). Beamline 10.0.1 of the ALS utilizes the U10 undulator which is 4.5 meter long, containing 43 10-cm period dipole magnets (43). The U10 undulator provides radiation in the 5-950 eV energy range. Beamline 7.0.1 uses the U5 undulator, whose parameters include a 5-cm period and a 5-m length with an 0.837-T maximum field at a 14-mm gap (44).

The crucial advantage for using synchrotron source in ARPES experiments is the selectivity of incoming photon energies. As will be discussed in some detail in Section 3.7.3, varying the incoming photon energy in ARPES effectively changes the momentum offset along the direction perpendicular to the sample surface. In iron pnictide superconductors, this direction...
corresponds to $k_z$ - perpendicular to the Fe-As layers. Mapping the entire three dimensional electronic structure requires a study of $k_z$ band dispersion; this simply cannot be done in a fix-wavelength discharge-lamp-based ARPES system. Because of this (and insufficient number of lab systems), experiment time in synchrotrons (beamtime) is precious and highly competitive. Research proposals must go through a peer-reviewing and grading process before beamtimes can be assigned. A reasonably good proposal may win about 120 hours of beamtime per half a year, during which researchers often work 24 hours a day. A visit to synchrotron is an exciting and challenging experience that often includes sleepless nights, lots of junk food and coffee and, hopefully, scientific discoveries.

3.4 Vacuum chamber and sample stage

In this section we discuss the components and basics of construction of the ultra-high vacuum chamber and the sample stage for ARPES experiments. The reason why ARPES requires a good vacuum condition is two-folded. First, for a photoelectron to be able to travel from the sample surface to the micro-channel plate (MCP) detector (see Section 3.5), an electron mean free path ($l$) of at least 2 meters is required. According to a kinetic theory, $l$ is inversely proportional to the pressure and the scattering cross section of the particle. $l \sim 2 \text{ m}$ thus correspond to a vacuum better than $p \sim 10^{-4} \text{ torr}$ (1 torr $\equiv 1 \text{ mmHg} = 133.3 \text{ Pa}$). Second, for a reasonably long lifetime of the sample inside the chamber, the sample surface must not be covered with gas molecules too quickly. In a gas system obeying the Maxwell-Boltzmann distribution, the typical scale for particle speed is $v \sim \sqrt{k_B T/m}$. In a given time $t$, the number of times these molecules would hit the sample surface is given by $n \sim vtsp$, where $s$ is the area of the sample surface, and $\rho$ is the density of gas molecules. Assume that all particles hitting the surface would stick to it, the threshold pressure for the formation of a single layer of gas molecules on the sample surface within a time period $t$ is $\rho_c \sim \sqrt{m/k_B T}/ts_0$, where $s_0$ is the molecule cross section. Therefore, a sample total-loss time of 1 hour in an oxygen gas environment at $T = 10 \text{ K}$ requires a vacuum better than $p \sim 10^{-9} \text{ torr}$, which is in the range of ultrahigh vacuum. The vacuum requirement for a realistic chamber is even 100 times higher.
than this, since in most cases one needs a sample lifetime of several days, and a significant signal loss can be easily visible long before the above total-loss time.

Figure 3.11 gives a general idea of what a typical ARPES chamber looks like. The total volume of the chamber varies with each design, typically fits a \( \sim 30 \text{m}^2 \times 3 \text{m} \) room. In order to maintain a vacuum condition better than \( \sim 3 \times 10^{-11} \text{torr} \) within the chamber, several components are crucial: the vacuum pumps, the vacuum gauges, and the connecting components that link them without any leakage to the atmosphere. Usually the sample sits on a stage that is temperature controllable down to \( \sim 10 \text{K} \) or lower. This requires a helium-based cooling system. Moreover, for sample transferring process, we need vacuum valves connecting regions with different vacuum conditions, and transfer arms that enables handling of the samples from outside air to the center of the vacuum chamber. Below we discuss them separately.

### 3.4.1 Vacuum pumps

A vacuum pump is a device that removes gas molecules from a sealed volume in order to create a partial vacuum. Base on the residual pressure, vacuum condition is generally divided into three major categories: rough vacuum [ambient pressure (760 torr) to \( 10^{-3} \text{torr} \)], high vacuum [\( 10^{-3} \text{ to } 10^{-9} \text{torr} \)], and ultrahigh vacuum [lower than \( 10^{-9} \text{torr} \)]. Different types of
pumps work in different pressure ranges and have different pumping speed. For example, in Figure 3.12 we see that the scroll pump (rotary pump) works the best from ambient pressure down to $\sim 10^{-3}$ torr, while the operating range of an ion pump goes from $10^{-4}$ to $10^{-12}$ torr. It is therefore apparent that for an ion pump to work properly, the chamber must be pre-pumped to at least a rough vacuum. In an operating vacuum chamber these pumps are often arranged in series (e.g. turbo pump backed up by a roughing pump) or in parallel to reach the desired vacuum condition. Below we show the operating mechanism for two of the most widely used pumps - the turbo pumps and the ion pumps.

A Turbomolecular (turbo) pump operates by using high-speed rotors to physically kick the gas molecules toward the back side of the pump. It is mainly composed of the rotors and stators - rotating and fixed disks with multiple axial propellers (Figure 3.12). When properly operating the rotors obtain a frequency of 12,000 to 90,000 rpm depending on the model. Modern turbo pumps have considerable pumping power from a pressure as high as $10^{-2}$ torr to as low as $10^{-12}$ torr.
\( \sim 10^{-10} \) torr, they are one of the most useful type of pumps in a ultrahigh vacuum chamber.

A typical ion pump consists of a central (positive charged) anode that takes the shape of an array of short metal tubing (Right of Figure 3.12). Opposite to each open end of the tubing is a plate of titanium that is properly grounded to form the cathode structure. An external permanent magnet generates a magnetic field parallel to the anode cell axis (51). In operation, the anode tubing maintains a cloud of electrons that are forced to undergo spiral trajectories by the magnetic field. The electrons collide with gas molecules to form positive ions. These ions are then accelerated away from the positive anode voltage and collide into the titanium cathode plates. This results in the removal of titanium atoms by “sputtering”. The sputtered titanium is deposited on the internal surfaces of the pump where it reacts with absorbed active gases to form stable compounds (51). “Active gases are those such as oxygen, nitrogen, CO, \( \text{CO}_2 \), and water, as opposed to the noble gases like helium, neon, argon, krypton, and xenon, which are nonreactive. The latter are pumped by ‘ion burial’ (ion burial is the ‘plastering over’ of inert gas atoms by the sputtered getter atoms)”, quoting Ref. (51). The ion pump is one of the most powerful pumps in the ultrahigh vacuum region; it serves as the workhorse of an ultrahigh vacuum chamber.

### 3.4.2 Vacuum gauges and residual gas analyzer (RGA)

Vacuum gauges are used to monitor the pressure inside a vacuum chamber. As an example, two types of gauges are used in the ARPES chamber at the Ames Laboratory: the Pirani gauge for measuring rough vacuum (\( 10^{-3} \) torr to ambient pressure) in the load-lock area; and hot cathode ionization gauges (ion gauges) for measuring high to ultrahigh vacuum everywhere else. In an ion gauge, electrons generated by thermal emission collide with gas atoms, generating positive charged ions. These ions are then attracted to a suitably biased electrode known as the collector. The collector current is a monotonic function of pressure, which is measured by an electrometer in units of picoamps (pA). By definition, ion gauges are not able to distinguish different types of gas molecules; they measure a sum of all partial pressures.

Due to the different probability that a molecule of different gases stick with the sample
surface, the “harm” to the sample varies with gas type. For example, oxygen and water molecules are poison to the sample since they react easily with the sample surface. On the other hand, inert gases such as helium and argon do almost no harm to the sample. At Ames Laboratory the ARPES chamber is commonly operated under a relatively high partial pressure of $1 \times 10^{-8}$ torr for helium; samples survive up to 16 days under this condition. In light of this fact, it is crucial to know exactly what gases are left inside the chamber. We utilize the residual gas analyzer (RGA) to accomplish this. An RGA operates by creating a beam of ions from samples of the gas being analyzed. The resulting mixture of ions is then separated into individual species through their charge-to-mass ratios by a quadrupole mass spectrometer. The output of an RGA is a spectrum of relative intensities versus the atomic mass of the gas (mass spectrum). In many chambers [e.g. Beamline 7.0.1 (ESF) of the ALS] an RGA is permanently connected to the chamber to continuously monitor the partial pressure of the residual gases.

### 3.4.3 Sample stage and cold finger

Next we discuss the sample stage and the cold finger - the place where sample is located in the vacuum chamber. Besides the normal position control ($x, y, z$), modern sample stages often have the ability to rotate about at least three axes: the polar axis $\beta$, the azimuthal axis $\omega$, and the perpendicular polar axis $\theta$ (Figure 3.13). Changing the sample direction in the chamber is equivalent with changing the detector position with respect to the sample surface normal, thus enables the exploration on different parts of the reciprocal space. One subtlety of such a design is that when the sample rotates on the stage, the incoming photon beam would change slightly its exact location on the sample. Therefore if the sample is highly inhomogeneous (rough surface and/or physical properties change rapidly with position), the good portion of the sample can be moved out of the beam. The two beam lines at the ALS have different solution to this. At Beamline 7.0.1 (ESF), the detector is fixed. One compensates this misalignment by automatically adjust the $x$-$z$ position of the sample stage itself. At Beamline 10.0.1 (HERS), the entire electron analyzer rotates about the $\beta$-axis (called $\alpha$ there), eliminating all possible distortion.
Most APRES studies focus on examining the elementary excitations of an electronic system, which requires temperatures lower or comparable to the temperature scale of the system of interest. In some cases this can be as low as, for example, the boiling point of helium (4.2 K). To obtain such low temperature, a helium-based cooling system through the sample stage is required. There are two types of cooling systems - open-cycled liquid helium cryostat and close-cycled helium gas refrigerator. The first one operates more or less by brute force: one uses an external tank of liquid helium, guides the liquid to the sample stage through proper tubing. The advantage of this method is the high cooling power, yet such advantage is accompanied by the vibration due to boiling and a waste of expensive liquid helium. The lowest temperature such a system can produce at the sample location is \( \sim 2.5 \) K (Shin group, Tokyo, with associate helium pumping). The other method utilizes a commercial close-cycled helium refrigerator (Right of Figure 3.13). This refrigerator operates via the four-step Gifford-McMahon refrigeration scheme, which is manifested in the \( p-V \) graph as a clockwise squared loop (53; 54). Using this method, the sample can be cooled down to \( \sim 10 \) K with proper grounding and good thermal contact. One possible way to obtain lower temperature is the usage of an \(^3\)He-based system, whose base temperature is as low as \( \sim 0.25 \) K (54). We will not go into detail for this method.
Figure 3.14  Load-lock and Sample transfer system at the Ames chamber. When loading samples, they are first placed in the load-lock area where subsequent rough and turbo pumping lowers the pressure from 760 torr to $\sim 10^{-8}$ torr. Then the samples are transferred using the transfer arms to the main chamber, whose pressure is maintained at $\sim 10^{-11}$ torr.

### 3.4.4 Sample transfer and vacuum valves

Now we examine how we put a sample into the ultrahigh vacuum chamber. We use a load-lock system and transfer arms to accomplish this task. As an example we show in Figure 3.14 the load-lock system of the ARPES chamber at the Ames Laboratory. First we insert the properly mounted (Section 3.6) samples into the load-lock area, which is filled with nitrogen gas before it is opened to the outside air. After isolating the load-lock area we perform subsequent rough and turbo pumping, lowering the load-lock pressure to $\sim 10^{-8}$ torr. Depending on the pumping power this process can be lengthy - typically 5 hours. After that we use transfer arms to move the sample holder from the load-lock to the transfer area, then to the main chamber. Such a process is very similar to the way ships pass the dam: by opening first Valve 2 (Figure 3.14) we level the pressures in the load-lock and transfer area; after the sample holder enters the transfer region we close Valve 2 and wait, until the pressure there drops down again to $\sim 10^{-9}$ torr. Further transferring to the main chamber is exactly the same, using Valve 1 for
isolation. The common vacuum valves used in an ARPES system are the manual or pneumatic
gate valves and ball valves, which provide a total isolation for pressures down to $10^{-11}$ torr.

3.4.5 System maintenance

Maintenance of the complicated ARPES system can be lengthy and tedious. Here we focus
on two common procedures: system bake-out and leak checking. More information on this topic
can be found in e.g. Ref. (55). The process of bake-out is required each time when the chamber
(or a part of it) is exposed to the atmosphere, since once exposed, extra gas molecules will stick
to the inner walls of the stainless-steel chamber; they are not easy to detach and pump away. As
a result, a system without proper baking will never reach the pressure of $\sim 10^{-11}$ torr. During
the bake-out process the entire chamber (or the part that is exposed to atmosphere) is heated
up to elevated temperatures, usually about $150^\circ$C, higher than the evaporation temperature
of all the stuck gas molecules. These molecules will then release and be pumped out of the
chamber volume. The bake-out process generally takes several days, depending on the baking
volume, the baking temperature and the target pressure.

Any leakage of gas into the chamber should be checked before the experiment starts. Large
amount of gas leakage is easily detected by spraying ethanol to the leaking part and observing
a jump of pressure reading at the corresponding ion gauge. Smaller leaks are more subtle to
detect. One way to check it is by spraying small beam of helium gas to the suspected area. If
there is a leak, the helium partial pressure will increase and be displayed at the RGA (Section
3.4.2).

Even with all the above efforts the sample will inevitably age inside the chamber. Typical
symptom of sample aging include the suppression of signal intensity, and more importantly
changes of the band locations and the superconducting gap value. These can be explained
by change of surface properties due to external molecule deposition. An oxidation layer at
the sample surface may result in a change of surface doping, which results in a shift of the
detected chemical potential (hence the bands), and in high-$T_c$ cuprates a change of $T_c$ and the
superconducting gap. To test the severeness of aging we typically monitor the gap value and
peak intensity over extended period of time for a sample of high-$T_c$ cuprate. Usually a gap shift of $< 5$ meV over a few days is considered acceptable for studies with highest statistics.

A final remark for this section is that all material used in the ARPES chamber should be strictly non-ferromagnetic. In the electron analyzer (Section 3.5) the electron path is further protected by $\mu$-metal magnetic shielding to eliminate the effect of earth’s magnetic field. This is easy to understand, since the trajectories of electrons will be altered by external magnetic fields.

3.5 Hemispheric electron analyzer

Selected photoelectrons enter the hemispheric electron analyzer after traveling through the vacuum chamber. In this section we intend to discuss the basic operating principles of the electron analyzer optimized for ARPES studies. In operation, the entire analyzer should also be kept under ultrahigh vacuum. The most common analyzers used in state-of-the-art ARPES systems are commercial products of VG Scienta, a company in Sweden. In Figure 3.15 we show the exterior of a Scienta R8000 analyzer about to be used at the Ames Laboratory. It is
Figure 3.16 Schematics of the electrostatic lens setup for Scienta R3000 electron analyzer. $d$ is the working distance, $\phi$ is the acceptance angle of the analyzer. Red curves show the calculated electron trajectories for photoelectrons emitted from different angles or from the same angle with different energies. From Ref. (56). In the “angular mode”, different emitting angle of the photoelectrons are transferred to different positions at the plane of the entrance slit.

seen that the analyzer consists of two major parts: the electrostatic lens and the hemispheric capacitor. Below we use the Scienta 200 mm electron spectrometer series (R2002, R3000, R4000 and R8000) as examples to discuss these two parts in greater detail.

The electrostatic lens portion of an analyzer maps the emitting angle of the photoelectrons onto different positions at the plane of the analyzer slit. After being emitted from the sample, photoelectrons enter the electron analyzer through a circular opening at the beginning of the electrostatic lenses (leftmost part in Figure 3.15). The diameter of the circular opening and its distance from the sample (working distance $d$, Figure 3.16) define the acceptance angle $\phi$ of the analyzer, which in turn gives the maximum $k$ range in the raw data. There are usually 3 or 4 lens elements in total. In what is called the “angular mode” these lenses work similarly as a regular concave lens in optics: at the focal plane of the lens set (slit plane), electrons emitted at different angles are focused to different locations, creating a one-to-one mapping from the real space to the reciprocal space. Modern analyzers also include the option of the “transmission mode”, which gives information of the real space distribution: electrons that come from different parts of the sample are focused on different locations at the slit plane. The transmission mode is often used in ARPES experiments to accurately locate the sample with respect to the analyzer. It should be noted that even electrons emitting at the same angle will
Figure 3.17  Left: Schematics of a hemispheric capacitor and several electron paths. Yellow and blue curves denote two trajectories for electrons with the same energy but different $k$; Red and green curves denote two trajectories for electrons with different energies but the same $k$. From Ref. (57). Right: Raw data at the MCP screen. The horizontal and vertical axes are $E$ and $k$, respectively.

have different energies due to the intrinsic electronic structure. These electrons must not be dispersing at the focal plane. This goal is achieved by proper lens setup and voltage control (see Figure 3.16).

The analyzer slit located between the electrostatic lens and the hemispheric capacitor; it expands vertically in the setup of Figure 3.15. The length of the slit determines the maximum $k$-range, whereas the width of the slit controls the electron intensity, the energy and lateral momentum resolutions of the analyzer (discuss later). In a Scienta R4000 analyzer one can choose the slit width from 0.1 mm to 0.8 mm (denoted as 100 ∼ 800). This is done by manually tuning a knob at the back of the hemispheric capacitor.

After entering the hemispheric capacitor, electrons with different energies travel along different paths due to the voltage difference between the inner and outer hemispheric plane. As shown by the red and green curves in the left panel of Figure 3.17, electrons with lower kinetic energies bend more severely by the capacitor, ending up at locations closer to the inner sphere on the MCP/CCD screen. On the other hand, electrons with higher kinetic energies end up at locations closer to the outer sphere. By this means the axis of energy is created. A second requirement of the hemispheric capacitor is that electrons with different $k$ but the same $E_k$ must travel along a plane to the MCP/CCD screen that is perpendicular to the $E$-axis. As shown
by the yellow and blue curves in the same panel, this is done in a reversed fashion: electrons come from the right side (top) of the slit travel to the left side (bottom) of the screen and *vice versa*. The “straightness” of the $k$-axis depends on the shape of the analyzer slit. Before a real experiment, detailed calibration must be done to determine exactly how the $k$-axis is curved (or simply how the chemical potential is shifted with different $k$’s).

The final destination of the photoelectrons is the micro-channel plate (MCP) detector located at the opposite end of the hemispheric capacitor (Figure 3.17). A micro-channel plate is a slab with a regular array of tiny tubes or slots (microchannels) leading from one face to the opposite, densely distributed over the whole surface. Each microchannel works as a usual electron multiplier, in which the number of electrons are multiplied by an electric-field driven secondary emission process. The voltage across the MCP is generally $> 1400$ V. After the MCP, electrons hit a fluorescent phosphor screen and images are collected by a high-speed CCD camera. A typical image of the CCD camera is shown in the right panel of Figure 3.17. It is interesting to notice that such a camera image (not even the raw data) already shows the band structure of the detected material: the brighter “tail” in the image is actually an energy band in the sample, and the sudden drop of overall intensity at roughly the middle of the image comes from the Fermi cut-off.

Now we introduce the concept of *pass energy* which generally determines the overall transmission and the energy resolution of an electron analyzer. A measurement with pass energy $PE$ (unit eV) is such that the electrons traveling to the central vertical line of the MCP detector have kinetic energy $PE$. Note that this energy is not the original kinetic energy of the photoelectrons. Photoelectrons undergo accelerating/decelerating processes within the electrostatic lens, yielding a certain range of energies with which electrons are allowed to pass through the analyzer slit. This energy range is centered at the pass energy, its width depending on the pass energy. For example, in the setting of Pass Energy 5 ($PE = 5$ eV) the energy range is $4.84 < E < 5.16$ eV, the width of energy range is 0.32 eV. In the setting of Pass Energy 10 ($PE = 10$ eV) the width is exactly twice of that in PE 5 setting (0.64 eV); the energy range is thus $9.68 < E < 10.32$ eV. Since the pixel number in the MCP is fixed, we expect a measure-
ment of higher pass energy to have higher intensity and lower energy resolution. In a typical Scienta 2002 or higher version detector, eight pass energies can be chosen: they are 1, 2, 5, 10, 20, 50, 100 and 200 eV. Different pass energies are used for different ARPES maps in the present thesis. We do not mention them explicitly; instead we give an overall energy resolution to each map.

Another factor that affects the intensity and the energy resolution is the slit size. The bigger the slit, the higher the number of transmitted electrons. However in the bigger slit settings some electrons with slightly different $k$'s would end up in the same $k$-channel in the MCP detector, rendering a lower $k$ and $E$ resolution. As a result, the energy resolution of an ARPES experiment is a monotonic but non-linear function of the pass energy and the slit size (in the synchrotron the limited resolution of the beam line further complicates this). The momentum resolution, on the other hand, is better defined by the ratio between the acceptance angle and the number of $k$-channels in the MCP.

Finally we examine how to construct a map of ARPES raw data base on the CCD images. A single image is generally not applicable for two reasons. First, the energy range of an ARPES map is better not fixed and can be set by the experimentalist, yet a single CCD image has a fixed energy range. Second, each microchannel in the MCP may have different gain, some of them may even be not working at all. The usage of a single CCD image will result in losing physical information at these “dead pixels”. A way to proceed is to scan the whole energy range of interest plus the MCP energy range. This is called the “scan mode”. For example, if we want to scan from 16.5 to 17.1 eV with Pass Energy 5, the first frame of the scan will be set such that electrons with initial kinetic energy $16.5 - 0.32 = 16.18$ eV is located at the leftmost column of microchannels in the MCP; while the last frame will be set such that electrons with initial kinetic energy $17.1 + 0.32 = 17.42$ eV is located at the rightmost column of microchannels. In this case, the physical information for each $E$-point will be collected by a row of microchannels. The intensity for that specific $E$-point in the ARPES raw data is a sum of intensities collected by each channel in the row. This is the default setting of the ARPES software. Its shortcoming is the requirement of longer scanning time. An alternative way to proceed is the so-called
“dithering mode” used routinely at Beamline 7.0.1 and 10.0.1 of the ALS. The idea is the same as the scan mode except that the scanning range is much smaller. This allows some degree of pixel averaging while keeping a relatively short scanning time. It is best used for eliminating the effect of a metallic mesh placed at the hemispheric detector.

3.6 Sample preparation

The basic idea of sample preparation is to achieve an atomically clean surface so that photoelectrons can escape, and a good electrical contact between the sample and the chamber so that the samples are not charging up. For a crystal with layered structure, such as the cuprates and the pnictides, the most common way of sample pre-processing is to cleave them inside the vacuum chamber (Figure 3.18). To do this, we first glue a “cleaving bar” to the sample before it is loaded; then we remove the cleaving bar mechanically inside the chamber. If the glue is stronger than the sample, the sample will be cleaved, resulting in a fresh surface. The electrical contact is achieved by using conductive glues (e.g. the EPO-TEK H21D silver epoxy) or adding a layer of graphite connecting the sample to the sample holder.
3.7 Data processing and interpretation

After discussing the ARPES system in detail, we intend to conclude the chapter with basic data processing and interpretation methods, i.e., generally how we extract useful physical information from a set of raw ARPES maps.

3.7.1 Raw data

A typical ARPES raw data set is a map of photoelectron intensity within a certain $k$-$E$ range, constructed from a series of CCD images using the scan or dithering mode (Section 3.5).
The horizontal and vertical axes for the raw data are the slice number (ARPES intensity in a slice is the integration of intensities from several rows of CCD pixels) and the kinetic energy of the photoelectrons. Usually such an ARPES map is not used directly for presentation in papers. Below we use a map taken from a half-Heusler GdPtBi sample as an example to explain what might need to be done before the raw data can be presented in scientific papers. We present in Figure 3.19a the raw data for an ARPES cut along the $k_{(110)}$ direction across the Brillouin zone center $\Gamma$, higher electron counts are shown by brighter grey scales. Even at the first glance one realizes the main advantage of the ARPES technique - the band structure is so apparent and clear even in the raw data, the most important physical information is unambiguously presented without any complicated analyzing process. Some mild analytical methods are nonetheless needed, since after all, machine defects, distortions and unevenness need to be corrected before the raw data shows the accurate physical picture. A few common pre-processing methods include the Fermi level and $k$-scale determination, data normalization, correction of grid distortion, margin truncation, etc.

The first thing to do is to change the scale of the $E$ axis in the raw data from channel number to binding energy in units of eV. This is equivalent with determining the chemical potential and set it to binding energy zero. Even without a proper technique one can guess more or less the chemical potential $\mu$, since ARPES intensity typically experiences a dramatic decrease at $\mu$, yielding essentially no information above. For example in the raw data of Figure 3.19c, $\mu$ locates roughly at the kinetic energy of 95.55 eV (which means a work function of 4.45 eV for 100 eV photons). A more proper way to determine $\mu$ is by measuring a polycrystalline gold or aluminum reference in electrical contact with the sample inside the vacuum chamber. ARPES intensity in such a gold sample is uniform except for the Fermi cut-off. We then determine the accurate $\mu$ by fitting each energy distribution curve with a resolution convoluted Fermi-Dirac function. Figure 3.19d shows the result of $\mu$ correction.

Grid correction is usually done with data taken from detectors with large acceptance angle (Scienta R4000 with $\phi \sim 30^\circ$). Typically we perform this by putting a metal grid with straight parallel sections between the sample and the detector. If the lens voltages are not optimized,
this grid will transform to a non-parallel shape in the CCD image. We then correct the observed
grid shape back to parallel by proper data interpolating. The grid correction process is shown
in Figure 3.19a-d.

Raw data generally requires a normalization process in which the total ARPES intensity
within a certain energy range at a specific $k$ point is set to be unity:

$$I_{\text{nor}}(k) = \int_{E_1}^{E_2} I(k, E) dE = 1,$$

the integration limit varying with application. In Figure 3.19d the normalization range is the
whole detection range. In some cases, we further subtract the background intensity by fitting
a linear function to the background above $\mu$.

After necessary pre-processing, data is ready for analytical use. Now we formally define
two important physical concepts routinely used in data analysis: the energy distribution curve
(EDC) and momentum distribution curve (MDC). As is shown in Figure 3.19e-f, an EDC is
a curve of ARPES intensity versus binding energy at a specific momentum; while a MDC is a
curve of ARPES intensity versus momentum at a specific binding energy. Theoretically, both
EDC and MDC give information for the one-particle self energy $\Sigma$ which enters the spectral
function via Eqn. 3.12,

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

Among the two quantities, analysis for EDC has the advantage of being able to examine the
raw data without the normalization process, yet in the EDC the spectral function is dressed
by the Fermi-Dirac distribution (ignoring the dipole matrix element),

$$\text{EDC}_k(\omega) \propto A(k, \omega) f(\omega).$$

On the other hand, analysis for MDC requires high momentum resolution of the facility and a
proper normalization process, yet it is more directly linked with the spectral function,

$$\text{MDC}_\omega(k) \propto A(k, \omega).$$

The analysis using MDCs is proven to be an important tool for revealing the mechanism in
high-$T_c$ cuprates (58; 59; 60).
Figure 3.20  Principle of Fermi mapping.  a, Schematics of the Fermi mapping procedure. Photoelectrons at the Fermi surface emitted by fixed-energy photons span a spherical surface at the three dimensional $k$-space. In a typical Fermi mapping, the analyzer with acceptance angle $\phi$ scans a certain $\theta$ region, constructing a $\phi$-$\theta$ map (b). The corresponding region in $k$-space is marked with orange color on the spherical surface. A properly rotated Fermi map with axes $k_x$ and $k_y$ (c) is then constructed by projecting the $\phi$-$\theta$ map onto the two dimensional $k_x$-$k_y$ plane. Data in Panels b-c is taken from a LuPtBi sample with 21.2 eV photons at $T = 12$ K, using a Scienta 2002 analyzer ($\phi = 14^\circ$).

Special attention should be paid to the fact that the $k$-axis of an ARPES map is not a straight line in the $k$-space. Instead it is a circular arc curving around a spherical surface defined by the incoming photon energy. This fact is depicted at Panel g of Figure 3.19. Thus for a sample with apparent $k_z$-dispersion, even a $\Gamma$-$\Gamma$ cut shows significant difference between the two zone centers.

3.7.2 Fermi mapping

After confirming the quality of a sample using a single ARPES map, a common next step is to map the Fermi surface of the sample, i.e., construct a $k_x$-$k_y$-$E$ map out of large number of ARPES maps with different inclining angle $\theta$. In order to do this, the analyzer should be
arranged such that the entrance slit (with acceptance angle $\phi$) is perpendicular to the scanning direction. By taking consecutive ARPES maps at a series of $\theta$ angles, we obtain a three dimensional data set with axes $\theta$, $\phi$ and $E$ (See Figure 3.20a,b). Since a fixed incoming photon energy defines a spherical surface in the $k$-space, such a $\phi$-$\theta$ map covers a spherical region. The Fermi maps presented in this thesis are projections of the spherical region onto the $k_x$-$k_y$ plane (Figure 3.20a). As a result, the conversion from $\phi$-$\theta$ values to $k_x$-$k_y$ values requires the usage of the three Euler angles $\theta$, $\phi$ and $\psi$, which are defined as the angles at Figure 3.20a for each individual data points. The rotation matrix is

$$A \equiv \begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} = \begin{pmatrix} \cos \psi & \sin \psi & 0 \\ -\sin \psi & \cos \psi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & \sin \theta \\ 0 & -\sin \theta & \cos \theta \end{pmatrix} \begin{pmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

(3.19)

The projection process is then given by

$$K_{xy}^\prime = A_{xy}K_{xy}^0$$

(3.20)

where $A_{xy} \equiv \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix}$, $K_{xy}^\prime = (k_x^\prime, k_y^\prime)^T$ ($K_{xy}^0 = (k_x^0, k_y^0)^T$) is the $k$-space location after (before) the spatial rotation. The rotation along the $k_z$ axis is subsequently defined by a fourth rotation angle $\Omega$ via

$$\begin{cases} k_x = k_x^\prime \cos \Omega - k_y^\prime \sin \Omega, \\ k_y = k_x^\prime \sin \Omega + k_y^\prime \cos \Omega. \end{cases}$$

(3.21)

Figure 3.20b-c show the result of such a rotation. In Figure 3.20c the Euler angles are set such that the high symmetry points (e.g. the zone center $\Gamma$) locate at the special positions in the $k$-space (e.g. $\Gamma = (0, 0)$). For a previously unexplored sample, finding the $\Gamma$ point is not always trivial. One recognizes this by examining several equal-energy surfaces and check for high translational and rotational symmetries. Figure 3.21 show a set of high quality ARPES Fermi maps taken from different samples. Even the first look to these Fermi surfaces gives an exciting experience, as they show the power of the ARPES technique in revealing the hidden beauty of Nature.
Figure 3.21  Gallery of Fermi mapping. Brighter colors represent higher intensity. a-b, Mapping at constant binding energies for Ce$_2$RhIn$_8$. Incident photon energy is 105 eV, binding energies are a, 0 eV ($\mu$); b, 1 eV. c, Fermi mapping for GdPtBi with 48 eV photons. $k_0 \equiv \sqrt{6}/a$. d, Fermi mapping for BaFe$_2$As$_2$ with 105 eV photons.
3.7.3 “$k_z$ dispersion”

For a material whose bands are dispersive along the axis perpendicular to the cleaving plane ($k_\perp$, $k_z$ for the tetragonal cuprate and Fe-based systems), the shape of Fermi surface will depend on incoming photon energies. That is because for different photon energies, the mapping region of the $k$-space intersect differently with the underlying electronic structure. Ideally one would like to have a set of ARPES Fermi maps for consecutive photon energies. In this way a full three dimensional Fermi map as well as a full four dimensional electronic structure ($k_x, k_y, k_z, E$) can be constructed. Since this procedure requires considerable machine time, a more feasible way is to make a “$k_z$ dispersion map” by changing the photon energy while maintaining the $\theta$ angle (Figure 3.22a) at a high symmetry axis. Figure 3.22 shows the principle and an example of such a map. By fixing the $\theta$ angle of the analyzer and varying the photon energy, a sector-shaped $k_x$-$k_z$ cross-section of the $k$-space is measured. This schematics also explains the energy dependence of the momentum resolution. Since the pixel number is fixed, the higher the photon
energy (hence the wider the detection range), the worse the $k$-resolution.

The basic idea of extracting the $k_z$ value come from the principle of photoemission (Eqn. 3.2) and a proper usage of the Euler angles. However, in real crystals the potential barrier across the crystal surface consists of not only the work function $\phi$ but also a potential difference $E_0$ between the electron kinetic energy inside the crystal and that in the vacuum, if the final state of this electron were a free electron:

\[
E_k^\text{free} = \frac{\hbar^2 k^2}{2m} - V_0, \tag{3.22}
\]

where $V_0 = E_0 + \phi$ is the inner potential of a specific crystal. In this case, the momentum of the photoelectron (second equation of Eqn. 3.2) is changed to

\[
\begin{aligned}
k_\perp &= \sqrt{\frac{2m}{\hbar^2} (E_k \cos^2 \theta + V_0)} \\
k_\parallel &= \sqrt{\frac{2m}{\hbar^2} E_k \sin \theta}
\end{aligned} \tag{3.23}
\]

where $\theta$ is the polar angle with respect to the surface normal. Since the inner potential $V_0$ enters only the perpendicular part of the momentum ($k_\perp$ or $k_z$), we usually determine $V_0$ by seeking the high symmetry points in the $k_z$ map and choose a proper $V_0$ such that these points has a $k_z$ value of multiples of $\pi/c$ (or $2\pi/c$ depending on the crystal structure). Quasi two dimensional electronic systems (e.g. the cuprates) and surface states shows no $k_z$ dispersion. In these cases the inner potential has no proper definition.

### 3.7.4 Typical data interpretation

Now we discuss some typical electronic structures that often appear in ARPES data sets. Only those relevant to later discussion of the pnictides are included. We begin with the definition of two most commonly seen Fermi topology - the electron pocket and the hole pocket. From Figure 3.23 we see that an electron pocket has the shape of an upward paraboloid in the $k_x$-$k_y$-$E$ map; a quasiparticle circling around an electron pocket has positive effective mass, like a free electron. On the other hand, a hole pocket has the shape of a downward paraboloid in the $k_x$-$k_y$-$E$ map; a quasiparticle circling around a hole pocket has negative effective mass, acting like a hole in semiconductors. The important Luttinger theorem states that in a normal
metallic state, the Fermi contours enclose a volume in the $k$-space which is proportional to the number of valence electrons in the system,

$$n = \frac{N}{V} = 2 \int_{G(k, \omega = 0) > 0} \frac{d^3k}{(2\pi)^3},$$  \hspace{1cm} (3.24)

where $G(k, \omega = 0) > 0$ defines a $k$-space region where the single particle Green's function at zero energy (Fermi surface) has a positive phase. Simply put, the volume enclosed by an electron pocket contributes positively to the integral, whereas the volume enclosed by a hole pocket contributes negatively to the integral. If we assume that external electron or hole doping to the system affect negligibly to the shape of the bands (rigid band approximation), the only effect it has is the position of the chemical potential $\mu$. If more electrons are doped to the system, $\mu$ shifts upward in Figure 3.23, and vice versa. It is clear that electron pockets will expand under electron doping and shrink in size under hole doping; hole pockets will shrink under electron doping and expand under hole doping. This is consistent with the Luttinger theorem (Eqn. 3.24).

The word “nesting” is used when parallel parts exist in different Fermi contours. Note that the parallel parts need not be straight - as is demonstrated in Figure 3.23. It is generally believed that such “nesting” regions in the electronic structure help the forming of density wave states, and perhaps the emergence of superconductivity. That is because parallel parts of bands
would reduce the local $k$-space to quasi one dimensional. Unlike the higher dimensional cases, the one dimensional solution of the density wave problem gives a finite energy decrease for the system (22).

Another important application of ARPES maps is the direct observation of superconducting energy gaps and their momentum dependence. We have shown before in Section 2.7.2 that the existence of a superconducting gap will lead to typical back-bending of the bands and zero density of states within the gapped region $2\Delta$. All of these can be seen by ARPES. Figure 3.24 shows the superconducting gap observed for selected cuprate superconductors. From the EDCs in Panels a and c we see that in the superconducting state, the local density of states for a superconductor exhibit a peak structure close to the chemical potential $\mu$, rendering a vanishing spectral weight at $\mu$. This behavior is well reproduced by the BCS theory (see Figure 2.8). We call this the quasiparticle peak, and the gap value is approximated by the energy

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**Figure 3.24** Superconducting gap measured by ARPES. a, ARPES spectra (EDCs) at the superconducting state of Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4}$ for Bi2201 ($n = 1$, $T_c = 19$ K), Bi2212 ($n = 2$, $T_c = 91$ K), and Bi2223 ($n = 3$, $T_c = 108$ K) measured at $(\pi,0)$ point where the gap has the biggest value. Measurement temperatures are 13.5 K for Bi2201 and 40 K for both Bi2212 and Bi2223. Inset shows the EDC/cut position(s) of each panel. From Ref. (61). b, Normalized ARPES spectra at 60 K divided by the resolution-convoluted Fermi-Dirac function. Blue and red broken lines are the BCS band dispersions below and above $\mu$. Open circles show the experimental normal-state band dispersion, and the white solid line ($\epsilon_k$) is the fitting with a parabolic function. c, Corresponding EDCs of Panel b. b-c taken from Ref. (62).
difference between the top of the peak and $\mu$. From Figure 3.24a we also notice that the gap value depends on the transition temperature of the superconductor. This fact is understood by recalling that the coupling strength is the proportionality constant between the gap at zero temperature and $T_c$ (Eqn. 2.39).

The back-bending effect of a band (Figure 2.8) is best seen in Figure 3.24b where the ARPES spectra is divided by the resolution-convoluted Fermi-Dirac function. Compared with the normal state spectra (white circles) we clearly observe a back-bending for the two halves of a band crossing the Fermi level. The excellent agreement with BCS theory (dashed lines) further confirms the validity of BCS predictions even in strong coupling superconductors. Theoretically the superconducting gap is best described by the Dynes function (63; 64) which includes the thermal broadening effect in the BCS equation (Eqn. 2.35):

$$D(\omega, \Delta, \Gamma) = \text{Re} \left[ \frac{\omega - i\Gamma}{\sqrt{(\omega - i\Gamma^2 - \Delta^2)}} \right],$$

(3.25)

with $\Delta$ the gap value and $\Gamma$ the broadening parameter. By fitting the Fermi momentum EDC with the Dynes function at Figure 3.24c (bold green line) we can obtain a more accurate $\Delta$-value than measuring the energy difference. This procedure, however, is not always possible, since the coherent peak above the chemical potential is generally difficult to observe experimentally. One simplified procedure is to symmetrize the raw EDCs at Fermi crossing points with respect to $\mu$,

$$I_{\text{sym}}(\omega) \propto I_{\text{raw}}(\omega) + I_{\text{raw}}(-\omega),$$

(3.26)

where $\omega = 0$ at $\mu$. If the symmetrized EDC show two peak structure centered by a valley at $\mu$, the corresponding $k$-point is considered to be “gapped”, with the gap value approximated by a half of the energy difference between the two peaks. If the symmetrized EDCs show only one peak (or no peaks) centered at $\mu$, the gap value is most likely zero.
CHAPTER 4. Physical properties of iron pnictide superconductors

With the physical and technical introduction to ARPES in Chapters 2 and 3, we now begin to discuss the main subject of the present thesis - ARPES studies of the iron-arsenic (pnictide) superconductors. In this chapter we intend to give a brief introduction to the physical properties of the pnictides, both theoretically and experimentally. For a general overview of the whole subject, the reader is referred to two review papers by Johnston [Ref. (11)] and by Canfield and Bud’ko [Ref. (10)]. Earlier developments are best summarized in Physica C’s special issues on pnictide superconductors: Physica C: Superconductivity, Volume 469, Issue 9-12, May 2009.

Periodic Table for Pnictide Superconductors

![Periodic table of the iron pnictides](image)

Figure 4.1 Periodic table of the iron pnictides. Different colors represent different groups of elements that act as stoichiometric components or dopants.
High temperature superconductivity in iron-based layered compounds was first discovered in February 2008 by Prof. Hosono and co-workers (6), attracting unprecedented attention in the scientific community in the past three years, as they “break the tyranny of copper, offering high transition temperatures without requiring the presence of copper oxide”, quoting Ni et al (65). Among various families of the pnictides, the most extensively studied are the $R{\text{FeAsO}}_{1-x}{F}_{y}$ family (6) (“1111”, $R$ being the rare earth elements), the carrier-doped $A{E}{\text{Fe}}_{2}{\text{As}}_{2}$ family (“122”, $AE$ being Ba, Sr, Ca, etc.) (66), the $A{\text{FeAs}}$ family (“111”, $A$ being Li, Na, K, etc.) (67), the $A{\text{Fe}}_{1+y}{\left(\text{Te}_{1-x}\text{Se}_{x}\right)}$ family (“11”) (68), and the lastest discovered $A{\text{Fe}}_{2-y}{\text{Se}}_{2}$ selenide compounds (69). The highest $T_c$’s found in these families to date are 56 K (1111), 38 K (122), 18 K (111), 8 K (11) (11) and $\sim$ 30 K (selenides) (69). The 1111 and 122 series superconduct at temperatures higher than the BCS limit of about 40 K for electron-phonon interactions (70). In Figure 4.1 we show positions of the constituent elements of the Fe-based superconductors in the periodic table. The present thesis focuses on the 122 and 1111 series (check marks in Figure 4.1). We begin the discussion with their crystallographic structures, showing how their superconducting properties are sensitive to certain structural parameters; then we gradually construct their phase diagrams by introducing experimental data on the temperature-doping (external pressure) evolution of transport, thermodynamic and superconducting properties. A brief summary on theoretical models of their electronic structure and symmetry of superconductivity is also included.

4.1 Crystallographic properties

Figure 4.2 shows the crystallographic structures of the 1111, 122, 111 and 11 pnictide series. Despite the vast difference of constituents, there are important similarities among these structures. First, all of them are layered structures with a crystallographic $c$ axis much longer than the $a$ and $b$ axes [the 1111’s have similar $c$ and $a$ ($b$)]. Second, they all contain a FeAs [or more generally, MPn ($M$ = Fe, Mn, etc.; Pn = As, P)] atomic layer. Compared with the relatively flat CuO$_2$ layers in the cuprates, the FeAs layers in pnictides consists of a square lattice of iron atoms, sandwiched by As atoms located alternatively above and below the iron layer, forming tetrahedral chemical bonding. Other elements form layer or planar structures in between the
Figure 4.2  Crystallographic structures of a, $R$FeAsO$_{1-x}$F$_y$; b, $AE$Fe$_2$As$_2$; c, $A$FeAs and d, Fe$_{1+x}$Te. Black arrows in a and b show the directions of long range magnetic order obtained from neutron scattering experiments. It is seen that all iron pnictide families contain FeAs layers with tetrahedral bonding. From Ref. (11).

FeAs layers. Since the electron density of states at the Fermi level for pnictides is dominated by Fe 3$d$ orbitals, the FeAs layer is believed to be responsible for their superconducting behavior. The intrinsic three dimensionality of this layer thus gives rise to unique physical properties to the pnictides, distinct from the quasi two dimensional cuprate superconductors.

Figure 4.3 $T_c$ vs. selected structural parameters on iron-based superconductors. Pn and M stand for the pnictide (e.g. As) and the metallic element (e.g. Fe), respectively. Each data point represents a sample with an individually measured $T_c$ and crystal structure refinement. Vertical arrows indicate that superconductivity is not observed above the indicated temperature. Vertical dashed line marks the band angle for a perfect tetrahedron (109.47°). From Ref. (11).
The superconducting transition temperature $T_c$ of the pnictides may correlate with certain structural parameters. Figure 4.3 shows two of the best examples. In Figure 4.3a we see that the highest $T_c$s of the pnictides appear when the As-Fe-As chemical bonding angle is close to that of a perfect tetrahedron ($\theta = 109.47^\circ$). A mere $5^\circ$ distortion would result in total disappearance of superconductivity. Similar gross sensitivity exists in the plot of $T_c$ vs. the $z$-axis arsenic (pnictide) distance to iron (Figure 4.3b), where the optimized value is around 1.4 Å. The lattice ratio $a/c$ is also indicated earlier to be coupled with superconducting and other phase transitions (11), yet further measurements found that such a correlation only applies to a limited subset of transition metal doped pnictides (10). These correlations pointed to the possibility that the superconducting ground state in pnictides takes place within a very narrow window of physical parameters (bonding angle and pnictide height), and more importantly, superconductivity can be induced by fine tuning the structural parameters with e.g. application of mild external pressure and/or proper choice of interlayer elemental sizes.

4.2 Electronic properties

Understanding the electronic structure of a material is a need for experimental/theoretical studies on its physical properties, since a lot of useful information for the transport, thermodynamic and superconducting behavior is derived from the band structure and interactions. In this section we will focus on studies of the electronic structure of the iron pnictides; ARPES studies are not included and will be detailed in Section 5.1. Despite the differences in the crystal structure, all families of pnictide show common features in the bands and Fermi surfaces. We show this by first presenting the calculated band structure for the iron pnictide “parent compounds” - stoichiometric compounds without carrier doping. In Figure 4.4 we present the calculated electronic structures for LaFeAsO (71) and BaFe$_2$As$_2$ (72). From Figs. 4.4a,d we notice that the electron density of state at the Fermi level comes mostly from Fe $d$ orbitals, evident of the FeAs layer being responsible for their low energy excitation spectra as well as superconductivity. The next observation is that both the 1111 and 122 compound contain quasi two dimensional (cylindrical) Fermi sheets along the zone center $\Gamma-Z$ and the zone corners $M$...
Figure 4.4  Calculated electronic structures for iron pnictide parent compounds LaFeAsO [Panels a-c, from Ref. (71)] and BaFe$_2$As$_2$ [Panels d-f, from Ref. (72)] in the high temperature tetragonal state. Calculations were performed within the local density approximation (LDA) using the general potential linearized augmented plane wave (LAPW) method.  

- **a, d**, Density of states close to the Fermi level.  
- **b, e**, Band structure close to $E_F$. Dashed lines in **b** show the band location dependence of the As position along $z$.  
- **c, f**, Calculated Fermi surfaces. Different colors in the Fermi surfaces represent different Fermi velocities. Note that $\Gamma$ points are at the corners of each graph.  

This can also be seen from the $\Gamma$-$Z$ section of the band structures [Figs. 4.4b,e]: the bands along $k_z$ for both parent compounds are mainly independent of energy, except for one band that crosses $\mu$ halfway between $\Gamma$ and $Z$ in the 1111 compound, making an ellipsoid-shaped hole pocket around $Z$. From the band structure we can also see that the center cylindrical pockets are holelike, while the corner pockets are electronlike - a signature of the iron pnictides being semimetals. The sizes for the $\Gamma$ and $M$ ($X$) pockets are similar to each other, indicative of a nearly perfect nesting condition and electron-hole compensation. This observation may have very important implications for understanding the pairing mechanism, which we will discuss in the following chapters. Such quasi low dimensionality is naturally
Figure 4.5 Calculated Fermi surfaces for iron pnictide parent compounds BaFe$_2$As$_2$ (left), SrFe$_2$As$_2$ (middle) and CaFe$_2$As$_2$ (right) in the low temperature orthorhombic/antiferromagnetic state. Calculations were performed within the density functional theory framework, using the plane wave basis method with the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof. From Ref. (74).

derived from the FeAs layers being two dimensional planes, and has long been considered as an important ingredient for possible high temperature superconductivity. Compared with the high-$T_c$ cuprates who contain relatively flat CuO$_2$ layers, the tetrahedral arrangement of As atoms in the FeAs plane and thus increased hopping between layers is likely responsible for the three dimensional component in the electronic structure. This is one of the most important differences between the cuprates and the pnictides.

It is important to note that the given electronic structures in Fig. 4.4 apply only to the high temperature tetragonal (paramagnetic) phase of the pnictides. At temperatures between 100 $\sim$ 200 K the pnictide parent compounds undergo structural and magnetic phase transitions [detailed in Section 4.3], yielding a low temperature orthorhombic (antiferromagnetic) phase. The band structure changes dramatically across the phase line. Figure 4.5 shows the density functional calculation result for the antiferromagnetic phase for three 122 parent compounds. We see that the Fermi surfaces as well as the Brillouin zone shape are different from the high temperature phase, a result of the change of the space group from tetragonal ($I4/mmm$) to orthorhombic ($Fmmm$). Generally speaking, the Fermi surfaces for the antiferromagnetic phase are more complicated and three dimensional than that for the paramagnetic phase [note as first indicated by the observation of changes in the anisotropic superconducting upper critical-field
data $[H_{c2}(T)]$ between the high and low temperature phases (75)]; the cylindrical Fermi contours change to a four starlike shapes which are discontinuous along $k_z$. This shape originates from the antiferromagnetic zone boundary bisecting the $\Gamma-M$ line segment. Its crucial importance to superconductivity will be discussed in great detail in Section 5.3.

Fermi surfaces of the iron pnictides have been studied also by quantum oscillation experiments. These experiments utilize the oscillatory behavior in transport and magnetic properties [magnetization (de Haas-von Alphen effect), conductivity (Shubnikov-de Hass effect), etc.] at low temperatures as a function of strong applied magnetic field to probe the electronic structure of the sample. Compared with ARPES, quantum oscillation data is sensitive only to the extremum area of the Fermi surface cross sections perpendicular to the field direction, lacking the detailed shape information for each Fermi contours, though oscillation frequencies for different field directions give useful indications about some details of the Fermi surface shape (20; 21). The advantage of this technique is that it always probes the bulk properties of the sample and not just surface properties. Quantum oscillation studies for the 1111 and 122 parent compounds (76; 77; 78) reveal a Fermi surface structure similar to calculational results. In Ref. (76) it is found that the $\Gamma$ and $X$ Fermi contours are two dimensional and have similar shape and size. In Ref. (78) the 122 parent compounds are found to have several small Fermi pockets, consistent with calculational result for the antiferromagnetic phase. Please note that although ARPES data is consistent with results from the 122 compounds, it shows clear deviation for the 1111 systems. Such a deviation has been known from the beginning of ARPES studies on the pnictides (79), and is recently explained by a surface driven electronic structure. This will be the main subject for Section 6.2.

Upon increasing carrier concentration, the temperature of the phase transition is decreasing and the quasi two dimensional paramagnetic electronic structure is expected to prevail to lower and lower temperatures. It is an important question to ask whether or not superconductivity favors certain type of Fermi surface topology. In Section 5.3 we will show with our ARPES data that superconductivity occurs mainly in the doping region where the paramagnetic Fermi topology exist down to the lowest measurable temperature. This reveals the crucial importance
for the underlying Fermiology for the superconducting behavior in the pnictides. Here we point out one study showing the calculational Fermi surfaces for highly overdoped 122 compounds: Ref. (80).

4.3 Transport and thermodynamic properties

In this section we discuss the temperature dependent transport and thermodynamic properties of single crystal iron pnictides and how they vary as a function of doping or external pressure. We focus on results from the Ames collaboration, since ARPES studies were done on the same batches of crystals. First we would like to list the theoretical expressions for the measured transport and thermodynamic quantities. First, within the assumption of the Drude model, the DC resistivity of a metallic system can be written as (20; 21)

$$\rho = \frac{m^*}{ne^2\tau},$$  \hspace{1cm} (4.1)

where $m^*$, $n$, $e$ are respectively the effective mass, number density and charge of the electron; $\tau$ is the relaxation time (mean free time) of the electron, defined as the average time between two consecutive electron-ion collisions. Since $\tau$ is proportional to $dE/dk$, the resistivity is reversely proportional to the density of states at the Fermi level (20; 21).

Next, in a grand canonical ensemble the Helmholtz free energy $A(B,T)$ can be obtained from the partition function $Q(B,T)$ via

$$A(B,T) = -k_B T \log Q(B,T).$$  \hspace{1cm} (4.2)

The internal energy, the specific heat and the magnetic susceptibility is subsequently calculated by (73)

$$U(B,T) = -T^2 \frac{\partial}{\partial T} \left( \frac{A}{T} \right),$$  \hspace{1cm} (4.3)

$$C(B,T) = -T \frac{\partial^2 A}{\partial T^2},$$  \hspace{1cm} (4.4)

$$\chi(B,T) = -\frac{1}{B} \left( \frac{\partial A}{\partial B} \right)_T.$$  \hspace{1cm} (4.5)

In a first order phase transition, the first derivative of the free energy is discontinuous, thus the internal energy $U$ and the magnetic susceptibility $\chi$ experience a jump across the critical
Figure 4.6 Transport and thermodynamic properties of iron pnictide parent compounds LaFeAsO [left panels, reproduced from Ref. (81)] and CaFe$_2$As$_2$ [right panels, from Refs. (10) and (82)]. Data of the electric resistivity (first row), magnetic susceptibility (second row) and specific heat (third row) is shown. The pnictide parent compounds experience two phase transitions at low temperatures: a structural transition at $T_S$ from the high-$T$ tetragonal phase to the low-$T$ orthorhombic phase, and a magnetic transition at $T_N$ from the high-$T$ paramagnetic phase to the low-$T$ antiferromagnetic phase. In 1111 compounds these two transitions are separated in temperature; in 122 compounds they are equal in temperature and is first-order.
temperature. The heat capacity $C$, the second derivative of the free energy, shows a $\delta$-function anomaly at the critical temperature. We will utilize this feature to identify experimentally the nature of the phase transition(s) in the Fe-based superconductors.

We begin our discussion with the transport and thermodynamic properties of the pnictide parent compounds. In the 1111 and 122 series, the parent compounds are not superconducting. Figure 4.6 shows temperature dependence of the resistivity $\rho$, magnetic susceptibility $\chi$ and specific heat $C_p$ for two model compounds LaFeAsO and CaFe$_2$As$_2$. In LaFeAsO and other 1111 parent compounds, two separate phase transitions are observed at low temperatures. At about 155 K the crystal experiences a structural phase transition from the high temperature tetragonal phase to the low temperature orthorhombic phase, as confirmed by temperature dependent powder X-ray diffraction analysis (81); at about 143 K a second, magnetic, phase transition takes place from the high temperature paramagnetic phase to the low temperature antiferromagnetic phase (83; 84). Magnetic moments of the Fe atoms are aligned ferromagnetically along one planer crystal axis ($a$), and antiferromagnetically along another axis ($b$) (See also Figure 4.2). In CaFe$_2$As$_2$ and other 122 parent compounds, on the other hand, these two transitions happen at the same temperature, the combined transition being first order (10; 85). This fact is clearly shown in Figure 4.6, where the resistivity data shows a rapid increase followed by a large-scale downturn when the crystal is cooled below the transition temperature. Such a peak feature in the $\rho$-$T$ graph displays apparent hysteresis in temperature cycling, which is a signature of the transition being first order. Also, a discontinuous jump is unambiguously presented at $\sim$ 170 K in the magnetic susceptibility data, and a $\delta$-function-like anomaly is seen at the same temperature in the specific heat data (10). In theory, the occurrence of an antiferromagnetic ground state is controlled by the relative strength of the coupling constants between neighboring atoms (11). In fact this state (regardless of series) is predicted by first principle calculations. A spin density wave instability based on strong Fermi nesting is proposed for this state (86; 87; 88; 89), although clear first order nature of the phase transitions in the 122 parent compounds point to limitations of this assumption.

Next we examine the effect of doping in the pnictides, focusing on how these phase transi-
Figure 4.7 Structural, transport and thermodynamic properties of carrier-doped iron pnictide superconductors. **a-b**, Neutron scattering data of CeFeAsO$_{1-x}$F$_x$ at low doping levels. Data reconstructed from Ref. (91). **a**, Doping dependence of the structural transition. $T_S$ is obtained by measuring the (2,2,0)$_T$ nuclear scattering peak. **b**, Doping dependence of the magnetic transition. $T_N$ is obtained by measuring the (1,0,2)$_M$ magnetic scattering peak. In 1111 compounds, it is currently under debate whether or not the antiferromagnetic phase coexists with superconductivity (91; 92). **c-d**, Doping dependence of resistivity and magnetic susceptibility for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [from Refs. (10) and (75)]. Both the structural and superconducting transition are clearly seen. **e-g**, Transport, magnetic, X-ray and neutron scattering studies of Ba(Fe$_{0.953}$Co$_{0.047}$)$_2$As$_2$ [from Refs. (10) and (93)]. Both the structural transition at $T_S \sim 60$ K, the magnetic transition at $T_N \sim 47$ K, and the superconducting transition at $T_c \sim 17$ K are unambiguously observed. Bulk superconductivity coexists with long range antiferromagnetic order in this doping level.
tions evolve with temperature, and how superconductivity manifest itself. Figure 4.7 shows the structural, transport and magnetic properties of carrier-doped iron pnictide superconductors. For both the 1111 (Figures 4.7a-b) and 122 (Figures 4.7c-g) series, the structural and magnetic transition is suppressed in temperature with increasing doping. These two transitions are apparently coupled, since the critical temperatures $T_S$ and $T_N$ are either the same or with $T_S$ greater and similar to $T_N$ (11), the latter being the case in doped 122 compounds. In intermediate doping levels of electron-doped 122 systems (e.g. Figures 4.7e-g), superconductivity emerges before the full suppression of the phase transitions; the presence of the magnetic scattering peak (Figure 4.7g) indicates the coexistence of superconductivity and long range antiferromagnetism. As quoted from Ref. (93), although “neutron diffraction alone cannot provide direct evidence for homogeneity of antiferromagnetism, suppression of the low energy spin excitations [not shown; see Figure 4(b) of Ref. (93)] together with the reduction of the static moment provides strong evidence that antiferromagnetism and superconductivity coexist homogeneously and are in competition with one another.” In 1111 and hole-doped 122 systems, superconductivity also takes place close to the antiferromagnetic phase, yet their coexistence is not yet firmly established, partly due to doping inhomogeneities in single crystals (91; 92; 94; 95). It should be noted that such interplay between the superconducting and antiferromagnetic phase is not observed in high-$T_c$ cuprates (29), but is common in the $R$Ni$_2$B$_2$C compounds (96).

Another difference is that parent compounds of the cuprates are Mott insulators, whereas that for the pnictides are semimetals - metals that consist of a half-filled conduction band and a half-filled valence band. These two types of high-$T_c$ superconductors have distinct electronic and superconducting properties. Interaction between antiferromagnetism and superconductivity in the pnictides are extensively studied by theorists [see e.g. Refs. (90; 97; 98; 99; 100)]. We intend to leave this discussion to the following sections.

### 4.4 Superconducting properties

For both the 1111 and 122 series, superconductivity emerges for intermediate doping levels (external pressures) and subsequently disappear at higher doping levels. Based on the data from
Figure 4.8  $s^\pm$-wave superconductivity for the iron pnictides - theory and experiment.  

**a**, Schematics for the $s^\pm$-wave order parameter between the two sets of Fermi pockets. From Ref. (28). See also Figure 2.9 for comparison with other superconductors.  

**b**, Functional renormalization-group study result for two typical inter-Fermi-surface pair transfer (Josephson) processes that drive pairing (red and blue arrows). From Ref. (114).  

**c**, Functional exchange calculation for the gap value across the $k$-space. A gap smaller than zero means a $\pi$ phase shift. Calculation uses realistic coupling parameters and a temperature of 70 K. From Ref. (115).  

**d-f**, Experimental evidence for the $\pi$ phase shift. From Ref. (116).  

**d**, Experimental setup for the Nb-NdFeAsO$_{0.88}$F$_{0.12}$ loop. Magnetic flux threading the loop [(a)+(b)] is introduced by currents through a Nb toroidal coil (d). A commercial dc-SQUID (e) serves as a readout magnetometer.  

**e**, Typical data showing half integer $\Phi_0$ jumps that result solely from sign-reversal order parameter of the pnictide. $\Phi_0 = h/2e$ is the flux quanta.  

**f**, Corresponding histogram for data in e.
Section 4.3 we find that superconductivity occurs in both the paramagnetic and antiferromagnetic phases in the 122 compounds. In this section we review the theoretical and experimental studies of the superconducting properties of the pnictides, especially the superconducting gap symmetry.

Unlike the cuprates whose $d$-wave superconductivity is established long after their discovery, there has been a general consensus (with exceptions) about the gap symmetry of the pnictides since almost the beginning of the subject. Most studies believe that the pnictides have a unique "$s^\pm$-wave" gap symmetry, meaning that the phase of the superconducting gap flips by $\pi$ between the two sets of Fermi pockets, whereas the size and phase remaining constant within a single Fermi sheet [Figure 4.8a-c]. This behavior was first proposed theoretically by Mazin and coworkers (101). Based on an insufficient phonon-mediated coupling to explain the high $T_c$ values, the authors argued that the pairing interaction in the pnictides is mediated by spin fluctuations, which arise mainly due to a nearest-neighbor antiferromagnetic superexchange and a strong nesting [with vector $Q = (\pi, \pi)$] between the $\Gamma$ and $M$ Fermi pockets. Such spin fluctuations are repulsive between different Fermi sheets, therefore a sign reversal order parameter is required to cause pairing. After the initial work, extensive theoretical and experimental effort has been carried out to further study the gap symmetry. Most of them support the $s^\pm$ scenario (88; 98; 102; 103; 104; 105; 106; 107; 108; 109; 110; 111; 112; 113; 114; 115; 116), some argued against it (117; 118; 119). The first phase sensitive experiment presenting evidence for a sign reversal superconducting gap is performed by Chen et al. [Figure 4.8d-f, Ref. (116)]. In that study the authors detected the dynamic magnetic flux output of a niobium - (polycrystalline) iron pnictide loop versus the induced flux. It is remarkable that there are cases where the flux changes by one half of the flux quanta [Figure 4.8e-f]. This fact can only be explained by intergrain transport between the hole and electron pockets, i.e., a $\pi$ phase shift in the order parameter.

In an $s^\pm$-wave superconductor, the gap size between distinct Fermi pockets need not be the same. Indeed such two-gap superconducting behavior is observed by numerous experimental studies besides ARPES (120; 121; 122; 123). A summary for most published results of the
superconducting gap sizes is presented in Ref. (11), pp. 87. For both the 1111 and 122 compounds, it is found that the larger gap is about 2 ~ 3 times the size of the smaller one. From later chapters we see that such ratio is consistent with the ARPES results.

Noticeably, a number of studies point to the possibility for a “nodal $s^{±}$” state in systems without physical parameters optimized for the highest $T_c$ (124; 125; 126; 127). In such a state the gap function goes to zero at specific Fermi crossing momenta (“nodes”), in contrast to being constant along the entire pocket. In the $k_z$ direction these nodes either form a line or remain point-like. Theoretically, such a nodal state may result from exactly the same pairing mechanism as for the nodeless state. The presence of a particular case depends on the relative strength between the coupling parameters (124). These gap nodes allow for zero temperature excitation of the quasiparticles, dominating the transport and magnetic properties at lowest temperatures. They are responsible for e.g. the non-exponential temperature dependence of the London penetration depth (125) and the rapid increase of the in-plane thermal conductivity versus magnetic field (127).

The three dimensionality of the electronic structure also greatly affects the superconducting properties of the pnictides. For example, superconducting gap nodes along the $k_z$ axis for three dimensional Fermi pockets are suggested by numerous theoretical and experimental works (128; 129; 130; 131) to possibly reconcile the discrepancy between certain transport results and ARPES. It is speculated that the superconducting gap along the $k_x$-$k_z$ plane has an “applelike shape” - when the pocket has a largest $k_x$-$k_y$ intersection size, the gap is the biggest; when the intersection shrinks to a point, the gap also vanishes. This behavior does not conflict with the $s^{±}$-wave picture: after all the gap in the $k_x$-$k_y$ plane is still $s$-wavelike.

4.5 Phase diagrams

We conclude this chapter by presenting the phase diagrams for the iron pnictides. Figure 4.9 shows a number of typical examples. Compared with the famous temperature-doping phase diagram for the high-$T_c$ cuprates, the pnictides also display superconductivity in close proximity to an antiferromagnetic instability. The ordering temperatures are suppressed upon
doping (external pressure); superconductivity exists in a domelike region in intermediate doping levels (pressure). Another important similarity is that in some electron-doped cuprates (29) and pnictides, there is a region where superconductivity coexists microscopically with antiferromagnetism [Figure 4.9b,d,e], while in hole-doped compounds these two phenomena coexist much less likely [one exception is found in the phase diagram of SmFeAsO$_{1-x}$F$_x$, Figure 4.9c, constructed by muon spin rotation data (132)]. As mentioned in Section 4.3, one important differences between these two types of high-$T_c$ superconductors is that the undoped compounds of the cuprates are Mott insulators, whereas that of the pnictides are semimetals.

We begin the discussion by pointing out the similarity between the phase diagrams for carrier-doped and isovalent doped (pressure applied) compounds. In Figure 4.9a such similarity is shown by constructing a two dimensional parameter space for these two physical quantities. Linking with the remarkable sensitivity of superconductivity to certain structural parameters (Figure 4.3), it is suggested that the underlying driven force for superconductivity may be an electronic one: the optimization of e.g. the As position and the As-Fe-As bonding angle alters the electronic structure of the pnictides; superconductivity then emerges with properly tuned number of extra electrons, or alternatively, Fermi surfaces and density of states. Doping or external pressure serve as means to adjust the carrier concentration and, to some extent, structural parameters. Evidence for this argument is given in a recent report by Kimber et al. where a gross proportionality of pressure and carrier doping on adjusting the structural parameters is pointed out (136). However, universal scaling of certain structural parameters with doping or extra electron count does not exist at least in carrier-doped 122 compounds (10), casting the above argument into doubt. Despite such complication, a direct study of the electronic structure (i.e., by ARPES) is still of importance for unveiling the mechanism of superconductivity.

From Figure 4.9 it is also apparent that long range antiferromagnetism is competing with superconductivity. In intermediate doping (pressure) levels, suppression of one order parameter always accompanied by the emergence and increase of another one. Even in the rare region of coexistence, superconductivity would markedly “push” the structural/magnetic transition
Figure 4.9  Phase diagrams for various iron pnictide superconductors. a, Schematic phase diagrams for the pnictides. Acronyms: AFM - antiferromagnetism; SC - superconductivity; O - orthorhombic phase; T - tetragonal phase. b-e, Temperature-doping phase diagram of b, LaFeAsO$_{1-x}$F$_x$ [Ref. (92)]; c, SmFeAsO$_{1-x}$F$_x$ [Ref. (132)]; d, Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [Ref. (133)] and e, Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ [Ref. (134)]. f, Temperature-pressure phase diagram of BaFe$_2$As$_2$. From Ref. (135).

back to lower doping [Figure 4.9e, Ref. (134)]. More convincingly, in neutron scattering experiments one observes a suppression of the magnetic peak height when the system enters the superconducting state [Figure 4.7g, Ref. (93)]. Interesting enough, competition between superconductivity and another region in the phase diagram seems to be universal for high-$T_c$ superconductors. In the cuprates it is recently suggested, by ARPES, that superconductivity is competing with the pseudogap region (36). Such competition may be a fundamental ingredient for high temperature superconductivity.

Despite remarkable similarity, there are differences between phase diagrams of the hole-doped and electron-doped systems. We mentioned before that microscopic coexistence of superconductivity and antiferromagnetic order is not well established in hole-doped compounds.
Figure 4.10  Phase diagrams of transition metal (TM) doped BaFe$_2$As$_2$. From Ref. (10). a, $T$-$x$ phase diagrams for various dopants. b, $T$-$e$ phase diagrams for the same dopants as in a. c, $T$-$x$ phase diagrams for single valance dopants Co and Rh. d, $T$-$x$ phase diagrams for double valance dopants Ni and Pd.

Not only does the doping level changes dramatically with location on a single sample (65), there are also evidences that the two phases are separated microscopically by domain walls (94; 95). It is then an interesting question why the hole-doped systems generally have even higher $T_c$'s than the electron-doped systems. Moreover, superconductivity in hole-doped systems extend to 100% doping (e.g. KFe$_2$As$_2$ as in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ has a $T_c \sim 3$ K), compared with a high-hoping disappearance of superconductivity in electron-doped systems [e.g. $T_c = 0$ for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with $x > 0.15$]. Is the pairing mechanism between the two types of doping different? This important question needs to be answered in future studies.

There are further evidences pointing to the possibility of an electronic origin of supercon-
ductivity. In Figure 4.10 we present the phase diagrams for BaFe$_2$As$_2$ doped with various transition metals (i.e. electron doping). In a temperature-doping phase diagram, these dopants yield different onset and offset doping of superconductivity, while the trend of suppression for the structural/magnetic transition seems to share a universal scaling (Figure 4.10a). Remarkably, if we change the horizontal axis of the phase diagrams to the number of extra electrons per Fe site [for example, according to the periodic table (Figure 4.1), cobalt would give one extra electron per Fe site, while nickel gives two], the superconducting “dome” scales very well among all measured dopants (Figure 4.10b). Denoting the onset (offset) doping of superconductivity to be $x_{on}$ ($x_{off}$), we have $x_{on}$(Co) $\sim 2x_{on}$(Ni), $x_{off}$(Co) $\sim 2x_{off}$(Ni), and so on. This fact is also clearly seen by comparing Panel 4.10c with Panel 4.10d. An important implication for this observation is that superconductivity in electron-doped pnictides is linked directly with their underlying electronic structure. Within a rigid band shifting scheme (Section 3.7.4), the electron “sea level” increases twice as fast with nickel than with cobalt. It is likely that superconductivity emerges in the phase diagram when the chemical potential reaches a point where the intrinsic electronic structure experience a rapid change. Such a change is then critical for superconductivity.

Theoretical studies of the phase diagrams bring about important insights for the competition between antiferromagnetism and superconductivity as well as its pairing mechanism (90; 97; 98; 99; 100). Here we give a brief introduction to the results in Refs. (99; 100), focusing on a simple Ginzburg-Landau type approach to study the quantum critical behavior at intermediate doping levels, where the phase transition from static magnetism to superconductivity is either first order or coexist microscopically, depending on the specific compounds. In the phase diagrams, the quantum critical point corresponds to the $T$-$x$ point where the magnetic ordering temperature $T_N$ drops to zero within the superconducting dome. At vicinity of this point, the authors in Refs. (99; 100) write the Helmholtz free energy via a phenomenological Ginzburg-Landau expansion up to the fourth order,

$$A(\Delta, M) = \frac{a_s}{2} |\Delta|^2 + \frac{u_s}{4} |\Delta|^4 + \frac{\gamma}{2} |\Delta|^2 M^2 + \frac{a_m}{2} M^2 + \frac{u_m}{4} M^4,$$  \hspace{1cm} (4.6)
with a subsequent definition for a dimensionless parameter

\[ g = \frac{\gamma}{\sqrt{u_m u_s}} - 1, \quad (4.7) \]

where \( \Delta \) as a complex number and \( \mathbf{M} \) as a 3 \times 3 matrix are the superconducting and magnetic order parameters. In the case of \( g > 0 \), the transition is first order; antiferromagnetism expels superconductivity. In the case of \( g < 0 \), these two order parameters can be finite simultaneously; there exist a region where antiferromagnetism coexists microscopically with superconductivity, as is the case for Ba(Fe\(_{1-x}\)Co\(_x\))\(_2\)As\(_2\). Two key consequences for such coexistence are (1) \( dT_N/dx > 0 \), i.e. the phase line separating the antiferromagnetic and paramagnetic states has a positive slope in the superconducting region. This prediction is remarkably verified by neutron diffraction measurements [Figure 4.9e, Ref. (134)]. (2) \( d\mathbf{M}^2/dT > 0 \) for \( T < T_c \), i.e. the magnetic signal increases with temperature up to \( T_c \) and peaks at \( T_c \). Unambiguous neutron scattering data [Figure 4.7g, Ref. (93)] proves this statement.

In light of the Ginzburg-Landau model, the authors of Refs. (99; 100) perform an analytical mean-field analysis for an effective two-band model of the pnictides. Their main assumptions are (1) magnetism and superconductivity in the pnictides are resulted from \textit{interband} interaction for the same Fe \( d \)-electrons; (2) magnetism has an itinerant nature. The authors begin with the simplest case where the hole pocket and the electron pocket have exactly the same circular shape and size (complete particle-hole symmetry). In this case they found the Ginzburg-Landau expansion to have the form

\[ \delta A = A(\Delta, \mathbf{M}) - A(0, 0) = \frac{a}{2}(\mathbf{M}^2 + \Delta^2) + \frac{u}{4}(\mathbf{M}^2 + \Delta^2)^2 + \frac{u}{2}g(\theta)\mathbf{M}^2\Delta^2. \quad (4.8) \]

where, importantly, \( g(\theta) = 1 + \cos \theta \) and \( \theta \) is the phase difference between the order parameter in the hole pocket and that in the electron pocket. This quantity is proportional to the \( g \) defined in Eqn. 4.7. In a conventional \textit{s}-wave superconductor, \( \theta = 0 \) and \( g = 2 > 0 \). According to the discussion above, this allows no coexistence of magnetism and superconductivity. In an \textit{s}±-wave state, however, \( \theta = \pi \) and \( g = 0 \), meaning a system in the border between mutual phase separation and coexistence. Moreover, a solution with \( g < 0 \) is possible by adding finite
particle-hole asymmetry and ellipticity of the electron pocket, only to the $s^{\pm}$-state. For realistic values for Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$, $g \sim -0.52 < 0$.

On the overdoped side of the phase diagram, the same model suggests that the high doping offset of superconductivity links with the total disappearance of the $\Gamma$ hole pocket. By solving a set of BCS-type gap equations, the authors found that the gap size decreases dramatically in vicinity of the doping level where the central hole pockets are filled entirely with extra electrons. We will come back to this idea in much greater detail when we discuss our ARPES results (Section 5.3).

It is worth noting that this model allows determination of the pairing symmetry based on the appearance of the phase diagram, free from intricate phase sensitive experiments [e.g. Ref. (116)]. It also captures all main characteristics of a typical phase diagram [as in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$] with minimum technical complexity. In general, it endorses the idea that superconductivity in iron pnictides has an electronic origin rather than a phonon-mediated one. Limitations of this model come from the fact that all five Fe $d$-orbitals contribute to the pairing process, instead of only one hole- and one electron pocket. In the antiferromagnetic state these bands further hybridize with respect to the antiferromagnetic zone boundary, resulting in a more complicated 10-band electronic structure. The discussion on competition between antiferromagnetism and superconductivity is thus incomplete. Despite such short-comings, this model serves as a theoretical platform for discussion of our ARPES results in Chapter 5.
CHAPTER 5. ARPES studies on $AEFe_2As_2$ systems

In the following two chapters we present the main results of the ARPES studies of the $AEFe_2As_2$ (122) and $RFeAs(O,F)$ (1111) iron pnictide superconductors. For the purpose of the present thesis, we will focus on studies that the author of the thesis was personally involved, with a brief introduction on works done by other groups. We begin with ARPES results for the 122 family of compounds. Studying them as model systems for the pnictides has great advantages. Technically, single crystals of the 122 systems are easily grown using the flux method with samples measuring several square millimeters ($65; 66; 82; 75$). Experiments on larger crystals are considerably easier, yielding much more reliable and reproducible results. For the transition metal doped 122 systems, one further advantage is that the dopants spread quite homogeneously throughout the volume of the sample ($75$); contamination caused by spatial inhomogeneity is minimized. This is especially important for ARPES studies, since the typical spot size of incoming photon is from hundreds of micrometers to a millimeter. These advantages present us with the opportunity to explore the entire phase diagram with unprecedented doping accuracy, revealing doping-dependent properties that would be otherwise difficult to discover. Thanks to this, the author of the thesis was able to contribute in two aspects of the field: (1) the confirmation of three dimensionality of the pnictide electronic structure, and (2) the evidences supporting the discovery of a series of Lifshitz transitions that are linked directly to the onset of superconductivity. These works are published in Refs. ($13; 14; 15$) and are described extensively in Sections 5.2 and 5.3.
5.1 Introduction

The number of ARPES results from the 122 compounds greatly exceeded that of the 1111 systems in the literature. In this section we will review a number of important results from other groups as well as members of our group other than the author of the thesis. These studies roughly belong to three main categories: (1) ARPES on the undoped parent compounds, (2) doping evolution of the ARPES data/results, and (3) ARPES studies on the superconducting properties, especially on the gap function.

Physical properties of the undoped 122 parent compounds $\text{AFe}_2\text{As}_2$ ($\text{AE} = \text{Ba, Sr, Ca, etc.}$) are qualitatively very similar. As reviewed in Section 4.3, the high temperature tetragonal and low temperature orthorhombic/antiferromagnetic phase is separated by a simultaneous structural and magnetic transition ranging between $100 \sim 200$ K, with details depending on specific alkali metals or even the preparation procedure. ARPES studies of these systems were mainly focused on differences of electronic structure between these two phases, as well as physical interpretation of the low temperature band structures. For example, results in Refs. (137; 138; 139; 140; 141; 142; 143) reveal a band reconstruction across the ordering temperature. Fermi surfaces in the antiferromagnetic state consists of not only the original hole and electron pockets at zone center and zone corners but also four (sometimes two) bright spots close to the high symmetry points, making a typical flower-petal shape. Detailed band analysis reveal that these petallike spots are actually small hole pockets, with tops of the hole band very close to the chemical potential. Some studies even suggest that these are indications of Dirac cone dispersion in the pnictides (144), signature for massless Dirac fermions that have been observed in graphene and topological insulators, although their data quality is likely insufficient for far reaching conclusions. It should be noted here that the above studies measured only the “twinned” samples, which means that both magnetic domains with the ferromagnetically aligned in-plane moments along the $a$ and $b$ axes are measured, resulting in a combined electronic structure. Besides this, there is a number of viewpoints about the origin of these small pockets. Refs. (138; 139) suggest a band splitting scenario in which one holelike band at the zone corner ($X$ point) splits into two at the phase transition temperature. Other studies [e.g. Ref. (137)]
indicate that the small pockets come from antiferromagnetic back-bending of the Γ and X bands. These ideas are not necessarily in conflict with each other.

One ARPES study from our group (145) finds an unexpected incommensurate Fermi surface nesting at the central Fermi contours, making a typical squared shape that extends along the $k_z$ axis. This observation is consistent with a nematic electronic structure with wave vector $\mathbf{q} = \pm 2\pi/8a_{Fe-Fe}$ observed by scanning tunneling microscopy (146). Such nematic state reveals the difference in electronic structure between the crystallographic $a$ and $b$ axis, which are close in length but after all different in the low temperature phase (75). Notably, this spontaneous breaking of the tetragonal $C_4$ symmetry also results in the in-plane anisotropic physical properties, as revealed by measurements on “detwinned” samples (i.e., elimination of nematic domain walls by application of external strain) (147; 148; 149).

Unlike studies of undoped parent compounds, ARPES experiments aiming at doping dependence of the electronic properties require measurements of a number of samples at different doping levels. The limited sample accessibility is resulted in a smaller number of reports than for the parent compounds. A main question for such a study is the validity of the rigid band shift scheme, namely, the electron occupancy (doping level) controls the chemical potential, while keeping the band structure essentially unchanged (see Section 3.7.4). In Ref. (150) the authors examined the As 3$d$ core level chemical shift for the (Ba,K)(Fe,Co)$_2$As$_2$ series. They found that the core peaks shift monotonically to high binding energies with increase electron doping, strongly supporting the rigid band picture. There are also studies on the doping dependence of the three dimensionality of the electronic structure; we intend to discuss this subject in Section 5.2.

The properties of the superconducting gap are some of the most interesting subjects of ARPES studies since almost the beginning of pnictide history. On July 3, 2008 two papers (151; 152) appeared on the arXiv about the superconducting gap symmetry of Ba$_{1-x}$K$_x$Fe$_2$As$_2$, marking the beginning of this quest. Figure 5.1 shows the main results of these two papers. Based on analysis of the symmetrized energy distribution curves (Section 3.7.4), both papers concluded that the superconducting gap in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ is nodeless and $s$-wave-like, different
Figure 5.1  Superconducting gap symmetry of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ revealed by ARPES. From Ref. (151) (a-c) and Ref. (152) (d). a, Symmetrized EDCs at 15 K measured at various Fermi crossing points on three different Fermi sheets. b, Extracted Fermi surface and superconducting gap values plotted with polar coordinates. c, Three dimensional visualization of the superconducting gap size on the three observed Fermi sheets. d, Results from Ref. (152) showing similar contents with a-c.

gap values are observed for different Fermi sheets. Near the Γ point, the inner hole pocket shows a gap size of ~12 meV, about twice as that for the outer hole pocket. The corner electron pockets also has a gap of ~12 meV. The values of $2\Delta/k_BT_c$ are about 7.5 for the bigger gap, and 3.7 for the smaller one. This result indicates an intermediate coupling strength compared with the BCS value of 3.53 (Section 2.7.2) and the cuprate value of ~10. After these two papers, reports from other groups (153; 154) reproduced the study and supported their conclusions. Notably, gap symmetry studies from electron-doped Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ reveal a reversed relative size between the inner and outer Γ pockets (155). This is explained as evidence
for “an intimate connection between Fermi surface nesting and superconducting pairing”, since in this case the outer Γ pocket and the X pocket are similar in size. A recent progress in this area was the observation of $k_z$ dependence of the gap. In Ref. (156) the authors probe gap sizes for various pockets near Γ using different photon energies (i.e. different $k_z$s, Section 3.7.3). They conclude that the gaps in most pockets (except one) remain nodeless and constant for all three dimensional $k_F$ points. This result is not in conflict with the proposed $k_z$ nodes (128; 129; 130; 131), since all pockets are quasi two dimensional (cylindrical) in the doping level they measured.

Another research highlight is the observation of renormalization effects and mode coupling of the low energy electronic structure (153; 157; 158). These effects lead to apparent “kink” structure (sudden decrease of band velocity) and a drop in the scattering rate (MDC peak width) at low binding energies, similar to that found in cuprate superconductors (29; 159). There is a consensus between these reports that the typical energy scale of the kink in the pnictides is $\sim$ 25-55 meV. However, different temperature dependence and origin of this kink is suggested, rendering this issue unresolved. Possible reasons for the present conflict come from the multiband nature of the pnictides, limited momentum resolution of the facility and unsatisfactory data quality [Refs. (157; 158)].

In summary, ARPES studies on iron pnictide superconductors reveal a complicated multiband in-plane electronic structure for the 122 systems. Basic band structure include several hole pockets around the zone center Γ and two electron pockets around the zone corner X, reducing the tetragonal $C_4$ symmetry to $C_2$ within one magnetic domain. In the antiferromagnetic state these bands will hybridize to form a typical flower-petal shape. Carrier doping can be described by the rigid band shifting scheme, obeying the Luttinger summation rule (Section 3.7.4). In superconducting samples, ARPES finds a multiband, $s$-wave-like superconducting gap that remains nodeless along the $k_z$ direction. A kink structure at low binding energies is also observed, indicating renormalization and mode coupling effects in the pnictides.
5.2 Three dimensionality of electronic structure

In the following two sections we present ARPES measurement on the 122 systems that are mainly performed by the author of the thesis. In this section we report the first observation of a three dimensional electronic structure of a 122 parent compound, CaFe$_2$As$_2$. The main content of this section can be found in Ref. (14).

The dimensionality of electronic structure plays an important role in the superconductivity of solids. The cuprate superconductors have the highest known transition temperatures, and they have quasi two dimensional electronic structure. In contrast, the RNi$_2$B$_2$C family (96; 160), a filled variant of the 122 structure and another class of relatively high transition temperature superconductors, have a strictly three dimensional electronic structure (161). The situation in the iron pnictides is less clear. The 122 family share the same ThCr$_2$Si$_2$ structure as the borocarbides, and both display interesting interplay between magnetism and superconductivity. Some band structure calculations predict strong $k_z$ dispersion and three dimensional Fermi surfaces (74) in the magnetic state of the parent compounds; however, up to the point when our study (14) was published, this had not been observed by ARPES (13; 137; 151; 152; 153). On the other hand, a number of physical properties display an anisotropy that is a few orders of magnitude smaller than that found in the cuprates (65; 121; 162), which hints at a strong hopping of electrons between the layers. In terms of the pairing mechanism, most theoretical models depend on nesting between the $\Gamma$ and $X(M)$ pockets (89; 101), for which the dimensionality of the Fermi surfaces is very important.

CaFe$_2$As$_2$ shows a first-order tetragonal-orthorombic transition with a transition temperature (160 $\sim$ 170 K) depending on the growth method (82; 163; 164). Superconductivity is found when moderate (nonhydrostatic) pressure is applied, or by doping with cobalt (163), or sodium (164). Such a rich phase diagram makes CaFe$_2$As$_2$ an ideal system for studying the electronic properties of the parent compounds. It is important to note that pressure-induced superconductivity in CaFe$_2$As$_2$ attracted considerable scientific interest, although further research showed that superconductivity in CaFe$_2$As$_2$ is found only in samples subjected to nonhydrostatic pressure conditions. See Refs. (165; 166; 167; 168; 169) for details. In this study, platelike single
crystals of CaFe$_2$As$_2$ were grown out of a FeAs flux as well as Sn flux using conventional high-temperature solution growth techniques (82; 170) with typical dimensions ranging from $2 \times 2$ mm$^2$ up to $10 \times 10$ mm$^2$. Following the growth, the FeAs flux-grown samples were annealed at 500°C for 24 hours. Resistivity measurements showed a first-order tetragonal-orthorombic transition at $\sim 160$ K for the FeAs flux grown samples and $\sim 170$ K when using Sn flux. The ARPES measurements are performed at beam lines 10.0.1 (HERS) and 7.0.1 (ESF) of the Advanced Light Source (ALS), Berkeley, California, and the SIS beam line of the Swiss Light Source, Switzerland. Energy resolution was set at 20 - 30 meV; vacuum conditions were better than $5 \times 10^{-11}$ torr. All samples were cleaved in situ along the $a$-$b$ plane, yielding mirrorlike, clean surfaces. Lattice constant values from Ref. (171) are used to determine the $k$-space positions. The high symmetry points $X$ and $Z$ for both two phases (orthorhombic and tetragonal) are defined to be $[\pi/a, \pi/a(b), 0]$ and $(0, 0, 2\pi/c)$ in the tetragonal Brillouin zone, respectively, with $k_x$ ($k_{(100)}$) and $k_y$ ($k_{(010)}$) axes along the Fe-As bonds.

Fermi surface maps of CaFe$_2$As$_2$ obtained at several different photon energies in the orthorombic phase are shown in Figure 5.2 along with ARPES intensity plots and energy distribution curves (EDCs). Varying the photon energy in ARPES effectively changes the momentum offset along the direction perpendicular to the sample surface (in our case, this direction corresponds to $k_z$ - perpendicular to the Fe-As layers, see Section 3.7.3). The striking feature of Figure 5.2 is that the dispersion of one of the bands that form the $\Gamma$ pocket changes dramatically with photon energy. At $h\nu = 40$ eV, three different bands $\alpha$, $\beta$ and $\gamma$ cross the chemical potential ($\mu$) as seen in Figures 5.2e and g, and this gives rise to three Fermi surface sheets. The $\gamma$-band crosses $\mu$ again near the $X$ point, forming a characteristic flower shape of the $X$ pocket. The other two bands ($\alpha$, $\beta$) are relatively close to each other. They form two hole pockets around $\Gamma$. Similar behavior has been reported in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ (138; 140; 151; 152; 172). However, at $h\nu = 50$ eV, the top of the $\alpha$ band is located below $\mu$ and the corresponding $\alpha$ pocket disappears. The $\beta$ and $\gamma$ pockets continue to cross $\mu$ at about the same $k_F$ as for 40 eV photons (Figures 5.2c, f, and h). These data conclusively demonstrate that the electronic structure in the orthorombic phase of CaFe$_2$As$_2$ is three dimensional. On the other hand, no
Figure 5.2 ARPES data of CaFe$_2$As$_2$ low temperature orthorhombic phase (T = 12 K) for a few photon energies. a-d, ARPES intensity integrated within 10 meV about the chemical potential $\mu$ for $h\nu = 35$, 40, 50, and 60 eV, respectively. Bright areas mark the location of the Fermi surfaces. e,f, Band dispersion data along the $\Gamma$-$X$ direction for $h\nu = 40$ and 50 eV. $\alpha$, $\beta$, $\gamma$ correspond to different bands that cross $\mu$. g,h, Energy distribution curves (EDCs) for data in panels e-f over the same $k$ range.

A comprehensive study of the evolution of the $\Gamma$ and $X$ pocket with different incident photon energies is shown in Figure 5.3 for the orthorhombic phase of CaFe$_2$As$_2$. The photon energy ranges from 35 to 105 eV. The Fermi surface map along the $k_z$ direction is shown in Figure 5.3a over a range corresponding to several Brillouin zones. The $\alpha$ Fermi pocket forms an ellipsoid centered at $Z$ in the respective Brillouin zones with a $4\pi/c$ periodicity. It should be noted that the observation of $k_z$ dispersion with such periodicity clearly demonstrates that ARPES data from these samples reveals intrinsic, bulk electronic properties. In Figure 5.3b,
we extract the Fermi crossing momenta \( (k_F) \) from the momentum distribution curve (MDC) peaks at \( \mu \) for each photon energy. It is clear that only the \( \alpha \) band (black solid dots) but not the \( \beta \) and \( \gamma \) bands show a strong \( k_z \) dispersion. Almost no dispersion of the X pocket is observed, which indicates its quasi two dimensional nature. The consistency of this map with that of Figure 5.2 is better seen at Figures 5.3c-e where ARPES intensity maps are shown for three high symmetry points. At \( h\nu = 58 \text{ eV} \) \( (k_z = 16\pi) \), the \( \alpha \) band does not cross \( \mu \), while at \( h\nu = 80 \) and \( 41 \text{ eV} \) \( (k_z = 18 \) and \( 14\pi) \), all three bands form Fermi pockets.

Now we turn our attention to the high-temperature tetragonal phase of CaFe\(_2\)As\(_2\).
Figure 5.4  $k_z$ dispersion data for CaFe$_2$As$_2$ in the high-temperature tetragonal phase ($T = 200$ K). a, Brillouin zone structure in the $k_x$-$k_y$ plane for the measured range. b, Same as a but in the $k_x$-$k_z$ ($\Gamma$-$Z$) plane. c, Fermi surface maps for $h\nu = 100$ eV. d, $k_z$ dispersion data parallel to $\Gamma$-$M$ [marked by magenta arrow in panel e]. The corresponding photon energy range was 80 to 190 eV. e, Fermi crossing momenta $k_{FS}$ extracted from the data in panel d. f-i, Band dispersion data along a direction parallel to $\Gamma$-$M$ for $k_z = 18, 19, 20, \text{ and } 21\pi$ at $k_x = 0$ (corresponding to incident photon energies of $h\nu = 80, 89, 99, \text{ and } 110$ eV). The data was divided by the resolution convoluted Fermi function to reveal the dispersion in the vicinity of $\mu$.

demonstrate in Figure 5.4 the two dimensional character of the band structure in the tetragonal phase. Panel 5.4c shows the Fermi surface map at $h\nu = 100$ eV. An arrow represents the $\Gamma$-$Z$ direction along which data in panels 5.4d and 5.4e were obtained. Schematic arrangement of the Brillouin zones along in-plane and out-of-plane directions for the tetragonal phase are shown in panels 5.4a-b. Panels 5.4d and 5.4e present the actual $k_z$ intensity data integrated within 10 meV about $\mu$ as a function of $k_z$ and $k_x$ and the Fermi surface extracted using MDC peaks, respectively. The photon energy range used here is 80 - 190 eV, which corresponds to $18\pi \leq k_z \leq 25\pi$. The most important observation here is that the bands around $\Gamma$ cross $\mu$. 
Figure 5.5  Direct comparison of band dispersions for low and high-temperature phase of CaFe$_2$As$_2$. Each panel shows the EDCs in vicinity of the Γ point (black solid curve) along $k_{(110)}$ direction. High-temperature data was divided by the resolution convoluted Fermi function to reveal dispersion in the vicinity of μ. Insets show the corresponding plot of band dispersion. Data was obtained at temperatures and momenta indicated in the panels.

at all $k_z$s measured, no apparent $k_z$ dispersion is visible. For further clarification, in panels 5.4f-i, we show ARPES intensity maps divided by the resolution convoluted Fermi function for $k_z = 18, 19, 20,$ and $21\pi$, respectively. The band crosses μ for all these $k$ points, in clear contrast with the situation for the low temperature orthorhombic phase. The data in Figure 5.4 is consistent with a quasi two dimensional nature of the Fermi surface in the high-temperature tetragonal phase of CaFe$_2$As$_2$.

In Figure 5.5, we directly compare the band dispersion of low- and high-temperature phase for the two $k_z$ values that correspond to high symmetry points. The data is taken along Γ-X direction on the same sample under exactly the same experimental conditions to avoid possible complications due to scattering matrix elements or polarization of incident photons. Though the data in Figure 5.5 is taken from different samples and beam lines than that in Figure 5.3, the three dimensional nature of the low-temperature orthorhombic phase reproduces nicely. At high temperature, we divided the data by the resolution convoluted Fermi function to better
see the location of the band in the proximity of $\mu$. At low temperature, this is not necessary, as the width of the Fermi edge is much sharper than the leading edge of the peaks, and band crossings are clearly visible. At $T = 200$ K, the $\alpha$ band crosses $\mu$ at both points ($k_z = 16\pi$ and $k_z = 18\pi$, Figures 5.5a,b). At low temperature in the orthorhombic phase, the same band crosses $\mu$ at $k_z = 18\pi$ (Figure 5.5d), but is located several tens of meV below $\mu$ at $k_z = 16\pi$ (Figure 5.5c). This dramatic change of the Fermi surface shape with temperature may be the origin of the sudden but relatively small drop in the electric resistivity found by transport measurements (Figure 4.6, upper right panel) when the material is heated above the transition temperature (82, 164).

In conclusion, we have measured the in-plane and out-of-plane band dispersion for both the orthorhombic and tetragonal phase of the iron-arsenic 122 parent compound CaFe$_2$As$_2$. A number of theoretical models of the pairing mechanism and magnetic ordering in these materials are based on nesting between different sheets of the Fermi surface (89, 101). Our results demonstrate that some Fermi surface sheets are three dimensional, therefore put significant constrains on possible nesting scenarios since the degree of nesting will strongly depend on the dimensionality of the Fermi surfaces. Our finding also has important implications for understanding a number of other physical properties such as the anisotropy in electrical and thermal conductivity which depend on the dimensionality of the electronic structure.

At the same time or soon after the above work, several groups reported the three dimensionality of the electronic structure observed by ARPES (173; 174; 175) and other techniques (176). In the three ARPES studies the authors found three dimensional Fermi surfaces in not only the parent compound but also the electron-doped superconducting samples. It is clear from these studies that the iron pnictides belong to a totally different class of superconductors compared with the cuprates where a quasi two dimensional Fermiology persists for most part of the superconducting dome. Also in the ARPES reports the authors claim that the detailed arrangement of the three dimensional bands are different from our model. They found the outer $\Gamma$ pocket to be strongly $k_z$ dispersing, instead of the inner one proposed by us. These results, however, do not conflict with each other, since after all different materials (CaFe$_2$As$_2$ versus
BaFe$_2$As$_2$) are probed in different reports. On the other hand, inelastic neutron scattering (176) finds a change from three dimensional spin wave excitation to two dimensional when a 122 system reaches the antiferromagnetic phase, a phenomenon indicative of a similar change in electronic structure. Thus low dimensionality as a factor for enhancement of superconductivity is still a possible hypothesis.

5.3 Doping effects: Fermi topology as essential for superconductivity

In this section we discuss in great detail the doping dependence of electronic structure in the 122 pnictides. A series of studies were carried out by our group on both the hole and electron doped compounds. These studies lead to two main conclusions: (1) Rigid band shift scheme is valid in the doped pnictides, and (2) superconductivity in electron-doped 122 systems (as seen by transport measurements) is closely related to the underlying electronic structure. The latter point is argued based on the discovery of a series of Lifshitz transitions (irreducible change of Fermi surface topology due to carrier doping) that happen on both the low doping onset and high doping offset of superconductivity [except for the Cu-doped BaFe$_2$As$_2$ (not shown) where the low doping Lifshitz transition happens away from the superconducting dome (10)]. Superconductivity in 122 pnictides (at least in the electron doping side) is best supported by a band structure in which the $\Gamma$ and $X$ points are surrounded by non-reconstructed, quasi two dimensional hole pockets and electron pockets, respectively. We begin our discussion by demonstrating the rigid band shifting scheme.

5.3.1 Validity of rigid band shift scheme

In order to prove the validity of the rigid band shift scheme, we use ARPES to investigate the electronic properties of the parent and hole doped 122 compounds, BaFe$_2$As$_2$ and Ba$_{1-x}$K$_x$Fe$_2$As$_2$. In fact this was one of the first published ARPES results on the iron-arsenic superconductors. Our study indicates that the Fermi surface of the undoped compound BaFe$_2$As$_2$ consists of hole pocket(s) at $\Gamma$ and larger electron pocket(s) at $X$, in general agreement with a full-potential linearized plane wave (FLAPW) calculations. Upon doping with
Figure 5.6  Measured Fermi surface of BaFe$_2$As$_2$ and Ba$_{1-x}$K$_x$Fe$_2$As$_2$, compared with calculated Fermi surface for the undoped case. a, Fermi map of BaFe$_2$As$_2$ - Intensity of the photoelectrons integrated over 20 meV about the chemical potential obtained with 40.8 eV photons. Experiment was done at $T = 100$ K. Areas of bright color mark the locations of the Fermi surfaces. b, Fermi map of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with nominal $x = 0.45$ measured under the same conditions as a. c, Three dimensional Fermi surface of BaFe$_2$As$_2$ obtained from FLAPW calculations. d, Fermi surface cross section for $k_z = 0$ ($X$-$\Gamma$ plane) obtained by FLAPW calculations. e, Same as d but for $k_z = 1$ ($R$-$Z$ plane).

potassium, the hole pocket expands and the electron pocket becomes smaller with its bottom approaching the chemical potential. Such an evolution of the Fermi surface is consistent with hole doping within a rigid-band shift model. Our results also indicate that the full-potential linearized plane wave calculation is a reasonable approach for modeling the electronic properties of both undoped and K-doped iron arsenites. This result is published in Ref. (13).

In this study, single crystals of BaFe$_2$As$_2$ and Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with nominal doping $x = 0.45$ were grown out of a Sn flux using conventional high temperature solution growth techniques (65). The experimental data were acquired using our laboratory-based ARPES system (Figure
Measurements on multiple samples yielded similar results for the band dispersion and Fermi surface. All data were acquired using the He-IIα line with a photon energy of 40.8 eV (Section 3.3.1). The momentum resolution was set at 0.014 Å\(^{-1}\) and 0.06 Å\(^{-1}\) parallel and perpendicular to the slit direction. The energy resolution was 30 meV for the Fermi surface scans and 15 meV for the intensity maps. All measurements are taken at \(T = 100\) K. The FLAPW calculations (177) used the local density approximation (178) and the experimental lattice constants (66) for undoped BaFe\(_2\)As\(_2\) and potassium-doped Ba\(_{1-x}\)K\(_x\)Fe\(_2\)As\(_2\) with \(x = 0.4\). Total energy minimization was used to determine the \(z\) location of the arsenic atom \(z_{\text{As}} = 0.341c\).

The shape of the Fermi surface is normally illustrated by plotting the photoelectron intensity at the chemical potential \(\mu\) (Section 3.7.2). In Figures 5.6a-b we plot this quantity integrated within 20 meV of \(\mu\) for the undoped and potassium-doped samples. The Fermi surface of undoped BaFe\(_2\)As\(_2\) consists of a smaller circular-shaped hole pocket centered at \(\Gamma\) and larger electron pockets at \(X\) points with a characteristic “starrish” shape (more clearly seen in Figure 5.7a), in reasonable agreement with the FLAPW calculations shown in Figures 5.6c-e. In the potassium-doped samples (Figure 5.6b) one can see that the \(\Gamma\) pocket becomes larger and the \(X\) pocket decrease in size. This observation is consistent with hole doping of the material. Although there is also a variation in the intensity around the \(\Gamma\) and \(X\) pockets, it is only a signature of photoemission matrix elements and not the material itself.

In Figure 5.7 we show how the shapes of both the \(\Gamma\) and \(X\) bands evolve with binding energy as well as potassium doping. With increasing binding energy, the contour of the \(\Gamma\) pocket becomes larger - consistent with its holelike topology, while the \(X\) pocket becomes smaller - consistent with its electronlike topology. One notable fact shown in Figure 5.7 is that the size of the pockets at a binding energy 40 meV in the parent compound are similar to those of the potassium-doped compound at the Fermi level. In other words, based on a rigid-band shifting scenario, we could approximately say that the potassium hole doping lowers the chemical potential by \(\sim 40\) meV. We note also that with potassium doping the bottom of the \(X\) band is located in very close proximity to the chemical potential.
Figure 5.7 Electron intensity maps for selected binding energies of the undoped and potassium-doped samples. All data were taken at $T = 100$ K. Panels a-f present the data of undoped BaFe$_2$As$_2$, while panels g-l present the data of Ba$_{1-x}$K$_x$Fe$_2$As$_2$ with nominal $x = 0.45$. The three rows of panels present the data at the chemical potential $\mu$, binding energy $E = 40$ and 80 meV, respectively; the two columns of panels for each doping present the intensity map covering a $k$-space area near the $X$ point (a-c, g-i) and the $\Gamma$ point (d-f, j-l), respectively.

In Figure 5.8 we plot the experimental band dispersion data perpendicular to the $\Gamma$-$X$ direction along cuts through the $X$ and $\Gamma$ points (i.e., along the $k_{(1,-1,0)}$ direction). For both the $x = 0$ and $x = 0.45$ doping levels, the hole pockets at $\Gamma$ and the electron pockets at $X$ (see also Figure 5.7) are in general agreement with band calculations. Here we can examine the relative size of the hole pockets and the electron pockets in more detail by studying the Fermi crossing momenta ($k_{FS}$s) marked by darker curves in Figure 5.8c,d,h,i. These $k_{FS}$s were determined from the most intense points in the momentum distribution curves at the Fermi level. The number of $k$ curves between two $k_{FS}$s is proportional to the actual size of each pocket. The calculated Fermi surface (Figure 5.8e) of BaFe$_2$As$_2$ is quite sensitive to the $z$ location of As (179). When $z_{As}$ is changed from the experimental value to the one determined by energy minima calculations, we found that the $\Gamma$ hole pocket (shown in the middle of Figure
Figure 5.8  Band dispersion of BaFe$_2$As$_2$ and Ba$_{1-x}$K$_x$Fe$_2$As$_2$ ($x = 0.45$). a, ARPES intensity map in the $X$ region for undoped sample. b, ARPES intensity map in the $\Gamma$ region for undoped sample. c,d, EDCs for the same cuts in a and b. Curves at Fermi momenta are darker. e, Results of FLAPW band calculation for parent compound BaFe$_2$As$_2$. f-j, same content as a-e but for the K-doped compound.

5.6c) changes from a cylinder without dispersion along the $k_z$ direction (180) to a modulated cylinder with strong dispersion along $k_z$. The band structure for the doped material performed using the virtual crystal method is shown in Figure 5.8j. Clearly, in the undoped parent compound, both experiment and calculation give the $X$ pocket as larger than the $\Gamma$ pocket, whereas in the $x = 0.45$ potassium-doped samples, the opposite is the case. This effect is consistent with the idea of rigid-band shifting, namely, potassium doping lowers the chemical potential of the parent compound, while the shapes of the bands are left essentially unchanged. A second notable doping dependent feature is the energy shift of two fully occupied bands, marked by black arrows in Figures 5.8b,e,g,j. Upon potassium doping, the upper band shifts to lower binding energy by $\sim 130$ meV, while the lower band shifts to lower binding energy by $\sim 180$ meV. This fact is in qualitative agreement with the calculations. These doping dependent
features point to the conclusion that the FLAPW approximation is valid in both undoped and hole-doped iron-arsenic superconductors. Band structures of $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ can be described using the rigid band shifting scheme.

5.3.2 Lifshitz transitions in electron-doped systems - the low doping side

In light of the above study, an immediate quest would be to reveal the link between this seemingly complex electronic structure and the physical properties of the 122 systems, especially the superconducting properties. On the hole doping side, there is indication that the small flower-petal-like Fermi dots caused by magnetism persist for the entire doping range (172). Are they friends or foes to superconductivity? The observed superconducting gaps on these small Fermi dots (154) do not answer this question directly, since antiferromagnetism and superconductivity may not coexist microscopically in the hole doped systems (94; 95), the gaps may result from possible proximity effect (superconductivity penetrates through domain walls or $k$-space regions to exhibit itself in non-superconducting regions). Below we present a complete survey of the Fermi surfaces for electron-doped $\text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$ where antiferromagnetism is confirmed to coexist microscopically with superconductivity, and doping level is uniform across a given piece of sample. In this survey we measured the Fermi surface for samples from every region of the $T$-$x$ phase diagram. We conclude with clear evidence that the reconstructed Fermi dots are competing with superconductivity; their disappearance defines the low doping onset of superconductivity in the phase diagram. In other words, these hole pockets vanish - that is, the Fermi surface undergoes a Lifshitz transition (181) - as the cobalt concentration is increased sufficiently to support superconductivity. Superconductivity and magnetism are competing states in this system: when petal-like hole pockets are present, superconductivity is fully suppressed, whereas in their absence the two states can coexist. On the other hand, the high doping offset of superconductivity is marked by the disappearance of the central $\Gamma$ hole pocket. Electron doped 122 systems are solid examples of high temperature superconductors whose superconducting behavior is controlled primarily by the underlying Fermiology. In this section we begin our survey from the low doping side of $\text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$, with $0 \leq x \leq 0.114$. 
This study is published in Ref. (15). It should be noted that the low doping Lifshitz transition was first (as in publication date) observed by transport and thermodynamic measurements (182); the ARPES study was performed in the same time period, partially motivated by the transport results.

In the studies on Sections 5.3.2 and 5.3.3, single crystals of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ were grown by self-flux using conventional high-temperature solution growth techniques. The doping level $x$ for each sample batch was determined using wavelength dispersive X-ray spectroscopy in a JEOL JXA-8200 electron microprobe; the doping inhomogeneity is kept as low as $\Delta x/x < 7\%$ [Ref. (75)]. Transport and thermodynamic measurements report a tetragonal to orthorhombic structural transition with a paramagnetic to antiferromagnetic transition at $T_S \simeq T_N \simeq 135$ K for the undoped ($x = 0$) samples. Increasing the doping significantly suppresses and splits the two transition temperatures (10; 75; 93). Superconductivity appears around $x_{on} = 0.038$ and vanishes between $0.135 < x_{off} \leq 0.166$. A maximum onset $T_c$ of $\sim 24$ K was observed for the $x = 0.058$ samples (75). In Section 5.3.2, the ARPES measurements were carried out at a laboratory-based ARPES system consisting of a Scienta SES2002 electron analyser, GammaData ultraviolet lamp and custom-designed refocusing optics at Ames Laboratory, as well as Beamline 7.0.1 (ESF) of the Advanced Light Source (ALS), Berkeley, California with a Scienta R4000 electron analyser. Vacuum conditions at ALS were better than $3 \times 10^{-11}$ torr. The energy resolution was set at $\sim 25$ meV for Figures 5.9, 5.11, 5.13 and $\sim 9$ meV for Figure 5.10. All samples were cleaved in situ yielding mirror-like, clean $a$-$b$ surfaces. Cleaved surfaces of all samples were stable for at least 24 h. Results were reproduced at the ALS Beamline 7.0.1 as well as Ames Laboratory on several samples. The high symmetry point $X$ is defined to be $\left(\pm \pi/a, \pm \pi/a(b), 0\right)$ with the $k_x$ and $k_y$ axes along the Fe-As bonds.

We begin in Figures 5.9a,b by presenting the Fermi-surface maps of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ at $T = 20$ K for two extreme doping levels: $x = 0$ where antiferromagnetic order is present and $x = 0.114$ where it is fully suppressed by cobalt doping. In the undoped samples the $X$-pocket Fermi surface looks like four flower petals - high-intensity peaks are visible along the diagonal $k_{(110)}$ and $k_{(1,-1,0)}$ directions. For $x = 0.114$ samples, the $X$-pocket Fermi surface changes
Figure 5.9 The Fermi-surface reconstruction and its magnetic origin. a, b, Fermi-surface mappings of Ba(Fe_{1−x}Co_{x})_2As_2 - Intensity of the photoelectrons integrated over 10 meV about the chemical potential. Data are taken with 105 eV photons in the antiferromagnetic (x = 0) and paramagnetic (x = 0.114) phases at T = 20 K. The bright areas indicate higher intensity. The orange arrows in a emphasize the Fermi peaks along the k_{(110)} direction. c-f, Expanded ARPES intensity plots in the vicinity of the X-points for two different binding energies indicated at the top of each graph. g-j, Results of a five-band tight-binding model calculation for the same binding energies. ∆_{AF} is a measure of the antiferromagnetic order parameter; ∆_0 is a measure of the inter-orbital coupling strength.
to an oval shape and the peaks along the $k_{(110)}$ direction are absent. In Figures 5.9c-j we point out the magnetic origin of this Fermi-surface reconstruction by comparing the $X$-pocket details to the prediction of a model calculation. We use a five-band tight-binding model [See Supplementary Information in Ref. (15) for detail] with and without an antiferromagnetic order. The presence of the antiferromagnetic order is measured by mean-field order parameters $\Delta_{AF}$ and $\Delta_0$ that represent intra-orbital and inter-orbital magnetic interactions, respectively, and lead to opening of gaps in the antiferromagnetic state. The observed Lifshitz transition (detailed later) occurs only as a consequence of $\Delta_0$ and is evidence for the importance of inter-orbital magnetic interactions, which were argued to be essential for spin-fluctuation-induced superconductivity (115). The comparison shown in Figure 5.9 clearly demonstrates that the observed Fermi-surface reconstruction is consistent with the effects of a long-range antiferromagnetic order and inter-orbital coupling on the electronic structure. In the undoped sample with antiferromagnetic order, the four Fermi peaks that make up the “flower petals” appear in both the experimental data and the theoretical calculation, and they are hole-like: increasing the binding energy results in a larger size of the petals in the constant-energy cuts. In the overdoped paramagnetic state, however, these petals are absent in both the experiment and theory. The main $X$-pocket is electron-like: increasing the binding energy results in smaller pockets. We will use these features to study the effects of doping on the Fermi surface and its relation to superconductivity in electron-doped pnictides.

In Figure 5.10 we plot the ARPES Fermi-surface maps at $T = 13$ and 150 K for several different cobalt doping levels obtained with a photon energy of 21.2 eV (He-I line). It is clear that the reconstructed hole pockets are present for $x < 0.034$ at low temperatures and vanish at $T = 150$ K, above the magnetic transition temperature $T_N$. It is worth noting that the temperature dependence of the Fermi surface is not due to thermal broadening, because the low- and high-temperature data for higher doping levels are very similar. The first and most important observation in Figure 5.10 is that the small hole-like pockets vanish from the Fermi level rather rapidly at intermediate doping levels. At low temperature the intensity of those petals starts to decrease at a doping level of $x = 0.024$, and effectively the intensity has vanished
Figure 5.10 The vanishing of the Fermi-surface reconstruction coincides with the onset of superconductivity. This figure shows Fermi-surface mappings of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ for temperatures $T = 13$ and 150 K measured at various cobalt doping levels. The incident photon energy is 21.2 eV. (Note: the image slice is rotated by 45° with respect to Figure 5.9.)
Figure 5.11 Temperature and doping dependence of the Fermi surface in \( \text{Ba(Fe}_{1-x}\text{Co}_x)\text{As}_2 \) measured with 105 eV photons. Bright areas indicate higher intensity. Orange arrows in a and b emphasize the Fermi peaks along the \( k_{\langle 110 \rangle} \) direction. Panels a and e are the same as Figures 5.9a and b.
Figure 5.12 Analysis for the Lifshitz transition and the nesting condition. a, b, Maximum intensity of electrons around the X-pocket for the low-temperature data taken from a, the lab-based system and b, the synchrotron, shown as a function of an angle $\alpha$ defined in the inset. The intensities are normalized at a, $\alpha = 90^\circ$; b, $\alpha = 50^\circ$ and symmetrized with respect to $\alpha = 0^\circ$. c, $\Gamma$- and X-pocket location of the low-temperature data extracted through the peak position of the momentum distribution curves for $0.038 \leq x \leq 0.114$. The X-pocket is shifted to the $\Gamma$-pocket by rescaling the $k_{(110)}$ axis through $k' = k - \sqrt{2}$ for easier comparison of their areas.

by $x = 0.038$. This is due to the fact that the top of the hole bands moves below the Fermi energy, which is a classic signature of a Lifshitz transition (181) (see Figure 5.14c), and it coincides with the emergence of superconductivity in the phase diagram.

ARPES data consistent with this picture was also collected at a higher photon energy, corresponding to a different value of $k_z$. Figure 5.11 shows the Fermi mappings of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ measured via a linearly polarized, monochromatic synchrotron photon beam with photon energy $h\nu = 105$ eV. With a choice of the inner potential $V_0 = 15$ eV (145), the $k_z$ value for 105 eV and 21.2 eV photons differs by $10.9\pi$ (or $1.1\pi$ in the reduced zone scheme) at $\Gamma$. It is a notable
fact that no apparent difference of the Fermi surface reconstruction is observed for these two different \( k_z \) values. “Petals” and ovals are seen for antiferromagnetic and paramagnetic states, respectively, and the Fermi surface reconstruction occurs up to the doping level \( x = 0.020 \) and is gone by \( x = 0.038 \).

In Figure 5.12a,b we quantify this transition by plotting the maximum intensity around the \( X \)-pocket Fermi surface (from panels in Figures 5.10 and 5.11) as a function of the angle (\( \alpha \)) with respect to the \( k_{(110)} \) direction. Data from both two facilities is included. With hole pockets present (\( 0 \leq x \leq 0.024 \)) there is a strong peak at \( \alpha = 0^\circ \). This peak decreases monotonously with increasing doping for the data from both two facilities, and essentially vanishes by \( x = 0.038 \). Beyond this doping these small hole pockets are absent. The fact that data from the synchrotron (Figure 5.12b) shows a small peak at \( \alpha = 0^\circ \) at the doping level of \( x = 0.038 \) is due to the different scattering matrix element effective for different polarization condition of the photon beam in the two facilities (137; 183).

In Figure 5.12c we focus on the doping evolution of the nesting condition by examining the contours of the \( X \)- and \( \Gamma \)-pocket Fermi-surface sheets in the doping region where the petals are absent. For \( 0.038 \leq x \leq 0.073 \), both pockets are roughly similar in shape and size, indicating reasonably good nesting conditions. For \( x = 0.114 \), however, the \( X \)-pocket is significantly larger than the \( \Gamma \)-pocket, yet the sample is still superconducting (\( T_c = 12.8 \) K). Thus, superconductivity can exist in these materials even in the absence of perfect nesting, in contrast to what was previously suggested (155).

Neutron scattering experiments (93; 184) clearly demonstrate that long-range antiferromagnetic order coexists and competes with superconductivity beyond \( x = 0.04 \), and probably extends up to \( x = 0.06 \). Indeed, in ARPES data (Figure 5.13) the reconstruction of the electronic structure is observed up to \( x = 0.058 \), but only at higher binding energies. As the doping increases beyond \( x = 0.03 \), the small hole pockets disappear and superconductivity can take place even in the antiferromagnetic state. In Figure 5.13, the electronic structure of \( \text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2 \) for different Co doping levels and binding energies at \( T = 20 \) K is presented. It is clear that the electronic structure reconstruction due to presence of the magnetic order is
Figure 5.13  Doping and binding energy dependence of the electronic structure in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$. Data is taken with 105 eV photons at $T = 20$ K. Doping values are indicated at the top of each column and energy values with respect to $E_F$ are shown to the left of each row. Note that at the doping level of $x = 0.058$ where superconductivity is present with the antiferromagnetic order, the electronic structure reconstruction due to the antiferromagnetic order is present at higher binding energies ($E_b > 60$ meV) but not at the Fermi level. This fact is indicated by orange arrows in the figure.
seen up to $x = 0.058$, where antiferromagnetism is coexisting with superconductivity, and the crystal undergoes a magnetic transition at $\sim 30$ K (75), above the measurement temperature of 20 K. Such a reconstruction presents itself as a typical band back-folding effect, forming hole bands around the $X$-point at higher binding energies. Therefore the ARPES intensity maps for the $x = 0$ and $x = 0.058$ samples are very similar at binding energies $E_b > 60$ meV. The important fact is that this effect is absent at the Fermi level for the superconducting samples. Typically for $x = 0.058$ ($T_c \sim 24$ K), the bright peaks at $E_F$ along the $k_{(110)}$ and $k_{(1,-1,0)}$ directions are absent, in sharp contrast with the Fermi surface topology for the undoped sample. This observation fully verifies the main argument of the paper that maintaining the paramagnetic-like electronic structure at the Fermi level at low temperatures is a critical ingredient for superconductivity in the electron-doped iron pnictides. The fact that the hole bands along the $k_{(1,-1,0)}$ direction exhibit a much more pronounced hole-like dispersion and seem to undergo the transition at higher doping suggests a noticeable (but not crucial) difference between the actual data and the present theoretical model, and implies that the $k_{(110)}$ pockets are linked closer to the rapid change in transport properties and the onset of superconductivity. Further theoretical investigation is needed for explaining this interesting observation.

Our ARPES results verified the hypothesis of a Lifshitz transition inferred from Hall effect and thermoelectric power (TEP) measurements (182) as well as more general trends in the Hall effect data (185; 186). In Figure 5.14a we plot the Hall coefficient $R_H$ as a function of doping at $T = 25$ and 150 K [Ref. (182)] measured on samples from the same batch as those used for the ARPES measurements. We compare this with the maximum ARPES intensity of the reconstructed Fermi surface at the chemical potential (defined in the caption) for the data from both the helium lamp and the synchrotron, which is a way to quantify the changes in the Fermi-surface topology. The two ARPES data sets are qualitatively consistent with each other. From the helium lamp data, one can observe that not only does the change in the above-defined ARPES intensity correlate with the marked increase in the Hall coefficient, it also coincides with the onset of superconductivity at $0.024 < x < 0.028$. In a similar
Figure 5.14 Summary of the Lifshitz transition at low doping. a, Left axis: the $a$-$b$-plane Hall coefficient $R_H \equiv \rho_H/H$ versus $x$ of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ with magnetic field $H = 90kOe$ \parallel c, $T = 25$ and 150 K [Ref. (182)]. Right axis: ARPES intensity $I_{\text{ARPES}}$ at $\alpha = 0^\circ$ extracted from both helium lamp and synchrotron data, minus $I_{\text{ARPES}}$ at $x = 0.114$. b, Schematic phase diagram of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ based on ARPES and transport measurements (182). Both the magnetic transition temperature $T_N$ and the onset temperature of superconductivity are determined by resistivity measurements. c, Schematic band dispersion for three different doping levels at the vicinity of the $X$-point. In the antiferromagnetic state ($0 < x < 0.058$) the electron bands and hole bands fold back onto each other, and hybridize because of the existence of inter-band coupling. The Lifshitz transition takes place when the tip of a hybridized band sinks below the Fermi level because of increasing electron occupation.
manner to the Hall coefficient, the TEP [Ref. (182)] (not shown) changes abruptly with doping between $x = 0.02$ and $x = 0.024$ (right at the onset of the changes in the Hall coefficient) for a surprisingly wide range of temperatures ($T_c < T < 300$ K). This implies that TEP is much more sensitive to the underlying electronic properties. The current ARPES data does now show a abrupt change of Fermi topology between different doping levels at 150 K. This disagreement needs to be reconciled with future studies. The Hall effect and TEP measurements together set a finer range for the Lifshitz transition as they reflect the effects of the electronic structure on the macroscopic physical properties of the sample. It is also noteworthy that other electron-doped 122 systems show essentially the same phase diagram as that of the cobalt-doped samples (187; 188) and similar changes in Hall coefficient and TEP are also observed [for Cu-doped BaFe$_2$As$_2$ (Ref. (187)) and for Ni-doped SrFe$_2$As$_2$ where the onset of the Hall coefficient and TEP anomaly also occurs right at the onset of superconductivity (188)]. This suggests that the Lifshitz transition reported here is a general property for the electron-doped 122 systems. It is not clear whether or not this conclusion can be extrapolated to the hole-doped side of the phase diagram. On one hand, assuming a simple rigid band shift, one would expect the petals to be present in the hole-doped 122 system and indeed they were observed by ARPES in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ [Refs. (140; 154)]. On the other hand, the situation in Ba$_{1-x}$K$_x$Fe$_2$As$_2$ is significantly complicated by spatial inhomogeneity (154) and evidence from local probes (for example, nuclear magnetic resonance) suggests that antiferromagnetism and superconductivity are microscopically separated (94; 95). In this case the impact of down folding on the superconducting state is not an issue and superconductivity is suppressed at low hole doping by the emergence of a first-order phase boundary between the two states (99). The question of why superconductivity is compatible with the petals in the hole-doping regime is an important one and requires further detailed experimental investigation.

We summarize our main findings in Figure 5.14b, where we plot the locations of each ARPES spectrum on the $x$-$T$ phase diagram. Figure 5.14b shows that the emergence of superconductivity in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ coincides with the disappearance of the reconstructed pieces of the Fermi surface. Our observation explains that the changes in Hall coefficient, namely the
rapid increase of $R_H$, are caused by rapid changes of the Fermi-surface topology with doping. As shown in Figure 5.14c, a Lifshitz transition takes place at a doping level close to the emergence of superconductivity, when the hybridized petal-like hole pockets fill up because of an increase in electron occupation. Long-range magnetic order has a particularly strong impact on the pairing interaction in the case of unconventional superconductivity because of magnetic fluctuations. The pairing interaction resulting from spin fluctuations on the reconstructed Fermi surface is reduced because of the requirement that the quasiparticle-induced spin wave damping vanishes at the ordering vector ($q_{\text{ord}}$). In the context of the pnictides, this effect leads to the reduced pairing interaction of the magnetically ordered state because the modified wavefunctions in the magnetically ordered state couple less efficiently to magnetic fluctuations (98). This effect is strongest for large magnetization with pronounced down folding and demonstrates the sensitivity of an electronic pairing mechanism with respect to an antiferromagnetic Fermi-surface reconstruction. The finding of the present study demonstrates that avoiding the Fermi-surface reconstruction may be the key to establishing the superconductivity in electron-doped iron arsenic high-temperature superconductors.

*Note:* Subsequent data analysis on the Fermi maps taken from the ALS (Figures 5.9, 5.11, 5.13) reveals signal of magnetic reconstruction even for high temperature (150 K) measurements at doping levels ranging from $x = 0$ to $x = 0.059$. At 150 K, such reconstruction is absent at the Fermi level, but is clearly resolved for binding energies $E_b > 50$ meV. This effect is first observed in Ref. (140); the authors argued against “any direct connection between the observed Fermi surface topology and the static magnetic order” based on this observation. We argue here that the persistence of band reconstruction at high temperature may result from magnetic fluctuation that was claimed to exist up to room temperature [see e.g. Ref. (190)]. This statement is supported by the ARPES observation of strong itinerant spin fluctuations in the normal state of CeFeAsO$_{0.89}$F$_{0.11}$ (191). As a result, our conclusion of the magnetic origin of the Fermi reconstruction remains valid.
5.3.3 Lifshitz transitions in electron-doped systems - the high doping side

The study in Section 5.3.2 reveals that superconductivity emerges at a doping level ($x_{on}$) where a topological change of the Fermi surface [Lifshitz transition (181) at doping $x_1$] reduces the magnetically reconstructed Fermi surface to its paramagnetic appearance, i.e. $x_1 \simeq x_{on}$. This transition exhibits itself as a rapid change of Hall coefficient and thermoelectric power in transport measurements (182). An immediate question is whether we can observe a similar change of Fermiology in the high-doping offset of superconductivity. It is likely that the hole pockets surrounding the central axis of the Brillouin zone ($\Gamma$-Z) will shrink in size and inevitably vanish at some higher doping $x_2$. The question is whether this Lifshitz transition happens before, after, or right at the offset of superconductivity ($x_{off}$). Based on a solution of the two-band BCS gap equations assuming only interband coupling, Fernandes and Schmalian (100) showed that the disappearance of superconductivity is directly linked to the vanishing of the central hole pocket(s), i.e. $x_2 \simeq x_{off}$. Experimentally, Hall coefficient and TEP vs. temperature on Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ (185) experiences a change of base slope around $x_{off}$, hinting at a possible Lifshitz transition close to the offset of superconductivity.

Below we show a systematic ARPES study on Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ for $0.073 \leq x \leq 0.42$. This study is posted on the arXiv in Ref. (16). Along with the study in Section 5.3.2 we performed a complete survey of the electronic structure of this material on 15 different doping levels ranging from $x = 0$ to 0.42. This survey reveals that topological changes of the Fermi surface link directly to superconductivity in electron-doped pnictides. In the overdoped side, superconductivity starts to suppress in temperature around the doping level ($x_{2\Gamma}$) where the cylindrical hole pocket surrounding the zone center ($\Gamma$-Z) changes to ellipsoids centering at $Z$. The vanishing of superconductivity happens before the disappearance of $Z$-ellipsoids at $x_{2Z} \sim 0.2$. In short, we found that $x_{2\Gamma} < x_{off} < x_{2Z}$. This finding reveals that the underlying Fermiology is essential for superconductivity in this class of materials. A necessary condition for superconductivity is the existence of the central hole pockets rather than a perfect nesting between the $\Gamma$ and $X$ pockets. Superconductivity in electron-doped iron pnictides is consistent with a inter-band coupling picture (100).
Figure 5.15 Fermi maps and band dispersion around the upper zone edge $Z$ of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ for $x = 0.073$ (optimal doping), $x = 0.166$ (edge of superconducting dome) and $x = 0.42$. Upper Row: Fermi mappings for the three doping levels, taken with incident photon energy $h\nu = 35$ eV at temperature $T = 20$ K. Red arrows show the exit slit direction of the hemispheric analyzer and the cutting direction of the band dispersion maps (Lower Row). The same direction is also used in Figure 5.16.

In this section, the ARPES measurements were performed at Beamline 10.0.1 (HERS) of the ALS, using a Scienta R4000 electron analyzer. Vacuum conditions were better than $3 \times 10^{-11}$ torr. The energy resolution was set at $\sim 25$ meV. All samples were cleaved in situ yielding mirror-like, fresh $a$-$b$ surfaces. High symmetry points were defined the same way as in Section 5.3.2.

To get a general idea of this Lifshitz transition, we begin by showing in Figure 5.15 the ARPES Fermi maps and corresponding band dispersion data for three different doping levels of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$. Direction of the band dispersion maps is perpendicular to the exit-slit because the ARPES intensity of the $Z$ electron pocket along the exit-slit direction is suppressed by the transition matrix element. The incident photon energy is $h\nu = 35$ eV, corresponding to $k_z \simeq 2\pi/c$, the upper edge of the first Brillouin zone ($Z$) (145). From Figure 5.15 it is clear that
Figure 5.16  Band location analysis for the Lifshitz transitions at high doping levels - Z intersection. a-i, Band dispersion maps along the direction shown in Figure 5.15 for six different doping levels (top of each column) at low and high temperatures (left of each row). All data is taken with 35 eV photons. The high temperature data is divided by the resolution convoluted Fermi-Dirac function for better pinpointing the band positions above the Fermi level. The red vertical line indicates that a Lifshitz transition happens between \( x = 0.195 \) and \( x = 0.27 \) at \( Z \). j, Energy distribution curves (EDCs) at \( Z \) for the doping levels in panels a-i. Measurement temperature is \( T = 20 \text{ K} \) unless specifically mentioned in the graph.
as electron doping increases, the Fermi contours around $Z$ first shrink in size. At $x = 0.166$, the edge of the superconducting dome, the $Z$-pocket becomes almost a single point, meaning a complete closing of the hole pocket. This observation is consistent with the data in Refs. (175; 192). As more electrons are doped in, the $Z$ pocket expands again, yielding a diamond shape at $x = 0.42$ (the intensity in two edges of this “diamond” is suppressed due to the dipole matrix element). Band dispersion clearly reveals that this “diamond” is electron-like. Such an electron pocket is not expected by band structure calculations (185). The $X$ pocket, on the other hand, keep expanding from $x = 0.073$ to $x = 0.42$, its carrier nature remaining electron-like. The central message of this figure is that the $Z$-pocket undergoes a drastic topological change from hole-like to electron-like at roughly the high doping offset of superconductivity.

Based on this observation we perform two independent procedures of data analysis with finer doping steps to further pinpoint the doping level at which the Lifshitz transition takes place.

The first procedure to obtain a more accurate value for $x_2$ is to extract the energies for the hole band top and the electron band bottom, and examine them as a function of cobalt doping. As shown in Figure 5.16, we plot the band dispersion maps along the same direction as in Figure 5.15 for six different doping levels ranging from $x = 0.166$ to $x = 0.42$. This gives us a comprehensive picture on how the $Z$-pocket evolves as a function of doping. Combining with the energy distribution curves (EDCs) in Figure 5.16j, we see that both the hole band and the electron band shift to higher binding energies as more electrons are doped in, the shape of these bands remaining the same during the process. Note that in Figure 5.16j the $x = 0.166$ and $x = 0.195$ high temperature data is divided by the Fermi function in order to better locate the band positions above $E_F$. There is a small gap ($\sim 25$ meV) between these two bands, as revealed in e.g. the $x = 0.27$ data in Figure 5.16j where two peaks are clearly visible. At $0.195 < x < 0.27$ the bottom of the electron band evolves above the Fermi level, defining the Lifshitz transition (see also Figure 5.18a). Figure 5.16 send us a clear message that, at the $Z$ intersection of the Brillouin zone, the Lifshitz transition takes place at $0.195 < x_{2Z} < 0.27$, higher than $x_{off} \sim 0.15$.

Intrinsic three dimensionality of the electronic structure (14; 173; 174; 175) results in dif-
Figure 5.17  Band location analysis for the Lifshitz transitions at high doping levels - Γ intersection. a-j, Band dispersion maps along the direction shown in Figure 5.15 for seven different doping levels (top of each column) at low and high temperatures (left of each row). All data is taken with 49 eV photons. Insets in f and g show increased contrast for better revealing the bands near $E_F$. The high temperature data is divided by the resolution convoluted Fermi-Dirac function. The red vertical line indicates that a Lifshitz transition happens between $x = 0.073$ and $x = 0.166$ at Γ. k, Energy distribution curves (EDCs) at Γ for the doping levels in panels a-j. Measurement temperature is $T = 20$ K.
Figure 5.18 Evolution of binding energy for the top of the hole band and the bottom of the electron band with respect to cobalt doping. Data is extracted from ARPES intensity maps taken with a, 35 eV and b, 49 eV photons, corresponding to $k_z$ values of Z and $\Gamma$ points, respectively. Data points in a are extracted from the EDCs at Figure 5.16 by fitting with two Lorentzian functions (times the Fermi function for low temperature data). Data points in b are extracted the same way from the EDCs at Figure 5.17 except for the lowest doping where a parabolic function is fitted to the MDC peaks at 5.17a to reveal the hole band top above $E_F$.

We note that this doping level corresponds to the onset of $T_c$ decreasing in the phase diagram. This observation also supports the theoretical prediction that three dimensionality of the Fermi surface makes a more gradual decrease of $T_c$ in the overdoped side (100).

In Figure 5.18 we summarize the data from both the Z and $\Gamma$ intersection. Data taken with 35 and 49 eV photons is extracted by fitting two Lorentzian functions to the EDCs shown in Figures 5.16 and 5.17, respectively, except that we use a parabola fitting to the MDC peaks of the 49 eV low temperature data to estimate the top of the hole band above $E_F$, since the Fermi function divided high temperature data (Figure 5.17) is generally too noisy. The linear behavior of the band locations again confirms the validity of the rigid band shifting scheme.
Figure 5.19 Pocket size analysis for the Lifshitz transition at upper zone boundary Z. a, Z pocket extraction for seven doping levels, done by fitting the momentum distribution curves (MDCs) at the chemical potential with several Lorentzian functions. Positions of hollow circles are symmetrized from experimental data points (solid circles), proposing the band positions where ARPES intensity is suppressed by the transition matrix element. b, Evolution of Z pocket area with cobalt doping. Green shaded area indicates the boundary of the superconducting dome. c, Visualization of the Lifshitz transition. Data in a is plotted against the cobalt doping $x$ as a third dimension. Shaded areas are approximate size and shape of the pockets. Panels b and c show a Lifshitz transition at $x_{2Z} \sim 0.2$. 
From Figure 5.18, we estimate based on a linear fit to the band locations that, the top of the hole band also evolves below the Fermi level at $\sim 0.18$ at $Z$, and $\sim 0.11$ at $\Gamma$. At a slightly higher doping the bottom of the electron band evolves below $E_F$, changing the carrier nature of the central pocket from holelike to electronlike. Compared with the doping level $x_{\text{off}}$ at which superconductivity disappears, we conclude that $x_{2\Gamma} < x_{\text{off}} < x_{2Z}$. A necessary but not sufficient condition for superconductivity in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ is the existence of the central hole pocket.

In Figure 5.19 we perform a pocket size analysis at $Z$ to further pinpoint $x_2$. This second procedure is independent from the above energy extraction method. To do this we first find the $Z$ pocket location for seven doping levels (ranging from $x = 0.073$ to $x = 0.42$) by fitting the momentum distribution curves (MDCs) at the chemical potential with several Lorenzian functions. From Figure 5.19a we see a clear evolution of the $Z$ pocket size with doping. As $x$ increases, the hole pocket shrinks in size up to $x = 0.195$, then it expands again as an electron pocket up to the highest doping measured. As seen in Figure 5.19b, both the hole and electron pocket size evolves in a linear fashion, a signature of the validness of the rigid band shifting scenario (13; 150), and of the pockets being paraboloids in shape. The cross-over takes place around $x = 0.2$. This Lifshitz transition is best visualized in Figure 5.19c where data in Figure 5.19a is plotted against the cobalt doping $x$ as a third dimension. This figure reveals that, as cobalt is doped in, the electron sea level rises and the $Z$ hole bands gradually sink. At $x \sim 0.2$ the total occupation of the outer hole band marks the Lifshitz transition. Beyond this point the $Z$ pocket changes to electron-like, and superconductivity vanishes. One may argue, however, that there are at least two hole bands surrounding $Z$ at low doping levels, and the Lifshitz transition marked by the vanishing of the inner hole pocket might weaken the present interpretation. We argue based on Figure 5.19c that the outer hole pocket has much closer relation to superconductivity in electron-doped pnictides. One supporting observation is that the strong pairing strength switches to the outer hole pocket in Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ (155).

Figure 5.20 summarizes the main finding of the present study along with that in Section 5.3.2. In these two studies we performed a systematic ARPES survey on the Fermi surface
Figure 5.20 Summary for the Lifshitz transitions. a, location of the known Lifshitz transitions in the phase diagram. $T_N$ and $T_c$ data is taken from Refs. (75) and (15). Left insets (A-E) show schematic Fermi surface topology for each region in the phase diagram, out of which Fermi configurations B-D supports superconductivity. b, Thermoelectric power vs. doping for four different temperatures. Lifshitz transitions exhibit as sudden jumps of changes of slope.
topology of Ba(Fe\textsubscript{1−x}Co\textsubscript{x})\textsubscript{2}As\textsubscript{2} for 0 ≤ x ≤ 0.42, covering all regions of the phase diagram. The most important finding of this survey is that the onset and offset of the superconducting region is closely linked to topological changes of the Fermi surface. Excellent agreement with this finding is shown in the thermoelectric power vs. doping curves for several temperatures [Figure 5.20b, see also Ref. (182)] in which “jumps” or changes of slope occur right at each proposed Lifshitz transition: \(x_1 \simeq 0.03\), \(x_{2\Gamma} \simeq 0.11\) and \(x_{2Z} \simeq 0.2\). At the doping range of \(0 < x < 0.03\), the Fermi pockets experience a significant reconstruction caused by long range antiferromagnetic order. Both \(\Gamma(Z)\) and \(X\) points are surrounded by central contour(s) plus four petal-like small hole pockets. Such Fermi surface configuration do not support superconductivity (Section 5.3.2). At \(x \simeq 0.03\), electron doping causes the petal-like pockets to sink below \(E_F\), reducing the Fermi topology to its paramagnetic appearance - the \(\Gamma(Z)\) pockets are hole-like, and the \(X\) pockets are electron-like. At about the same doping level, superconductivity emerges in the phase diagram. \(x_1 \simeq x_{\text{on}} \simeq 0.03\) marks the first Lifshitz transition that defines the low doping onset of superconductivity (Section 5.3.2). At the doping range of \(0.03 < x < 0.11\), superconductivity persists and no relevant transition is found. The antiferromagnetic reconstruction shifts to higher binding energy until it disappears at the boundary of antiferromagnetism, \(x \sim 0.06\). Microscopic coexistence of superconductivity and antiferromagnetism is allowed as long as the Fermi surface appears to be paramagnetic-like.

The region of \(0.11 \leq x < 0.2\) is where the second Lifshitz transition occurs on the high doping side of the superconducting dome. This transition happens first at the \(\Gamma\) cross-section of the three dimensional Fermi surface \(k_z = 0\) at \(x_{2\Gamma} \simeq 0.11\) when the shape of the quasi-cylindrical outer Fermi contour changes to an ellipsoid centered at \(Z\). As doping increases, this \(Z\) ellipsoid shrinks in size until it disappear altogether at \(x_{2Z} \simeq 0.2\). On the other hand, superconductivity vanishes at \(x_{\text{off}} \simeq 0.15\). At \(x > 0.2\), the region of the highest doping, the central pocket changes to electron-like, and superconductivity does not exist.

Importantly, the above conclusion can most likely be applied to other electron doped 122 systems. We are specially interested in \(AE(\text{Fe}_{1-x}\text{Ni}_x)\textsubscript{2}\text{As}_2\) where each nickel atom gives two extra electrons per Fe site compared to one in the cobalt doped system. There, similar to
the cobalt doped system, the Hall coefficient and thermoelectric power anomaly occurs right at the onset of superconductivity (15; 188). Based on a similar ARPES survey (not shown) we indeed find Lifshitz transitions at close vicinity to the boundaries of superconductivity, the only difference being that the corresponding doping levels are roughly one half as those of the cobalt system. As the phase diagram changes to $T$ vs. $\epsilon$, the extra electron count, these two systems match perfectly.

Our finding has important implications for understanding of the nature of superconductivity in the pnictides. First, our observation reveals the crucial importance of the underlying Fermi surface topology: a necessary condition for the emergence of superconductivity is the existence of the non-reconstructed central hole pockets rather than a perfect nesting condition for the central and corner pockets. Superconductivity in not supported only if either one set of these pockets vanishes or changes its carrier nature. Second, our result implies that the suppression of superconductivity in the underdoped side is related to the competition between the antiferromagnetic and superconducting phases (10), whereas in the overdoped side it is due to the disappearance of the central hole pocket rather than the decrease of the pairing interaction magnitude (100). This finding supports similar statements made based on thermodynamic and transport measurements (9; 10; 187). Electron doped 122 systems are, therefore, solid examples of high temperature superconductors whose superconducting behavior is controlled primarily by the underlying Fermiology.

5.4 Discussion and outlook

As discussed in this chapter, our ARPES studies on electronic structures of the 122 pnictides point to an electronic origin of the pairing mechanism. On the electron doping side, the universality of the superconducting region in the $T$-$\epsilon$ phase diagram and the discovery of Lifshitz transitions bracketing the superconducting region strongly support this idea. Rapid changes in the Fermi surfaces and transport parameters can be readily explained by electron filling of the bands. Naively, one would imagine that the same idea can be applied to the hole doping side, since the electronic structure of the 122 systems are highly symmetric for electron and
hole doping: the parent compound Fermi pocket size and shape is very similar at the zone center and zone corner, which are evolved in a similar manner for hole and electron doping. However, there are apparent differences between the phase diagrams for the hole and electron doped systems. Particularly, the superconducting region in the hole doping side extends to the 100% doped KFe$_2$As$_2$ system, in sharp contrast with the electron doping side. In an ARPES study of KFe$_2$As$_2$ (172), one even observes the flower-pedal-like Fermi dots near the X point. As we have seen in Section 5.3.2, these features have a clear magnetic origin and are thought to be pair-breaking. It is therefore mysterious why they appear in a nonmagnetic compound and coexist with superconductivity. Similar features also appear in the near optimally doped samples (154), where one even observes a superconducting gap at those “pedals”. Further detailed studies are in need to explain such discrepancy.

Another promising route to explore the electronic structure of the 122 systems is by measuring the isovalent doped compounds. Special attention should be given to these systems because they likely mimic the effect of external pressure (193) as another means of adjusting the sensitive crystallographic parameters, thereby defining the third axis in the phase diagram (Figure 4.9a). At the present stage, the most studied isovalent doped systems are $AE$Fe$_2$(As$_{1-x}P_x$)$_2$, where phosphor substitutes for arsenide, and $AE$(Fe$_{1-x}$Ru$_x$)$_2$As$_2$, where ruthenium substitutes for iron. Both systems have reasonably high $T_c$s with phase diagrams similar to the electron doped ones (194; 195; 196). For BaFe$_2$(As$_{1-x}P_x$)$_2$, quantum oscillation experiments reveal a doping evolution of Fermi surface nesting condition resembling that for the cobalt doped samples (197). Importantly, the reduction of the c-axis length as well as pnictogen height and increase of the inter-layer hopping due to phosphor substitution may lead to more three dimensional Fermi surfaces (198) and even the existence of line nodes in the superconducting gaps, as indicated by various transport, magnetic (199; 200) and nuclear magnetic resonance (201) experiments. These observations raise immediate question on whether the carrier doping and physical/chemical pressure induced superconductivity share the same pairing mechanism. For Ba(Fe$_{1-x}$Ru$_x$)$_2$As$_2$, one ARPES study (202) reports that hole and electron pockets are twice as large compared to the carrier doped compounds, indicative of a “substantial reduction of
the band renormalization. Systematic surveys of the electronic structure of these systems, like the one we presented in Sections 5.3.2 and 5.3.3, would surely give important constraints on possible pairing mechanism for the pressure induced superconductivity in the pnictides.

The three dimensional temperature-doping-pressure phase diagram does not stop only on the axes. There is a huge, essentially unexplored territory in which both physical/chemical pressure and carrier doping are applied to the stoichiometric parent compounds. As for a possible next step project, it is instructive to synthesize these compounds and preform ARPES (and any other type of) measurements on them. For example, does a similar superconducting dome exist in Ba(Fe$_{1-x}$Co$_x$)$_2$(As$_{1-y}$P$_y$)$_2$? If so, what are the implications for its pairing mechanism? Answers to these important questions may pave way to a full understanding of the interplay between various external/internal parameters and the superconducting/magnetic behaviors in the second family of high temperature superconductor ever discovered.
CHAPTER 6. ARPES studies on $R$FeAs(O,F) systems

In this chapter we focus on ARPES studies for the $R$FeAs(O,F) (1111) systems performed mainly by the author of the thesis. Compared with the 122 systems discussed in the last chapter, ARPES studies on the 1111 systems are difficult due to both technical and physical problems. Technically, large (millimeter-sized) single crystals were not available until recently [successful growth reported by Yan et al., Ref. (203)], causing a low success rate of sample preparation and handling process. In some of our first experiments, the sample size we used are no bigger than $200\mu m \times 200\mu m$, far beyond the reach of the smallest tweezers commercially available. This extra difficulty is, we believe, the main reason for a much smaller number of publications compared with that for the 122s. Physically, as will be discuss in detail in this chapter, the 1111 systems experience surface relaxation and/or reconstruction much stronger than the 122 compounds. These surface effects lead to a surface-driven electronic structure different from the bulk. This fact was revealed from our ARPES studies (17) as well as results from other groups, which is the main subject of Section 6.2. Understanding the relation between the two types of electronic structures is a prerequisite for further ARPES investigations on the 1111 systems.

There are even less ARPES studies on the superconducting properties of these systems. To our best knowledge, the only published ARPES observation for the momentum dependence of the superconducting gap is done by members of our group (204). An $s$-wave-like gap of $\sim 15$ meV was reported in that study, putting the 1111 systems in the class of strongly correlated materials. In Section 6.2 we will also discuss briefly this result.
6.1 The first ARPES attempts

Despite the difficulties, successful ARPES electronic structures of the 1111 systems was obtained only a few months after their discovery. Two independent studies were posted on the online arXiv at roughly the same time. In the paper by Lu et al. [Ref. (205), later published in Nature], the Fermi maps of the phosphor-based parent compound LaFePO was experimentally observed for the first time (Figure 6.1). It was found that its Fermi surface contains several central hole pockets and corner electron pockets. In the other paper posted by our group [Ref. (18), which was finally published in a later review article, Ref. (19)], measurements were taken on a true high temperature superconductor NdFeAsO$_{1-x}$F$_x$ with $T_c > 50$ K. We found that the Fermi surface consists of a cylindrical hole pocket centered around $\Gamma(0,0,0)$ and a cylindrical electron pocket at each corner of the Brillouin zone ($M$ points), similar to most calculations (71; 89; 206; 207). Some band calculations yield also an ellipsoidal Fermi surface around $Z(0,0,1)$ (71; 206). We did not observe this for the studied photon energies, however we did find a flat top band just below the chemical potential centered at $\Gamma$. Even with a very small $k_z$
dispersion, this band could cross the chemical potential and give rise to the ellipsoidal Fermi surface at \( Z \). We observed for the first time a superconducting gap of 20 meV at the \( \Gamma \) hole pocket for \( T = 20 \) K. This corresponds to \( 2\Delta/T_c = 8 \) and indicates that this system is in the strong coupling regime. We note that this ratio is similar to that of the cuprate family of high temperature superconductors. The emergence of the coherent peak below \( T_c \) and diminished spectral weight at the chemical potential above \( T_c \) closely resembles the spectral characteristics of the cuprates.

High pressure synthesis of samples with the nominal composition of NdFeAsO\(_{0.9}\)F\(_{0.1}\) was carried out in a cubic, multianvil press, with an edge length of 19 mm from Rockland Research Corporation. Stoichiometric amounts of NdFe\(_3\)As\(_3\), Nd\(_2\)O\(_3\), NdF\(_3\) and Nd were pressed into a pellet with a mass of approximately 0.5 g and placed inside of a BN crucible with an inner diameter of 5.5 mm. The synthesis was carried out at a pressure of 3.3 GPa. The temperature was increased, over one hour, from room temperature to 1350 - 1400°C and then held there for 8 hours before being quenched to room temperature. The pressure was then released and the sample was removed mechanically. This synthesis produced a high density pellet that contained large grains (up to \( 300 \times 200 \) \( \mu \)m in cross section) of superconducting \( (T_c \sim 53 \) K) NdFeAsO\(_{0.9}\)F\(_{0.1}\) as well as non-superconducting NdFeAsO. In addition there are inclusions of FeAs and Nd\(_2\)O\(_3\). Magneto optical measurements (208) indicate that on average the samples are over 50% superconducting. The single crystals were mechanically extracted from the pellet. They were then mounted on an Al pin using UHV compatible epoxy and cleaved \textit{in situ} yielding flat mirrorlike surface. The data was acquired at the PGM beamline of the Synchrotron Radiation Center, Wisconsin, using a Scienta 2002 analyzer and at the Advanced Light Source using beamline 7.0.1 equipped with a Scienta R4000 analyzer. The energy and angular resolution were set at 30 meV and 0.5 degree, respectively. The beam profile on the sample was slightly elliptical, with a mean diameter smaller than 100 \( \mu \)m. The photoelectron energy corresponding to the chemical potential was determined by measuring spectra from polycrystalline aluminium in electrical contact with the sample. Measurements carried out on several samples yielded similar results for the band dispersion and Fermi surface. For comparison with experi-
Figure 6.2 Measured and calculated Fermi surface of NdFeAsO$_{1-x}$F$_x$. a, Angle integrated spectra from polycrystalline and single crystal samples for selected photon energies. b, Fermi surface map - intensity of the photoelectrons integrated over 20 meV about the chemical potential obtained with 22 eV photons at $T = 70$ K. Bright color represents higher intensity. c, The locations of the Fermi crossings extracted from the raw data by fits to the MDCs. d, same data as in b but obtained with 77 eV photons. e, same data as in c but obtained with 77 eV photons. f, Three dimensional Fermi surface of NdFeAsO$_{1-x}$F$_x$ with $x = 0.1$ obtained from FLAPW calculations. g, A Fermi surface cross-section at $k_z = 0$ ($X$-$\Gamma$-$M$ plane) obtained by FLAPW calculations.

Experimental data, we use a full-potential linearized plane wave (FLAPW) calculation (177) with the local density approximation (LDA) (178) and the experimental lattice constants (209) for the undoped parent compound NdFeAsO. The As internal parameter ($z_{As} = 0.639c$) was obtained by total energy minimization that gave reasonable value to compare to the experimental result for undoped and $x = 0.2$ fluorine doping ($z_{As} = 0.6580$ and 0.6599 respectively) (210). The virtual crystal approximation was employed for the nominal level of $x = 0.1$ fluorine doping and Nd 4$f$ electrons were treated as core electrons.

The presence of multiple phases in polycrystalline samples can often contaminate the pris-
Figure 6.3  Measured and calculated band dispersion for NdFeAsO$_{1-x}$F$_x$. Locations of the cuts are indicated by green lines in Figure 6.2b. a, Measured ARPES intensity along the X-Γ-M direction ($T = 70$ K). Black dashed curves are guides to the eye. b, Energy distribution curves (EDCs) for data in panel a at $T = 70$ K. c and d, EDCs ($T = 70$ K) in the directions shown in Figure 6.2b. Blue curves mark the Fermi crossing momenta $k_F$. e, Band dispersion along the symmetry directions for NdFeAsO$_{1-x}$F$_x$ with $x = 0.1$ obtained from FLAPW calculations.
tine spectra. As an example we plot in Figure 6.2a a comparison of the photoemission data from polycrystalline samples and angle integrated measurements from single crystals. The strong intrinsic peak just below the chemical potential is very strongly suppressed in the polycrystalline samples. In Figures 6.2b,d we plot the ARPES intensity integrated within 20 meV about the chemical potential from data obtained using 22 eV and 77 eV photons. To obtain more accurate information we have extracted the exact locations of the Fermi momentum from momentum distribution curves (MDCs) and plot them in Figures 6.2c and e. Our data show that indeed this system has a Fermi surface that consists of two main contours: a larger one centered at $\Gamma$ (0,0) and a smaller one centered at the corners of the Brillouin zone. For comparison we plot the three dimensional Fermi surfaces based on FLAPW band calculations for NdFeAsO$_{1-x}$F$_x$ with $x = 0.1$ in Figure 6.2f. A two dimensional cut at $\Gamma$ ($k_z = 0$) is shown in Figure 6.2g. We note that there are both similarities and differences between the data and calculations. Overall the calculation predicts Fermi surface sheets centered at $\Gamma$ and $M$, in agreement with our measurements. The main difference between theory and experiment is the number and relative size of the Fermi surface sheets. According to calculation there should be two sheets around each symmetry point. It is quite possible that the separation between the sheets is smaller than the calculated result and not sufficient to resolve in the experiment. A second disagreement is in the size of the $\Gamma$-pocket. Experimentally the Fermi “tube” crosses the band(s) about half-way from $\Gamma$ to $X$, while theory has the band crossing $E_F$ at about 0.27 of the $\Gamma$ to $X$ distance. Band theory and experiment is not yet in quantitative agreement.

The band dispersion along selected cuts (indicated by green arrows in Figure 6.2b) is shown in Figure 6.3. Panel 6.3a shows the intensity map along the $X-\Gamma-M$ symmetry line. Bright areas on this graph mark the locations of the bands. From these data we can identify the topology of the main Fermi surface components. The Fermi surface centered at $\Gamma$ is hole-like, i.e., the unoccupied states are on the top of this band. In contrast, the Fermi surface centered at $M$ is electron-like with the bottom of the band located at $\sim 50$ meV below the chemical potential. In addition to these two conduction bands, there are also two very prominent fully occupied bands for this particular value of $k_z$. The tops of both are centered at $\Gamma$. The first is
located just 50 meV below the chemical potential. The second band has a rather flat top which is located at \( \sim 200 \) meV below the chemical potential. This band is most likely responsible for the strong peak observed in angle integrated measurements \((211; 212; 213)\). EDCs for the above data are shown in Panel 6.3b. The dispersion of the peaks in this plot agrees with the above description of the Fermi surface topology. The band dispersion close to the chemical potential for the \( \Gamma \) pocket and \( M \) pocket are plotted in Panels 6.3c and d respectively. The location of the Fermi momenta are marked by blue solid lines. In Panel 6.3e the calculated band structure at the high symmetry points for \( \text{NdFeAsO}_{1-x}F_x \) \((x = 0.1)\) is presented for comparison.

We now proceed to discuss the measurements of the superconducing gap in this material. The EDCs and ARPES intensity along a selected cut at the \( \Gamma \) pocket are shown in Figure 6.4a-b. The Fermi momentum was determined using the peak position of the MDCs and it is marked in blue. The inset of Panel c shows the EDCs below (red) and above (blue) \( T_c \), whereas in the enlarged panel we plot the magnified part of EDCs close to the chemical potential. The black curve is a chemical potential reference measured using polycrystalline aluminium in electrical contact with sample. The peak of the EDC above \( T_c \) is very broad and its leading edge is slightly shifted (\( \sim 10 \) meV) towards higher binding energies, which indicates the possible existence of a pseudogap. At present we do not have extensive temperature dependent data to definitely confirm whether these effects are similar to the pseudogap observed in the cuprates. We have performed these measurements with varying photon flux and confirmed that this shift is not due to charging effects. Below \( T_c \) the spectrum changes quite dramatically - a coherent peak develops at a binding energy of \( \sim 20 \) meV which roughly corresponds to the value of the superconconducting gap. In addition, a characteristic back-bending of the band is observed in the dispersion (Panels 6.4a,b) which arises due to particle-hole mixing in the superconducting state. The spectral signatures of the superconducting transition are strikingly similar to the ones widely reported in cuprates. Namely, below \( T_c \) a sharp peak appears, violating the conservation of low energy spectral weight. This additional weight in the case of the cuprates correlates reasonably well with the superfluid density \((214; 215)\). Following the ARPES experiments we have performed measurements of the temperature dependence of the
Figure 6.4 Superconducting gap at the Γ pocket, location marked in the upper-left inset. a, EDCs along the cut. Blue line indicates the EDC at the Fermi momentum. b, Intensity map along this cut with a clearly visible dispersion and back bending of the band close to Fermi energy $E_F$ caused by the superconductivity. The white line marks the range of momenta for which the EDCs are plotted in Panel a). c, Magnified low binding energy region from inset, where EDCs at $T = 60$ K and $T = 20$ K are plotted. Black curve is a reference spectra from polycrystalline Al. d, The penetration depth data measured using the tunneling diode resonator technique on the same crystal after the ARPES measurement. A strong superconducting signal is shown.
penetration depth on the same crystal. Due to the small size of the crystals (200×200×30 µm),
the measurements were performed using a very sensitive tunneling diode resonator technique
(216). Penetration depth data (Figure 6.4d) confirms that the crystals measured by ARPES
are indeed superconducting.

In summary, we use angle-resolved photoemission spectroscopy (ARPES) to investigate
the electronic properties of the oxypnictide superconductor NdFeAsO₁₋ₓFx. We find a well-
declared Fermi surface that consists of a large hole pocket at the Brillouin zone center and smaller
electron pockets in each corner of the Brillouin zone. The overall location and shape of the
Fermi surface agrees reasonably well with calculations. The band dispersion is quite complicated
with many flat bands located just below the chemical potential. We observe a superconducting
gap of 20 meV, which is indicative of strong coupling. Emergence of a coherent peak below
the critical temperature \( T_c \) and diminished spectral weight at the chemical potential above \( T_c \),
closely resembles the spectral characteristics of the cuprates.

Within a month after the above study, members of our group succeeded to measure the
momentum dependence of the superconducting gap at the large hole pocket around \( \Gamma \). With
such small single crystals (most of them almost invisible by bare eye), one can imagine that it
was not a trivial experiment, not to mention that the difficulty is multiplied by the imperfect
chamber condition that leads to substantive aging effect. In fact near one hundred crystals
are cleaved in the vacuum chamber in order to obtain a good and accessible surface. At
the end, however, we succeeded in obtaining important results that are later published in
Ref. (204). The main conclusion of this paper was the observation of a nodeless, \( s \)-wave-
like superconducting gap at the \( \Gamma \) hole pocket. Superconducting gaps at each Fermi crossing
momenta was determined using the EDC symmetrization method (Section 3.7.4). As shown in
Figure 6.5, the superconducting gap around the entire pocket has nearly a constant value of
15 ± 3 meV, no gap zeros (nodes) were observed. This observation is of course consistent with
the \( s^\pm \)-wave scenario and the above-mentioned ARPES gap symmetry of the 122 compounds,
but the fact that it is obtained at the large \( \Gamma \) hole pocket adds possible limitation to its
physical interpretation, since it is now believed that the large pocket arises solely due to the
Figure 6.5 Momentum dependence of the superconducting gap at the \( \Gamma \) pocket of \( \text{NdFeAsO}_{1-x}\text{F}_x \). From Ref. \( (204) \). Blue dots indicate the measured data, and red dots are the reflected ones. It is clear from this graph that the gap is always open, with a magnitude that varies between \( \sim 13 \) and \( \sim 18 \) meV, indicating conventional \( s \)-wave or slightly anisotropic \( s \)-wave behavior at the \( \Gamma \) pocket. Green line indicates a model with a slight gap anisotropy of 20% that would still be consistent with this data.

sample surface. On the other hand, the observed gap value and the resulting coupling strength \( 2\Delta/k_BT_c \sim 8 \) puts the system on the strong coupling side. This is not consistent with the ratio of 3 \( \sim 6 \) in the 122 systems \( (151; 152; 153; 154; 155) \). In the following section we intend to discuss this issue in greater detail.

### 6.2 Surface driven electronic structure

From the study presented in the last section, it is clear that the ARPES Fermi surface for the 1111 systems is inconsistent with the theoretical predictions and other experimental probes of the bulk electronic structure. More specifically, theoretical calculations and quantum oscillation measurements \( (76) \) suggest similar sizes of the hole and electron pockets, while ARPES shows a larger circular hole pocket around the zone center \( \Gamma \), which covers almost 40% of the Brillouin
zone (18; 204; 205). Base on the fact that ARPES can probe only a few top layers of the crystal, many authors believe that the large hole pocket comes from surface-driven electronic structure, i.e. an atomic reorganization and/or lattice relaxation at the sample surface (217; 218; 219). The answer to this question is a prerequisite for any further ARPES investigation of the 1111 system.

The most important purpose of the study in this section is to verify the observation of a surface-driven electronic structure in the 1111 parent compound LaFeAsO. By comparing with an electronic structure calculation for the surface layers, we show that indeed the extra $\Gamma$ hole pocket arises from a surface FeAs or LaO layer. Despite this, the observation does not exclude the possibility that electronic structure from the bulk crystal is also present in the same ARPES map. Furthermore, it is likely that such a surface-driven hole pocket may contain the superconducting information of the bulk crystal via the proximity effect, resulting in e.g. the observation of an $s$-wave-like superconducting gap by Kondo et al (204). Keeping this in mind, we discuss the strong polarization dependence of the band structure and an unusual temperature-dependent hole-like band around the $M$ point. This study is published in Ref. (17).

In this study, millimeter-sized single crystals of LaFeAsO were grown out of a NaAs flux using conventional high-temperature solution growth techniques (203). As-grown crystals have typical dimensions of $3 \times 4 \times 0.05 \sim 0.3 \text{ mm}^3$ with the crystallographic $c$-axis perpendicular to the plane of the plate-like single crystals. The characteristic temperatures for the separated structural and magnetic transitions are $T_S \sim 154 \text{ K}$ and $T^* \sim 140 \text{ K}$, respectively. The ARPES measurements were performed at beamline 10.0.1 of the Advanced Light Source (ALS), Berkeley, California using a Scienta R4000 electron analyzer, as well as a laboratory-based ARPES system consisting of a Scienta SES2002 electron analyzer, GammaData UV lamp and custom designed refocusing optics at Ames Laboratory. Vacuum conditions were better than $3 \times 10^{-11}$ torr. The energy resolution was set at $\sim 15 \text{ meV}$ for measurements at the ALS, and $\sim 9 \text{ meV}$ for measurements at Ames Laboratory. All samples were cleaved in situ yielding mirror-like, clean $a$-$b$ surfaces. Cleaved surfaces of all samples are stable for at least 24 hours.
Figure 6.6  ARPES Fermi surface maps of LaFeAsO, integrated within ±10 meV with respect to the chemical potential. Bright areas indicate high intensity. Data is taken with a polarized monochromatic synchrotron beam at $T = 10$ K. Incident photon energies are indicated at the top of each panel. Inset of the 45 eV panel shows the labeling of the high symmetry points. Note that $M_1$ and $M_2$ represent two zone corners showing different band structures due to different polarization arrangements.
for a given temperature. High symmetry points $M_1$ and $M_2$ are defined to be $(\pi/a, \pi/a(b), 0)$ and $(\pi/a, -\pi/a(b), 0)$, respectively, with the $k_x$ and $k_y$ axes along the Fe-As bonds.

Figure 6.6 shows the ARPES FS maps of LaFeAsO taken with a linearly polarized synchrotron beam for four different incident photon energies [probing at four different $k_z$ momenta, Ref. (12)]. More than half of the first Brillouin zone is covered. The data in Figure 6.6 is consistent with previous ARPES studies on LaFePO, LaFeAsO, CeFeAsO and NdFeAsO$_{0.9}$F$_{0.1}$ single crystals (19; 217; 220). The most apparent difference between the ARPES data on these 1111 systems and that on the 122 systems is a ultra large Fermi pocket around $\Gamma$, which is denoted as $\alpha_3$ throughout the paper. Subsequent band structure analysis (Figure 6.9a) shows

Figure 6.7 Top: $k_z$ dispersion maps of LaFeAsO taken with incident photon energies $30 < h\nu < 70$ eV for the $\Gamma$-$M_1$ (left) and $\Gamma$-$\Gamma$ (right) directions respectively. Locations of each Fermi crossing band are indicated by their symbols and orange arrows. Red arrows show the locations of the four maps in Figure 6.6. Bottom: Peak extraction of the corresponding momentum distribution curves (MDCs) at the top panel. Different colors represent different bands.
that this pocket is hole-like. This pocket is not expected from theoretical calculations (18) and experimental results for the bulk electronic structure (76). Recall that the electron escape depth for ARPES experiments are of the order of only a few angstroms (comparable with the lattice constant $c$), ARPES is essentially a surface probe (12). It is thus reasonable to speculate that the existence of the $\alpha_3$ pocket is a result of a surface-driven electronic structure. The $k_z$ dispersion maps in Figure 6.7 give further evidence for this speculation. It can be easily seen from Figure 6.7 that the detected electronic structure, including the $\alpha_3$ pocket, is essentially two dimensional along both $\Gamma-\Gamma$ and $\Gamma-M$ directions. This observation is in sharp contrast with the three-dimensional electronic structure observed in 122 compounds (14; 173; 174; 175), while consistent with the two dimensional nature of the sample surface layer.

In Figure 6.8 we present the results of a model theoretical calculation to verify the existence of the surface-driven electronic structure. It should be noted here that although this calculation is performed for NdFeAsO, the results for LaFeAsO will be essentially the same [see also Ref. (219)], since the 4$f$ electrons of the Nd atoms were treated as core electrons, the valence electrons of the Nd atoms are the same as those of the La atoms. In this calculation we use a full-potential linear augmented plane wave (FPLAPW) method (177) with a local density functional (178). The structural data was taken from a reported experimental result (210). The presence of the crystal surface is imitated by constructing a supercell with four NdO and FeAs layers, and a 12 a.u. vacuum located between the Nd2 and Fe4 layer (Figure 6.8a). To obtain the self-consistent charge density, we chose 28 $k$-points in the irreducible Brillouin zone, and set $R_{MT} \times k_{\text{max}}$ to 7.5, where $R_{MT}$ is the smallest muffin-tin radius and $k_{\text{max}}$ is the plane-wave cutoff. We use the muffin-tin radii of 2.4, 2.1, 2.1 and 1.6 a.u. for Nd, Fe, As and O respectively. In this calculation, the atoms near the surface (Nd1-O-Nd2, As-Fe4-As) were relaxed along the $z$-direction until the forces exerted on the atoms were less than 2.0 mRy/a.u. With this optimized structure, we obtained a self consistency with 0.01 mRy/cell total energy convergence. After that, the three dimensional Fermi surface calculation was performed with 420 $k$-points in the irreducible Brillouin zone (Figure 6.8b). We used a graphic program called XcrysDen for presenting the three dimensional Fermi surface. Details at http://www.xcrysden.org/. For
Figure 6.8 Results of the full-potential Linear Augmented Plane Wave calculation for the surface-driven electronic state of NdFeAsO. The results of LaFeAsO will be essentially the same (see discussion in the text). 

a, Calculational setup of the crystal lattice. The red, yellow, lilac and purple spheres represent the Fe, As, Nd and O atoms, respectively. Labels such as Fe1 and Nd2 indicate atoms at different locations. The 12 a.u. distance between Nd2 and Fe4 layers is added manually to imitate the existence of the crystal surface. 

b, Calculation result of the three dimensional Fermi surface for the crystal in a. 

c, Fermi surface sheets generated from different atomic layers.
the two dimensional electronic structure, we chose $k_z = 0.5$ (the $k_x$-$k_y$ plane that crosses the $\Gamma$ point) and divided the Brillouin zone ($-0.5 < k_x, k_y < 0.5$) into a $51 \times 51$ mesh that resulted in 2601 $k$-points (Figure 6.8c).

From Figures 6.8b-c, one essential statement must be pointed out: The surface layer of NdFeAsO (and LaFeAsO), regardless of its elemental nature (NdO/LaO or FeAs), will generate an extra large hole pocket at the Fermi surface, and this large hole pocket can only be generated at the surface layer of the Nd/LaFeAsO crystal. In contrast, even though it is just the second layer from the surface, the Fe1 layer generates two $\Gamma$ pockets which are even smaller than the $M$ pockets from the same layer. Similar sizes of the $\Gamma$ and $M$ pockets are seen only from the Fe2 and Fe3 layers, which are farther away from the surface and can thus be considered “bulk” states. Assuming the validity of the rigid band shifting scheme, this effect can be explained by the transfer of charge near the surface: electrons are retrieving from the surface layer (Fe4 or Nd2) to the adjacent layer (Fe1), leaving the opposite sign of the electron-hole imbalance for these two layers.

Another interesting observation of Figure 6.6 is the strong polarization dependence of the $M$ electron pockets. As seen from Figure 6.6, the two $M$-points $M_1$ and $M_2$ which are $90^\circ$ away in the $k$-space show fundamentally different electronic structures. Figure 6.9 shows their detailed band structure analysis; the schematics of the experimental setup is shown in Figure 6.9c. Clearly the $M_1$ point is surrounded by four petal-like intensity peaks at the chemical potential. The ones along the $k_{(110)}$ direction (perpendicularly intersected by Cut#a) are much more pronounced in intensity, and they are indeed hole-like bands, the top of which located at $\sim 20$ meV below the chemical potential (see left panel of Figure 6.9d). We denote this band as $\beta_h$ (Figure 6.10a). The intensity peaks along the $k_{(1,-1,0)}$ direction are actually part of an elliptical electron pocket. On the other hand, the bands around the $M_2$ point manifest themselves as two crossed elliptical electron pockets (right panel of Figure 6.9d). We denote them as $\beta_{e1}$ and $\beta_{e2}$ (Figure 6.10a). We speculate that one of these electron pockets - the one whose long axis is perpendicular to the $\Gamma$-$M_2$ direction, $\beta_{e2}$ - is the same pocket as the one observed around $M_1$. The only way to explain this unusual behavior is that these $M$-pockets are highly sensitive to
Figure 6.9 Band structure analysis for the 45 eV data in Figure 6.6. a, Measured band structure for two diagonal cuts Γ-$M_1$ and Γ-$M_2$. Strong polarization dependence on the electronic structure in both the Γ and $M$ pockets are clearly visible. b, Constant energy maps for binding energies $E_b = 0$, 30 and 60 meV in the vicinity of $M_1$ and $M_2$ points. Binding energies are indicated to the top of each column. Cut#1 and #2 indicate the locations of the band structure maps in panel d. c, Schematics of the experimental setup. Note that the electric field vector of the incoming light is polarized along the $k_{(1-1,0)}$ direction. The entrance slit of the electron analyzer is along the mirror plane.
Figure 6.10  a, Notations of the Fermi pockets and bands of LaFeAsO measured by ARPES. The existence of these pockets/bands is proved by the data from the synchrotron (Figures 6.6 and 6.9). The three hole pockets around $\Gamma$ are labeled as $\alpha_1$, $\alpha_2$ and $\alpha_3$; $\beta_{e1}$ ($\beta_{e2}$) is the $M$ electron pocket with the long axis along (perpendicular to) the $\Gamma$-$M$ direction; $\beta_h$ represents the intensity from a hole–like band located right below the chemical potential $\mu$ at the vicinity of $M$.

b, ARPES intensity map at $\mu$ measured with a helium lamp ($h\nu = 21.2$ eV), along with locations of the ARPES band structure cuts shown in Figures 6.11 and 6.12. The direction of these cuts is defined as $k_n$. Arrows in the cuts indicate the $k_n$ ranges in the corresponding panels in Figures 6.11 and 6.12.

the polarization of the incoming beam. In fact such phenomena are observed and discussed in detail in the 122 systems (137; 139; 142; 143; 183). The fact that the $\beta_{e1}$ and $\beta_{e2}$ pockets have different parity nature is consistent with tight-binding calculations (221).

We now move on to a detailed discussion of how these bands/pockets behave at the Fermi level. The high energy resolution data is taken with a partially polarized helium lamp ($h\nu = 21.2$ eV). We begin this discussion with Figure 6.11 where we analyze three $k$-$E$ maps marked #1, #2 and #3 in Figure 6.10b. These maps are chosen so that all three $\Gamma$ hole pockets $\alpha_1$, $\alpha_2$ and $\alpha_3$ are visible. The main conclusion of this figure is that there is no gap opening at
Figure 6.11 Band structure analysis for the $\Gamma$ hole pockets. Locations of the cuts #1, #2 and #3 are indicated in Figure 6.10b. Top row: MDCs integrated within $\pm 10$ meV with respect to the chemical potential $\mu$ for the three cuts. $\mu$ is determined by fitting a Fermi function to the spectra of polycrystalline gold. The MDCs are fitted with several Lorenzians for extracting the peak positions which are used to determine the Fermi crossing momenta ($k_F$s). Middle row: Band dispersion maps obtained by ARPES measurements at $T = 12$ K. The incident photon energy is 21.2 eV. Bottom row: Energy distribution curves (EDCs) for the corresponding maps in the middle row. Each EDC is integrated within a momentum range of $0.011\pi/a$ and is symmetrized with respect to $\mu$. Insets show an expanded region at the vicinity of the $k_F$s.
Figure 6.12  Band structure analysis for the $M$ hole band $\beta_h$ at three different temperatures. Location of the cut #4 is indicated in Figure 6.10b. Top row: Band dispersion maps obtained by ARPES measurements at $T = 12$, 120 and 200 K. The incident photon energy is 21.2 eV. Vertical dashed lines indicate the location of the high symmetry point $M$. Bottom row: EDCs at the $M$ point for the three temperatures. Data is integrated within a momentum range of $0.011\pi/a$, symmetrized with respect to $\mu$, and normalized for high binding energies.

the $\Gamma$ pockets. In the symmetrized energy distribution curves (EDCs) at each Fermi crossing momenta, we see one single peak instead of two peaks separated by a valley. This is a typical indication of a vanishing gap. Linking this result with the findings by Kondo et al. [Ref. (204)], we obtain an interesting picture for the low lying electronic excitations of this 1111 system. Resulted solely from the surface layer, the $\alpha_3$ pocket shows no gap in the undoped sample, while exhibits an $s$-wave-like gap as large as $\sim 15$ meV in the fluorine-doped superconducting sample (204). The coherent peak for this gap vanishes at a temperature close to $T_c$ (18). To date we have no information on whether the surface layer of the 1111 crystal is superconducting itself, so a possible scenario is the proximity effect. The proximity effect offers us the possibility that the
superconducting properties of the bulk sample affects the surface. In that case the momentum
dependence of the superconducting gap observed for the surface will be similar to that of
the bulk crystal. For high-$T_c$ cuprates, it is proposed that the proximity effect may result
in “$d+s$”-wave superconductivity at the metallic layer that is coated on the superconductor
\cite{222, 223, 224}. This scenario is consistent with scanning tunneling spectroscopy (STS) results
on polycrystalline 1111 samples where a reduced superconducting gap is observed at the sample
surface \cite{225, 226}. It is not understood why the gap size shown by ARPES is much bigger
than by STS and other methods.

In Figure 6.12 we discuss the temperature dependence of the $\beta_h$ band. Cut#4 is located
right through the $M$ point where the binding energy is the lowest for this band. One can
easily see from Figure 6.12 that the peak location of the $\beta_h$ band gradually shifts to higher
binding energies with increasing temperature. At $T = 12$ K the maximum intensity is located
at $E_b \sim 10$ meV, whereas at $T = 200$ K it shifts to $E_b \sim 60$ meV. The peak intensity decreases
at the same time. Such changes are intrinsic, since multiple measurements are performed in
multiple samples, and both increasing and decreasing the temperature during the measurement
reveals the same behavior. As a reminder, in the 122 systems the bands locate at the same
binding energies until the magnetic transition temperature is reached \cite{14, 138, 139, 141}. Here the band location shifts even below the transition temperature (between 12 and 120 K).
This is not expected from the bulk properties - transport measurements unambiguously show a
magnetic transition at 140 K. It is thus an evidence for the existence of a temperature-dependent
surface layer.

To summarize, the main conclusion of our study is that the surface-driven electronic struc-
ture plays an important role in the ARPES data of the iron arsenic 1111 systems. It is a
fact that ARPES data on these systems shows more discrepancies rather than agreements
with theoretical and experimental bulk properties. ARPES shows a temperature-dependent $\beta_h$
band, and most significantly an extra large hole pocket around $\Gamma$. However, bulk calculations
and experiments suggest a Fermi surface reconstruction associating with a well-defined mag-
netic transition temperature, and similar sizes of $\Gamma$ and $M$ pockets. By comparison with a
full-potential linear augmented plane wave calculation on the surface layers of the crystal, we confirm that at the very least the large $\Gamma$ pocket is generated solely by the sample surface. The $s$-wave-like superconducting gap that exists in this pocket in the superconducting samples is most likely a result of the superconducting proximity effect.

The availability of sizable single crystals (203) also provided opportunity for researchers from other groups to study in detail the electronic structure of the 1111 systems. Here we give a brief overview of two recent reports by Chinese scientists, Refs. (220) and (227). In Ref. (220), ARPES studies are performed using another 1111 parent compound CeFeAsO. Although the data shows similar overall shape and sizes of Fermi surfaces with our LaFeAsO result, the authors could resolve four different $\Gamma$ Fermi sheets. In the vicinity of the $M$ points, the authors claim to observe a small central electron pocket plus four petallike Fermi dots (hole pockets), similar to the situation of the 122 compounds. Ref. (227) gives a more comprehensive and detailed ARPES study on LaFeAsO. With the help of a second derivative analysis, the authors revealed a more complicated band structure with at least nine bands close to $\mu$ and five Fermi contours. In particular, one $M$-shaped band centered at $\Gamma$ (called $\omega$ in the paper) displayed considerable $k_z$ dispersion and insensitivity to deposition of sodium onto the surface. More importantly, the exact energy location of the $\omega$ band is found to change dramatically across the magnetic ordering temperature. These facts indicate that this band is related with the bulk electronic structure.

One common observation for these two papers is a “kink” structure located at $E_b \sim 25$ meV, accompanied by a drop in the MDC width (proportional to the imaginary part of the self energy). The authors find that the energy scale of the kink is similar to an intrinsic phonon mode in the system, indicative of electron-phonon interaction as a likely origin. One should note here that even if electron-phonon interaction is the origin of the kink, it does not mean that electron-phonon interaction is responsible for superconductivity in the pnictides. As it is discussed in the last chapters, a large body of evidence points otherwise, i.e., superconductivity in the pnictides is likely to be non-phonon-mediated.

Similar to our reports, these two papers draw specific attention to the unusual temperature
dependence of band location near the $M$ point. Both papers report exactly the same behavior as our study: a sharp and narrow EDC peak develops gradually as temperature decreases, at $\sim 15$ K the peak width is no more than 30 meV. The authors believe that this behavior is caused by a drastic decrease of the scattering rate, which is “a clear signature of the magnetic transition” [Ref. (220)]. This interpretation is somewhat different but does not conflict with our claims, since the exact origin of the behavior is not clear at this point. To summarize the present knowledge for the 1111 systems studied by ARPES, we are certain that (1) there exists a surface driven electronic structure caused by surface relaxation and/or surface carrier exchange; (2) a dispersion kink at $\sim 25$ meV appears at least in one of the surface bands; and (3) a sharp EDC peak develops at low temperatures for at least the bands near $M$. Physical interpretations of these unusual behaviors call for detailed investigation of these fascinating high temperature superconductors in the future.

6.3 Discussion and outlook

The $R$FeAs(O,F) systems hold the record for the highest $T_c$ found in the pnictides and are thus in a sense the true second class of high-$T_c$ superconductors. ARPES studies of these materials, however, are still in their infancy compared to the 122 compounds. Generally speaking, the electronic structure of the 1111 compound are “more two dimensional” than the 122s, while it is not certain whether low dimensionality alone accounts for the higher $T_c$s. It is mentioned above that although there exists a surface-driven electronic structure, tracks for bulk bands are also found in the same ARPES map [e.g. the $M$-shaped band observed in Ref. (227)]. This important fact ensures us that the surface sensitive ARPES technique is still useful for probing bulk electronic properties in these systems. An immediate follow-up question is the size of the bulk superconducting gap. This is an unexplored territory since the only available data (204) shows the gap at a surface band. The research procedure is straightforward: we need to find the Fermi crossing momenta for the bulk band and measure the gap there. The authors of Ref. (227) believe that the inner two $\Gamma$ hole pockets and the $M$ electron pockets come from the bulk. Thus a gap survey on these Fermi pockets is both instructive and feasible, given the patience
of sample handling. Similar measurements can also be performed to study the $k_z$ dependence of the superconducting gap, same as what have been done for the 122 systems (156).

Along the same route, we also propose measurements on the 1111 systems using laser-based or synchrotron-based ARPES with low incoming photon energies. Presumably the longer electron mean escape depth (Chapter 3) will help us to obtain information of the crystal bulk. The higher energy resolution of the laser system would also help measuring the superconducting gap with higher accuracy.

One concern about the current result of the superconducting gap (204) is the lack of detailed temperature dependence of the gap size. In Section 6.1 we showed EDCs at $T = 20$ K where the coherent peak is present, and $T = 60$ K just above $T_c$ where the coherent peak disappears (Figure 6.4). Interestingly the symmetrized EDCs (not shown) indicate a gap-like feature even above $T_c$, reminescent of the pseudogap behavior in the cuprates. The pseudogap in the pnictides have been suggested by theoretical works (228; 229) as well as early angle-integrated photoemission (211; 212; 213) and other experimental studies (230; 231; 232; 233), but was not observed with clear evidence by ARPES so far. In the 122 compounds, different ARPES groups draw contradicting conclusions even with essentially the same data set (151; 152). The reconciliation of this problem would provide important insight to the origin of the pseudogap in the cuprates, or even the origin of high-$T_c$ superconductivity. Detailed, reproducible temperature dependence of the superconducting gap in 1111 (and 122) pnictides is thus of urgent need, although such a study require near perfect vacuum condition to eliminate possible aging effect during temperature cycling.

To conclude the last two chapters, the ARPES studies for the pnictide superconductors, preformed mainly by the author of the thesis, reveal a comprehensive picture of their electronic structures. We performed some of the first ARPES measurements on the pnictides, followed by detailed ARPES studies on a wide range of members, including the carrier-doped $AEFe_2As_2$ (122) and $RFeAsO$ (1111) systems. Our experimental results show the quasi two dimensionality of electronic structure in the 1111 systems, versus three dimensional Fermi surfaces in the 122
systems; a surface-driven electronic structure with the presence of a large \( s \)-wave-like superconducting gap in the 1111 systems; a magnetically reconstructed electronic structure revealing an unexpected nesting condition in undoped as well as underdoped 122 systems. Most importantly, a comprehensive survey on cobalt-doped \( \text{BaFe}_2\text{As}_2 \) led to the discovery of several Lifshitz transitions (topological changes in the Fermi surface due to doping-driven rigid band shifting) that have direct impact on their superconducting properties. Both the low doping emergence and the high doping disappearance of superconductivity are linked with such Lifshitz transitions. For the first time, we found that superconductivity favors a specific Fermiology in high-\( T_c \) superconductors.
CHAPTER 7. Summary and conclusions

This thesis presents a series of experimental studies on the electronic structure of the newly-discovered iron arsenic (pnictide) high temperature superconductors, using angle resolved photoemission spectroscopy (ARPES). The technique of ARPES utilizes photoelectric effect as a probe to study the energy band structure and related low energy excitation states for a given metallic/semimetallic material. Specially designed electron analyzers collect photoelectrons for a certain range of kinetic energy and azimuth angle with respect to the sample, and transfer such information into a momentum-energy map. The entire four dimensional electronic structure is subsequently obtained by collecting data from different polar angles with different incoming photon energies. ARPES is proven to be one of the leading techniques for studies in high temperature superconductors, including the pnictides. Discovered in spring 2008, the iron arsenic superconductors are compounds with layered structures resembling the copper-oxide superconductors. Their superconducting transition temperatures are found to be sensitive to the extra electron counts and certain crystallographic parameters. By adjusting these parameters via carrier doping or chemical or physical pressure, superconductivity up to $\sim 55$ K is well established. Phase diagrams of the pnictides show first or second order phase transitions between a high temperature tetragonal/paramagnetic phase and a low temperature orthorhombic/antiferromagnetic phase. The temperatures of such transitions decrease as charge carriers are doped in, or external pressure is applied. Superconductivity emerges before, and vanishes after the full suppression of the structural/magnetic transition, forming a domelike region in the phase diagram. In electron-doped $AE\text{Fe}_2\text{As}_2$ systems, superconductivity is found to be able to coexist with long range antiferromagnetic order. The superconducting order parameter is found consistent with a unique $s^\pm$ symmetry in which the energy gap experience a $\pi$ phase
shift between the central hole Fermi pockets and the corner electron pockets, while remains a constant within each Fermi sheets. These intriguing behaviors triggered enormous volume of theoretical and experimental efforts within the last three years.

ARPES studies on both the $AE\text{Fe}_2\text{As}_2$ (122) and the $R\text{FeAs(O,F)}$ (1111) systems are shown in the present thesis. These studies reveal a comprehensive electronic structure of the pnictides. For the undoped parent compounds of the 122 systems, it is found that two distinct Fermi surface configuration exist for the two structural/magnetic phases. In the low temperature orthorhombic and antiferromagnetic phase, the Fermi surface is found to be strongly dispersive along all three momentum axes, with apparent in-plane reconstruction caused by long range magnetic order and a reduction of symmetry from $C_4$ to $C_2$ in a single magnetic domain. In the high temperature tetragonal and paramagnetic phase, the reconstruction is not present; the Fermi surface changes to be quasi two dimensional. Carrier doping affects the electronic structure in a way that can be described by simple rigid band shifting model, i.e., carrier concentration controls only the energy position of the chemical potential but not the shape of the bands. When extra holes are doped into the system, the central hole pockets grow larger, whereas the electron pockets shrink in size, in accordance with the Luttinger summation rule. The opposite trend applies to the electron doping side of the phase diagram. In the high temperature ARPES data on $\text{Ba(Fe}_{1-x}\text{Co}_x\text{)}_2\text{As}_2$, electron pockets expand and hole pockets shrink as $x$ increases.

The most important finding of the present thesis is a series of topological changes of Fermi surface (Lifshitz transitions) that occur in close vicinity of the low and high doping boundaries of the superconducting dome. At the low doping side, our ARPES data demonstrates that the Fermi surface reconstruction caused by long range antiferromagnetic order evolves below the Fermi level (i.e. to higher binding energies) at the doping level where superconductivity emerges at the phase diagram. From the ARPES Fermi maps, this Lifshitz transition appears as the disappearance of the four pedal-like Fermi dots near the zone corner $X$. In transport measurements, the same transition exhibits itself as a sudden increase of the Hall coefficient and an abrupt jump of thermoelectric power. On the high doping side, the vanishing of $T_c$
corresponds to the vanishing of the hole pocket at the zone center: the quasi two dimensional \( \Gamma \) cylinders first break down to ellipsoids centering around the upper boundary \( Z \); these ellipsoids vanish slightly after the disappearance of superconductivity. Beyond these Lifshitz transitions, the central pockets change to electron-like, and superconductivity no longer exists. Superconductivity in electron-doped iron pnictides favors a specific Fermi surface configuration in which the center and corner of the in-plane Brillouin zone are surrounded by simple hole and electron pockets. Additional three dimensionality of the Fermi surface results in lower \( T_c \)s of the system, yet superconductivity is not vanished until either set of the pockets shows considerable reconstruction, completely vanishes or even changes its carrier nature. In transport measurements, these high doping Lifshitz transitions signifies themselves as a change of slope in the curves of thermoelectric power vs. doping at fixed temperatures. Unambiguous experimental evidences support our statement that electron-doped iron pnictides are examples of high temperature superconductors whose pairing behavior is governed primarily by their underlying Fermi topology.

Our ARPES studies of the 1111 systems also show similar electronic structure. One important difference from the 122 compounds is that relaxation and/or reconstruction from the sample surface leads to the formation of a surface driven electronic structure, which adds on top of the bulk bands in the same ARPES map. By comparison with a first principle calculation for the surface bands, we find that the extra large \( \Gamma \) hole pocket observed by ARPES comes from the sample surface. We also observe a temperature dependent hole band located at the zone corner, which serves as a side evidence of the surface electronic structure.
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