Laser-based angle-resolved photoemission spectroscopy (ARPES) and studies of topological insulators and heavy fermions

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Laser-based angle-resolved photoemission spectroscopy (ARPES) and studies of
topological insulators and heavy fermions

by

Rui Jiang

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

Major: Condensed Matter Physics

Program of Study Committee:
Adam Kaminski, Major Professor
   Patricia A. Thiel
   Paul C. Canfield
   Jigang Wang
   James Cochran

Iowa State University
Ames, Iowa
2014
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DEDICATION

I would like to dedicate this thesis to my parents, Zhanqing Jiang and Ping Dai, without whose support I would not have been able to complete this work.
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ABSTRACT

Angle-resolve photoemission spectroscopy (ARPES) as an experimental method that can directly measure electronic structure has been playing an important role in studies of novel materials, such as high temperature superconductors, topological insulators and many others. In this thesis, we will discuss the development of a tunable vacuum UV Laser ARPES system as well as ARPES studies of topological insulators and heavy fermion materials. The main results are as follows:

1. We developed an angle-resolved photoemission spectrometer with tunable vacuum ultraviolet laser as a photon source. The photon source is based on the fourth harmonic generation of a near IR beam from a Ti:sapphire laser pumped by a CW green laser and tunable between 5.3 eV and 7 eV. The most important part of the set-up is a compact, vacuum enclosed fourth harmonic generator based on potassium beryllium fluoroborate crystals, grown hydrothermally in the US. This source can deliver a photon flux of over $10^{14}$ photon/s. We demonstrate that this energy range is sufficient to measure the $k_z$ dispersion in an iron arsenic high temperature superconductor and rare-earth antimonides, which was previously only possible at synchrotron facilities.

2. We studied a nontrivial surface state in a pseudobinary Bi$_2$Te$_{2.28}$Se$_{0.58}$ topological insulator. We demonstrated that, unlike in previously studied binaries, this is an intrinsic topological insulator with the conduction bulk band residing well above the chemical potential. Our data shows that under a good vacuum condition there are no significant aging effects for more than two weeks after cleaving. We also demonstrated that the shift of the Kramers point at low temperature is caused by UV-assisted absorption of atomic hydrogen.

3. We systematically studied the electronic structure of quasi-2D heavy fermion material
Ce$_2$RhIn$_8$. The lack of significant $k_z$ dispersion confirms the quasi two dimensionality of the electronic structure. Fermi surface is quite complicated and consists of several hole and electron pockets. Using comparison with DFT calculation we demonstrated that the data is consistent with a localized picture of f electrons. This provides clues to understanding their unusual transport and thermodynamical properties.
CHAPTER 1. THEORETICAL BACKGROUND FOR ARPES

1.1 Introduction

Application of quantum mechanics to the theory of solids fundamentally changed the understanding of the origin of their properties. Sommerfeld’s free fermion model for metals successfully explains wide range of properties, especially for good metals. It assumes electrons move freely among atomic lattice and gives a dispersion relation of kinetic energy and momentum of electron as

\[ E = \frac{\hbar^2 k^2}{2m} \]  

(1.1)

However, this oversimplified theory not only fails to explain properties of insulators, but also fails to explain the temperature dependence of resistivity for a conductor. Setting aside the independent electron approximation, the band theory of solids takes into account the interaction between electron and periodic potential generated by atomic lattice, which results in much more realistic model. The Schrödinger equation for an electron has a general form

\[ H\psi = \left(-\frac{\hbar^2}{2m} \nabla^2 + U(r)\right)\psi = E\psi \]  

(1.2)

where \( U(r) \) is a periodic potential of an atomic lattice. Those eigenstates of electrons associated with a wave vector \( k \) and kinetic energy \( E \) are the allowed states for electrons. Since the atomic lattice “felt” by an electron is the same for wave vector \( k \) and \( k + 2\pi R^{-1} \) (\( R \) is Bravais lattice vector) due to periodic form of \( U(r) \), all the allowed states can be folded into first Brillouin zone. This representation is called the reduced-zone scheme. Due to the interaction of atomic lattice, the dispersion relation for electrons is much more complicated than a parabolic shape. Fig 1.1 shows a band structure of BaFe\(_2\)As\(_2\) along high symmetry cut calculated by local density approximation (LDA).
Since the room temperature (300K) corresponds to the energy of roughly 30meV, only the electrons close to Fermi energy can be thermally excited. Electronic states near $E_f$ determine many properties of a solids, such as thermal and electrical conductivities, magnetism, superconductivity, etc. Therefore, the shape of Fermi surface and band structure close to Fermi energy is essential to our understanding of the properties of solids.

Photoemission spectroscopy is a very useful technique to determine the band structure of solids. Utilizing low photon energy, UV light ranging from 5eV to 100eV, ultraviolet photoelectron spectroscopy (UPS) is mainly focused on studies of the density of states in the valence band and near Fermi energy. Angle-resolved photoemission spectroscopy (ARPES), which further provide angular resolution, is the most direct method of measuring the electronic structure of solids. It plays an important role[2] in studies of unconventional superconductors, topological insulators and many other novel materials.
1.2 Principle of APRES

Photoemission spectroscopy is an experimental technique based on photoelectric effect, which was first discovered by Hertz and Hallwachs in 1887 and explained by Einstein in 1905. Electrons inside of solids are excited by the photons from light source with energy $h\nu$ and have enough energy to overcome surface work function $\phi$. The emitted photoelectrons will carry the information of electronic structure of solids. In a band structure picture, by applying conservation of energy and momentum, we have

\[ E_{\text{kin}} = h\nu - \phi - |E_B| \quad (1.3) \]

\[ p_\parallel = \hbar k_\parallel \quad (1.4) \]

Figure 1.2: Energetics of the photoemission process.[2]
Where, $E_{\text{kin}}$ and $p_\parallel$ is measured energy and momentum of photoelectron, and $E_B$ and $k_\parallel$ describe the bad structure of sample. Here the momentum of photon $\hbar k_{h\nu}$ is neglected, because at the low photon energy ($<1\text{KeV}$), it is much smaller than the momentum of photoelectron. Note that only the component of momentum parallel to sample surface is conserved in Eq. 1.4. This is because even though the perpendicular component of momentum $k_\perp$ is conserved during the interaction of photon and electron, it is not conserved when electrons travel though the sample surface interface. This is due to the lack of translational symmetry along normal direction to the surface. The kinetic energy $E_{\text{kin}}$ and momentum $p_\parallel$ of photoelectron can be measured by electron analyzer. By using Eq. 1.3 and 1.4, binding energy $|E_B|$ and corresponding momentum of electron inside crystal, the band structure, can be derived.

The simple discussion above didn’t include the interaction of electrons and neglects the effect of left-over state after emission of photoelectron. One rigorous approach to this problem is to consider photon absorption, electron removal and electron detection as a single coherent process, which is called one-step model, as shown in Fig. 1.3. After electron absorption, photoelectron will interact with “left-over” bulk state, forming a damped final state. The surface excitations also need to be considered when calculating phase matching of wavefunction at the surface. All the complexities of one-step model not only make it hard to calculate, but also have no intuitive relation to well-known physics quantities.

Therefore, to gain more insight into photoemission process, a simple three-step model is widely used to discuss result of ARPES measurement. In this model, shown in Fig. 1.3, the photoemission process is separated into three steps: (i) Optical excitation of electron from ground state to excited state. (ii) Excited electron travels to the surface. (iii) Electron escapes into vacuum and is measured by the electron analyzer. The first step carries most of the information about solid and will be discussed below. The second step can be described by elastic and inelastic scattering of photoelectrons by atomic lattice. during the third step, electrons overcome work function and change the $k_\perp$.

In “one-step” model, the measured photoemission intensity will be proportion to the sum of all possible transition probabilities $w_{fi}$ between a $N$-electron ground state $\Psi_i^N$ and a final excited state $\Psi_f^N$, which can be expressed by Fermi’s golden rule
\[ I \propto \sum_{f,i} w_{fi} = \sum_{f,i} -\frac{2\pi e}{\hbar c} |\langle \Psi_f^N | \mathbf{A} \cdot \mathbf{p} | \Psi_i^N \rangle|^2 \delta(E_f^N - E_i^N - h\nu) \tag{1.5} \]

\( \mathbf{A} \cdot \mathbf{p} \) describes the interaction of electron with momentum \( \mathbf{p} \) and a photon with vector potential \( \mathbf{A} \). If the photoelectrons have high kinetic energy, the interaction between photoelectron and the system left behind will be small. Therefore, the damped final state can be approximated as two separate states without interaction. This approximation is called sudden approximation, which is widely used in discussions of many-body system. The final and initial state can be written as,

\[ \Psi_f^N = A\phi_f^k \Psi_f^{N-1} \tag{1.6} \]
\[ \Psi_i^N = A\phi_i^k \Psi_i^{N-1} \tag{1.7} \]

Please note that the left over final state \( \Psi_f^{N-1} \) in an interacting system are usually associated with several exited states also having N-1 electrons. Therefore \( \Psi_f^{N-1} \) should be replaced by \( \Psi_m^{N-1} \) with \( m \) for all possible excited states. Consider \( E_f^N = E_m^{N-1} + E_{\text{kin}} \) and \( E_i^N = E_i^{N-1} - E_B^k \), Eq. 1.5 will become
\[ I \propto \sum_{f,i} |M_{f,i}^k|^2 \sum_m |c_{m,i}|^2 \delta(E_{\text{kin}} + E_{m}^{N-1} - E_i^N - h\nu) \]

where \( M_{f,i}^k \propto \langle \phi_f^k | A \cdot p | \phi_i^k \rangle \) is the dipole matrix element for photon-electron interaction and \( c_{m,i} = \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle \). In non-interacting picture, there is only one \( m \) state and \( m = i \). Then the delta function gives us \( E_{\text{kin}} = h\nu - |E_E| \), which is the same result in Eq. 1.3. In this situation the data will be a sum of delta function of band structure, as shown in Fig. 1.4(a).

Figure 1.4: Noninteracting system and Fermi-liquid system[2]

### 1.3 One-particle Spectral Function and Self Energy

When interactions between electrons are considered, more states can be excited. Beside the state at band position, which gives a delta-function-like peak, many other states with \( m \neq i \) will show up in spectrum. In Fermi-liquid system, interaction causes a hump after main peak, as shown in Fig. 1.4(b). A more theoretical formalism for interaction includes one-electron Green’s function \( G^\pm(k, \omega) \) and one-particle spectral function \( A^\pm(k, \omega) \).

After removing or adding an electron, the response function of the system can be written as one-electron Green’s function,
where the operator $c_k^\pm$ creates or annihilates an electron and $\eta$ is a positive infinitesimal. With $\eta \to 0^+$, one can easily connect Green’s function with ARPES spectrum. Taking one-particle spectral function $A(k, \omega) = A^+(k, \omega) + A^-(k, \omega) = -(1/\pi)\text{Im}G(k, \omega)$ and noticing that $\Psi_i^{N-1} = c_k \Psi_i^N$, the spectrum function of removing or adding an electron can be written as

$$A^\pm (k, \omega) = \sum_m |\langle \Psi_m^{N+1} | \Psi_i^{N-1} \rangle|^2 \delta(\omega - E_m^{N+1} + E_i^N)$$ (1.10)

By comparing with Eq. 1.8, the photoelectron intensity measured by ARPES is just the one-electron removal spectral function $A^-(k, \omega)$ times cross product of photon-electron interaction and cut-off by Fermi distribution function $f(\omega)$ due to finite number of electrons in system, that is,

$$I(k, \omega) \propto \sum_{f, i} |M_{f,i}^k|^2 f(\omega) A^-(k, \omega)$$ (1.11)

The imaginary part of Green’s function can therefore be determined directly from ARPES spectrum. Since Green’s function needs to satisfy causality, the real part and imaginary part are related by Kramers-Kronig relations. Therefore, the total one-electron Green’s function, which fully described the interactions in the system can be derived from ARPES data.

One particularly useful quantity that can be extracted from this approach is self-energy $\Sigma(k, \omega)$. The real and imaginary part of the self energy describes the renormalization of the band energy and lifetime of a quasiparticle. The Greens’ function and one-electron spectral function can be expressed in terms of self-energy,

$$G(k, \omega) = \frac{1}{\omega - c_k - \Sigma(k, \omega)}$$ (1.12)

$$A(k, \omega) = -\frac{1}{\pi} \frac{\Sigma'(k, \omega)}{[\omega - c_k - \Sigma(k, \omega)]^2 - [\Sigma(k, \omega)]^2}$$ (1.13)

According to the Fermi liquid theory, weak repulsive interactions of electrons will broaden the peak in $A(k, \omega)$ to a Lorentzian function. The half-width of peak in energy distribution
gives the imaginary part of self-energy. To obtain the real part of self-energy, one may utilize
the Kramers-Kronig relations. However, since ARPES can only measure spectral function
below $E_f$, this approach does not work easily. The analysis of real part of self-energy is usually
performed under certain approximation[30].

1.4 Matrix Element Effect

The intensity of photoelectrons also greatly dependents on matrix elements of photon-
electron interaction $M_{f,i}^k$, as shown in Eq. 1.11. This will give a selectivity of measured data
depending on photon energy and polarization.

![Figure 1.5: Illustration of polarization and photon energy effect[2].](image)

When changing photon energy, the cross-section can change in a non-necessarily monotonic
way, as shown in Fig. 1.5(a). The cross-section of of Cu 3d and O 2p orbit shown a maximum
at around 50eV and 20eV. At some photon energies, the cross-section of certain bands can be
small enough so that they will not be measurable. Therefore, ability to tune photon energy is
important to reveal full electronic structure of the sample.

Another effect of matrix element is a selective suppression of intensity for some parts of the
band due to polarization. Recall that $M_{f,i}^k \propto \langle \phi_f^k | \mathbf{A} \cdot \mathbf{p} | \phi_i^k \rangle$. Since the wave vector of final
state $\langle \phi_f^k |$ is always in the mirror plane, as shown in Fig. 1.5(b), it must be an even function. If
the photon source is polarized, the usual setup will have the vector potential $\mathbf{A}$, the direction
electric field, either within the mirror plane (S polarization) or perpendicular to mirror plane (P polarization). Because the \( \mathbf{p} \) has the same direction as \( \mathbf{x} \), since \( \hbar \mathbf{p}/m = -i[\mathbf{x}, \mathbf{H}] \), \( \mathbf{A} \cdot \mathbf{p} \) will be odd at P polarization and even at S polarization. To have a non-zero intensity at mirror plane, \( \langle \phi_{f}^{k} | \mathbf{A} \cdot \mathbf{p} | \phi_{i}^{k} \rangle \) must be a even function. Therefore,

\[
\begin{align*}
|\phi_{i}^{k}\rangle & \text{ even } \langle + | + \rangle \Rightarrow \mathbf{A} \text{ even } \\
|\phi_{i}^{k}\rangle & \text{ odd } \langle + | - \rangle \Rightarrow \mathbf{A} \text{ odd }
\end{align*}
\]

(1.14)

For example, for a \( d_{x^2+y^2} \) orbit, the initial state is odd in XZ plane. Electron can only be detected in P polarization. Therefore, information of symmetry can be extracted by changing polarization.

### 1.5 Universal Curve

The second step of three-step model is the travel of the excited electron to the surface, which can be described by elastic or inelastic scattering of photoelectrons by atomic lattice. The electrons scattered inelastically are usually called secondary electrons. Those electrons will add to the background at higher binding energies. Since this background does not carry any important information, it can be modeled and subtracted from measured data, for example using Shirley background function[31].

The mean free path of the excited electrons is controlled by scattering processes. Fig. 1.6 shows the dependence of mean free path on the incoming photon energy. This curve, also known as universal curve, typically applies to most metals and can be a good guide for other materials. The curve has a minimum at around 50eV with increasing mean free path for lower or higher photon energies. The most commonly used photon energies in ARPES are in 20-100eV range, therefore only the electronic structure of top layer is measured. The Laser photon source at lower photon energy will have better bulk sensitivity and we will discussed this in details in the next chapter.
1.6 \( k_z \) Dispersion

For a quasi-1D or quasi-2D material, electronic structure has little dispersion along \( k_z \) direction. Therefore the whole band structure can be measured without changing photon energy. This is not the case for 3D materials, and alternation of \( k_z \) at surface has to be considered. Let’s assume that a band near Fermi surface has a parabolic dispersion,

\[
E_B(k) = \frac{\hbar^2 k^2}{2m} - |E_0| = \frac{\hbar^2 (k^2_z + k^2_z)}{2m} - |E_0| \tag{1.15}
\]

where \( E_0 \) is the bottom of conduction band. By using conservation of momentum parallel to surface (Eq. 1.4) and considering the free electron nature of outgoing electron, we have

\[
k_z = \sqrt{\frac{2m}{\hbar^2} (E_{kin} \cos^2 \theta - \hbar \nu + V_0)} \tag{1.16}
\]

where \( V_0 = E_0 + \phi \) is called inner potential. From this equation, we can see that the \( k_z \) is not only dependent on photon energy, but will also change with angle of photoelectrons. In a more complex system, the inner potential is usually considered to be an artificial parameter. It
can be determined by comparing the periodicity of the measured dispersion along \( k_z \) direction with band calculations.

Although the parallel component of momentum is strictly conserved at surface, it is not true for \( k_z \)[32]. With finite life time of quasiparticle, the wave vector takes a complex number form \( k_z = k_z^R + i k_z^I \). The cross-section can be expressed as a convolution of two Lorentzian functions,

\[
\sigma \propto \frac{1}{(k_{z,f}^R - k_{z,i}^R)^2 + (k_{z,f}^I + k_{z,i}^I)^2}
\]

with maximum at \( k_{z,f}^R = k_{z,i}^R \) and half maximum at \( k_{z,f}^R - k_{z,i}^R = \pm (k_{z,f}^I + k_{z,i}^I) \). If electronic structure has a dispersion along \( k_z \) direction, this finite cross-section over some range of \( k_z \) will result in broadening of spectrum and limitation of \( k_z \) resolution. Since the broadening effect increases with increasing \( k_z \) dispersion, this limits the ability of ARPES to measure the electronic properties in a 3D system.

1.7 Electronic Structure at Surface

The band theory assumes that the lattice size is infinite, which is valid for bulk state since the normal sample is much larger than unit cell. This assumption led to periodic boundary conditions for solving the band structure. However, at the surface of solids, the boundary condition may be quite different, due to surface relaxation and reconstruction.

![Figure 1.7: Schematic illustration of (a) relaxation in the top atomic plane and (b) one possible type of reconstruction of a semi-infinite crystal.](image)
When solid is terminated at certain plane, the force that acts on the atoms at surface is altered, which changes the equilibrium positions of atoms. This change can take form of a relaxation or reconstruction. Fig 1.7 shows a schematic diagram for both cases. Relaxation changes the position of entire planes of atoms, vertically or horizontally, but maintains the same periodic structure as bulk lattice. This usually does not affect the band structure a lot. The reconstruction, on the other hand, rearranges the atoms within plane, and, most likely, causes the changes in the surface periodicity. The larger unit cell at surface will results in a smaller Brillouin zone, which will fold the Fermi surface.

Besides the surface relaxation and reconstruction, the interaction between solid and semi-infinite vacuum region will also change the band structure or introduce new states that only exist at surface. One example of such surface state will be the Dirac-cone shaped band in topological insulators, which will be discussed in detail at Chapter 3. Since ARPES system usually measure cleaved sample, the orientation of surface is also a critical effect to be considered. For a bad cleave, the surface can have multiple orientation, which results in a integrated spectrum for several momentum directions. This effect can reduce the momentum resolution and in some severe situation, the spectrum can be so blurred that no band structure can be extracted. This also limit the samples that can be measured by ARPES measurement. Only samples that give a flat surface can result in a shape spectrum.
CHAPTER 2. SETUP OF LASER ARPES

2.1 Introduction

An ARPES spectrometer consists of three essential parts: photon source, experimental chamber and electron analyzer, as shown in Fig. 2.1. Over last decade and a half, ARPES technique matured as an important tool in studies of electronic properties of solids due to technological advances in photon sources and electron optics. We will begin the discussion with photon sources.

Figure 2.1: Schematic illustration of ARPES measurement.[5]
2.2 Photon Sources

Photon sources for ARPES measurements usually deliver photons of energy greater than 6eV, to overcome the work function, which is typically around 4.5eV. In comparison with XPS, the lower photon energy translates to better energy resolution, which is essential to study the fine details of single-particle spectral function. Typical photon sources for ARPES include discharge lamp, synchrotron radiation and laser.

2.2.1 Discharge lamp

The discharge lamp used in ARPES can utilize either low or high pressure gas. For low pressure discharge lamp, the gas inside of the lamp is ionized by high voltage or microwave radiation generating plasma. A schematic diagram of a typical helium lamp used in our lab is shown in Fig. 2.2(a). The electrons released by ionization are accelerated by microwaves in a magnetic field inside the plasma cavity. Those high energy electrons further ionize gas and excite ions into high energy state. Due to low pressure in the lamp (below mTorr), excited ions have enough time to relax back to ground state and emit photons with discrete energies that depend on the type of gas used. Helium gas is most often used due to high energy and only few emission lines. Majority of photons from He lamp are due to He I\(\alpha\) emission line (21.2 eV, \(\sim 80\% \) of total intensity), He I\(\beta\) emission line (23.1 eV, \(\sim 10\% \)) and He II\(\alpha\) emission line (40.8eV, \(\sim 10\% \)). The narrow spectral bandwidth (\(\sim 1\text{meV}\)) and small size of the source make He lamp suitable for use in laboratory setting, often in combination with other light sources to increase number of available photon energies. The disadvantage of using a He lamp is inability to tune photon energy and presence of He plasma which can be source of sample contamination.

The high pressure discharge lamp produces continuous spectrum of photons. Due to the high pressure in the lamp (\(\sim 50\) bar), the collisions between excited ionized gases will interrupt and shorten the time for the emission process. This increases the uncertainty in the energy of photons emitted. Such a pressure broadening effect will result in almost continuous tunable photon energy from 5eV to 7eV\[34\] for Xeon bulb. A monochromator then selects certain photon energy with spectral bandwidth of about 5meV. The intensity of this type of lamp
depends on the photon energy and bandwidth as shown in Fig. 2.2(b). This light source offers small range of tunable photon energies with comparable intensity to a He lamp, but worse energy resolution and lower photon energy.

### 2.2.2 Synchrotron radiation

It is well known that electromagnetic radiation is emitted when charged particles are accelerated. This so-called synchrotron radiation is one of the major photon sources for ARPES measurement. At a synchrotron facility, electrons are usually confined to a fixed orbit of the storage ring and move close to the speed of light. Number of bunches of electrons are circulating in the storage ring and produce synchrotron radiation when passing through undulators or bending magnets, as shown in Fig. 2.3.

An undulator consists of a periodic structure of dipole magnets. When high-speed electrons pass though this device, they wiggle periodically and generate collimated photon beam, which are then guided through beamlines to produce monochromatic photons for ARPES measurement. Synchrotron radiation is typically fully polarized within the plane of the storage ring. By changing the magnetic field strength, photon energies can be tuned over a very wide range. For example, the energy range of Beamline 10.0.1 of the Advanced Light Source (ALS) is 17 - 350 eV, which is enough to cover several Brillouin zones in $k_z$ direction. By adjusting monochromator in the beamline, photon flux can be increased at the expense of energy...
resolution and vice versa. At Beamline 10.0.1, with intensity set at $\sim 10^{12}$ photons/s, energy resolution is around 30meV. The synchrotron radiation can work with small number of bunches of electrons to achieve also time resolution. For example, at ALS, the time resolution of 2 ns can be achieved with 2 bunches of electrons.

Typically, synchrotron radiation center has a storage ring with circumference of several hundred meters, which requires large space and consumes significant amount of electricity and is a very expensive operation. This limits the number of synchrotron radiation centers, resulting in a very tight schedule for experiments and tough competition for beam time.

### 2.2.3 Laser

Laser is an ideal photon source for many applications in physics and engineering. However, utilizing laser as a photon source for ARPES measurement was not possible until recently, due to the lack of sufficiently high photon energy and repetition rates. To overcome work function, photon energy needs to be higher than 4.5 eV, which limited possible sources to excimer lasers with low repetition rate and high pulse energy. High pulse energy is favorable for many applications, but in ARPES measurement, the space-charge effect from high number of
simultaneously ejected photoelectrons within single laser pulse will cause electrostatic repulsion and perturbation of their trajectories. As a result the data is broadened and shifted in energy making the studies of the initial state of the electrons difficult. Thanks to the development of techniques based on high harmonic generation and deep-UV nonlinear crystals, high repetition rate lasers with low photon energy can now be used for ARPES measurement.

Both of those approaches require high peak intensity to achieve a usable conversion efficiency. Therefore, the fundamental photon source needs to be a pulsed laser. From Fourier transform, we know that a pulsed output in time domain covers a range of spectrum in frequency/energy domain, as shown in Fig. 2.4(a). Therefore, a broad band inhomogeneous gain medium is typically required so that multiple modes can saturate independently and be present in the cavity simultaneously. But board spectrum is not the only necessary condition for a pulsed output. For example, light bulb contains whole visible spectrum. However, since the phases for different modes in a bulb are random, this produces a constant average intensity with random spiking. If the phases of number of modes are somehow fixed, the peak intensity becomes much larger and the random spiking is suppressed, as shown in Fig. 2.4(b). This principle is referred to as “mode-locking”.

Figure 2.4: Principle of pulsed Laser.

There are two main types of pulsed lasers used in ARPES measurement: Q-switched neodymium-doped yttrium aluminum garnet (Nd:YAG) laser and titanium-doped sapphire (Ti:sapphire) laser utilizing Kerr-lensing effect principle. The former one outputs photons with a fixed wavelength of 1064 nm. By applying several kilovolt pulse to a Pockels’ cell in optical patch, the loss introduced by Pockels’ cell modulates the amplitude and phase of the modes. Due to interaction of the Pockels cell with laser medium and cavity, this type of laser has a long
pulse duration (several nanoseconds), giving an excellent energy resolution (below μeV). An alternative to Pockels cell is use of saturable absorber (SESAME) that produces much shorted pulses (10 ps) at higher repetition rates.

The Ti:Sapphire laser can output photons with tunable wavelength from 700nm to 1000nm. Since the pulse duration is much shorter than Nd:YAG Laser, of the order of a picosecond or hundreds of femtoseconds, the peak intensity is much higher. When high intensity plus propagates in a crystal, non-linearity effects need to be taken into a consideration. The refractive index of crystal will depend on the intensity of light, $n(I) = n_0 + n_2 I$. Because of the non-uniform power density distribution in the light beam (usually Gaussian shape), the refractive index experienced by the beam is higher at the center of the beam than edge. Therefore, a Kerr medium, in this case Ti:sapphire crystal, functions like a lens for high intensity beam. This so called self-focusing or Kerr-lens effect will focus the pulsed beam but not affect the continuous wave (CW) beam, due to its much lower intensity. If a slit is placed near the focus point, a loss can be introduced only for CW beam and the system will automatically favor pulsed beam.

Very high order harmonics of the fundamental laser can be generated when an intense femtosecond laser pulse is focused on dilute noble gases. This can be illustrated by a three-step model shown in Fig. 2.5. The intense electric field from laser pulse can shift the electrostatic potential in a gas atom. The electrons are first ionized and then accelerated by the electric field. When the electric field reverses, electrons will accelerated towards the remaining ion and can recombine at significantly higher energy than initial excitation. This leads to the emission of an odd harmonics of the fundamental beam. This so called high harmonic generation process provides a broadband ultrashort coherent radiation in the XUV range.

![Figure 2.5: Illustration of the three-step model for high harmonic generation](image-url)
The high harmonic generation opens the door for a table-top system with wide tunable range of photon energies. Unlike in the case of synchrotron radiation, the whole system is small enough to fit in a typical laboratory. However, since the high harmonic generation requires a femtosecond laser pulse, the energy resolution is not great. For example, at $h\nu=43\text{eV}$, a 32 fs pulse gives a $\sim350\text{meV}$ energy resolution\[35].

The other way to generate UV photons is second harmonic generation (SHG) or third harmonic generation (THG) using nonlinear crystals. In a classic picture, an electron can be excited inside the crystal by sinusoidally-oscillating electric field of a light beam. If the electron is in an anharmonic potential, in a sufficiently large electric field, its motion is no longer sinusoidal. Based on Fourier transform, in addition to a oscillation at the same frequency as the exciting beam, i.e. linear susceptibility, higher orders of motion are also possible. With the lowest order corresponding to doubling the frequency of incoming beam, also known as second harmonic generation. Depending on the the polarization of fundamental light and SHG light, the SHG can be characterized as three types, 0, I and II. The difficulty of this method is that most nonlinear crystals have short wavelength SHG limit, as shown in Fig. 2.6. Since it is hard for electron analyzer to measure electrons with kinetic energy less than 0.5 eV, by assuming the work function is around 4.5 eV, only light source with photon energy greater than 5 eV can be used in ARPES measurement over a reasonable binding energy range. Therefore only BBO with 6eV SHG limit and KBBF with 7.5eV SHG limit can be utilized in ARPES spectrometer.

One of the first working laser ARPES systems utilized two BBO crystals to generate a fourth harmonic at 6eV\[36]. Although Ti:sapphire laser used in this system can output photons with higher photon energy, the phase matching of BBO crystal limits the achievable photon energy to 6eV. A laser system with KBBF crystal was subsequently introduced by Prof. Shin and Prof. Zhou\[37, 8], which greatly extends measurable binding energy range. Although the energy resolution and photon flux are far exceeding any other photon source, it’s still difficult to use such system due to the fact that photon energy is fixed. This problem can make measurements difficult due to low matrix element for certain bands and limits the access of momentum space to a single sphere. One solution to the above limitations is to design a tunable fourth harmonic generation stage so that phase matching conditions can be tuned over large photon energy
Table 2.1: Photon source comparison.

<table>
<thead>
<tr>
<th></th>
<th>Ti: sapphire Laser</th>
<th>Nd:YAG Laser</th>
<th>Helium Lamp</th>
<th>High pressure lamp</th>
<th>Synchrotron</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Intensity</strong></td>
<td>$10^{15}$ photons/s</td>
<td>$10^{15}$ photons/s</td>
<td>$10^{13}$ photons/s</td>
<td>$10^{12}$ photons/s</td>
<td>$10^{12}$ photons/s</td>
</tr>
<tr>
<td><strong>Energy resolution</strong></td>
<td>submeV</td>
<td>$\mu$eV</td>
<td>$\sim$8meV</td>
<td>$\sim$5meV</td>
<td>1-50meV</td>
</tr>
<tr>
<td><strong>Spot size</strong></td>
<td>1-30µm</td>
<td>1-30µm</td>
<td>1mm</td>
<td>0.5mm</td>
<td>50µm</td>
</tr>
<tr>
<td><strong>Momentum resolution</strong></td>
<td>$10^{-3}$Å$^{-1}$</td>
<td>$10^{-3}$Å$^{-1}$</td>
<td>$10^{-2}$Å$^{-1}$</td>
<td>$10^{-2}$Å$^{-1}$</td>
<td>$10^{-1}$Å$^{-1}$</td>
</tr>
<tr>
<td><strong>Time resolved</strong></td>
<td>100fs - ps</td>
<td>ps - ns</td>
<td>none</td>
<td>none</td>
<td>$\sim$10ns</td>
</tr>
<tr>
<td><strong>Polarization</strong></td>
<td>easy to change</td>
<td>easy to change</td>
<td>unpolarized</td>
<td>unpolarized</td>
<td>changeable</td>
</tr>
<tr>
<td><strong>Bulk sensitivity</strong></td>
<td>10-100ML</td>
<td>10-100ML</td>
<td>$\sim$5ML</td>
<td>10-100ML</td>
<td>$\sim$5ML</td>
</tr>
<tr>
<td><strong>Photon energy</strong></td>
<td>small range</td>
<td>fixed</td>
<td>fixed</td>
<td>small range</td>
<td>large range</td>
</tr>
<tr>
<td><strong>Momentum range</strong></td>
<td>partial BZ</td>
<td>partial BZ</td>
<td>2 BZ</td>
<td>partial BZ</td>
<td>several BZ</td>
</tr>
</tbody>
</table>
range. Indeed a design of a tunable VUV laser was described in the literature recently, but was never used for ARPES studies.

We have developed a laser-based ARPES system with tunable light source based on FHG that has ability to adjust photon energy from 5.4eV to 7eV. We will discuss the setup of this system in details in the following sections. The summary of the properties of various photon sources used for ARPES are shown in table 2.1.

### 2.3 Instrument

The laser-based ARPES system consists of VUV laser based photon source, beam delivery optics, experimental chamber and a modern, multiplexing electron analyzer. The approximate drawing and a picture of the whole system are shown in Fig. 2.7. We will describe each of the key components in details.
2.3.1 Tunable VUV Laser

The fundamental photon beam is produced by a passively mode locked Ti:Sapphire oscillator Mira HP-D made commercially by Coherent Inc. The oscillator is pumped by 18 W CW Verdi laser at 532 nm, which is close to the maximum in absorption spectrum of Ti:sapphire crystal. The oscillator also features dual, ps or fs mode of operation. The picosecond mode has a narrow pulse width (typically \( \sim 5 \text{ps} \), corresponding to \( \sim 0.4 \text{meV} \) bandwidth) and offers a better energy resolution. At the expense of energy resolution, the femtosecond (\( \sim 120 \text{fs} \)) mode allows us to use the same laser system for pump-probe measurements, which will be added into the system.
in the future. This dual-mode feature allows the high energy resolution ARPES measurement
and time-resolved ARPES measurement to share the same laser and optical path. Since shifting
between ps and fs modes only requires replacing of the birefringent filter and output coupler,
it can be done within a hour, which is well below the lifetime of sample. Hence both high
resolution spectroscopy and excitation dynamics can be measured using the same sample.

The infrared beam has power in excess of 3.6W in its tunable range from 710 to 980nm
with maximum power of 5W at 790nm for fs mode. The ps mode has slightly lower power
and we will show that in next section. This high power of fundamental beam is essential for
obtaining sufficient photon flux in the VUV range for high-resolution ARPES measurement.
The intensity of FHG is actually so high that the laser can be set at a much lower power,
for example 12W at 740nm, to extend the lifetime of the laser diodes. The laser runs at a
high, 76MHz repetition rate, which is essential to avoid problems of space charge that can
significantly reduce energy and momentum resolution of the spectrometer. The setup is very
stable and the oscillator can remain mode locked for several days at a time.

2.3.2 Conversion box

The conversion box is based on fourth harmonic generation. The fundamental IR beam is
directed into conversion box, where the IR beam will pass through BBO and KBBF crystals to
generate fourth harmonic of the fundamental beam. The schematic layout of optical compo-
nents and a picture of conversion box during construction are shown in Fig. 2.8. The box has
to be kept under in rough vacuum ($\ll 10$ mTorr), since UV photons below 200 nm are readily
absorbed by oxygen and that is why radiation in this range is called Vacuum UV. The optical
components are mounted on a 3×12 inch aluminum plate enclosed in a 4"OD stainless steel
tube with 6”CFF flanges on each end. Two 2-3/4” viewports at bottom of the tube are used
for pumping port and electrical feed throughs.

To achieve a tunable photon energy, many optical components need to be mounted on a
motorized stage, which also have to be vacuum compatible. Typically, vacuum compatible
motorized stages are large and expensive (several thousands dollars). Here we choose Newport
Agilis Series, since the motorized stages from this series are small enough to fit into a 4”OD
Figure 2.8: (a) Schematic layout of the fourth-harmonic generation. Red, blue and purple arrow indicate the optical path for fundamental light, SHG and FHG. Lens L1 and L2 has a focus length of 200mm and 50mm. Mirror M1 is a cold mirror, only reflecting SHG light. (b) A picture of plate with all optical components before assembled into conversion box. (c) FHG light detected by fluorescent effect.

stainless steel tube and the price is reasonable. The main drawback of using those stages are lack of absolute position for rotational stage. The linear stage and optical mount can have an absolute position by counting steps between two limit switches. Therefore, it’s important to have some viewports at proper position for observation.

The Ti:sapphire laser has a horizontally polarized IR beam. The beam is first focused by lens L1 (f=200mm) inside a BBO crystal for maximum conversion efficiency. Lens L1 is mounted on a translational piezo stage (Newport AG-LS25v6) that allows compensation of chromatic dispersion. The BBO crystal is mounted on a piezo driven rotation stage (Newport AG-PR100v6) that allows adjusting the phase matching angle. A viewport is above the BBO crystal to see the visible SHG from BBO. A dichroic mirror separates the fundamental light from the UV beam after it leaves the BBO crystal. Right now the IR beam is dumped on a
heat sink. For future pump-probe measurement, the IR beam will be reflected out of conversion box to use as a pump.

The SHG is reflected twice and focused by L2 lens (f=50mm) inside a KBBF crystal assembly. Since the KBBF crystal is very thin (\(~1\)mm), it’s necessary to have a short focal length with a small depth of focus, which offers higher conversion efficiency. Mirror M2 is mounted on a piezo tilt mount, that allows adjustment of the beam direction and scans the area of KBBF crystal. This is a must have feature, since the KBBF crystal will “age” under high intensity beam with gradually decreasing conversion efficiency. Note that the phase matching angle of the KBBF crystal for shortest wavelength is larger than the critical angle, which prevents the FHG from leaving the crystal on the opposing side due to total internal reflection. This problem can be solved by sandwiching the KBBF crystal between pair of CaF\(_2\) prisms\([39, 40, 41]\), as shown in Fig. 2.9. In our setup, we utilize the Type I SHG of BBO and KBBF, which changes the polarization of light from an ordinary polarization (fundamental light) to an extraordinary polarization (SHG light). Therefore, the SHG beam is vertically polarized and the KBBF assembly is mounted on a piezo rotation stage that rotates about a vertical axis.

![Figure 2.9](image)

**Figure 2.9:** (a) Schematic diagram of the prisms pair\([39]\). (b) A picture of prisms pair used in our setup.

The FHG beam leaves the assembly at an angle of \(3^\circ\) to \(17^\circ\) away from SHG for wavelengths between 700nm and 930nm. In order to maintain the same location of the beam on the sample, we utilize two mirrors, M3 and M4, to compensate for changes of the beam direction. Since M4 mirror can be adjusted within only \(\pm 2^\circ\), M3 is mounted on a piezo rotation stage, which can rotate 360\(^\circ\), and is used for coarse positioning of the beam onto M4. M4 is then be able to do fine adjustment of the beam angle. This setup offers wide tunable range of fourth-harmonic
generation from 230nm to 177nm (5.4eV - 7eV), while maintaining the beam at the roughly same position on the sample.

The free rotation of M3 also gives a way to observe the generation of FHG by mounting a crystal on the back of the mirror. The FHG light is in VUV range, which cannot be seen by naked eyes. The fluorescence effect of the crystal gives a visible green light under FHG, as shown in Fig 2.8(c). This is an easy way to detect FHG light down to 20µW. A viewport is placed above the KBBF crystal to view both the angle of KBBF and the crystal.

Overall, the use of very small, vacuum compatible piezo driven linear, tilt and rotational stages allows very compact conversion system that fits inside a 12.5-inch-long 4-inch OD chamber. The VUV beam is focused on the sample by a CaF\textsubscript{2} lens with focal length of 150 mm mounted inside of the main chamber.

### 2.3.3 Experimental chamber and ultrahigh vacuum

The experimental chamber is a modified standard design supplied by VG Scienta. The walls are manufactured from stainless steel and lined up with mu-metal shield to reduce the magnetic field around the sample. The outgoing photoelectrons, especially at low kinetic energies, can be easily deflected by even slightest magnetic field. This has very adverse effects on the performance of the ARPES spectrometer, due to the distortion of the paths of the photoelectrons as they travel from sample to the lens of the analyzer. To reduce the magnetic field inside the main chamber, the earth and stray magnetic fields need to be shielded. The orientation of main chamber and electron analyzer needs to be along east-west direction, so that the earth magnetic fields are blocked by mu-metal shield instead of entering the lens of electron analyzer. The main chamber must be degaussed by application a AC magnetic field inside the main chamber starting at \( \sim 600A \) and slowly decreasing its amplitude. This minimizes the stray magnetic fields inside of the mu-metal shield. After carefully connecting the mu-metal in the chamber and electron analyzer together and demagnetizing the system, the magnetic fields can be less than 3 mGauss in the sample-lens area.

The main chamber needs to remain in ultrahigh vacuum (UHV) at all times during measurement. According to the Langmuir Rule, if every particle hitting a surface sticks, then
an exposure of one Langmuir ($1L = 10^{-6}$ Torr$^s$) is sufficient to cover whole surface. Though the possibility of particles sticking on the surface is controlled by sticking coefficient, which is a function of coverage, the Langmuir Rule gives the order of vacuum we should achieve for ARPES measurement. Since photoemission is really sensitive to the surface of sample and some measurements can last for days ($10^5$ s), the pressure needs to be maintained at the order of few $10^{-11}$ Torr.

The main pumps for our UHV system are turbo pumps and ion pumps. Turbo pump includes multiple layers of fixed and rotating fan-like blades mounted on an axis. The molecules hit by the blades will gain a momentum towards to the outside of vacuum chamber. This maintains a pressure difference between front and back side of turbo pump. Since the blades are rotating at a very high speed, 30,000 to 90,000 rpm depending on the model, turbo pump can only operate at a pressure below $10^{-2}$ Torr. Therefore, a rough pump, preferably an oil-free scroll pump, needs to pump the system to rough vacuum prior to turning on the turbo pump.

![Figure 2.10: Partial pressure spectrum of the residual gas after bake of two weeks measured by RGA.](image)

Although turbo pumps can pump the system down to $10^{-11}$ Torr in an ideal situation, ion pumps are usually used in many systems to increase pumping power at ultra high vacuum. Molecules inside of ion pump can be ionized by high voltage, usually 3kV to 7kV, and then
accelerated to strike a titanium anode. Since titanium is very chemically active, ions reacting with titanium will be buried in the anode. An ion pump also needs to operate in a high vacuum condition, because too high ion current will burn through the titanium plate and in some cases stainless steel wall. During the operation, unlike turbo pump, ion pumps have no vibration and can stay active even without a voltage supply for several hours due to presence of sputtered titanium.

The final pressure of a system is a result of a balance between pumping speed and degasing rate. At room temperature, it would take years until molecules attached to the inner surface area of the system degas. A common way to accelerate this process is baking the system to a high temperature, usually around 120°C. During the bake, the pressure inside the chamber can go up to $10^{-5}$ Torr depending on how “dirty” the system was. After a bake of three weeks, the vacuum of system then can easily go down to $10^{-11}$ Torr, if there is no leak. Fig. 2.10 shows gas pressure measured by a residual gas analyzer (RGA) after a two-week bake. The absent of oxygen (mass=32) indicates no leak in the system.

2.3.4 Electron analyzer

The main chamber is connected to the R8000 electron analyzer (supplied by VG Scienta) that was especially tuned for performance at very low kinetic energies. Electron analyzer measures the momentum and kinetic energy of electrons at the same time. When electrons enter into the electron analyzer, they will be first “sorted” by their momentum, then “sorted” by their kinetic energy and finally detected by a 2D detector.

To separate electrons with different momentum, an electrostatic lens is used. As shown in Fig. 2.11, photoelectrons come out of sample at all angles and an aperture at the front of lens will select electrons within certain angular range. Depending on the model of electron analyzer, this angle can be $\pm 7^\circ$ to $\pm 40^\circ$. The larger acceptance angle will require larger aperture and a closer distance between the aperture and the sample. The electrons then travel through a four element lenses, which generate electrical field to focus electrons. Fig. 2.11(b) shows the trajectories of electrons in the lens. The electrons with same momentum will be focused on the same position at the back of lens regardless of the initial positions they left the sample. Due
to the axisymmetric lens, the distribution of electrons is also axisymmetric at the focus plane, as shown in Fig. 2.11(c).

![Figure 2.11](image)

**Figure 2.11:** (a) Geometry of photoelectrons. (b) Trajectory of electrons in the lens. (c) Entrance slit cut out electrons along one direction.

To distinguish electrons with different energies, time-of-flight (TOF) analyzer or hemispherical sector analyzer (HSA) can be used. R8000 electron analyzer is a HSA consisting of two precision machined hemispheres positioned concentrically with an average radius of 200mm. A voltage difference is applied between the inner and outer hemisphere, which generates an electrostatic field allowing electrons with certain kinetic energy (so called "Pass Energy" or PE) to go through the analyzer along the median equipotential surface of radius. HSA allows electrons with slightly different energy (7% of PE for R8000) to pass though and be detected as shown in Fig. 2.12(a).

![Figure 2.12](image)

**Figure 2.12:** Schematic illusion of structure of HSA and electron trajectory within hemispheres.[9]
To limit the HSA “start” position of electrons, an entrance slit is used. As shown in Fig. 2.11(c), the entrance slit selects electrons along one direction. A smaller slit will offer a better energy resolution and R8000 electron analyzer is equipped with a much smaller slit (0.05mm) than previous models, which can deliver a sub-meV energy resolution. R8000 electron analyzer works at several discrete pass energy modes, 5eV, 2eV and 1eV. Smaller pass energy offers better energy resolution, but lower throughput. R8000 electron analyzer allows us to measure spectrum in sweep mode providing kinetic energy range from 0.5eV to 25eV. Since electrons with low energy are very sensitive to electrical noise, R8000 is equipped with a new voltage supply that has very low electrical noise and long-term stability.

2.4 Troubleshooting

After assembling the main chamber, electron analyzer and photon source together, we noticed two major problems during several test. First of the problems was a shift of the focus point with kinetic energy and the second significant distortion of the dispersion for low kinetic energies. In this section, we will discuss the troubleshooting of the system and the way we resolved these two problems.

2.4.1 Focus point shift

The effect of residual magnetic field in the experimental chamber is inevitable even after degaussing and carefully aligning the mu-metal shield. Typical symptom of this is a deflection of photoelectrons and resulting shift of the focal point. When scanning the kinetic energy, photoelectrons with lower kinetic energy will deflect more than ones that have higher kinetic energy, as shown in Fig. 2.13 (a). Therefore, the focus point of lens will shift with kinetic energy. The focus point of lens is determined by finding the maximum intensity of electrons emitted from a thin wire (100 µm). The shift of focus point measured in a test run as a function of kinetic energy of electrons is shown in Fig. 2.13 (b). With typical beam size of 100 µm for the laser used in our setup, changing the energy by 1eV can easily shift the focus point out of beam spot resulting in a nearly zero intensity.
The shift we encountered had to two main reasons: a large residual magnetic field and faulty lens assembly. Before the degaussing process, the residual magnetic field can be of the order of tens of mGauss. After several degaussing procedures and carefully attaching the mu-metal in chamber and lens together, the magnetic field was lowered to less than 3 mGauss in the sample-lens area, which is comparable to the residual magnetic field in other setups [8]. However, the persisting shift of focus point we detected required field larger then 20 mGauss, shown as the red line in Fig. 2.13 (b). This hinted us that there are other reasons beside the residual magnetic field that must cause the shift of focus point. After minimizing the influence of all the possible factors, we narrowed the problem to the lens itself. After very long negotiations, we sent the R8000 analyzer back to manufacturer for repairs and it turned out that there was a problem during lens assembly that caused horizontal “sagging”. The repair took nearly one year to complete and delayed setup of the whole system substantially. In addition to fixing the lens problem, we also asked the manufacturer to remove the apertures behind the slits that serve no important function in solid state spectroscopy, by can distort the photoelectron image. All these efforts resulted in a greatly improved analyzer performance and stability of the focal point over the whole kinetic energy range.

2.4.2 Distortion in angular spectrum

One of the key performance requirement for electron analyzer is a distortion-free angular trajectories of the photoelectrons on the output of the lens. The test device for studying the
photoelectron trajectories is shown in Fig. 2.14 (a). A thin wire at the back side of the device is excited by electron gun or photons and emits photoelectrons in wide energy and momentum range. The narrow slits cut in graphite sheet at the front of the device select photoelectrons only for certain angles, which should produce straight lines along energy direction in measured detector image. One example of which provided by Scienta R4000 data sheet is shown in Fig. 2.14 (b). The initial test with Scienta R8000 in our system for pass energies set at 5eV, 2eV and 1eV reveals a similar straight behavior for kinetic energy larger than 2eV. However, a visible distortion for kinetic energy lower than 2eV can be clearly observed. Considering that R8000 is designed for outstanding performance for low energy spectrum, the results are clearly well below expectations.

Figure 2.14: (a) Illusion of the device for test angular distribution. (b) Angular spectrum provided in Scienta R4000 data sheet. (c) Measured angular spectrum for 30 degree angle range with passing energy set at 5eV, 2eV and 1eV.

A distortion-free spectrum is critical for ARPES measurement, since the distortion can influence the results of band structure measurement. For example, the Dirac cone can appear to be bent instead of straight lines for a graphene or a topological insulator samples. The initial suspect was the stray fields from the electron gun used as excitation source that would deflect mostly photoelectrons with low kinetic energy. But a comparison of an image from shielded and unshielded electron gun revealed no difference in spectrum image and ruled out this as a factor. Since trajectory of photoelectrons inside of lens is controlled by the voltages applied to all four elements of the lens, these voltages need to be adjusted for each individual kinetic energy. This
information is stored in a lens table for each pass energy. By optimizing the lens table, one can minimize the distortions as a function of kinetic energy. Because the construction and dimensions of the lens is classified, we contacted the Scienta company to perform optimization of the lens table based on our test data. After several iterations the distortion of spectrum image was minimized to a tolerable level.

2.5 Instrument Characterization

2.5.1 Beam properties

The fundamental beam of Ti:Sapphire laser is generated with a horizontal polarization, tunable between 710nm and 1000 nm with typical power of 3.6 W to 4.6 W at 18 W pump power. At 16W pump power, the laser intensity is slightly lower, as shown in Fig. 2.15. After second harmonic generation the wavelength of UV beam is between 355nm and 470nm and the power is typically between 0.8 and 1.2 W. The wavelength of FHG VUV beam varies between 177nm and 230nm, which corresponds to 7eV to 5.4eV. In pico second mode, the peak power of the VUV beam is close to 1mW at 205nm and more than 20\(\mu\)W at 177.5nm, as shown in Fig. 2.15. The power of VUV beam changes non-monotonically with wavelength - most likely due to the fact that in the ps mode the pulse width can change with wavelength, which affects the conversion efficiency. The power of the VUV beam is somewhat lower than pervious work\cite{41}, due to use of thinner KBBF crystal. However, this intensity at peak pump power of 18W is more than enough for ARPES measurement and able to saturate the detector even in lowest pass energy/slit combination. We normally adjust the pump power down to about 60% of its maximum to avoid saturation problems.

To get a small beam size, ideally a movable lens should be used to compensate focus length difference. Since the focal length of CaF\(_2\) lens used in this system is large, the depth of focus is long enough to avoid having to make such adjustments. The beam size on the sample is around 30\(\mu\)m at 200nm wavelength, and is essential for measurements of samples with very small portions of flat surface after cleaving. The beam size gradually increases to around 0.1mm at 177nm, which is still much smaller than a Helium lamp.
2.5.2 First results

The described above system is capable of measuring angular and energy distribution of photoelectrons down to 0.5 eV without noticeable distortions of their paths. To demonstrate very good instrumental resolution and usefulness of having ability to tune phonon energy, we used this instrument to obtain ARPES data from several samples, including optimal-doped cuprate Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ (Bi2212), polycrystalline gold, iron arsenic high temperature superconductor BaFe$_{1.82}$Co$_{0.12}$As$_2$, rare-earth antimonides YSb, multiband superconductor MgB$_2$ and topological insulators. Significant portion of this initial data is being analyzed and is in various stages of publication.

2.5.2.1 Optimally doped cuprate Bi$_2$Sr$_2$CaCu$_2$O$_{8.16}$ - Bi2212

In Fig. 2.16 we plot the Fermi surface map of Bi2212 at optimal doping, intensity map and momentum distribution curve at E$_f$ measured along nodal cut. Due to a low photon energy of 6.61 eV, electronic structure at anti-node cannot be measured. The width of the MDC, which
is a measure of the scattering rate[42] broadened by experimental resolution is $\sim 0.011\text{Å}^{-1}$, comparable to some of best previous results obtained using fixed photon energy laser ARPES [36, 37, 8] and significantly sharper than typical data obtained at synchrotron facilities. The momentum resolution measured by the thin slit device results in a much smaller number around $0.001\text{Å}^{-1}$, which indicates the broadened peak of Bi2212 is most likely due to intrinsic effects in the sample.

Note that at the time of writing we used an old design of closed cycle refrigerator capable of cooling the sample down to only 15K. Therefore, the energy line widths are limited by sample temperature rather than electron analyzer or the light source. Based on the data measured using gold sample, we can estimate that the upper limit of energy resolution is around 3meV.

### 2.5.2.2 MgB$_2$

One of the first systems we measured using newly constructed laser ARPES system was multiband superconductor MgB$_2$. The small spot size of laser system and ultra-high resolution is of critical importance, since the size of high quality single crystal is smaller than 500μm. With a beam size only around 30μm, we obtained much sharper data of MgB$_2$ with many more fine details as compared to previously published results[43], as shown in Fig. 2.17. In the intensity plot of $\sigma_2$ band shown in Fig. 2.17 (c), we can easily observe a kink at 75meV resulting from strong coupling of conduction electrons to phonons, which was not previously
Figure 2.17: Data from MgB$_2$ multi band classical superconductor. (a) previous intensity plots showing multiple broad bands from Ref [43]. (b) previously measured EDCs at $\sigma$ and $\pi$ bands below and above $T_c$ showing emergence of the superconducting gap from Ref [43]. (c) dispersion of the $\sigma$ band measured with our laser ARPES system. Series of EDCs in the proximity of Fermi momentum for $\sigma$ band. Arrow marks the dip in the spectrum that arises due to presence of a Leggett mode.

reported in published literature. Additionally, with the benefit of ultra-high resolution, a new low energy excitation at 10meV is observed as shown in Fig. 2.17 (d). The quasi-particle peak shows a dispersion less feature, which is not expected for classical Bogolubov quasiparticle, and all the features of this spectrum are consistent with Leggett mode. Such data demonstrated excellent capability of the new system for finding new phenomena in a well-studied material by utilizing the small beam size and ultra-high resolution.
Figure 2.18: Photon energy dependence of BaFe$_{1.82}$Co$_{0.12}$As$_2$ and YSb. (a)-(c) Fermi Surface mapping of BaFe$_{1.82}$Co$_{0.12}$As$_2$ with photon energy 6.61eV, 6.05eV and 5.51eV. (d)-(f) Intensity plot cut of (a)-(c) along Γ-X direction. (g) MDCs at Fermi level for various photon energies. Red points mark peak positions. (h) $k_z$ dispersion extracted from (g). Solid red circles mark momentum of Fermi crossing. Dashed red circle shows absence of Fermi crossing at 6.61eV. Green line is a guide to the eye for $k_z$ dispersion. (I) Intensity plot cut of YSb along Γ-X direction. (J) $k_z$ dispersion extracted from (I).
2.5.2.3  BaFe\textsubscript{1.82}Co\textsubscript{0.12}As\textsubscript{2} and YSb

There are two key benefits of tuning photon energy in ARPES measurements. The intensity of emitted photoelectrons often strongly depends on the photon energy due to matrix elements. At a particular photon energy some bands can be therefore too weak to observe. Tuning to a different photon energy can reveal such “hidden” bands\cite{44, 45}. Perhaps more importantly, majority of materials have 3D electronic structure and performing measurements using fixed photon energy allows access to only a spherical cut through 3D momentum space. By tuning the photon energy one can “change” the radius of this sphere and therefore map a 3D volume in the momentum space.

As an example, in Fig. 2.18 we show the data revealing the 3D dispersion of the hole pocket in iron arsenic high temperature superconductor Co-doped BaFe\textsubscript{2}As\textsubscript{2} and rare-earth antimonides YSb. Top panels (a-c) show the ARPES data measured at $E_f$ for three different photon energies of Ba122, which is used to reveal Fermi surface. The intensity is clearly shows a dependence on photon energy. With lower photon energy, intensity along $k_x$ direction becomes weaker, which is mostly likely due to cross section effects (i.e. matrix elements). In the panels below we present binding energy-momentum intensity plots. Areas of high intensity (red and green) mark locations of the bands. In the panel (d) we plot data measured at 6.61 eV (which corresponds to $k_z$ value of 3.98 with inner potential set to 12eV), the top of the band is located below the $E_f$, which signifies absence of central hole pocket for this value of $k_z$ momentum. Upon lowering of the photon energy this band is moving to higher binding energy and crosses the $E_f$ creating a hole pocket (panels e,f). The data is summarized in panel h, where we plot the locations of the Fermi crossings along the z-direction. Indeed the Fermi surface measured at synchrotron facility at higher photon energies includes a ellipsoidal sheet centered at Z-point (i.e. center of the Brillouin zone boundary, $k_z$=3). The date of YSb shows a similar behavior. Since YSb has a cubic crystal structure, it shows a more dramatic change with photon energy. It should be emphasized that such data long $k_z$ direction was previously only possible to obtain at large synchrotron facilities.
2.5.2.4 $k_z$ dependence of the superconducting gap in Ba$_{0.61}$K$_{0.39}$Fe$_2$As$_2$

![Image](image.png)

Figure 2.19: Superconducting gap in optimally doped Ba$_{0.61}$K$_{0.39}$Fe$_2$As$_2$ measured with various photon energies and temperatures. Symmetrized EDCs for optimal-doped Ba$_{0.61}$K$_{0.39}$Fe$_2$As$_2$ at photon energy of (a) 5.7eV (b) 6.05eV and (c) 6.7eV. (d)-(f) Extracted gap values as a function of temperature from data in (a)-(c) by fitting with two lorentzian peaks.

Iron arsenic superconductor has a 3D electronic structure. Therefore, measuring gap symmetry along $k_z$ direction is necessary to reveal the full symmetry of gap. Traditionally, this kind of measurement is carried out at synchrotron radiation center, which usually has a tight schedule and limited energy resolution. The small gap size of iron arsenic superconductor can be only reliably measured using laboratory based laser ARPES system. Here, we measured optimal-doped Ba122 sample with different photon energies, as shown in Fig. 2.19. The optimally doped sample is chosen due to the good sample quality and high $T_c$, which makes the gap measurement easier considering that we can only cool sample down to 13K at present. In Fig. 2.19 (a)-(c) we plot symmetrized EDCs measured using 870nm (5.7eV), 820nm (6.05eV) and 740nm (6.7eV) photons and at temperatures above and below $T_c$. We can then fit two Lorentz peaks to find the size of gap, which is shown in Fig. 2.19 (d)-(f). With high energy resolution, the gap size for different $k_z$ can be measured accurately. Within our measurement range, the size of the gap has the same value around 7.5±0.5meV.
CHAPTER 3. INTRODUCTION TO TOPOLOGICAL INSULATORS

3.1 Introduction

Understanding the nature of the phases of solids is one of the most important and challenging goals in condensed matter physics. Before the quantum Hall effect was discovered by Klaus von Klitzing in 1980[10], all phases were differentiated by symmetry breaking, which gives a unique order parameter with a nonzero expectation value in associated ordered state. For example, the ferromagnetism breaks the rotation symmetry in spin space, which leads to a nonzero magnetization $m(x)$. The quantum Hall effect, on the other hand, is classified by a topological invariant, the Chern number. Similar to quantum Hall effect, topological insulator, existence of which was theoretically predicted in 2005[46, 47, 48] and experimentally observed in 2006[49], is also a state associated with a novel $Z_2$ topological invariant. A lot of research has been carried out in this field. In this chapter, we will introduce the basic concepts and materials of this research area.

3.2 Hall Effect

The 2D topological insulator is a quantum spin Hall insulator, which is a close cousin of the integer quantum Hall state. To better understand the origin and concept of topological insulator, we will begin with Hall effect and integer quantum Hall effect.

When a magnetic field points in a perpendicular to the current in a metal or semiconductor, electrons will be deflected and accumulate on one side of the sample, forming an electrical field that counteracts the force of magnetic field (Lorentz force). In equilibrium state, the total force acting on electrons will be zero and the voltage $V_H$ across the sample perpendicular to current and magnetic field will be
\[ V_H = -\frac{IB}{ned} \]  

Figure 3.1: Hall effect. \( F_L \) and \( F_E \) are the Lorentz force acting on electrons.

where \( n \) is the density of carriers and \( d \) is the thickness of the sample. This effect was first discovered by Edwin Hall in 1879. Since the voltage is perpendicular to current, resistivity and conductivity will be a second-order tensor with non-zero Hall resistivity \( \rho_{xy} \) and Hall conductivity \( \sigma_{xy} \) being the off-diagonal elements,

\[ \rho_{xy} = \frac{1}{\sigma_{xy}} = \frac{E}{J} = -\frac{B}{ne} \]  

This classical picture works fine for small magnetic field, but fails to explain experimental results at low temperature and high magnetic fields. In 1980, Klaus von Klitzing\[10\] discovered that Hall conductivity was exactly quantized rather than a linear function of the magnetic field, as shown in Fig. 3.2. When Hall conductivity forms a step, resistivity of device also drop dramatically to nearly zero. This can be understood by a semiclassical idea of Landau Levels and current-carrying chiral edge state. Here, we try to use a different approach\[50\] of a Berry phase and Chern number to get a better sense of how topology plays a role in this system.
3.3 Integer Quantum Hall Effect

When a uniform magnetic field acts on a 2D non-interacting electron system, we have

\[ H \Psi = \left[ \frac{1}{2m} (p + eA)^2 + U(r) \right] \Psi = E \Psi \quad (3.3) \]

\( U(r) \) stands for crystal potential with periodicity of \( a \) and \( b \) along \( x \) and \( y \) axes. By applying Bloch theorem, wave function for band \( n \) with momentum \( k \) has a form of \( \Psi_k^n(r) = e^{ikr} u_k^n(r) \).

Equation becomes

\[ \hat{H}(k)u_k^n(r) = \left[ \frac{1}{2m} (-i\hbar \nabla + \hbar k + eA)^2 + U(r) \right] u_k^n(r) = E^n u_k^n(r) \quad (3.4) \]

When a small current flows through the device, response to an external electrical forces can be calculated using Kubo formula. Therefore, the Hall conductivity can be expressed in terms of Bloch wave function,
where $\sigma_{xy}^n$ is Hall conductivity of the completely filled $n^{th}$ band and the total Hall conductivity is the sum over all filled bands. $A^n(k) = i \langle u^n_k | \nabla_k | u^n_k \rangle$ is a real vector field known as Berry connection defined on the whole magnetic Brillouin zone $T^2_{MBZ}$. In presence of magnetic field, an enlarged magnetic unit cell, extended from a to qa, as shown in Fig. 3.3(a), with integral multiples of magnetic flux $p \ast (eB/h)$ is chosen so that magnetic translation operator and the Hamiltonian will commute with each other. Since the magnetic Brillouin zone is periodic, it can be folded by the boundary, forming a donut shape as shown in Fig. 3.3(b).

![Diagram of magnetic Brillouin zone](image)

Figure 3.3: (a) Illustration of magnetic Brillouin zone with q=3. (b) Folded magnetic Brillouin zone as a donut shape[11].

We know that for integral quantum Hall effect, the Hall conductivity forms precise plateau structure regardless the materials and disorder. This is deeply connected to the topological order and Berry connection. The Berry connection itself is gauge-dependent, so it is not a physical observable. For a gauge transformation $\hat{u}^n_k(r) = u^n_k(r) \exp[i\chi(k)]$, the observable physical quantities should stay the same, since only a overall phase is introduced. Under this transformation, the Berry connection will change to $\hat{A}^n(k) = A^n(k) + \nabla_k \chi(k)$. This transformation forms a U(1) fiber bundle on the magnetic Brillouin zone.

If the Berry connection is well defined on magnetic Brillouin zone, from Stokes theorem, the Hall conductivity will always be zero for every completely filled bands. However, when...
there are zero points on $u^n_n$, the phase of the wave function will not be well defined globally over the magnetic Brillouin zone. If we set a fixed phase for certain point, for example $u^n_n(r_0)$ is real, the phase can be continuously defined until it reaches another zero point (i.e. $u^n_n(r)$ is real again). Therefore, the magnetic Brillouin zone will be divided into multiple areas. Just like a unit interval $[0, 1]$ bound to a circle $S^1$, this object can either forms a trivial cylinder or a “twisted” Mobius strip depending how interval $[0, 1]$ is connected at the boundary. The $U(1)$ bundle can be connected trivially or “twisted”, which defines the topology of the system. Take two areas as an example shown in Fig 3.3(b). If the phase mismatch at the boundary $\partial H$ is

$$|u^n_H\rangle = \exp[i\xi(k)]|u^n_i\rangle$$  \hspace{1cm} (3.6)$$

since the Berry connection is well defined in both areas, we can then use Stokes theorem and Eq. 3.5 becomes

$$\sigma_{xy}^n = \frac{e^2}{\hbar} \frac{1}{2\pi} \int_{\partial H} d\mathbf{k} \cdot [A^n_I(k) - A^n_H(k)] = \frac{e^2}{\hbar} n$$  \hspace{1cm} (3.7)$$

with

$$n = \frac{1}{2\pi} \int_{\partial H} d\mathbf{k} \cdot [A^n_I(k) - A^n_H(k)] = \frac{1}{2\pi} \int_{\partial H} d\mathbf{k} \cdot \nabla_k \xi(k)$$  \hspace{1cm} (3.8)$$

When vector $k$ rotates one full turn at the boundary, $\nabla_k \xi(k)$ has to be back to the same point with rotation of integer number turns. This integer number is also known as winding number. This guarantees that $n$ must be an integer. Therefore, the Hall conductivity must forms precise plateau structure regardless the materials and disorder. This integer is also known as first Chern number. If Chern number is zero, a transformation can always be found to make $\xi(k)$ zero everywhere at boundary, which goes back to a well defined Berry connection, i.e. a trivial state. With non zero Chern number, the Chern number will not change unless the gap is closed at Fermi energy, which makes the definition of Chern number invalid. If we define that any insulator which has a nontrivial topological invariant is a topological insulator, the integer quantum Hall effect will be the first discovered example of a topological insulator.
3.4 Topological Insulators

In 2005, when studying the electronic structure of graphene, C. L. Kane and E. J. Mele[46] discovered that at sufficiently low energy, a single plane of graphene exhibits a quantum spin Hall (QSH) effect, which is topologically distinct from a band insulator. Later they showed[47] that this topological order can be characterized by $\mathbb{Z}_2$ invariant, which is the narrow definition of topological insulator. The topological insulator can be a 3D or 2D system, with 2D case also known as quantum spin Hall insulator. Unlike quantum Hall effect where time reversal symmetry is broken by magnetic field, in topological insulator the time reversal symmetry is preserved, which gives

$$H[-k] = \Theta H[k] \Theta^{-1} \quad (3.9)$$

where $\Theta = e^{i\pi S_y/h}K$ is the time reversal operator, $S_y$ is the spin operator and $K$ is complex conjugation operator. This constraint gives a zero Chern number, since the symmetry of clock and counter-clock rotation of $k$ in Eq. 3.8 forces $n=0$. Therefore, a globe smooth gauge can always be defined in a Brillouin zone. However, since the wave functions must satisfy time reversal symmetry, the Brillouin zone can then be divided into four parts with only two independent patches $A$ and $B$, as shown in Fig. 3.4. We can then follow the same process for Chern number by constructing a “twist” at the boundary between those two patches, which can gives a new topological invariant. The connection at boundary satisfies

$$|u_m(k,t)\rangle_A = t^{AB}_{mn} |u_n(k,t)\rangle_B \quad (3.10)$$

where $m$ and $n$ run over $N$ pairs of bands that follow Kramers degeneracy (I and II). We can then defined a number that is “nearly” gauge invariant similar to Eq. 3.7 with

$$v = \frac{1}{2\pi i} \int_{\partial\tau_1} d\mathbf{l} \cdot \left[ A^B(k) - A^A(k) \right] = \frac{1}{2\pi i} \int_{\partial\tau_1} d\mathbf{l} \cdot \text{Tr}[t^{AB}\nabla t^{AB}] \quad (3.11)$$

where $A$ is the Berry connection defined as before. This number is still not gauge invariant, since a gauge transformation for one band in Kramers doublets $u^I(k,t) = u^I(k,t) \exp[i\chi(k)]$
will give a transformation in the other band $\hat{u}^\Pi(-k,-t) = u^\Pi(-k,-t)\exp[i\chi(k)]$, which will change the number $v$ with plus or minus an even number[12],

$$v \rightarrow v + 2\int_{\partial \tau_{1/2}} dl \cdot \nabla \chi(k)$$

(3.12)

Therefore, a modulo two should be added to make it gauge invariant.

$$v = \frac{1}{2\pi} \int_{\partial \tau_1} dl \cdot [A^B(k) - A^A(k)] \mod 2$$

(3.13)

$v$ is called $Z_2$ topological invariant. For the trivial case,

$$|u_{-k,n}^I(-t)\rangle = \Theta |u_{k}^I(t)\rangle$$

(3.14)
, which is very like $\xi = 0$ in Eq. 3.6. This so called “TR-smooth” gauge will gives a $v = 0$, i.e. the trivial insulator, while $v = 1$ gives a non-trivial topological insulator. This construction of $Z_2$ topological invariant through incapability of shrinking the integral to vanish is formulated by Fu and Kane[12] and can be easily extended to 3D situation[51]. There are also several equivalent ways to evaluate $Z_2$ invariant[47, 52, 13]. Among them, Fu and Kane[13] combined the inversion symmetry and time reversal symmetry and obtained a simple way to calculate $Z_2$ invariant solely as a function of the parity eigenvalues of the filled bands at high symmetry point without the need to find globally well defined Berry connection, which is very impractical. The $Z_2$ invariant can be written as

$$2D: (-1)^v = \prod_{i=1}^{4} \delta_i$$

$$3D: \begin{cases} (-1)^{v_0} = \prod_{i=1}^{8} \delta_i \\ (-1)^{v_k} = \prod_{n_k=1; n_j=0,1} \delta_{i=(n_1, n_2, n_3)} \end{cases}$$

with

$$\delta_i = \frac{\sqrt{\text{det}[w_{mn}(\Gamma_i)]}}{\text{Pf}[w_{mn}(\Gamma_i)]} = \pm 1$$

where $\Gamma_i$ is the high symmetry point, $w_{mn} = \langle u_m(k)|\Theta|u_n(k)\rangle$ and Pf is the Pfaffian of a matrix, $\text{pf}(A)^2 = \text{det}(A)$. Any four points can define a topological invariant. For 2D situation, the Brillouin zone only has four high symmetry points, therefore only one $v$ can be constructed. For 3D situation, the Brillouin zone has eight high symmetry points, which gives four $v$: $v_0, (v_1, v_2, v_3)$. Several examples are shown in Fig. 3.5 to illustrate the situation for three dimensions.

The four $v$ in 3D are not all equal. The $v_0 = 1$ gives us a strong topological insulator with a robust surface state protected from impurities, while the weak topological insulator with $v_0 = 0$ and non-zero $v_i$ ($i=1, 2, 3$) does not. Since stack of 2D spin Hall insulator will have $v_0 = 0$, they are always weak topological insulators. Therefore, 3D topological insulator, which can not be constructed out of a 2D spin Hall insulator, is a new topological state.
3.5 Surface State

One of the most important features of topological state is the unique surface state at the boundary between a topological insulator and trivial band insulator (or vacuum). As we discussed above, the topological nature guarantees that a topological non-trivial state cannot be smoothly deformed into a trivial state. Since the topological state is only well-defined for completely filled bands, the surface state at the boundary must close the gap and cross the Fermi energy $E_f$, thus it must be a conductive surface state. The sensitivity of ARPES measurement to surface states, while it can be unfavorable in case of ordinary samples, is a major advantage in measuring topological surface state. Ever since the first experiment proved 2D quantum spin Hall effect in HgTe quantum wells\cite{49}, there is a very high research activity in studying the nontrivial surface state\cite{53, 54}.

Depending on the nature of topological order, the surface state can be quite different, as shown in Fig. 3.6. For integer quantum Hall effect, the spinless surface state is spatially separated at the two edges of 2D insulator. In a classical picture, the surface state can be understood in terms of the skipping motion of cyclotron orbits bouncing off the edge. The edge states are chiral, where electrons can only travel in one direction. Because the back scattering channel is suppressed, the surface has a very high conductivity.

The surface state of topological insulator has a linear dispersion and special spin texture. The surface state of 2D topological insulator can be treated as a combination of two quantum Hall states. Since the angular momentum needs to change sign under time reversal symmetry,
the two surface states with opposite momentum must have opposite spin. The 3D topological insulator can be much more complicated. For the single cross at $E_f$, the surface state forms a Dirac cone similar to graphene. The spin texture of the Dirac cone is fully spin polarized\[56\] where electrons at opposite momentum state have opposite spins. Although the spin of electron is always perpendicular to the momentum, it does not need to stay in the same plane. Due to the symmetry of crystal, the Dirac cone of topological insulators is usually deformed toward to a hexagon shape, as shown in Fig. 3.7(a)&(b). Theoretical studies\[57, 58\] have shown that when Dirac cone is deformed from circle shape, the spin will have an out-of-plane component. This was indeed confirmed\[59\] by spin-resolved ARPES, which can measure all three projections of photoelectron spin. As shown in Fig. 3.7 (c)&(d), the deformed Dirac cone of Bi$_2$Te$_3$ leads to a non-zero z component (out-of-plane) of the spin unlike a case of purely in-plane spin in TlBiSe$_2$, which has a nearly circular Fermi surface.

The unique spin texture of topological insulators makes the surface state very robust. This can be understood following argument proposed by Zhang\[60\]. Since the back-scattering channel for electrons requires a spin flip, the electrons scattered off nonmagnetic impurities will pick up a phase shift of $\pi$ or $-\pi$ due to time reversal symmetry. The electrons having opposite phases will interfere with each other. Because changing the phase by $2\pi$ leads to a negative
Figure 3.7: (a)&(b) Fermi surface mapping of TlBiSe$_2$ and Bi$_2$Te$_3$. (c)&(d) Component of spin within surface plane and out-of surface plane.[59]

sign for spin 1/2 particles, the interference is always deconstructive. Therefore, the back-scattering channel is suppressed. This was elegantly demonstrated by STM measurement[61] for Bi$_{0.92}$Sb$_{0.08}$. The magnetic and non-magnetic impurities can have quite different effect on the surface state, for example the magnetic impurities will open a gap at Dirac cone and cause back scattering[62]. We will discussed this in more details in the next chapter.

In addition to single crossing of $E_f$, the surface state can also have multiple crossings. Actually the first discovered 3D topological Bi$_{0.9}$Sb$_{0.1}$[15] has five crossing points at Fermi surface. When surface state crosses the Fermi surface, there can be even or odd number of such
crossings, as shown in Fig. 3.8 (a) and (b). With every crossing, the gap opens and closes once, which changes \( Z_2 \) invariant by 1. Therefore, for strong topological insulators with \( \nu_0 = 1 \), the number of crossing points is always odd. The surface state with even crossing points indicates a weak topological insulator with \( \nu_0 = 0 \). This surface state is not protected by time reversal symmetry and a gap will open when surface is contaminated with impurities.

3.6 Materials

Because a classification of a material as a topological insulator can be determined by a calculation, many materials have been predicted to be topological insulators. Yoichi Ando’s review paper[63] lists materials that have been experimentally studied as of May 2013. Without going into details about every system, here we will only focus on few that have very important influence on studies of topological insulators. And from now on, we will restrict our discussions only to 3D topological insulators.

\( \text{Bi}_{1-x}\text{Sb}_x \), also known as first-generation topological insulator, was theoretically predicted in 2007[13] and experimentally confirmed in 2008[15]. The antimony itself is a \((1;111)\) strong topological insulator with metallic bulk state due to H valence band crossing \( E_f \), as shown in Fig. 3.9(a) on the right side. Bi, on the other hand, is a \((0;000)\) trivial conductor with \( L_a \) band fully filled. When doped with antimony, the two bands \( L_a \) and \( L_s \) will flip at certain
doping. With further doping of antimony, a gap opens at $E_f$ due to the movement of the H and T valence bands away from $E_f$. We now have a 3D topological insulator state, marked as the grey area in Fig. 3.9(a). The ARPES measurement confirmed that this material is a true topological insulator, since the number of crossing points from $\Gamma$ to $M$ is five, an odd number, as shown in Fig. 3.9(b).

![Figure 3.9: (a) Band inversion in Bi$_{1-x}$Sb$_x$. (b) Surface state of Bi$_{0.9}$Sb$_{0.1}$ measured by ARPES](image)

Although the Bi$_{1-x}$Sb$_x$ conforms the concept of 3D topological insulators, it has many drawbacks for research and applications. First, the band gap is very small (<30meV). This makes the sample more close to a topological “conductor”. Therefore, most transport properties are determined by bulk state. Second, since the Fermi surface is too complicated, it’s hard to study the effect of various driving parameters on surface state. Finally, there may be some elemental inhomogeneities which make the detailed studies more difficult.

To overcome the drawbacks of Bi$_{1-x}$Sb$_x$, a topological insulator with stoichiometric crystals, simple surface states and large band gap will be important for research. In 2009, Bi$_2$Se$_3$, also known as second-generation topological insulators, was found by two groups[16, 17]. This material has a layered structure made of five layers (QL), where two Bi atomic layers are intercalated in three Se atomic layers as shown in Fig. 3.10. The bonding within each QL is largely covalent, while it is mostly van der Waals between QLs. This makes the crystal naturally cleave between two QL, forming a mirror-like flat surfaces suitable for ARPES measurement.

The theoretical prediction of topological nature of Bi$_2$Se$_3$ is shown in Fig. 3.11(a). By turning on the spin orbit coupling, energy levels $|P1_+\rangle$ and $|P2_-\rangle$ are flipped. Since those
two bands have opposite parity, the material becomes a topological insulator once the spin orbit coupling is taken into account. Since electronic structure around $E_f$ is dominated by four states, $|P1^+, \uparrow(\downarrow)\rangle$ and $|P2^-, \uparrow(\downarrow)\rangle$, the effective Hamiltonian can be written as

$$H(k) = \epsilon_0(k)I_{4 \times 4} + \begin{pmatrix} M(k) & A_1 k_x & 0 & A_2 k_- \\ A_1 k_x & -M(k) & A_2 k_- & 0 \\ 0 & A_2 k_+ & M(k) & -A_1 k_x \\ A_2 k_+ & 0 & -A_1 k_x & -M(k) \end{pmatrix} + o(k^2) \quad (3.17)$$

where $k_\pm = k_x \pm ik_y$, $\epsilon_0(k) = C + C_1 k_z^2 + D_2 k_\perp^2$ and $M(k) = M - B_1 k_z^2 - B_2 k_\perp^2$. With vacuum boundary condition, we can get an effective diagonalized Hamiltonian at (111) surface.
\[ H_s(k_x, k_y) = \begin{pmatrix} 0 & A_2 k_- \\ A_2 k_+ & 0 \end{pmatrix} \] (3.18)

where \( A_2 \) describes the Fermi velocity of Dirac cone. This equation tells us that the surface state of \( \text{Bi}_2\text{Se}_3 \) is a single Dirac cone located right at \( \Gamma \) point, as observed by ARPES measurement and shown in Fig. 3.11(b). Due to the simple surface state and easiness to grow single crystals, most of research so far was focused on this system. Based on the strong spin orbital coupling of Bi, this system has many variants, for example, \( \text{Bi}_2\text{Te}_3[64], \text{TlBiTe}_2[65], \) \( \text{GeBi}_2\text{Te}_4[66] \) and so on.

![Diagram](image)

**Figure 3.11:** (a) Band inversion in \( \text{Bi}_2\text{Se}_3[16] \). (b) Surface state of \( \text{Bi}_2\text{Se}_3 \) measured by ARPES[17].

Even though the gap size for \( \text{Bi}_2\text{Se}_3 \) is petty large (0.3eV), its bulk properties are rather metallic. This is because the Fermi energy lies on the top conduction band. Tuning the Fermi energy to the center of gap will therefore be important for this system. We will discussed it in more details in the next chapter.

Except for topological insulators based on Bi, the strong spin-orbit coupling can also be realized in many other materials. One famous example will be \( \text{SmB}_6[67, 68] \), a topological Kondo insulator, as the strong spin-orbit coupling is encoded in the hybridization between f
 electron and conduction electron. Due to an odd parity form factor of the f electrons, when hybridization happens at Fermi level, the parity changes at X or M point in the Brillouin zone for cubic Kondo insulator[69], as shown in Fig. 3.12. This leads to three Dirac cones with heavy quasiparticles and a (1;111) strong topological insulator. The surface conduction was confirmed by surface conductivity measurement[70] and three bands that not expected from calculations of the bulk electronic structure have been reported by ARPES[71, 72] to be consistent with surface states. All of those measurements indicate that SmB$_6$ is a possible topological Kondo insulator. However, the nature of SmB$_6$ is still need to be determined by extra measurements, such as a spin-resolved ARPES measurement shows that the surface state has a unique spin texture of topological insulator, that is for opposite momentum, electrons have opposite spin. At this time, we can only state that SmB$_6$ is a good candidate of topological Kondo insulator.
CHAPTER 4. REVERSIBLE TUNING OF THE SURFACE STATE

4.1 Introduction

Tuning of the properties of the surface state is one of important topics in the field of topological insulators. In this chapter, we will first demonstrate that under good vacuum condition, the electronic structure of the surface state in a “true” topological insulator Bi$_2$Te$_{2.28}$Se$_{0.58}$ remains unchanged over a period of two weeks even after temperature cycling. We will then show that the Dirac cone of this material can be reversibly tuned by UV–assisted absorption of atomic hydrogen. This presents a simple way to reversibly tune the carrier concentration at the surface by adjusting device temperature in a low–pressure hydrogen atmosphere. Before the discussions of our results, a brief summary of the effect of doping and deposition on topological insulators is presented in the following sections.

4.1.1 Effect of doping

One way to tune the surface state is doping or substitution by various elements into the topological insulators. As we mentioned before, the topological state is based on time reversal symmetry. Doping with magnetic elements will break the time reversal symmetry. Fig. 4.1 shows the result of doping with Fe and Tl. When doped with iron ((Bi$_{0.88}$Fe$_{0.12}$)$_2$Se$_{3.7}$ and (Bi$_{0.84}$Fe$_{0.16}$)$_2$Se$_{3.7}$), the magnetic moment of iron lifts the degeneracy at high symmetry point and forms a gap at Kramers point. When doped with Tl ((Bi$_{0.9}$Tl$_{0.1}$)$_2$Se$_3$), a nonmagnetic element, Fermi level shifts downward, due to the hole doping, without opening a gap. This clearly shows a way to tune the properties of the surface state. Various elements have been used to achieve this goal in Bi$_2$Se$_3$. 
Figure 4.1: (a) Illusion of Dirac cone in as grown sample. (b) Band structure of as grown Bi$_2$Se$_3$. (c) Band structure of (Bi$_{0.9}$Tl$_{0.1}$)$_2$Se$_3$ shows no gap at Kramers point. (d) Illusion of Dirac cone with a gap open at Kramers point. (e) & (f) Band structure of (Bi$_{0.88}$Fe$_{0.12}$)$_2$Se$_3.7$ and (Bi$_{0.84}$Fe$_{0.16}$)$_2$Se$_{3.7}$ with a gap open at Kramers point.[62]

Since most popular topological insulators Bi$_2$Se$_3$ and Bi$_2$Te$_3$ have different electronic structure i.e. Fermi surface topology and carrier concentration therefore Bi$_2$(Te-Se)$_3$ system, which substitutes Te with Se, is a good candidate to efficiently adjust many properties of the surface state. Indeed - for certain compositions, this material shows surprisingly large bulk resistivity[19] and low carrier concentration[73], as shown in Fig. 4.2. By substituting Te with Se, the Kramers point also moves to a higher binding energy as shown in Fig. 4.3. For Bi$_2$Se$_3$, the upper bulk band crosses Fermi level, while for Bi$_2$Te$_3$, the lower bulk band crosses Fermi level. When x is between 0.15 and 1.5, the Fermi level intersects only with the surface state bands, which makes it a “true” topological insulator.

Although in Bi$_2$(Te-Se)$_3$ the Dirac cone can be tuned significantly, the Fermi level never crosses the Kramers point. By partially substituting Bi with Sb, the Fermi level can be tuned to exactly the energy of the Kramers point, as shown in Fig. 4.4. This means the Dirac cone can be tuned between n–type and p–type topological insulator, which is significant for applications.
However, this type of tuning is not reversible and cannot be done in situ.

4.1.2 Effect of deposition

Compared with doping, the deposition has a more direct effect on surface state of topological insulators. Controlled deposition has been carried out for many elements and compounds, including NO₂, Fe[74], K[75], CO, Rb[76], water[77], Cs, Gd[22], N₂ and air[78]. The deposition effect of either magnetic or nonmagnetic impurities can be characterized in three stages, as shown in Fig. 4.5.

In stage one, the metallic impurities will donate electrons to the surface state, which will move the Fermi level upward and Kramers point downward. The chemical compounds are likely to have a reaction with topological insulators and leave a charged vacancy at the surface,
Figure 4.3: Surface state band structure of Bi$_2$Te$_{3-x}$Se$_x$ with various compositions, x, measured along Γ – K direction.[20]

Figure 4.4: Bi$_{2-x}$Sb$_x$Te$_{3-y}$Se$_y$ for four x values (x = 0, 0.25, 0.5 and 1.0) where y = 1, 1.15, 1.3 and 2.[21]
for example, \( \text{Bi}_2\text{Se}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{H}_2\text{Se}^+ + 2\text{Bi(OH)}_3 \)[77]. This has an overall effect that is similar to metallic impurities. Since donated electrons can move freely on the surface, those electrons will form a 2D electron gas (2DEG), which is shown as a sharp rim around the bottom of the upper conduction band in Fig. 4.5.

In stage two, with more electron doping, the Fermi level moves further up and 2DEG state splits into a pair of sharp parabolic states centered at equal and opposite momentum that shift away from \( \Gamma \) point. This is well known as Rashba splitting[79], where twofold spin degeneracy of 2DEG can be lifted by spin orbit coupling introduced by Bi. The splitting is comparable to one present in metal surface states in metals such as gold and orders of magnitude larger than one present in semiconductors. This may imply potential for application in spintronics devices[76].

In stage three, the deposition begins to saturate and Fermi level does not change any further. Depending on the type of elements used for deposition, final state can contain one or more pairs of Rashba split bands. Since the binding energy between deposited element and surface is very high, this process is an one-way ticket and can not be reversed easily.

As discussed in previous section, the magnetic doping will lift the degeneracy at high symmetry point and form a gap at Kramers point. The situation for deposition is not the same. The nonmagnetic impurities can also lift the degeneracy in the high-doping regime. This is shown in Fig. 4.5, which compares nonmagnetic elements Cs and Rb with strong magnetic element Gd.

The nontrivial surface state can surprisingly survive the exposure of the sample surface to atmospheric pressure[78], as shown in Fig. 4.6. Although the composition of air is complex and the pressure is several orders higher than deposition pressure, after cleaving samples in air, the surface state is still measurable (upon transferring the sample into UHV chamber) with only reduced intensity due to finite escape depth of the photoelectrons through the absorbed layer on top of the sample. This demonstrates that topological insulators may be suitable for practical devices, since ultra high vacuum environment is not a strict requirement for existence of a surface state.
Figure 4.5: Effect of surface deposition of (a) Cesium, (b) Gadolinium and (c) Rubidium on Bi$_2$Se$_3$.[22]
Figure 4.6: (A) Band structure of the fresh Bi$_2$Se$_3$ cleaved and measured in the UHV chamber at 30 K. (B)&(C) Band structure of Bi$_2$Se$_3$ cleaved in air and measured in UHV at 30 K and 300 K.[78]

4.2 Crystal Growth

Single crystals used in our measurement are pseudobinary Bi$_2$(Te-Se)$_3$. The crystals were grown using proper ratio of high purity elements of bismuth (99.999%), selenium (99.999%) and tellurium (99.999%) that were sealed in a quartz tube and melted into an ingot in an induction furnace to homogenize the composition. The ingot was then sealed in a quartz tube with a larger diameter and loaded into a Bridgman furnace. A crystal was grown by withdrawing the quartz tube at 1 mm/hr after being heated to 800°C.

The samples are cut into thin pieces of rectangular shape. Fig. 4.7 shows the resistivity curve for the samples from different batches, which are very similar to pervious results[19]. Chemistry of the samples was determined using electron probe micro-analysis (EPMA). We measured atomic ratio of Bi, Te and Se at 16 points on sample and the result shows a consistent values of 11.9% Se, 41.1% Bi and 46.9% Te, which means the sample is Bi$_2$Te$_{2.28}$Se$_{0.58}$. We
Figure 4.7: Resistivity curve for the samples with different batch numbers.

choose this composition for measurement due to the largest bulk resistivity at low temperatures.

4.3 Methods

ARPES data was acquired using a laboratory-based system consisting of a Scienta SES2002 electron analyzer and GammaData Helium UV lamp. Samples were cleaved in-situ at room temperature with base pressure in the vacuum system at $5 \times 10^{-11}$ Torr. All data were acquired using the HeI line with a photon energy of 21.2 eV. The angular resolution was 0.13° along and $\sim 0.5°$ perpendicular to the direction of the analyzer slits. The energy resolution was set at $\sim 6$ meV. Custom designed refocusing optics enabled us to accumulate high statistics spectra in a short time to study sample aging effects. The results were reproduced on several samples and temperature cycling.

All DFT calculations have been done using VASP[80] on the $(1 \times 1)$ surface unit cell for Bi$_2$Te$_3$(0001) with a slab of five atomic layers and 12 Å of vacuum. The bottom two layers are fixed at bulk positions and the top three layers are free to relax until the absolute magnitude of force on each atom is reduced below 0.02 eV/Å. A $k$-point mesh of $10 \times 10 \times 1$ with a Gaussian smearing of 0.05 eV and a kinetic energy cutoff of 300 eV were used.

4.4 Results and Discussion

In this section, we will demonstrate the long–term stability of surface state, Dirac cone can be tuned by temperature of sample and discuss the cause of this phenomenon.
4.4.1 Long–term stability

Figure 4.8: (a) Band structure of Bi$_2$Te$_3$ taken with $h\nu=30$ eV 8, 20 and 40 min after cleavage in UHV. Analogous Band structure of Bi$_{1.95}$Mn$_{0.05}$Te$_3$ 15 min, 4 h and 9 h after cleavage.[81] (b) Band structure of Bi$_2$Se$_3$ at $5 \times 10^{-11}$ Torr and $T = 6$ K 3 h and 34 h after cleaving.[75]

The electronic properties of topological insulators were shown to change significantly in vacuum with time[81, 76, 75, 78] with typical timescale of hours or even minutes after cleaving and usually results in formation of conventional 2D electron gas, as shown in Fig. 4.8. The delicate nature of sample surface presents therefore series of challenges such as long–term stability before it can be utilized in a new class of devices. This behavior was previously attributed to phonon effects[82] or photovoltaic effect[83]. Before discussion of the reason behind this phenomenon, we will first show that, if the vacuum is sufficiently good, the surface state can actually remain unchanged for a long time at high temperature.

In Figure 4.9, we demonstrate the temperature dependence and stability of surface band in Bi$_2$Te$_{2.28}$Se$_{0.58}$ sample. Intensity plots shows almost linear dispersion of the surface band and the absence of conduction bulk band at 300 K and 20 K, which is consistent with resistivity measurement and indicates that the bulk of the sample is insulating. The Kramers point is located 220meV below Fermi level - signature of n-type topological insulator. After cooling to 20 K (panel b) the Kramers point moves to higher binding energy of about 260meV. Remarkably, after the sample was warmed up back to 300 K, the band structure recovers to its original state even though its surface was kept for 15 days in vacuum and exposed to UV and extensive
Figure 4.9: Long term stability of the Dirac cone and temperature-induced changes in Bi$_2$Te$_{2.28}$Se$_{0.58}$. (a) Intensity plot along high-symmetry direction at 300K shortly after cleaving. (b) The data from the same cleave after cooling to 20K. The band moves to higher binding energy caused by electron doping. (c) The data from the same cleave as in (a) and (b) at 300 K after 15 days of continuous measurement and temperature cycling, also showing that the carrier concentration and band position is the same as in freshly cleaved sample.

4.4.2 Reversible tuning of Dirac cone

As shown in previous section, the temperature has a large effect on the binding energy of Kramers point. Here we will demonstrate a reversible tuning of the Dirac cone by changing the temperature. In a fresh cleaved sample, the energy of Kramers point is -0.22 eV at 300 K, as shown in Figure 4.9(a). We performed large number of consecutive measurements for each of the sample temperatures. Each measurement lasted for around 40 mins and results are shown in Figure 4.10. In panels a-d, we plot the ARPES intensity at various temperatures and exposure times. After the sample was kept at 20 K for 90 hours we can observe the bulk conduction band, which demonstrates that the chemical potential is located within the bulk band gap for a clean surface. In panel e, we show the evolution of the binding energy of the Kramers point with time and temperature. Each data point represents separate measurement and increases in sample temperature are marked by arrows. When sample was kept at 20 K,
Figure 4.10: Evolution of the band structure with time and temperature. (a)-(d) Intensity plot at temperatures and time indicated by arrows in panel (e). (e) Binding energy of the Kramers point as a function of time upon temperature cycling. Arrows mark the first measurement at a given temperature.

the Kramers point was moving to higher binding energies, consistent with electron doping of the surface state.

This process is relatively slow, which excludes scenarios involving phonons [82] or photovoltaic effect[83]. The associated large time constant suggests deposition of some element at the surface as the cause. The changes significantly slow down with time - a saturation effect that is most likely caused by the reduction of the sticking coefficient with increased coverage. The reverse effect, with a similar time constant, occurs upon warming up. Here, we rapidly increase the sample temperature to values indicated by the arrows and continuously perform multiple consecutive measurements at each temperature. The carrier concentration decreases with increasing temperature. In each case, a saturation level is reached when the sample is kept at fixed temperature for sufficiently long time. Therefore, just by changing the temperature, the Kramers point can be tuned. This process is also reversible as shown in Fig. 4.9(e).
4.4.3 Hydrogen absorption

We will now focus on the cause of the changes in the band structure at low temperature. The most likely suspect for the change of carrier concentration is the absorption of hydrogen. Even in the best vacuum system made of stainless steel, hydrogen is omnipresent due to the ability to diffuse through stainless steel and degassing from the mu-metal shielding that was annealed in hydrogen atmosphere. Upon cooling, the hydrogen can condense onto the surface of the sample and donate electrons to the surface state. The binding energy of molecular hydrogen is quite low (∼50 meV). It is possible, however, that UV light used for ARPES is causing its dissociation at the surface to atomic hydrogen that has a much larger binding energy. To validate our assertion about the origin of the shift, we dosed small amount of hydrogen into our vacuum system with and without UV. This is done by briefly firing the titanium sublimation
pump, which releases the hydrogen absorbed by titanium filament as verified by monitoring readings of residual gas analyzer.

The binding energy of the Kramers point during this process is shown in Figure 4.11. At the beginning of measurement, without additional hydrogen, the binding energy of the Kramers point increases as in previous case and shifts downward by about 70 meV. We inject hydrogen with UV light switched on for 10 seconds at $10^{-7}$ Torr at time marked by black arrow in Figure 4.11. We do not observe any significant change after the injection, as shown in Fig. 4.11(a)&(b). We then inject the same amount of hydrogen in the presence of UV light. Under those conditions the band shifts in energy by 36 meV, as shown in Fig. 4.11(b)&(c), measured immediately after injection. We repeat this process two more times. The drop is obvious each time, but with decreasing magnitude, indicating saturation of hydrogen on the surface of sample.

To support our proposition that the origin of electron doping and downward shift of Dirac point is due to absorption of atomic H, we used density functional theory (DFT)[84, 85] to calculate the adsorption of H$_2$ and H on Bi$_2$Te$_3$(0001) surface. Figure 4.12 shows the DFT adsorption energy of H$_2$ as a function of distance to the surface with different exchange-correlation functionals at the hcp site with an out-of-plane orientation for H$_2$. The data clearly shows that the interaction between H$_2$ and Bi$_2$Te$_3$(0001) surface is of van der Waals type. PW91[86] gives a very weak binding of $-28$ meV at 3.7 Å and LDA[87] gives a stronger binding of $-80$ meV at 2.4 Å, which is closer to $-71$ meV at 3.2 Å from the more accurate description of the system by the van der Waals exchange-correlation functional[88]. Upon full relaxation, the bond length of the adsorbed H$_2$ is 0.77 Å, only slightly longer than the 0.75 Å of the free H$_2$ molecule. The relaxation of the surface atoms is negligible. The adsorption energy at the three adsorption (fcc, BRIDGE (brg) and top) sites is 5, 11 and 36 meV higher than the hcp site, respectively. The difference in adsorption energy on the same site with different orientations of H$_2$ is less than 5 meV.

In contrast, the interaction between atomic H and Bi$_2$Te$_3$(0001) surface is much stronger, with a binding energy of $-1.41$ eV at the brg site (in reference to a free atomic H), followed by $-1.08$, $-0.99$ and $-0.92$ eV at the top, fcc and hcp sites, respectively. The space among the surface atoms can accommodate atomic H very well, the adsorbed H is in a co-planar position to
Figure 4.12: Adsorption energy of H$_2$ on Bi$_2$Te$_3$(0001) as a function of distance to the surface with LDA, PW91 and vdWDF-MK as exchange-correlation functional. The inset shows the top and side views of the relaxed structure. The (1×1) surface unit cell is highlighted in the top view. Red, gray and white spheres stand for Bi, Te and H, respectively.

surface Te atoms at all sites, except the top site, giving a binding distance of 1.73 Å. Although the adsorption energy in reference to a free H$_2$ molecule is 1.02 eV, which means that H$_2$ does not dissociate on Bi$_2$Te$_3$(0001) surface, the presence of UV light during ARPES measurement can produce atomic H, as confirmed experimentally. In supporting evidence, we also directly calculated the shift of Dirac point in the surface band with different H$_2$ coverage. The downward shift due to the weak H$_2$-surface interaction is about 20 meV, too small compared to the shift of 100 meV observed in experiment.

4.5 Conclusions

With extensive, long duration measurement by AREPS, we have demonstrated that the topological insulator behavior of Bi$_2$Te$_{2.28}$Se$_{0.58}$ remains unchanged over two weeks under good vacuum conditions, which is distinct from commonly observed Rashba effects with typical timescale of hours or even minutes after cleaving. We also showed that the Dirac cone electronic properties can be reversibly tuned by UV-assisted adsorption of atomic hydrogen.
CHAPTER 5. ELECTRONIC STRUCTURE OF Ce$_2$RhIn$_8$

5.1 Introduction

Heavy fermions, first discovered in 1975\cite{23}, are some of the most fascinating materials in condensed matter physics. The name originates from the enhanced effective mass of quasiparticles, as shown in Fig. 5.1. The Sommerfeld coefficient $\gamma = \lim_{T \to 0} C/T$ has an enhanced value two or three orders of magnitude higher than normal metal, while the functional form of resistivity $\rho \propto T^2$ indicates that the system is still a Fermi liquid. The behavior of this system is dominated by 4f and 5f electrons and arises due to competition between Kondo effect and Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction. Due to the complexity of this interaction, many marvelous phenomena are seen in heavy fermion compounds, such as Kondo insulator, unconventional superconductivity, quantum criticality and many others. Since electrons in heavy fermion materials are an important test-bed for understanding the interplay between magnetic and electronic quantum fluctuations, measurement of the electronic structure is a crucial step for further research. Before the discussion of our results, a brief introduction to this topic is presented below.

5.1.1 Kondo effect

Kondo effect arises from the interaction of conduction electrons and magnetic ions. Those magnetic ions are usually due localized magnetic moment of f or d electrons. As a result of this interaction, the resistivity $\rho(T)$ shows a logarithmic increase at low temperature and forms a minimum at certain temperature defined as Kondo temperature. This results was first explained by Kondo in 1964\cite{89} by considering the scattering of electrons by magnetic ion at low temperature, as shown in Fig. 5.2(a). This perturbation theory takes into account the
interaction described by

\[ \Delta H = J S \cdot s_0 \]  

(5.1)

Here \( S = 1/2 \) is the spin of impurities and \( s_0 \) is the local spin density of conduction electrons. This will give an extra term for resistivity \( \rho(T) \propto J \ln(1/T) \) in addition to the phonon contribution. Although the high-temperature properties agree well with experimental results, at low temperature this approach is clearly invalid, since resistivity diverges in the \( T \to 0 \) limit. This problem is known as Kondo problem and can be solved by considering a more detailed Anderson impurity model[90],

\[
H = \sum_{k,\sigma} \epsilon_k c_{k,\sigma}^\dagger c_{k,\sigma} + \epsilon_f \sum_{\sigma} f_\sigma^\dagger f_\sigma + U n_f n_f + V \sum_{k,\sigma} (c_{k,\sigma}^\dagger f_\sigma + \text{H.c.})
\]  

(5.2)

where \( J \propto V^2 \). This leads to a local Fermi liquid state with screened magnetic moment at impurities site, which can be calculated by numerical renormalization-group (NRG) method[91]. This approach works well for single or very dilute magnetic moments. When we have a dense lattice analog of the single ion Kondo effect, also known as Kondo lattice, the Anderson single impurity model need to be replaced with periodic Anderson model (PAM) with sum over all impurity sites,
\[ H = \sum_{\mathbf{k},\sigma} \epsilon_{k\sigma} c_{k\sigma}^{\dagger} c_{k\sigma} + \epsilon_f \sum_{i,\sigma} f_{i\sigma}^{\dagger} f_{i\sigma} + U \sum_i n_i^f n_i^f + V \sum_{i,\sigma} (c_{i\sigma}^{\dagger} f_{i\sigma} + \text{H.c.}) \] (5.3)

This results in a different low temperature behavior. Below \( T_K \), resistivity begins to increase until it reaches a maximum at certain temperature, usually called coherence temperature \( T_{coh} \). Then resistivity has a sharp drop that follows the same power law \( \rho(T) = \rho_0 + A T^2 \) of a Fermi liquid system. Although the detailed mechanism of how the coherent heavy quasiparticles form in the Kondo lattice is still not quite clear, the role of interaction between f electron and conduction electron is likely the key.

With lowering the temperature below \( T_K \), the size of screening clouds increases and they begin to “touch” each other. This allows for the conduction electrons to hop from site to site, which reduces the resistivity. Also due to the strong coupling between f and conduction electrons, f electrons can be injected into Fermi level resulting in a bigger Fermi surface and higher effective electron mass. Note that since the \( T_K \) and \( T_{coh} \) are just two loosely defined energy scales, \( T_K \) is not necessary smaller than \( T_{coh} \) in some cases.
5.1.2 RKKY interaction

Kondo effect is not the only result of coupling between f electron and conduction electron. The local moments can interact with each other through an indirect exchange of conduction electrons, also known as RKKY interaction. Since RKKY interaction preserves local moment while Kondo effect screens it, the competing of those two effects determines the phase diagram for a heavy fermion system.

Because the energy scales given by two interactions are different,

\[
T_K = D e^{-1/(2 J_p)} \\
T_{RKKY} = J^2 p
\] (5.4)

The phase diagram based on energy scales argument introduced by Doniach[92] is shown in Fig. 5.4. The antiferromagnetic (AFM) regime, where \( T_K < T_{RKKY} \), dominates for lower \( J_p \) range. At \( J_{p_c} \), if the AFM transition is a second-order phase transition, the critical temperature reaches zero Kevin indicating a quantum critical point in the phase diagram. The Kondo effect and Fermi liquid state dominate at large \( J_p \). However, how the system transits from a heavy-
fermion state to an AFM is still a matter of debate.

Two scenarios have been proposed for the transition from a heavy fermion to an AFM state, as shown in Fig. 5.5. In the first scenario[93], AFM arises from a spin density wave due to instability of the parent heavy Fermi liquid state. Here, Kondo screening is essentially intact and the local moments are completely quenched at zero temperature over the paramagnetic regime. In the second case[94], Kondo screening of local moments is absent at QCP and AFM states arises due to the ordering of local moments caused by RKKY exchange interactions. This is known as Kondo destruction. The dimensionality of the system plays a critical role here, with spin density wave being favored in 3D, while Kondo destruction scenario is more favorable in a 2D system [24].

Figure 5.4: Doniach diagram.[26]
5.1.3 CeₙMIn₃ₙ₊₂ family

Ce₂RhIn₈ with lattice parameters a=4.665Å, c=12.244Å[25] and tetragonal crystal structure is a member of CeₙMIn₃ₙ₊₂ (M=Co, Rh or Ir, n=1, 2 or ∞) family, which are antiferromagnetic heavy-fermion materials. Since the structure of Ce₂RhIn₈ can be viewed as inserting a CeIn₃ into CeRhIn₅, as shown in Fig. 5.6, one may expect that it shares some of the properties with both of those two compounds.

The value of the Sommerfeld coefficient $\gamma \sim 400 \text{ mJ/molCeK}^2$[95], determined by specific heat measurement, is consistent with heavy fermion nature of this material. The resistivity curve follows a $\ln(1/T)$ behavior between 55K and 130K[25] (shown in Fig. 5.3) as a result of Kondo screening. Single impurity model estimate of Kondo temperature $T_K$ yields value of 10K. The slope of resistivity changes at $T_N = 2.8K$ and $T_{LN} = 1.65K$ indicating two magnetic transitions, as shown in Fig. 5.7. Neutron scattering measurements[27] performed at 1.6K show presence of an anti-ferromagnetic state with ordering vector $Q = (\frac{1}{2}, \frac{1}{2}, 0)$. At this temperature magnetic moment of Ce is well screened to 0.55$\mu_B$, compared with 2.35$\mu_B$ per Ce at high temperature (200K). The slope of resistivity changes more dramatically[28] at $T_{LN}$ than $T_N$. $T_{LN}$ is also more sensitive to pressure with a $P_c \sim 0.04\text{GPa}$. It was suggested that the magnetic structure changes between an incommensurate and a commensurate structure at $T_{LN}$[28].

The nature of AFM order seems to fit better scenario of local moment ordering rather than SDW[95]. In case of CeRhIn₅, below $T_N$, the fitting of specific heat requires an additional term in the excitation spectrum to account for anisotropic gap in SDW state.
Figure 5.6: Crystal structure of CeₙMIn₃n+2 family.[27]

\[ C/T = \gamma_0 + \beta_M T^2 + \beta_M (e^{-E_g/k_BT})T^2 \]  \hspace{1cm} (5.5)

In case of Ce₂RhIn₈ this term is absent. Also the change of Sommerfeld coefficient \( \gamma \) above and below \( T_N \) (from 400 to 370 mJ/molCeK²) is much smaller than CeRhIn₅ (400 to 56 mJ/molCeK²), indicating that only a small part (~ 8%) of Fermi surface is gapped in Ce₂RhIn₈. \( T_N \) decreases linearly with pressure. According to conventional models of antiferromagnetic quantum criticality[93], \( T_N \propto (P_c - P)^1 \) indicate a effective 2D dimensionality of the spin-fluctuation spectrum.

Ce₂RhIn₈ becomes superconducting above 1 GPa with maximum \( T_c=2K \) near 2.3GPa[29]. Unlike conventional superconductors, Ce₂RhIn₈ shows non-Fermi-liquid behavior with \( \rho(T) \propto T^{0.95\pm0.05} \) and superconductivity co-exist with anti-ferromagnetism. The phase diagram is shown in Fig. 5.8. Some published works[96] also report that the resistivity of Ce₂RhIn₈ goes to zero at ambient pressure, which may be related to superstructure in Ce₂RhIn₈ rather than a sign of the bulk superconductivity[97].
Due to the layered structure, electronic properties of Ce$_2$RhIn$_8$ are believed to be quasi-2D, which is rarely seen in heavy-fermion superconductors. ARPES data of EDCs along high symmetry directions have been previously reported[98, 99]. But no reported measurements of the Fermi surface. To better understand the superconductivity and heavy-fermion phenomenon in this material, we examine the Fermi Surface and detailed band dispersion of Ce$_2$RhIn$_8$ using variable photon energy.

5.2 Methods

The ARPES measurements were performed using ARPES system at Ames Laboratory and beamline 7.0.1 of Advanced Light Source (ALS). Samples were cleaved in situ using Torr seal vacuum epoxy and had mirror-like surfaces. All ARPES data were taken at T=16K, above the AFM transition temperature (2.8K) but close to Kondo temperature (10K). Laboratory-based ARPES system consists of GammaData ultraviolet lamp (21.2eV He I$_\alpha$), custom-designed refocusing optics and a Scienta SES2002 electron analyzer. The UV spot size is around 1mm and the energy resolution was set at 10meV. Beamline 7.0.1 is equipped with Scienta R4000
Figure 5.8: Phase diagram of Ce$_2$RhIn$_8$ with pressure.\cite{29}

electron analyzer with energy resolution around 40meV.

First-principles band structure calculations were performed using spin-polarized density functional theory (DFT)\cite{85} within generalized-gradient approximation (GGA) with projector-augmented wave (PAW) method\cite{100, 101} by VASP code\cite{80}. The GGA exchange correlation functional parameterized by Perdew, Burke and Ernzerhof (PBE)\cite{102} was used. The semi core p states of Rh, as well as the lower lying d states of In, are treated as valences states, while the 4f electron of Ce are treated either as placed in the core or as valence state for comparison. The kinetic energy cutoff was 400 eV and the Monkhorst-Packs scheme\cite{103} was used for Brillouin zone sampling with a k-point grid of $2\pi \times 0.02\text{Å}^{-1}$.

The calculated lattice parameters, energies and magnetic moment of Ce atoms in different magnetic states are listed in table 5.1, together with the experimental results. The lattice parameters obtained from the GGA calculations are in good agreement with experiment, with about 1% overestimation. Magnetic moment of the Ce atom from the calculation also agrees well with the experimental measurement. From table 5.1, we see that the magnetically ordered states have slightly lower energy than the non-magnetic state. Between the AFM and FM states, FM state has lower energy, although the energy difference is as small as 1 meV per
Table 5.1: Optimized lattice parameters, energies and magnetic moment of Ce atom in different magnetic states.

<table>
<thead>
<tr>
<th></th>
<th>a(Å)</th>
<th>c(Å)</th>
<th>M(_{\text{Ce}}) (µ(_B)/Ce atom)</th>
<th>E (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>6.651</td>
<td>12.283</td>
<td>0.69</td>
<td>-4.029</td>
</tr>
<tr>
<td>FM</td>
<td>4.709</td>
<td>12.278</td>
<td>0.68</td>
<td>-4.030</td>
</tr>
<tr>
<td>Non-Mag</td>
<td>4.705</td>
<td>12.280</td>
<td>0</td>
<td>-4.027</td>
</tr>
<tr>
<td>Expriment[27]</td>
<td>4.664</td>
<td>12.238</td>
<td>0.55</td>
<td>-</td>
</tr>
</tbody>
</table>

atom.

5.3 Results and Discussion

Fig. 5.9 (a)-(d) shows the Fermi surface mapping of Ce\(_2\)RhIn\(_8\) by integrating electron intensity over \(E\_f \pm 5\text{meV}\) at various photon energy. Data in panel (a) was measured using laboratory He source - photon energy of 21.2eV, (b) at SRC using 80eV photons, data in panels (c)&(d) was measured at ALS using 94eV and 105eV photons. Since the cross section of bands can be quite different for various photon energies and polarizations, by performing measurements over large photon energy range, we can reveal the complete Fermi surface topology. To illustrate the orbital contributions to electronic structure, calculated Fermi surfaces with f electrons treated as localized and itinerant are shown in Fig. 5.9 (e)&(f) respectively. The magnetic moment for itinerant scenario is artificially set to zero, since the temperature for measured data is higher than \(T_N\). The Fermi surface for those two scenarios are nearly the same around M point. Close to \(\Gamma\) point, the measured Fermi surface more resembles a localized picture as shown in Fig. 5.10. The localized picture results in a diamond shape (marked by the arrow) of the FS sheet surrounding \(\Gamma\) point, which fits the experiment well in contrast to a square shape in itinerant scenario. This is not surprising since the data was measured at 16K. Although the temperature is comparable with \(T_N \approx 10K\) and screening of f electron by conduction electron should exist to some extent, it is still much higher than coherence temperature of 5K and most f electron will remain localized.
Figure 5.9: Fermi Surface measured with (a) He lamp (21.2eV) at 16K. (b) synchrotron (SRC, 80eV) at 20K. (c) synchrotron (ALS, 94eV) at 17K. (d) synchrotron (ALS, 105eV) at 17K. Black dashed lines show the position of first Brillouin Zone. (e)&(f) Fermi surface calculated by DFT with f electron set as localized and itinerant respectively.
Figure 5.10: Fermi surface close to Γ point with overlay of (a) local or (b) itinerant Fermi surface calculation.

The shape of the Fermi surface remains constant over studied range of the photon energies, which covers $19\pi/c$ to $25\pi/c$ range of the $k_z$ values. This demonstrates a quasi-2D character of the electronic structure of Ce$_2$RhIn$_8$, which is consistent with 2D effective dimensionality of the spin-fluctuation spectrum from phase diagram[29]. Such 2D character is further illustrated by $k_z$ dispersion shown in Fig. 5.11(a)&(c) along Γ-X ($k_y = 0$) and Γ-M ($k_x = k_y$) directions. This was accomplished by changing photon energy form 80eV to 157eV. The bands with high photoelectron intensity are almost vertical with little or no observable dispersion. The $k_z$ dispersion calculated within localized scenario, shown in Fig. 5.11(b)&(d), also predicts a nearly 2D electronic structure especially for the bands along Γ-M direction.

By performing measurements with different photon energies, the whole FS can be determined and consists of 2 pockets around Γ point, 4 pockets around M point and one pocket located between Γ and X point. The main difference between measured and calculated Fermi surface is that the band forming the pocket marked by arrow in Fig. 5.10(a) crosses the Fermi level along Γ-X direction at around $0.35\pi$, which would cut one pocket into two smaller pockets. This is more obvious in intensity plot shown in Fig. 5.12. The $\alpha$ band clearly crosses Fermi level along both Γ-X and Γ-M direction, which forms two electron pockets, one around Γ point
and one close to X point, while the calculated result places this band below Fermi energy along Γ-X direction. Band α also shows a nearly zero intensity along Γ-M direction at all photon energy at ALS data, which may due to the selection rules for horizontal polarization of light beam. Band δ forms a tiny electron pocket centered at Γ point.

Calculations and experiment agree well on the topology of Fermi surface around M point with four pockets β₁ - β₄. Based on intensity plot shown in Fig. 5.12, we can conclude that all four bands form electron pockets. Although the calculation shows a crossing between β₂ and β₃ pockets, there is no strong evidence for this in experimental data, although the momentum resolution may not be sufficient to detect such a crossing.

To reveal the nature of the AFM order, one needs to establish the presence of a nesting vector equal to AFM ordering vector \( \mathbf{q} = (0.5, 0.5, 0) \). In Fig. 5.10, the high intensity spot at the corner of bands β₂ and β₄ forms a vector slightly larger than ordering vector \( \mathbf{q} \), which should decrease due to injection of f electrons below coherence temperature.

Since the Fermi surface of Ce₂RhIn₈ contains multiple pockets, when nesting occurs for one of the pockets, large part of Fermi surface is not affected. This is consist with specific heat measurement[95], which predicts that only a small part (\( \sim 8\% \)) of Fermi surface is gapped. Therefore, the spin density wave scenario cannot be completely excluded from our measurement.

### 5.4 Conclusions

We used angle-resolved photoemission spectroscopy to measure the electronic properties of Ce₂RhIn₈. The lack of significant \( k_z \) dispersion confirms the quasi two dimensionality of the electronic structure. Fermi surface is quite complicated and consists of several hole and electron pockets. By comparing our data with DFT calculation, we find our results consistent with a localized picture of f electrons. This provides clues to understanding of unusual transport and thermodynamical properties of this important material.
Figure 5.11: $k_z$ dispersion along (a)&(b) $\Gamma - X$ direction and (c)&(d) $\Gamma - M$ direction from 80eV to 157eV comparing with local f electron calculation.
Figure 5.12: Intensity plot along high symmetry direction overlay with local f electron band structure calculation. Green arrow marked the band name and location.
6.1 Introduction

In a semiclassical model of current excitation, the momentum $k$ of electron is changed by electric field,

$$k(t) = k(0) - \frac{eEt}{\hbar} \tag{6.1}$$

For fully occupied band, the shift of momentum does not occur as there are no empty states in the proximity of $E_f$. The shift of momentum in partially occupied band in a perfect crystal will result in an oscillation of electrons in both phase space and real space, also known as Bloch oscillation. This phenomenon is not observed in real crystals due to the scattering of electrons by phonons and lattice defect, which give rise to resistivity. In this semiclassical picture, the band structure is not altered by electric field and the flow of current is a result of shift of electron distribution in momentum space. The average velocity (drift velocity) of electrons is typically very small in common metals. For example, a current of 1 amperes in a 1 mm diameter copper wire corresponds to drift velocity of only 0.01 cm/s. This velocity is orders of magnitude smaller than Fermi velocity, which approaches $10^7$ cm/s. Therefore, the effect of current is not observable in a common metal.

However, for topological insulators with protected surface Dirac states, the surface mobility is greatly enhanced over the bulk state. This high surface mobility is observed in many topological insulators, for example, $10^4$ cm$^2$/(V·s) in Bi$_2$Te$_3$[104], $8*10^4$ cm$^2$/(V·s) in Bi$_{0.91}$Sb$_{0.09}$[105], $2*10^4$ cm$^2$/(V·s) in Bi$_2$Se$_3$[106] and $2*10^3$ cm$^2$/(V·s) in Bi$_{2-x}$Sb$_x$Te$_3$-$y$Se$_y$[107]. Since the drift velocity is equal to surface mobility times magnitude of electric field, a large drift velocity can
be achieved even for modest voltages. This is particularly important for ARPES measurements, because strong electric field can disturb photoelectrons and introduce artifact in the data.

6.2 Method

The topological insulator sample used in this experiment is Bi$_2$Te$_{2.28}$Se$_{0.58}$. As discussed before, this sample has an insulating bulk state at low temperature. The sample is cut into 2mm long by 1 mm wide, thin rectangles. The resistivity measured in vacuum is very similar to data provided by the crystal growth group. The resistivity increases as temperature decrease and reaches to around 500 ohms cm at 15K, which is the temperature for all the measurement presented in this chapter.

Figure 6.1: Pictures of the device used in the current excitation experiment with (a) front view and (b) top view

The images of the device used to apply current in the sample are shown in Fig. 6.1. The bottom of sample is glued by Torrseal epoxy to a sapphire plate, which offers good thermal contact and electrical insulation from the ground of cold finger. The contacts at the top of sample are connected to two copper wires by silver epoxy and indium wire. In the new design of the device (not shown in this picture), a thin film of gold is deposited directly on top of the sample to reduce contact resistivity and achieve more uniform electric field. The copper wires are connected to two tungsten wires by two screws electrically insulated from the ground. After loading the sample into the cold finger under vacuum, the tungsten wires contact two copper plates mounted to the cold finger and connected to a power supply via several electrical
feedthroughs. An adjustable resistor connected between positive and negative output of power supply is used to adjust the voltage distribution in the sample so that the potential at the beam position is close to the electrical ground (0V). This ensures that the kinetic energy of the photoelectrons will not change significantly with voltage applied across the sample.

Because the ground of the sample floats on resistor network attached to a power supply, it is important to minimize the electrical noise as it would cause broadening of the spectra. The ground of low noise power supply, Keithley 2200-60-2, is connected to the metal part of electron analyzer to ensure common ground for both instruments. The cable used outside of vacuum was constructed from a standard USB 2.0 cable, that is double shielded and has twisted pairs of wires. This reduces the electrical noise picked up by wiring. A filter containing several capacitors and resistors is placed between the cable and electrical feedthrough to further reduce electrical noise. It attenuates large spikes and reduces unwanted AC components. The noise level, which is verified by an oscilloscope, measured as root mean square (RMS) voltage is smaller than 3mV at the feedthrough.

ARPES data was acquired using the tunable laser-based system mentioned in previous chapter. All data were measured with voltage applied vertically, along the direction of entrance slit. The “positive voltage” means the voltage on the top contact is positive and bottom contact is negative with respect to the ground of equipment, vice versa for the “negative voltage”. Samples were cleaved in-situ at 15K with base pressure in the vacuum system at $1 \times 10^{-10}$ Torr. All data were acquired with photon energy set at 6.7 eV. The angular resolution was around 0.001 Å⁻¹ with the analyzer slits set at 300. The energy resolution was better than $\sim 3$ meV.

6.3 Results

In this section, we will demonstrate the change of line shape and shift of Dirac cone in the momentum space with applied voltage. We then discuss the effect of electric field on photoelectron paths and plans for future experiments.
Figure 6.2: ARPES intensity plots for a topological insulator Bi$_2$Te$_{2.28}$Se$_{0.58}$ with applied positive and negative voltages.

6.3.1 MDC width

The ARPES intensity plots for a topological insulator Bi$_2$Te$_{2.28}$Se$_{0.58}$ with various applied voltages are shown in Fig. 6.2. It is quite clear that the data changes significantly when a voltage is applied to the sample. For positive voltages, the left branch (negative momentum) of Dirac cone becomes steeper (more dispersive) and broader while the right branch of Dirac cone becomes less dispersive and sharper. Note that the left side (negative momentum) of the intensity plot is corresponding to the up side in real space, which is the same direction of flow of electrons.

The width of the MDC and EDC peaks measured by ARPES is directly linked to imaginary part of self-energy ($\Sigma_{Im}$) which represents the scattering rate. As discussed in Chapter 1, the half-width of peak in EDC directly represents the imaginary part of self-energy. However, EDC’s are difficult to use due to complications of background and asymmetric line shape.
Therefore the MDCs are commonly used to extract imaginary part of self-energy, because the peaks are symmetric and have a simple linear background\[42\]. The imaginary part of self-energy is equal to half-width of the MDC peak times the slope of band dispersion (bare velocity).

Figure 6.3: Imaginary part of self-energy (Im\_SE) versus applied voltage for left and right branch of Dirac cone with (a)\&(b) positive voltage and (c)\&(d) negative voltage.

The measured imaginary part of self-energy are shown in Fig. 6.3 for various applied voltages. This data clearly demonstrates that electrons with negative momenta (i.e. traveling along the electron current direction) have increased MDC widths, while electrons with momenta opposite to the direction of electron current have narrower MDC widths. This reverses when the direction of the current is opposite. The increased imaginary part of self energy for electrons with momenta along the current direction points to shorter lifetimes, which implies higher scattering rates. Although the backscattering in topological surface state is prohibited, scattering which does not involve directly opposite momenta can still occur. The electrons with momenta along the current direction likely encounter more scattering in analogy to a windshield of a moving car in the rain.

### 6.3.2 Distortion of Dirac cone

The other change in band structure caused by applied voltage is distortion of the Dirac cone. We measured several Fermi surface scans with various voltage, with two of them at 0V...
and +0.7V shown in Fig. 6.4 (a)&(b). At 0V, the measured topological surface state shows a nearly circular Fermi surface, which is expected. With +0.7V applied to the sample, the whole Dirac cone shifts upwards and changes to an oval shape. The upward shift is a trivial effect due to the electric field in vacuum acting on the photoelectrons, while the distortion is very likely caused by the effect of current excitation on the electrons forming the topological surface state on the sample.

Figure 6.4: Fermi surface of topological insulator Bi$_2$Te$_{2.28}$Se$_{0.58}$ measured with (a) 0V and (b) +0.7V applied voltage. Slope of left branch (blue hollow triangle) and right branch (red solid triangle) of Dirac cone with -1V to +1V for (c) the sample with current and (d) grounded sample without current. Blue and red lines shows the simulated change of slope due to effect of electric field on the photoelectrons in the vacuum.
The distortion of the Dirac cone can be characterized by the change of slope in Dirac cone. As shown in Fig. 6.4 (c), for positive voltages, the left branch of Dirac cone becomes steeper while the right branch becomes flatter. Since the slope of band gives the velocity of quasi-particle, the steeper left branch of Dirac cone indicates that the left-moving electrons have a larger average velocity than right-moving electrons, which is consist with the direction of electron flow. For comparison purpose, we also measured the band structure of grounded sample without current. This is achieved by cutting out small parts of the sample located between the area of measurement and the contacts. The result is shown in Fig. 6.4 (d). With the nearly identical electric field (since the position of contacts nor voltage are not changed), the change of slope is dramatically reduced comparing to the case with current. Although the results indicate that the large component of slope changing is due to the effect of current excitation, a definitive conclusions can not be drawn without a more careful study of effect of electric field.

6.3.3 Simulation of the effect of electric field

Simulation of the effect of electric field on photoelectrons was performed using COMSOL Multiphysics Electrostatics and Charged Particle Tracing (CPT) modules. For the case of sample with current flow, two contacts are placed at a distance of 2.5µm with the source of photoelectrons in the center, as shown in Fig. 6.5 (a). The photoelectrons in the simulation go up towards the lens area and have the same kinetic energy and momentum as measured photoelectrons when no voltage is applied. The case of grounded sample without current is simulated by placing an additional grounded rectangular shape object right below the source of photoelectrons, as shown in Fig. 6.5 (b). Both of the simulations have a grounded boundary much larger than the distance between sample and lens in the experimental setup.

The simulated electric potential and electric field for 1.4V applied voltage are shown in Fig. 6.5. After photoelectrons left the source, the Lorentz force acted on the electrons will change the momentum and slightly alter the kinetic energy. For about 20ns, the momentum and kinetic energy become nearly stationary due to negligible electric field at area faraway from contacts. The change of the direction of the photoelectrons causes residual distortion
of Dirac cone due to the effect of electric field. The results are shown in Fig. 6.4 (c) & (d) as blue and red lines overlaid on experimental data. Since the electric field has a greater effect on slower electrons with lower kinetic energy, the electrons at Dirac point shift more than the electrons at Fermi level. This gives a similar behavior of distortion of Dirac cone as what we have been observed. For grounded sample without current, the magnitude of slope change from the simulation and experimental data agrees quite well, therefore the whole distortion of Dirac cone comes from effect of electric field.

For the sample with current, the situation is a little bit more complicated. The simulation shows a larger distortion than the case of grounded sample, because the grounded sample reduces the electric field along left-right direction as shown in Fig. 6.5. This increased change of slope fits well for experimental data of left branch, but is not agree with experimental data of right branch. This is most likely due to the measurement spot is closer to the right-side contact instead of in the middle of two contacts. And this also explains the asymmetrical shift between left branch and right branch, since right-moving electrons will feel larger electric force than left-moving electrons. Without knowing the exact position of measurement spot, the effect of electric field cannot be precisely simulated. However, if we consider that the total change of

Figure 6.5: Simulated photoelectron trajectories in presence of electrostatic potential. (a) the sample with current and (b) grounded sample without current.
slope consists two contributions from electric field and current excitation, the difference between the simulation and experimental data will be the effect of current excitation. Although this effect is smaller than the effect of electric field, it is still much larger than experimental error bar. And this tilt of Dirac cone is likely caused by the net flow of electrons in the topological surface state.

6.4 Discussions

We demonstrate the ability to perform ARPES measurements under applied current to the surface state of topological insulator. Our data demonstrates intrinsic effect of increasing the MDC width thus shorter lifetime of quasi-particles along the direction of the current in analogy to windshield rain drop effect for a moving car. We also observed distortion of the Dirac cone and Fermi surface induced by the current. To distinguish the effect of current excitation from artifact of electric field effects on the photoelectron paths we performed simulation using COMSOL package and compared it with experimental data. The modification of the photoelectron paths by the electrostatic potential present outside of the sample explains only part of the observed distortion of the Dirac cone. To fully disentangle these artifacts from the intrinsic effects of the current on the surface state it is important to reduce the electric field outside of the sample by improved shielding. This will make the assembly of the device more complicated, but hopefully will lead us to observation of intrinsic effects. Another approach would be to use other topological insulators with a higher surface mobility, so that the same drift velocity can be achieved at much lower applied voltages.
BIBLIOGRAPHY


