Quantum Transport on Topological Matter

Feixiang Xiang

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Quantum Transport on Topological Matter

Feixiang Xiang

This thesis is presented as part of the requirements for the conferral of the degree:

Doctor of Philosophy

Supervisors:
Prof. Xiaolin Wang,
Prof. Shixue Dou,
and Prof. Alex R. Hamilton(UNSW)

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School of Physics, Institute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials

30 Jan, 2017
I, Feixiang Xiang, declare that this thesis submitted in fulfilment of the requirements for the conferral of the degree Doctor of Philosophy, from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Name:

January 30, 2017
Abstract

Topological matter is a new state of matter which is characterized by topological non-trivial electronic structure. It not only has fundamental physical importance but also has practical applications. In this thesis, quantum transport measurement is used to study electronic structure and transport properties of various topological matter.

In Chapter 3, we report a magneto-transport study on single crystals of the topological insulator BiSbTe$_3$. Besides Shubnikov-de Haas oscillations and weak anti-localization (WAL) from the topological surface state, we also observed a crossover from the weak anti-localization to weak localization (WL) with increasing magnetic field, which is temperature dependent and exhibits two-dimensional features. The crossover is proposed to be the transport manifestation of the coexistence of the topological surface state and two-dimensional electron gas on the surface of TIs.

In Chapter 4, we use Shubnikov-de Haas oscillations to investigate the electronic structure of the bulk conduction band of BiTeCl single crystals with different carrier densities. We observe the topological transition of the Fermi surface (FS) from a spindle-torus to a torus. The Landau level fan diagram reveals the expected non-trivial $\pi$ Berry phase for both the inner and outer FSs. Angle-dependent oscillation measurements reveal three-dimensional FS topology when the Fermi level lies in the vicinity of the Dirac point. All the observations are consistent with large Rashba spin-orbit splitting in the bulk conduction band.

In Chapter 5, we use magneto-transport measurements to investigate the electronic
structure of WTe$_2$ single crystals. A non-saturating and parabolic magnetoresistance is observed from low temperature to high temperature up to 200 K with magnetic fields up to 8 T. Shubnikov–de Haas (SdH) oscillations with beating patterns are observed, the fast Fourier transform of which reveals three oscillation frequencies, corresponding to three pairs of Fermi pockets with comparable effective masses, $m^* \sim 0.31m_e$. By fitting the Hall resistivity, we infer they can be attributed to one pair of electron pockets and two pairs of hole pockets, together with nearly perfect compensation of the electron-hole carrier concentration. These magneto-transport measurements reveal the complex electronic structure in WTe$_2$, explaining the non-saturating magnetoresistance.

In Chapter 6, we use quantum oscillations from magneto-transport measurement to study the electronic structure of WTe$_2$ thin film with different thickness. The angle dependent quantum oscillations reveal a crossover from a three-dimensional to two-dimensional electronic system when the sample thickness is below 15 nm. The fast Fourier transform spectrum of quantum oscillations further shows the Fermi pockets get smaller when samples become thinner, suggesting the overlap between conduction band and valence band are getting smaller. We also use a back-gate to tune the carrier density of the thin film and to distinguish the electron and hole pockets. Our results support the potential nontrivial topological state in thinner samples and explain the carrier density decrease when thin film thickness is reduced in references.
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Dedication

To my family
List of publications

1. **Fei-Xiang Xiang** et al.
   Electronic structure change in atomically thin WTe₂. (under preparation)

2. **Fei-Xiang Xiang**, Xiao-Lin Wang, Menno Veldhorst, Shi-Xue Dou, and Michael S. Fuhrer

3. **Fei-Xiang Xiang**, Menno Veldhorst, Shi-Xue Dou and Xiao-Lin Wang
   Multiple Fermi pockets revealed by Shubnikov-de Haas oscillations in WTe₂. EPL 112, 37009 (2015) and arXiv:1504.01460

4. YJ Yan, MQ Ren, X Liu, ZC Huang, JQ Fan, J Miao, BP Xie, **F Xiang**, X Wang, T Zhang, D. L Feng

5. **Fei-Xiang Xiang**, Xiao-Lin Wang and Shi-Xue Dou
   Transport evidence for the coexistence of the topological surface state and a two-dimensional electron gas in BiSbTe₃ topological insulator. arXiv:1404.7572 (2014)
Chapter 1

Introduction

1.1 Review of topological matter

Topological insulators (TIs) are electronic materials that have a bulk band gap like an ordinary insulator but have protected metallic states on their edges or surface [1, 2]. The TIs can be categorized into two-dimensional topological insulators which were first discovered in experiments and three-dimensional topological insulators.

![Diagram of quantum Hall effect](image)

Figure 1.1: Quantum Hall effect. The left figure is the experimental set up for measuring the quantum Hall effect. The right figure are the measured Hall resistance (top) and longitudinal magneto-resistance. Adapted from [3].

The discovery of topological insulator can be traced back 1980s when the quantum Hall effect (QHE) was discovered [4]. K. von Klitzing et.al found that at low temperature
and high magnetic field when an longitudinal electric current is driven through a two-
dimensional electron gas (2DEG), the transverse resistance or the Hall resistance $R_{xy}$
exhibit quantized plateau $R_{xy} = \frac{h}{ie^2}$, where $i$ is an integer as a quantum number and
the longitudinal resistance $R_{xx} = 0$ (see Fig. 1.1). This is distinguished from the classical
Hall effect where the Hall resistance is proportional to the magnetic fields. Soon after
the discovery of the quantum Hall effect, Laughlin proposed that the quantization of Hall
conductivity of 2DEG is a consequence of gauge invariance and the existence of a mobility
gap due to the Landau quantization [5]. In the magnetic field, the electron undergoes
cyclotron motion. When the Hall resistance is quantized, the energy spectrum is gapped
due to the Landau quantization and the Fermi level locates in the gap and the electrons
in bulk are localized, \textit{i.e.} the bulk of quantum Hall state is insulating. And then in the
context of general explanation of Laughlin, Halperin pointed out that there are current
 carrying channels around the edge of the samples while the bulk is insulating and the
number of the chiral quasi one dimensional edge channels determine the quantum number
$i$ [6].

Then the question is what’s the fundamental difference between quantum Hall state and
conventional insulators. Thouless, Kohmoto, Nightingale and den Nijis (TKNN) [7] pro-
posed that in the quantum Hall system the $k$-space is mapped to a topologically-nontrivial
Hilbert space, whose topology can be specified by an integer topological invariant called
TKNN invariant $n$, which is nonzero and equals the quantum number in the quantized $R_{xy}$.
While for the conventional insulators $n = 0$. The topological classification also implies
there is a gapless edge state on the boundary of the quantum Hall insulators protected
by the topological nature. Because according to this theory one gapped state cannot be
deformed to another gapped state in a different topological calls unless a quantum phase
transition occur where the whole system turns to gapless state.
1.1. REVIEW OF TOPOLOGICAL MATTER

In 1988, F. D. M. Haldane for the first time shows, in principle, that the quantized Hall resistance may also be realized in 2D graphite without Landau quantization [9]. In 2004 during study of generation of spin current in graphene Kane and Mele found the spin-orbital coupling can drive the semi-metallic graphene into a quantum spin Hall insulator which is gapped in the bulk due to the spin-orbit coupling and supports the transport of spin and charge in the gapless edge states that propagate at the sample boundaries [8]. The band structure of such new electronic matter and its edge state are shown in Fig. 1.2, respectively. The direction of the charge current in the edge states is related with the spin, i.e. they are not chiral as in QHE, but they are insensitive to disorder. This phase is topologically distinct from a band insulator. In their subsequent paper they explained the difference of the quantum spin Hall insulator from the ordinary band insulator with the $Z_2$ topological invariant, which is similar to the TKNN number for quantum Hall effect [10].

Unfortunately, the spin-orbit coupling in graphene is too weak to realize the quantum spin Hall effect in real experiments. Nonetheless, another group led by Shou-Cheng Zhang works out that the quantum spin Hall insulator can be realized in mercury telluride-cadmium telluride (HgTe/HgCd) semiconductor quantum wells when its thickness is larger than 6.3 nm [11], see the left of Fig. 1.3. Due to the strong spin-orbit coupling in HgTe,
Figure 1.3: (left) (A) The experimental setup on a six-terminal Hall bar showing pairs of edge states, with spin-up states in green and spin down states in purple. (B) A two-terminal measurement on a Hall bar would give $G_{LR}$ close to $2e^2/h$ contact conductance on the QSH side of the transition and zero on the insulating side. (Right) The experimental results, which correspond to $G_{LR}$ in QSH side of transition. Adapted from [11] and [12].

the bulk gap can be more than 30 meV. One year after the theoretical prediction, the quantum Hall effect was observed in experiment [12], see right of Fig. 1.3.

Meanwhile, theorists have started to extend this topological classification of insulators to three-dimensional (3D) systems. It is found the topology can be characterized by four $Z_2$ invariants [13–15]. Moore and Balents used “topological insulator” (TI) for the first time to describe this new state of matter [13].

In a subsequent work, Fu and Kane predicted a series of specific materials which are strong 3D topological insulators such as semiconductor alloy Bi$_{1-x}$Sb$_x$ in certain composition range as shown in the left of Fig. 1.4 as well as $\alpha$-Sn and HgTe under uniaxial strain [16]. In 2008, the topological surface state was for the first time observed in Bi$_{1-x}$Sb$_x$ by Hsieh et al. in the angle-resolved photoemission spectroscopy (ARPES) experiment [17] and in their following paper the helical spin polarization of the surface states is also observed in Bi$_{1-x}$Sb$_x$ by using spin-resolved ARPES [18]. Later the topological surface state was also verified in the quantum oscillation measurement which resolves the Fermi surface belong to the 2D system [19] and in the scanning tunneling spectroscopy (STS)
1.1. REVIEW OF TOPOLOGICAL MATTER

Figure 1.4: (Left) Schematic representation of predicted band energy evolution of Bi$_{1-x}$Sb$_x$ as a function of $x$. (Right) experimental observation of the topological surface state. Adapted from [16] and [17].

study by observing the immunity from backscattering [20].

Figure 1.5: Theoretical prediction of second generation of three-dimensional topological insulators. Adapted from [21].

But the extremely complex surface band structure and the alloying disorder motivated the scientists to search for topological surface state in stoichiometric compounds with simple surface band structure and large bulk band gap. In 2009 Zhang et al. [21], predicted that Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ is 3D TIs with single Dirac cone at each surface while Sb$_2$Se$_3$ is not. These three materials are called second generation of 3D TIs in comparison
CHAPTER 1. INTRODUCTION

Figure 1.6: Experimental observation of topological surface state in Bi$_2$Se$_3$ (left) and Bi$_2$Te$_3$ (right). Adapted from [22] and [23].

with the first generation 3D TI the Bi$_{1-x}$Sb$_x$. Soon after the theoretical prediction, a single Dirac-cone surface state was observed in Bi$_2$Se$_3$ [22, 24] (see left of Fig. 1.6) and Bi$_2$Te$_3$ [23, 25] (see right of Fig. 1.6), and helical spin texture has also been observed in both materials [26] (see Fig. 1.7).

Figure 1.7: Helical spin texture of topological surface state. Adapted from [26].

Although the 2nd generation TIs has simple surface band structure, the bulk state is metallic rather than insulating. Because the defects formed during the materials preparation induce large amounts of bulk carriers, which shift Fermi level into conduction or
valence band. One example is Bi$_2$Se$_3$, the defects shift the Fermi level into conduction band as shown in Fig. 1.8. To measure the physical property of topological surface state and apply it to practical application requires the Fermi level locates near the Dirac point or in the bulk band gap. In order to bring the Fermi level back to the bulk band, chemical modification is used to reduce the bulk carrier density and tune the Fermi level as shown in Fig. 1.9 for calcium doping [26, 27].

Figure 1.8: Non-insulating bulk state. Adapted from [27] and [26].

Figure 1.9: Tuning the Fermi level with calcium doping. Adapted from [27] and [26].
Inspired by the energy band engineering in conventional semiconductors, Zhang et al. used an isostructural isovalent alloying of Bi\textsubscript{2}Te\textsubscript{3} (n-type) and Sb\textsubscript{2}Te\textsubscript{3} (p-type) to tune the Fermi level down to the bulk gap and the sheet carrier density can be reduced to $10^{12}$ cm\textsuperscript{-2} as shown in Fig. 1.10 [28].

As proposed in Fu and Kane’s paper, transport measurement is the most direct method to probe the topological surface state, however the residual resistivity in bulk as mentioned above makes it very difficult to study the topological surface state by transport measurement and limit the study of TIs in the surface sensitive method such as ARPES and STM. As the sample quality becomes better, the transport measurement begins to enter this field. The first important transport method is quantum oscillation which takes advantage of the high mobility surface carrier that exhibiting Landau quantization in low temperature and high magnetic field. Due to the 2D nature, the period of quantum oscillation from different angles can be reduced to the same in $1/B\cos\theta$. And the Landau level fan
1.1. REVIEW OF TOPOLOGICAL MATTER

Figure 1.11: Detection of topological surface state with quantum oscillations. Adapted from [29] and [30].

can give whether the oscillation have the non-trivial \( \pi \) Berry phase. The first quantum oscillation work is done by Qu et al. in Bi\(_2\)Te\(_3\) [29] and by Analytis et al. in Sb doped Bi\(_2\)Se\(_3\) [30] as shown in the top and bottom panel of Fig. 1.11.

Another effective method to probe the topological surface state is the weak anti-localization effect. Because the topological surface has non-trivial \( \pi \) Berry phase, the electric conductivity is corrected by the quantum mechanical coherence of the electron in the diffusive quantum regime, i.e. the phase coherence length of the electron is large than the elastic scattering length. The nontrivial \( \pi \) Berry phase makes the inference of two time-reversed paths destructive and therefore according to quantum mechanics, the return probability decrease and the conductivity is enhanced. When an external magnetic
field is applied, the phase coherene will be destroyed and the conductivity decrease rapidly in low field which exhibiting cusp-like shape as shown in Fig. 1.12 [31].

1.2 Bulk Rashba effect

Bulk Rashba effect refers to the momentum $p$ dependent spin-splitting at zero magnetic field observed in the polar semiconductors in BiTeX (X=Cl, Br and I) [32–34], as shown in Fig. 1.13(a). This effect is similar to the Rashba-Bychkov effect at the interface of semiconductor heterostructure, where the structure inversion symmetry is broken due to confinement potential, $V$, perpendicular to the heterostructure interface [35, 36]. Electrons moving at the interface experience a spin-orbital field $B_{SO} = (\nabla V \times p) \frac{\hbar}{mc^2}$. Due to the Zeeman interaction, $H_{SO} = (\nabla V \times p) \cdot \sigma \frac{\hbar}{mc^2}$, between the magnetic moment of electron spin and spin-orbital field, the energy states of electrons with opposite spin are split, which is called Rashba spin-splitting. The energy dispersion in parabolic bands can

Figure 1.12: Detection of topological surface state with weak anti-localization. Adapted from [31].
be approximately described by:

\[ E_{\pm}(k) = \frac{\hbar^2}{2m^*}(k \pm k_0)^2 \]  

(1.1)

where \( k = \sqrt{k_x^2 + k_y^2} \), \( k_0 \) is the momentum offset caused by the Rashba spin-splitting, \( m^* \) is the effective mass of the electrons, and \( \hbar \) is Planck’s constant divided by \( 2\pi \).

In the polar semiconductors in BiTeX (X=Cl, Br and I), the energy dispersion and spin polarization is found to be Rashba-like from angle-resolved photoemission spectroscopy measurement [32, 33, 37]. The Rashba-like spin-splitting is believed due to their bulk atomic configuration [32], instead of the structure inversion symmetry at the heterostructure interface. Because the inversion symmetry is broken and the electric affinity of Te and X (X=Cl, Br and I) is different, the charge inside materials distributes unevenly along the \( c \) axis. For example, in BiTeCl the positive and negative charges arrange alternatively along \( c \) axis, as shown in Fig. 1.13(b) [38]. Similar to heterostructure interface, an internal electric potential, \( V \), is build along \( c \) axis. When electrons move in the \( ab \) plane, which is perpendicular to \( c \) axis, they experience a spin-orbital field, which causes the momentum dependent spin-splitting.

Figure 1.13: (a)The band dispersions of BiTeI measured by angle-resolved photo-emission spectroscopy, which show Rashba-like spin splitting. (b) The charge distribution in BiTeCl crystals obtained by \textit{ab initio} calculation. Adapted from [32] and [38].
1.3 Shubnikov de Haas oscillations

Shubnikov-de Haas (SdH) oscillations is periodic oscillations of longitudinal resistance $R_{xx}$ in $1/B$, which are normally observed in high mobility samples at low temperature and high magnetic fields.

The SdH oscillations is due to Landau quantization of electrons in magnetic fields. In a magnetic field $B$, the Hamiltonian of a free electron is

$$\hat{H} = \frac{1}{2m}(\mathbf{p} - e\mathbf{A})^2$$  \hspace{1cm} (1.2)

where $m$ is the mass, $\mathbf{p}$ is the momentum, $\mathbf{A}$ is the vector potential related with the magnetic field $B$.

If the magnetic field $B$ is along the $z$ direction, then the vector potential related to the magnetic field is $\mathbf{A} = (-By, 0, 0)$ and the Schrodinger’s equation with Hamiltonian (1.2) become

$$\frac{1}{2m}[(\hat{p}_x - eBy)^2 + \hat{p}_x^2 + \hat{p}_z^2] \Phi = E \Phi$$  \hspace{1cm} (1.3)

To solve the Schrodinger’s equation with the Hamiltonian (1.3), we get the energy of the free electron

$$E = (n + \frac{1}{2})\hbar \omega_c + \frac{\hbar^2 k_z^2}{2m}$$  \hspace{1cm} (1.4)

Where $\omega_c = \frac{qB}{m}$. The first term in the equation (1.4) corresponding to the circular motion in the plane perpendicular to the magnetic field is quantized. Such quantized energy level is called Landau level. While the second term corresponding to the motion along the magnetic field direction is continuous.

The Fermi surface of free electrons in $k$ space is a sphere. When an external magnetic field is applied, the states of the free electrons coalesce on to a series of tubes as shown Fig.
1.4. WEAK LOCALIZATION AND ANTI-LOCALIZATION

1.14(a) and the corresponding energy dispersion along $k_z$ is shown in Fig. 1.14(b). By varying the magnetic field, the states at the Fermi surface will populate periodically in $1/B$ scale. The period is $\Delta_{1/B} = \frac{1}{B_{n+1}} - \frac{1}{B_n} = \frac{2\pi e}{hA_F}$, where $A_F$ is the extremal cross-section area of the Fermi surface.

![Figure 1.14](image)

Figure 1.14: (a) The states of the three-dimensional free electron gas in a magnetic field coalesce onto a series of tubes. Each tube represents a Landau level. The dotted sphere is the spherical Fermi surface of the electron gas at zero magnetic field. (b) The energy dispersion along $k_z$ at zero magnetic field (dotted line) and at non-zero magnetic field (solid lines). Adapted from [39].

1.4 Weak localization and anti-localization

In the diffusion transport regime, when the motion of electrons is elastically scattered by multiple impurities. The self-interference of the wave function can result in either the enhanced or depressed backscattering of the electrons due to the phase coherence. As shown in the Fig. 1.15(a), the trajectory of electrons form a closed loop by the multiple scattering centers, where the electron can travel in opposite ways. The wave function of the electrons can be represented by the complex numbers $A^+$ and $A^-$. Because the phase coherence is preserved after the multiple scattering, the two partial waves of electrons traveling in the opposite direction interfere with each other. The probability of the wave returning to the starting point or the backscattering is given by:
\[ P = |A^+ + A^-|^2 = |A^+|^2 + |A^-|^2 + A^+ A^-* + A^+* A^- = 2|A|^2 + 2|A|^2 \cos(\phi(i) + \phi(j)) \] (1.5)

Where the first term is the classical probability of the backscattering, the second term takes account of the interference of the wave interference of electrons.

Because the probability of electron going each direction is random, the amplitude of \( A^+ \) and \( A^- \) should be the same, \( |A^+| = |A^-| = |A| \). In addition, the length of the trajectory in the opposite direction is also the same, so the phase acquired during the motion in opposite direction is the same, \( \phi(i) = \phi(j) \). Therefore, the self-interference is constructive and the probability of the backscattering in equation 1.5 becomes \( P = 4|A|^2 \). In this case, the backscattering is enhanced, which is called weak-localization. The enhanced backscattering increases the resistance, as shown in the Fig. 1.15(b) that the resistance increase as the temperature decrease since the phase coherent length increase. However, in the material system with strong spin-orbit effect, the phase acquired during the motion in the opposite direction differs by \( \pi \). Therefore, the self-interference is destructive and the probability of the backscattering in equation 1.5 becomes \( P = 0 \). In this case, the backscattering is depressed. For example, in the Au/Mg film, as shown in Fig. 1.15(b), where the Au has strong spin-orbit coupling, the resistance does not increase as temperature decrease which is in contrast to the Mg film where the spin-orbit coupling effect is weak.

Furthermore, applying an external magnetic field could induce an extra phase [40], the probability of backscattering become

\[ P = 2|A|^2(1 + \cos(\frac{4\pi BS}{e/h})) \] (1.6)

Where the \( B \) is the magnetic field and \( S \) is the area enclosed by the trajectory. Because \( 1 + \cos(\frac{4\pi BS}{e/h}) \leq 2 \), the backscattering rate is reduced compared with the weak localization.
case, so the negative magnetoresistance occur as shown in Fig. 1.15(c) for Mg film, but the backscattering rate is increased compared with the weak anti-localization case, so magnetoresistance sharply increases in the magnetic field as shown in the Fig. 1.15(d) [41].

Figure 1.15: (a)Schematic diagram of the trajectory of the electrons. (b) The temperature-dependent resistance of Mg and Mg/Au film. (c),(d) Magnetoresistance of Mg and Mg/Au films, respectively, at various temperatures. (b), (c) and (d) adapted from [41].

1.5 References

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1.5. REFERENCES


CHAPTER 1. INTRODUCTION


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Chapter 2

Experiment Technique

2.1 Single crystal growth

Single crystal growth is an important technique for study of intrinsic physical properties of materials and also for practical applications in industry. Due to its single crystal form, it could be used for study of anisotropy of materials and problems from grain boundaries, inter-grain component and porosity in principle can also be eliminated. Because the growth of single crystals is also a purifying process, the grown crystals have higher purity than their starting materials. Therefore, single crystals are ideal candidates for exploring electronic structure of materials using quantum oscillation methods such as Shubnikov-de Haas oscillations, for transport measurement of topological insulator which need as low as possible bulk carrier density and for observing the large MR due to electron and hole compensation which is closely related with the carrier mobility.

The single crystal growth method used in this thesis is based on molten solutions. This method could be used for growth of both congruently and incongruently melt compounds. For congruently melt compound, the single crystal can be grown from stoichiometric starting materials, while for incongruently melt compound, a flux is needed, which has large enough solubility of the desirable single crystal material when the starting materials are melt. The flux can be one of the starting materials, called “self-flux”, or it can be another metal which has a low melting point, called “nonself-flux”. In general the self-flux method
is preferable because it can yield purer single crystal. The nonself-flux method is employed when self-flux method is not viable, for example, the melting point of all starting materials is too high for practical experiment. However, the flux need to be chosen carefully, otherwise the flux materials will also be incorporated into single crystals as impurity.

Figure 2.1: Binary alloy phase diagrams for (a) Bi–Te and (b) Sb–Te from ASM alloy phase diagram database.

2.1.1 \((\text{Bi}_{1-x}\text{Sb}_x)\text{Te}_3\) single crystal growth

Both Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are narrow gap semiconductors, which are good thermoelectric materials and have been studied for many years. Due to the defects formed during
growth such as anti-sites, A-on-B defects and vacancies, Bi$_2$Te$_3$ can be either n- or p-type semiconductor and Sb$_3$Te$_3$ is p-type semiconductor. Around 2010, non-trivial topological surface state are predicted to exist on their surfaces and observed in angle resolved photo-emission spectroscopy, which trigger new interests on them. The defects mentioned above make the bulk metallic, which prevent study of the topological surface state by transport measurement. Thanks to their same crystal structure and close lattice parameter, it was found isostructural isovalent alloy (Bi$_{1-x}$Sb$_x$)Te$_3$ single crystal can be grown to tune the bulk carrier density [1][]. Topological insulator, (Bi$_{1-x}$Sb$_x$)Te$_3$ single crystal, is grown to reduce the bulk carrier density.

Figure 2.1 shows the binary phase diagrams of Bi–Te and Sb–Te. It can be seen that both Bi$_2$Te$_3$ and Sb$_3$Te$_3$ are congruently melt compounds. Therefore they can be grown from stoichiometric starting materials. Because (Bi$_{1-x}$Sb$_x$)Te$_3$ single crystal are isostructural isovalent alloy, the $x$ can be any number between 0 to 1. So starting materials Bi, Sb, and Te with different ratio are mixed by an agate mortar and pestle in the glove box and loaded into quartz tube, and vacuum sealed. The temperature for stoichiometric liquid turning to Bi$_2$Te$_3$ and Sb$_3$Te$_3$ solids (or the melting points) are 588 °C and 617.7
CHAPTER 2. EXPERIMENT TECHNIQUE

Figure 2.3: Binary alloy phase diagrams for (a) Bi$_2$Te$_3$–BiCl$_3$ from ASM alloy phase diagram database.

$^\circ$C, respectively and the highest melting point of starting materials is Sb, 755 $^\circ$C, so the sealed quartz tube first heated up to temperature 800 $^\circ$C and held for 24 h and then slowly cooled down to 550 $^\circ$C in few days to grow the single crystals and annealed at 550 $^\circ$C for another 3 days to reduce the defects. Because when the stoichiometric liquid cools down melting point, the entire liquid freezes in very short time, the resulted single crystals are densely intergrown, but single crystals can be mechanically cleaved from intergrown polycrystalline ingots and further cleaved along $ab$ plane of crystal for final magneto-transport measurement. Figure 2.2(a) shows typical (Bi$_{1-x}$Sb$_x$)Te$_3$ intergrown polycrystalline crystal ingots and a flat single crystal cleaved from them, and the quartz tubes contains intergrown polycrystalline ingots before taking out. Figure 2.2(b) shows a typical X-ray diffraction (XRD) pattern of single crystal (Bi$_{1-x}$Sb$_x$)Te$_3$ and the (00l) peaks indicating the cleaved plane is $ab$ plane.
2.1.2 BiTeCl single crystal growth

BiTeCl single crystals are grown based on Bi$_2$Te$_3$ and BiCl$_3$ binary phase diagram as shown in Fig. 2.3. BiTeCl is not a congruently melt compound, so a flux is needed for growth of single crystals. According to the phase diagram in 2.3, the BiCl$_3$ can be a self-flux. In order to prevent the precipitation of the Bi$_2$Te$_3$ phase but also yield as much as possible BiTeCl single crystal, the ratio of starting material Bi$_2$Te$_3$ and BiCl$_3$ is set as 1:9. Bi$_2$Te$_3$ powder are grounded from high purity Bi$_2$Te$_3$ single crystal which grown in the previous section. As BiCl$_3$ is sensitive to moisture, the anhydrous BiCl$_3$ powder which is sealed in quartz ampule is purchased. All the processing such as weighing and mixing are carried out in glove box which control the inert gas atomosphere and moisture level.

The mixture of Bi$_2$Te$_3$ and BiCl$_3$ are loaded into a quartz tube and vacuum sealed. After putting the quartz tube into furnace, the furnace is heat up to 420 or 500 over several hours and maintained for 12h and then slowly cooled down to 200 over several days. The plate-like crystal as shown in the inset of 2.4(a) are obtained after chemically removing the residual BiCl$_3$ flux with ethanol. The lateral size is around 5 mm × 5 mm. Figure 2.4(a) shows a typical XRD pattern of a single crystal BiCl$_3$ and the (00l) peaks indicates the plate plane of the single crystal is ab plane. Figure 2.4(b) shows a typical XRD pattern of BiTeCl powder after grounding the BiTeCl single crystals. The red lines are the diffraction peaks from standard PDF card of BiTeCl. Some smaller peaks besides the peaks from BiTeCl are present due to the remaining flux BiCl$_3$. 
2.2 Device fabrication

In order to perform the magneto-transport measurement on nano-flake samples, nano-flake samples needs to be exfoliated from bulk single crystals and metal electrode need to attach on the nano-flake samples. Because the nano-flakes exfoliated by the Scotch tape
2.2. DEVICE FABRICATION

Figure 2.5: Basic steps of e-beam lithography. (a) Writing the pattern by exposing the PMMA with e-beam, (b) The structure after development in the mixture of MIBK:IPA (c) The structure after the Ti/Au deposition. (d) The final structure after lift-off.

method is randomly locate on the substrate and also the size of smallest feature is less than 1 μm, e-beam lithography (EBL), which is flexible and can write feature down to a few nanometers, is employed to fabricate the devices. Figure 2.5 shows the basic EBL steps. First, a substrate is spin-coated with a layer of e-beam resist, such as polymethyl methacrylate (PMMA), a type of positive e-beam resist and then baked until dry. Then some area of PMMA is exposed by the e-beam to break long chain polymer into smaller and more soluble fragments as shown in Fig. 2.5(a). After exposure, the substrate is immersed in certain solution, the exposed parts will dissolve in the solution much faster than the unexposed part. So the exposed part is removed and the unexposed part is left and a pattern is created, as shown in Fig. 2.5(b). This step is called development. Then certain metals will be deposited by thermal or e-beam evaporation (see Fig. 2.5(c)). The
thickness ratio of resist to metal is larger than 2:1, so that the PPMA can be removed in next step. After that the PMMA is immersed in certain solution such as N-methyl-2-pyrrolidone (NMP) or acetone, the exposed PMMA and the metal on top of it will be lift off. Only the metal on the area which has been exposed by e-beam will be left as shown Fig. 2.5(d).

2.2.1 Fabrication of alignment markers

To fabricate a 2D device, the first step is to fabricate alignment markers on the SiO$_2$/Si substrate, which are used to determine the relative position of desirable nano-flakes and correct the e-beam deflection before direct writing the patterns. The 8 mm × 8 mm SiO$_2$/Si substrate is cleaved from a wafer purchased from Graphene Supermarket. Normally the substrate is quite clean, which can be used for next process. If there are some debris produced on the surface during cleaving, the substrate is put into a beaker with IPA and left in an ultrasonic bath for 1 min and dry with N$_2$. When the substrate is ready, it is spin-coated with a thin layer (≈ 150 nm) of PMMA A3 (950, 3% in anisole), a type of positive e-beam resist, purchased from MICROCHEM and followed by a bake on a hot plat at 180 °C for 90 s. A drop of nano gold ball suspension is then place on the lower left corner of substrate.

When the suspension is dried, the substrate is loaded into RAITH150 Two for writing the pattern of alignment marker. The working distance is set at 8 mm and the accelerating voltage of electron beam is 20 kV and the aperture is selected as 30 µm. Before writing the pattern, the e-beam is corrected by the nano gold balls on the left corner so that the beam is in focus and no obvious stigmation, and the writefield is aligned. The writefield size is set as 200 µm × 200 µm. In each writefield, there is a cross-marker on each corner. The distance between two neighbor marker is 180 µm. The normal size of pattern is 2.2 mm × 2.2 mm, which consists of an array of such writefields designed before the experiment in
2.2. DEVICE FABRICATION

the RAITH150 Two software. During writing the pattern, the area dose of electron beam is 300 \( \mu \text{C/cm}^2 \). After that, the substrate is taken out from the RAITH150 Two, and put into a beaker with solution mixed with methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) in 3 to 1 ratio for 40 s. The PMMA exposed to the e-beam will be removed and then rinse the substrate with IPA for another 20 s and dry it with \( \text{N}_2 \). This step is called develop.

Now the substrate is ready for metal deposition. First the substrate is loaded into a chamber of a thermal evaporation system. The chamber is pumped until the vacuum is below 2 \( \times \) \( 10^{-6} \) mbar. To make sure, the deposited can be lift off, the PMMA to total metal ratio is large than 2. Before depositing a layer of Au with thickness 60 nm, a layer of Ti with thickness 10 nm is deposited to increase the adherence of Au on the substrate. The deposition rate for Ti and Au are 1 \( \text{Å/s} \) and 2.5 \( \sim \) 5 \( \text{Å/s} \).

The final step is lift-off. After taking the substrate from the deposition chamber, it is put into a beaker with N-methyl-2-pyrrolidone (NMP) and then heated on a hot plate with temperature 80 °C. After 1 hour, the metal on PMMA and the PMMA itself can be easily lift off by the pipette or in ultrasonic bath for 1 min and the metals is only left on the area exposed to the e-beam. The substrate is take out of the beaker, rinsed with IPA and dried with \( \text{N}_2 \). The substrate is cleaned in \( \text{O}_2 \) plasma (50 W, 245 mbar) for 3 min before next process.

2.2.2 Nano-flake exfoliation and electrode fabrication

The method to exfoliate nano-flakes from single crystals is the well-known scotch tape method, which is very effective to obtain very thin nano-flakes, even the mono-layer samples, from layered materials. First a small piece of single crystal cleaved from a large crystal and put on a cleanroom tape instead of the Scotch tape to reduce the residue. The crystal is cleaved for several times and then put the substrate with markers on it.
press the substrate with finger for 5 min and left it on the desk for another 20 min before peeling off the tape.

The substrate is quickly observed under optical microscope to identify desirable nano-flakes according to their color. The thick flake is brighter while the thin flake is darker, as shown in Fig. 2.6a. Accurate thickness is determined by atomic force microscope (AFM) either before electrode patterning or after transport measurement. Figure shows a AFM image which is scanned before electrode patterning and Fig. 2.6d show its thickness profile. The substrate with the flakes then is loaded into RAITH150 Two for record their relative position to the alignment marker. During this step, the accelerate voltage is 10 kV and aperture is 30 $\mu$m.

After recording the position, the substrate is spin-coated with PMMA and baked at a hot plate, which are the same as the process for alignment markers. Then substrate
is loaded into RAITH150 Two again for writing the pattern of electrodes and bonding pads. The accelerate voltage is changed back to 20 kV and aperture is 30 \( \mu \text{m} \). The beam correction and writefield alignment will be performed before writing the pattern. Then it followed by same develop, metal deposition and lift-off process as the alignment marker fabrication, except that substrate will be cleaned in Ar plasma before metal deposition to remove the native oxide on the sample surface. Most of Ar plasma cleaning is performed in a home designed hollow cathode reactive etching system (Ar 20 sccm, 5 Pa, 30 W) for 1 min.

### 2.3 Magneto-transport measurement

To carry out the magneto-transport, several system has been used, such as Physical Property Measurement System (PPMS) from Quantum Design company, Oxford dilution fridge and Oxford \(^3\)He fridge. They are used in different situations as detailed in the following subsections.

#### 2.3.1 Physical property measurement system

PPMS is used for magneto-transport measurement of bulk samples. Two kinds of PPMS are used in the work of this thesis. One can provide 14 T magnetic field and has both resistivity option and horizontal rotation option, and the other one can provide 9 T magnetic field but only have resistivity option. Both system can vary the temperature from 1.9 K to 400 K. Figure 2.7(a) shows the 14 T PPMS with the horizontal rotation option in use. An important part of PPMS is the probe as shown in Fig. 2.7(b) and 2.7(e). A superconducting magnet is attached at the bottom and immersed in liquid helium bath for generating the high magnetic field. The probe also encloses a sample chamber which is thermally insulated from the liquid helium bath. The base of sample chamber has a 12 pin connector, through which the samples on the puck are connected with the measurement
system. The temperature in chamber is controlled by impedance assembly and the resist heaters.

Figure 2.7: (a) Photo of 14 T PPMS. (b) PPMS probe. (c) Cross-section of the PPMS probe and its temperature-control components. Adapted from PPMS hardware manual.

Figure 2.8: (a) Sample puck for resistivity option. (b) Sample holder board for horizontal rotator option and the bottom of a horizontal rotator probe. (c) The horizontal rotator probe. Adapted from PPMS Resistivity and Horizontal Rotator option manuals.
2.3. MAGNETO-TRANSPORT MEASUREMENT

Normally resistivity option is used for magneto-transport measurement and the samples are mounted on a sample puck (see Fig. 2.8(a)). When angle-dependent measurement is needed, horizontal rotator option is used and the samples are mounted on a sample holder board (see Fig. 2.8(b)) which will be attached to rotator on a horizontal rotator probe (see Fig. 2.8(c)) after mounting the sample. Then the rotator probe is inserted into the sample chamber and its bottom end can be connected to the 12 pin connector in the sample chamber. The rotation axis is perpendicular to the magnetic field.

2.3.2 $^3\text{He}/^4\text{He}$ dilution refrigerator

The lowest temperature of PPMS can reach is around 1.9 K, but to measure some quantum effect such as SdH oscillations and weak anti-localizations, this temperature may not be low enough for some cases. For such situation, an Oxford $^3\text{He}/^4\text{He}$ dilution refrigerator is used. It can cool down 30 mK, has a superconducting magnet which could generate 10 T magnetic field and it also has a one-axis rotator. The electric measurement set up is based on the Stanford research lock-in amplifier and Keithly source measurement unit and the data is recorded by LabVIEW software from NATIONAL INSTRUMENTS.

Figure 2.9: Phase diagram of $^3\text{He}/^4\text{He}$ mixture. Adapted from Practical Cryogenics, Oxford.
The working principle of dilution refrigerator proposed by H. London in 1951 is as following: when a mixture of $^3\text{He}$ and $^4\text{He}$ is cooled below critical temperature, 0.86 K (see Fig. 2.9), it separates into two phase; one is rich in $^3\text{He}$, called concentrated phase and the other is poor in $^3\text{He}$, called dilute phase; because the concentrated phase is lighter than the dilute phase, it floats above dilute phase; In the dilute phase, $^3\text{He}$ is surrounded by the superfluid $^4\text{He}$ and behaves like a gas in a massive vacuum and the $^3\text{He}$ in the concentrated phase moves into dilute phase like “evaporation” of liquid; since the enthalpy of the $^3\text{He}$ in dilute phase is larger than it is in concentrated phase, certain cooling power can be obtained when $^3\text{He}$ moves from concentrated phase to dilute phase; this process still works even the temperature approaches absolute zero, because at that temperature the concentration of $^3\text{He}$ in dilute phase is still finite.
2.3. MAGNETO-TRANSPORT MEASUREMENT

Figure 2.10: Schematic diagram of dilution refrigerator. Adapted from Practical Cryogenics, Oxford.

Figure 2.10 is the schematic diagram of a dilution refrigerator and illustrate the cooling process. The first step is to condense the mixture of $^3$He/$^4$He. The storage dump is open and the mixture is released into condenser and condensed by 1 K pot. The cooling power of 1 K pot is generated by pumping $^4$He out from it and it can cool the mixture to 1.2
K. To reach the phase separation point, the next step is to start circulation by running a rotary pump. Because at that temperature, the vapor pressure of $^3$He is much larger than that of $^4$He, it is $^3$He that is mainly pumped away from the liquid surface in the still and the temperature reaches 0.6 to 0.7 K. Then the mixture can be cooled below 0.86 K to set the phase separation. The pumped out $^3$He passes through the LN2 and LHe cold traps returns into condenser and then into the concentrated phase in mixing chamber.
Chapter 3

Co-existence of topological surface state and two-dimensional electron gas in BiSbTe$_3$

Abstract

Topological insulators (TIs) are new insulating materials with exotic surface states, where the motion of charge carriers is described by the Dirac equations and their spins are locked in a perpendicular direction to their momentum. Recent studies by angle-resolved photoemission spectroscopy have demonstrated that a conventional two-dimensional electron gas can coexist with the topological surface state due to the quantum confinement effect. The coexistence is expected to give rise to exotic transport properties, which, however, have not been explored so far. Here, we report a magneto-transport study on single crystals of the topological insulator BiSbTe$_3$. Besides Shubnikov-de Haas oscillations and weak anti-localization (WAL) from the topological surface state, we also observed a crossover from the weak anti-localization to weak localization (WL) with increasing magnetic field, which is temperature dependent and exhibits two-dimensional features. The crossover is proposed to be the transport manifestation of the coexistence of the topological surface state and two-dimensional electron gas on the surface of TIs.

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CHAPTER 3. CO-EXISTENCE OF TOPOLOGICAL SURFACE STATE AND TWO-DIMENSIONAL ELECTRON GAS IN BISBTE$_3$

3.1 Introduction

Topological insulators (TIs) are new states of quantum matters characterized by a bulk gap, but gapless edge or surface states for two-dimensional (2D) or three-dimensional (3D) TIs, which host helical Dirac fermions. [1–3] These new states originate from the strong spin-orbit interaction of heavy elements, which causes inversion of the valence and conduction bands and therefore, generates a gap in the bulk, while there is a gapless state on the surface that is protected by time-reversal symmetry and robust against non-magnetic perturbations. The exotic topological surface state provides the opportunity to study the novel quantum Hall effect [4] and Majorana fermions [5], and promises applications in magneto-electric sensors [6], spintronics and quantum computation [1–3].

The topological surface state has been verified by surface sensitive techniques, such as angle-resolved photoemission spectroscopy (ARPES) and scanning tunnelling microscopy (STM) and spectroscopy (STS) [7–10]. It has also been revealed in various quantum phenomena by transport measurements, such as Aharonov-Bohm (AB) oscillations, Shubnikov-de Haas (SdH) oscillations, and weak anti-localization (WAL) [11–14].

Very recently, an inversion asymmetric topological insulator (IATI), BiTeCl, was discovered by ARPES [15]. The IATI not only exhibits new topological phenomena such as crystalline-surface-dependent topological electronic states, pyroelectricity, and an intrinsic topological $p-n$ junction, but also provides an ideal platform for the realization of topological magneto-electric effects [15]. The topological surface state in BiTeCl has been demonstrated by the observation of SdH oscillations, which exhibit the 2D nature of the Fermi surface and $\pi$ Berry phase [16]. In addition, when the Fermi level is close to the Dirac point, the topological surface electrons exhibit a small effective mass, $0.055m_e$, and quite large mobility, 4490 cm$^2$s$^{-1}$ [16].

We note that recent ARPES investigations have revealed strong evidence that a two-
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dimensional electron gas (2DEG) and the topological surface state (TSS) can coexist on the surface of topological insulators such as Bi$_2$Se$_3$ and Bi$_2$Se$_{3-x}$Te$_x$ [17–24]. It has been proposed that 2DEG is caused by the formation of quantum wells due to surface perturbations, which is believed to be generally present in narrow-gap topological insulators. The modification of topological electronic structure and the formation of additional quantum well states are expected to give rise to new phenomena. For example, by tuning the electric field gradient of the quantum wells, the 2DEG can exhibit large tunable Rashba spin splitting, which promises applications in non-magnetic spintronics [17, 20, 25].

In a transport study of topological insulators, the SdH oscillations of TSS exhibit 2D characteristics due to the 2D Fermi surface and the linear fit of the Landau level index in the Landau level fan diagram intercepts, with the $n$-index axis at $\pm 0.5$ due to the $\pi$ Berry phase. The $\pi$ Berry phase will also lead to weak anti-localization (WAL), as a result of the destructive interference of the electronic wave, while the 2DEG would show either WAL or weak localization (WL), depending on the phase coherence of the electronic waves. According to the ARPES observations, the 2DEG sub-bands do not split, which is indicative of little Rashba effect. The coexistence can lead to both the WAL and WL from the TSS and 2DEG. Furthermore, a crossover from WAL to WL can be expected, depending on the number of 2DEG channels. Little work has been done, however, on the transport properties associated with the coexistence of the topological surface state and the 2DEG so far.

In this work, by performing transport measurements on BiSbTe$_3$ single crystal with the Fermi level located in the bulk band gap, we detected the Shubnikov-de Haas oscillations and weak anti-localization from the topological surface state (TSS) with large carrier mobility. Moreover, we observed a crossover from weak anti-localization to weak localization, which is possibly the transport manifestation of the coexistence of the TSS.
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and conventional 2DEG.

3.2 BiSbTe$_3$ single crystal growth and magneto-transport measurement

The challenge for study of topological surface state with transport measurement is the bulk carrier contribution to the transport, which hinders the detection of the topological surface state. Electrostatic gating, chemical doping, more careful growth of the materials, and nanosization of material are the frequently used methods to suppress the bulk contribution [14, 26–28]. In particular, both Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are 3D topological insulators, and it has been verified that the isostructural and isovalent alloy of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ can effectively engineer the bulk properties while maintaining the topological surface state [27, 29], similar to the III-V semiconductor Al$_x$Ga$_{1-x}$As. By band engineering in Bi$_{1-x}$Sb$_x$Te$_3$ thin film and nanoplates, the chemical potential has been systematically tuned whenever the topological surface state still exists [27, 29]. But the carrier mobility of the topological surface state of Bi$_{1-x}$Sb$_x$Te$_3$ is so small that the quantum oscillation from the surface state of this material is hard to observe [29, 30]. Therefore, it is quite necessary to grow high quality single crystal with large carrier mobility, which is important for the study of its electronic properties by transport measurements. In this series of compounds, the Fermi level of BiSbTe$_3$ single crystal is located in the bulk gap, which is ideal for transport investigation, and we therefore chose BiSbTe$_3$ single crystal for our study.

Single crystals of BiSbTe$_3$ were grown by slowly cooling a melt of the high purity (5N) elements Bi, Sb, and Te. The mixture of three elements with molar ratio of 1:1:3 was put into a quartz tube, which was evacuated and sealed, and then heated up to 800 °C and held at that temperature for 24 h. It was then cooled to 550 °C over several days, annealed at that temperature for 3 days, and finally furnace cooled to room temperature. From the X-ray diffraction, only 00$l$ reflections appear with sharp peaks, indicating that
3.3 Signature of topological surface state

Figure 3.1: (a) Temperature dependence of the resistance at 0, 5, and 13 T. Below around 150 K, the resistance shows insulating temperature dependence. The inset contains the corresponding Arrhenius plot. (b) Hall resistance of the single crystal measured at 2.5 K. (c) Schematic diagram of the band structure for BiSbTe$_3$ single crystal. The Fermi level is located in the bulk band gap but close to the conduction band, the two-dimensional electron gas (2DEG) band and topological surface state band (SSB) coexist at the Fermi level. The 2DEG subbands are inferred from the crossover from WAL to WL.

For transport measurements, the single crystals were cleaved and cut into a rectangular shape. The dimensions of the sample used in this study, except for the Hall measurements, are $0.58 \times 0.85 \times 0.09$ mm$^3$ ($L \times W \times T$, where $W$ and $T$ are the width and thickness respectively, and $L$ is the distance between two voltage contacts). The standard four probe method was employed, and the Ohmic contacts were made with silver epoxy cured at room temperature. For the Hall resistance measurements, the standard six probe method was employed with the rectangular Hall bar shape. The magnetoresistance and Hall resistance were measured by sweeping the perpendicular magnetic field between $\pm 13$ T, except for the angular dependence of the magnetoresistance.

### 3.3 Signature of topological surface state

Figure 3.1(a) shows the temperature dependence of the resistance of cleaved single crystal BiSbTe$_3$ in magnetic field of 0, 5, and 13 T. From 300 K to 155 K, the resistance decreases with temperature, exhibiting metallic behaviour. The resistance increases with tempera-
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ture below 150 K, exhibiting insulating behaviour, which means that the the emergence of band gap. The activation energy deduced from the linear part of Arrhenius plot of ln \( \rho \) vs. \( 1/T \), as shown in the inset of Figure 1a, is 26.9 meV. It should be noted that there is a crossover between zero field and non-zero field \( R - T \) curves, which is an indication of negative magnetoresistance and will be discussed in detail below. Figure 3.1(b) shows the typical Hall resistance \( R_{xy} \) at 2.5 K for a BiSbTe₃ single crystal from the same batch, which indicates that the dominant carriers are electrons. To determine the relative position of the Fermi level in the band structure, the magnetic field dependence of \( R_{xy} \) of a sample cleaved from same single crystal was measured, as shown in Fig. 3.1(b). The negative value of \( R_{xy} \) in positive field and the non-linear magnetic field dependence of \( R_{xy} \) indicate that at least two types of charge carriers contribute to \( R_{xy} \), but that the dominant charge carriers are electron. So, according to our experimental data and the ARPES results on the thin film samples, the band structure of our sample could be schematically sketched, as shown in Fig. 3.1(c).

To detect the TSS by the Shubnikov-de Haas oscillations, the magnetoresistance was measured in magnetic field up to \( \pm 13 \) T. The SdH oscillation can be seen clearly at 2.5 K in Fig. 3.2(a) and gradually disappears with increasing temperature. Because the sample is already in the insulating regime, the oscillation of the magnetoresistance was inferred to be due to the electrons in the surface state. To verify the origin of the SdH oscillations, the angular dependence of the magnetoresistance was measured every 10°, as shown in Fig. 3.2(b), and the experimental set-up is shown in the inset of Fig. 3.2(b). In an electronic system with a two-dimensional (2D) Fermi surface (FS), the peak positions of the SdH oscillation depend only on the perpendicular component of the magnetic field \( B_\perp = B \cos \theta \) to the sample surface. It can be seen that the oscillation disappears as the angle increases from 0° to 90°, suggesting the 2D nature of the FS. To clearly confirm the 2D nature
of the SdH oscillation, \(dR/dB\) vs. \(1/B_\perp\) is plotted as shown in Fig. 3.2(c), in which the positions of its maxima and minima depend only on the perpendicular component of the magnetic field, \(B_\perp\), indicating that the SdH oscillations have a 2D character.

Figure 3.2: (a) Magnetoresistance up to 13 T was measured at various temperatures, and the weak anti-localization disappears with increasing temperature. (b) Angular dependence of magnetoresistance from \(0^\circ\) to \(90^\circ\) at 2.5 K. (c) \(dR/dB\) is plotted as function of the inverse perpendicular component of the magnetic field, \(1/B \cos \theta\), at various angles. (d) Landau level fan. Inset is the fast Fourier transform (FFT) of the oscillation, giving the oscillation frequency, \(F = 50.80\) T. (e) Temperature dependence of the oscillation amplitude, which yields the cyclotron effective mass, \(m_{cyc} = 0.105m_e\). (f) Dingle plot of the oscillation \(\Delta RB \sinh(\alpha Tm^*/B)\) vs \(1/B\).

The SdH oscillation originates from the Landau quantization of the FS, and the oscillation...
CHAPTER 3. CO-EXISTENCE OF TOPOLOGICAL SURFACE STATE AND TWO-DIMENSIONAL ELECTRON GAS IN BISBTE$_3$

The oscillation frequency is related to the extremal cross section of the FS, SF, which is quantitatively described by the Onsager relation: $F = (\hbar c/2\pi e)S_F$, where $S_F = \pi k_F^2$, where $k_F$ is the Fermi wave vector. Through the fast Fourier transform, the oscillation frequency, $F = 50$ T, is obtained; with this frequency, the Landau level fan is plotted, and the intercept is set to be 0.5. As shown in Fig. 3.2(d), all of the points are nearly located on the fitting line, which verifies the $\pi$ Berry phase of the surface state. Thus, it could be concluded that the SdH oscillations in our sample originate from the TI surface state.

After verifying the origin of the SdH oscillations, the temperature and magnetic field dependence of the oscillation amplitude were analysed to extract the information on the surface states. The oscillation amplitudes were obtained after subtracting the smooth background of magnetoresistance (MR). The temperature and magnetic field can affect the resolution of the Landau tubes: the lower the temperature and the higher the magnetic field is, the larger the oscillation amplitude will be. This is well described by the Lifszitz-Kosevich theory, in which the thermal damping factor $R_T$ and the Dingle damping factor $R_D$ describe the temperature and magnetic field dependence of the oscillation amplitudes as follows: $R_T = \alpha T m^*/B \sinh(\alpha T m^*/B)$ and $R_D = \exp(-\alpha T D m^*/B)$ where $\sinh$ is the hyperbolic function, the effective mass $m = m^* m_e$, and $\alpha = 2\pi^2 k_B/\hbar \approx 14.69$ T/K, and $T_D = \hbar/2\pi k_B \tau$ is the Dingle temperature, $\tau$ the scattering time. Fitting the temperature dependence of the oscillation amplitude with the thermal damping factor yields the effective mass $m_{cyc} = 0.105 m_e$. From $m_{cyc}$ and $k_F$ we obtain the Fermi velocity $v_F = \hbar k_F/m_{cyc} = 4.23 \times 10^7$ cm$s^{-1}$. Because $\Delta R/R_0 \approx R_D R_T$ (where $R$ is the resistance), the Dingle temperature, 25 K, and the scattering time $\tau$, $4.87 \times 10^{-14}$ s, are obtained from the slope in the semilog plot of $\Delta R B \sinh(\alpha T m^*/B)$ versus $1/B$, as shown in Fig. 3.2(d).

This gives the mean free path $l_s = v_F \tau$ of 20.62 nm, where $v_F$ is the Fermi velocity, and the mobility $\mu = e l_s/\hbar k_F = 821.95$ cm$^2$V$^{-1}$s$^{-1}$.
3.3. SIGNATURE OF TOPOLOGICAL SURFACE STATE

Figure 3.3: The magnetoconductance at 2.5 K and 5 K, which in low field, can be fitted by the HKN formula.

Besides the SdH oscillation at high field, another piece of evidence for the presence of a TSS in our sample is the weak anti-localization (WAL) in low field (Fig. 3.2(a)). The WAL emerges as the correction of coherent time-reversed closed paths to electronic transport when the phase coherent length, $l_\phi$, of electrons is much greater than the elastic scattering length, $l_e$. Applying the magnetic field will break the phase coherence and therefore results in a sharp increase (cusplike MR) of the resistance in magnetic field, which is the key signature of WAL. In topological insulators, the WAL is ascribed to the surface state with $\pi$ Berry phase, which causes the destructive interference. As shown in Fig. 3.2(a) the weak anti-localization is pronounced at low temperatures such as 2.5 K and gradually disappears with increasing temperature, since the phonon vibrations increase with temperature, which degrades the phase coherence of the electrons. The quantum correction to the Drude conductivity is well described by the Hikami-Larkin-Nagaoka (HLN) formula [31], as follows:
\[
\Delta_{HLN}(B) = \alpha e^2 \pi h \left[ \Psi\left( \frac{\hbar}{4eBL^2_\phi} + \frac{1}{2} \right) - \ln\left( \frac{\hbar}{4eBL^2_\phi} \right) \right] \tag{3.1}
\]

Where \( \Psi \) is the digamma function, \( B \) is the magnetic field, \( l_\phi \) the phase coherence length, and \( \alpha \) is the prefactor, while \( l_\phi \) and \( \alpha \) are fitting parameters. In our experiment, the low temperature magnetoresistance can be well fitted by this formula. As shown in Fig. 3.3, the low field magneto-conductance at 2.5 and 5 K is fitted well by the HLN formula, where \( \alpha \) is -1.1 and -1.1, and \( l_\phi \) is 40 and 31 nm, respectively. The prefactor, \( \alpha = -1.1 \), in our sample indicates that both the bottom and top TSS exist.

### 3.4 Signature of coexistence of a two-dimensional electron gas

![Figure 3.4: MR measured from 2.5 K to 75 K (a) and from 100 K to 300 K (b).](image)

Besides the ubiquitously observed WAL feature for topological insulators, a negative MR related to the weak localization (WL) is also observed in our measurements, as discussed below. As shown in Fig. 3.4(a) and 3.4(b), the WAL crosses to the negative MR at a field of around 1 to 2 T, which is clear at a low temperature such as 2.5 K, but with increasing temperature, the crossover become less pronounced and eventually disappears. At a high temperature such as 300 K, besides the disappearance of the WAL, the negative
3.4. SIGNATURE OF COEXISTENCE OF A TWO-DIMENSIONAL ELECTRON GAS

MR is transformed to positive MR, and the whole MR curve exhibits a parabolic shape corresponding to the MR caused by orbital scattering. Such temperature dependent negative MR is the signature of the WL effect. The theoretical calculations reveal that random magnetic scattering could drive the system from the symplectic to the unitary class, and if the magnetic doping can open a gap at the Dirac point, the weak anti-localization could be made to cross over to weak localization by tuning the gap or Fermi level [32]. The ARPES experiments have revealed a gap that opens at the Dirac point in magnetically doped topological insulators [33, 34] and a crossover from weak anti-localization to weak localization when they are magnetically doped or in proximity to ferromagnetic thin films [35]. In addition, WL can also emerge in the bulk quantization regime whenever the bulk WL channels outnumber the surface WAL channels [36–38]. Because the surface state bands and the lowest 2D bulk bands of a topological insulator thin film can be described by the two-dimensional modified Dirac model, a finite gap leads to the weak localization or the unitary behaviour. Neither of them, however is the reason for the behaviour of our non-magnetic bulk sample. The angular dependence of the MR shown in Fig. 3.2(b), however, gives us a clue as to the origin of the WL, where the crossover become less obvious with increasing angle and disappears from 50°, indicating the 2D nature of the negative MR. On the other hand, it has been reported that the 2D electron gas is present on the topological surface state when the surface is exposed to atmosphere, which is believed to be generally true for the topological insulators. The band structure of the 2D electron gas is similar to that of bulk quantized samples [17, 20, 25]. Because our transport measurements were performed under ambient atmosphere, a 2DEG can form on the surface of our sample, which will lead to the WL. Using the model in Ref. [36], we have calculated the magnetoconductance as a function of magnetic field. By assuming three pairs of subbands and one pair of topological surface state bands, the theoretical results show the similar
trends of the change of magnetoconductance as compared to our experimental data (Fig. 3.3). However, we can see that the simulation can account for the experimental data qualitatively, but not quantitatively. This implies there are some contributions from bulk carriers to magnetoconductance. Thus, the crossover from WAL to WL in our sample should arise from the coexistence of the 2DEG and TSS on the surface.

3.5 Conclusion

In conclusion, we studied the magneto-transport properties of single crystals of the topological insulator BiSbTe$_3$ with the Fermi level located in the bulk band gap. Shubnikov-de Haas oscillation was observed and identified as originating from the surface state by the angular dependence of the MR and $\pi$ Berry phase. The high mobility, 821.95 cm$^2$V$^{-1}$s$^{-1}$, explains why SdH oscillation was observed. In addition to the WAL from the TSS, a crossover from weak anti-localization to weak localization was observed; we propose that the crossover should be ascribed to the coexistence of the topological state and a two-dimensional electron gas on the surface.

3.6 References


CHAPTER 3. CO-EXISTENCE OF TOPOLOGICAL SURFACE STATE AND TWO-DIMENSIONAL ELECTRON GAS IN BISBTE$_3$


CHAPTER 3. CO-EXISTENCE OF TOPOLOGICAL SURFACE STATE AND TWO-DIMENSIONAL ELECTRON GAS IN BISBTE$_3$
Abstract

The recently observed large Rashba-type spin splitting in the BiTeX ($X = I, Br, Cl$) bulk states enables observation of the transition in Fermi surface topology from spindle-torus to torus with varying the carrier density and offers an ideal platform for achieving practical spintronic applications and realizing non-trivial phenomena such as topological superconductivity and Majorana fermions. Here we use Shubnikov-de Haas oscillations to investigate the electronic structure of the bulk conduction band of BiTeCl single crystals with different carrier densities. We observe the topological transition of the Fermi surface (FS) from a spindle-torus to a torus. The Landau level fan diagram reveals the expected non-trivial $\pi$ Berry phase for both the inner and outer FSs. Angle-dependent oscillation measurements reveal three-dimensional FS topology when the Fermi level lies in the vicinity of the Dirac point. All the observations are consistent with large Rashba spin-orbit splitting in the bulk conduction band.
4.1 Introduction

Spin-orbit coupling (SOC) is a relativistic effect present in a system with broken symmetry, where a charged particle moving in an electric field experiences an effective magnetic field, which interacts with its spin [1, 2]. In solids, electrons move in a crystal potential, and if there is a potential gradient, effective SOC arises [2] and manifests itself in the spin-split band structure. Such spin splitting was first described by the Dresselhauus [3] and Rashba [4] model in the zinc-blende and the wurtzite structure, respectively, and later by the Bychkov-Rashba model at surfaces and interfaces [5]. Although large spin splitting has been observed at the surface of heavy metals, it remains small in conventional semiconductors.

Recently, large Rashba-type spin splitting has been observed in the bulk bands of BiTeX (X = I, Br, Cl) polar semiconductors due to the broken inversion symmetry and charge polarity in the bulk [6–11]. The high energy scale of the Rashba effect in BiTeX provides opportunities for achieving practical spintronic applications [12, 13] and realizing non-trivial phenomena such as the intrinsic spin Hall effect [14], non-centrosymmetric exotic superconductivity [15, 16], Majorana fermions [17, 18], and topological transitions of the Fermi surface (FS) [9, 19, 20]. Among them, the topological transition of the FS takes place when the Fermi level is tuned down through the band crossing point (Dirac point), as shown in Fig. 4.1(a). When the Fermi energy, $E_F$, is larger than the Rashba energy, $E_R$, i.e., $E_F > E_R$, the FS is a spindle torus [(iv) of Fig. 4.1(a)]. When $E_F = E_R$, the spindle inner FS (IFS) disappears, and only the outer FS (OFS) remains [(v) of Fig. 4.1(a)]. When $E_F < E_R$, the FS becomes a ring torus [(vi) of Fig. 4.1(a)] [9]. In this transition, both the number and type of the FSs change by 1 [9]. Furthermore, due to the opposite spin helicity of the OFS and IFS, the ratio of carrier densities with opposite spin helicity changes with this transition. When $E_F > E_R$, two types of carriers with opposite
spin helicity are present [(i) of Fig. 4.1(a)]. When \( E_F \leq E_R \), the spin helicity of all the carriers is the same [(ii) and (iii) of Fig. 4.1(a)]. Therefore, such a transition would be an important step toward exploring spin-dependent transport and other exotic physical phenomena in the low-carrier-density regime [9, 19, 20]. In particular, it is highly desirable to tune the Fermi level into the vicinity of the Dirac point at zero momentum in the Rashba system, since schemes to realize Majorana fermions [18] involve opening a small energy gap at the Dirac point to realize a single spin non-degenerate band. Furthermore, the spin polarization of current is largest in the vicinity of the Dirac point [20, 21], and hence, such materials could be used as spin injectors, as has been proposed with topological insulators [22, 23], but the surface-dominated transport is not required in this case.

Magnetotransport is a powerful method to study the electronic properties of materials such as topological insulators [24, 25]. In particular, the Shubnikov–de Haas (SdH) oscillation can probe the electronic structure, reveal information on the Fermi surface (FS) topology [26, 27], and access the Berry phase [25, 28–30], so it is highly suitable for investigating topological transitions of the Fermi surface and detecting the potential topological surface states. Although BiTeCl has smaller spin splitting than BiTeI, it exhibits a larger band gap and more isotropic spin splitting [10], which are very desirable for transport measurements.

In this work, using the SdH effect, we observe a transition from two sets of oscillations to one as the carrier density varies in BiTeCl single crystals. The Landau level (LL) fan diagram reveals the non-trivial \( \pi \) Berry phase both in the inner FS (IFS) and the outer FS (OFS). We also resolve the three-dimensional (3D) FS topology when the Fermi level lies in the vicinity of the Dirac point by angle-dependent oscillation measurements. All the observations are consistent with a topological transition of the FS from a spindle torus to a torus in the large Rashba spin-split conduction band of BiTeCl.
CHAPTER 4. OBSERVATION OF TOPOLOGICAL TRANSITION OF FERMI SURFACE IN BULK RASHBA SEMICONDUCTOR BITECL

Figure 4.1: (a) (Left) Energy–momentum dispersion in the Rashba spin-split conduction band. The dashed lines represent different Fermi energies $E_F$. The blue and red colors indicate two opposite spin directions. (Middle) The constant energy contours at the $k_\parallel$ plane and (Right) the three-dimensional FS for $E_F > E_R$ [(i) and (iv)], $E_F = E_R$ [(ii) and (v)], and $E_F < E_R$ [(iii) and (vi)], respectively. The orange and green colours in the middle of Fig. 1(a) indicate different spin helicities, and the arrows show the spin direction. Longitudinal resistivity $\rho_{xx}$ (b) and Hall resistivity $\rho_{xy}$ (c) as functions of magnetic field $B$ for sample S4. (d) Evolution of the topological transition as the Fermi level shifts from well above the Dirac point down to the vicinity of the Dirac point. The arrows indicate the oscillation periods from the IFS that can be observed.

4.2 Experimental detail

Single crystals of BiTeCl were grown by the self-flux method according to the Bi$_2$Te$_3$–BiCl$_3$ binary phase diagram. Bi$_2$Te$_3$ was synthesized from high-purity (5N) Bi and Te powders. Bi$_2$Te$_3$ and BiCl$_3$ (5N) powders were weighed out with the molar ratio of 1 : 9 and thoroughly ground together, with these operations carried out in an oxygen and moisture monitored glove box to prevent the deliquescence of BiCl$_3$. The mixture of powders then was loaded into a quartz tube and sealed under vacuum before heating to above 420 – 500 °C over several hours. The temperature was maintained for 12 h, and then the samples were slowly cooled down to 200 °C over several days. The plate-like crystals were
obtained by chemically removing the residual flux of BiCl$_3$.

Single-crystal samples of BiTeCl with shining surfaces were cleaved from the as-grown crystals and used for standard four probe transport measurements. In some cases, a six-probe Hall measurement was employed to obtain the longitudinal resistance, $R_{xx}$, and the Hall resistance, $R_{xy}$, simultaneously. Gold wires were attached to the sample surface by silver epoxy, which was cured at room temperature before the measurements to ensure Ohmic contacts. The magnetic field B was applied perpendicular to the sample surface and varied up to 13.5 T, except for the angle dependent measurements. The temperature for magneto-transport measurements was 2.5 K, except for measurements of the SdH oscillations at various temperatures.

4.3 Observation of the topological transition of the Fermi surface

In contrast to BiTeI, the Rashba spin-orbit splitting in BiTeCl occurs in the $\Gamma K - \Gamma M$ plane of momentum space, denoted as the $k_\parallel$ plane, where momentum along the z direction, $k_z = 0$ [10, 11, 31, 32]. The energy-momentum dispersion can be described by the following equation, assuming a parabolic band.

$$E_{\pm}(k) = \frac{\hbar^2}{2m^*}(k \pm k_0)^2$$ (4.1)

where $k = \sqrt{k_x^2 + k_y^2}$, $k_0$ is the momentum offset caused by the Rashba spin-splitting, $m^*$ is the effective mass of the electrons, and $\hbar$ is Planck’s constant divided by $2\pi$. Besides the $k_0$, the other two Rashba parameters are the Rashba energy, $E_R = \hbar^2 k_0/2m^*$, and the Rashba constant, $\alpha_R = 2E_R/k_0$, which represent the energy when $k = 0$ and the strength of the Rashba effect, respectively. The spin-split conduction band dispersion of BiTeCl near the $\Gamma$ point is shown on the left of Fig. 4.1(a), and the right of Fig. 4.1(a) shows the 3D FS when the Fermi energy EF has different values. When $E_F > E_R$, the 3D FS is a
spindle torus, and both the IFS (spindle) and OFS (torus) are present [ (iv) of Fig. 4.1(a)]. While in a small Rashba spin-split system, the IFS and OFS result in beating patterns in the SdH oscillations; in a giant Rashba spin-split system, the two sets of oscillations are thoroughly decoupled from each other [29]. When \( E_F \leq E_R \), the IFS vanishes, and the FS is simply a torus, i.e. only the OFS is present [(v) and (vi) of Fig. 4.1(a)]. Thus, it is expected that the two sets of oscillations represent a transition to a single frequency in the Shubnikov-de Haas oscillation measurement when the Fermi level approaches the Dirac point, corresponding to the topological transition of FS from spindle torus to torus.

BiTeCl is a degenerate semiconductor due to the self-doping effect (nonstoichiometric effect or formation of defects), which is similar to what occurs in the topological insulators such as Bi\(_2\)Se\(_3\) and Bi\(_2\)Te\(_3\). Because the self-doping effect depends on the temperature gradient along the quartz tube during the single crystal growth, the carrier density of the crystal can vary in different positions in the quartz tube. To observe the expected topological transition of the FS as the Fermi level approaches the Dirac point, a group of single crystal samples with various carrier concentrations was selected from different positions in the tube. The samples are denoted as S1 to S7 and are ordered according to their increasing OFS oscillation frequency. Figs. 4.1(b) and 4.1(c) shows the typical longitudinal resistivity (\( \rho_{xx} \)) and Hall resistivity (\( \rho_{xy} \)) of the samples. The negative linear slope in Fig. 4.1(c) indicates that the dominant carriers are electrons. The calculated carrier density is \( 8.87 \times 10^{18} \) cm\(^{-3}\). A clear evolution of the transition from two sets of oscillations to a single frequency oscillation is shown in Fig. 4.1(d). From S7 to S1 the oscillations from the IFS indicated by the red arrows gradually disappear, and only oscillations from the OFS are left, consistent with the topological transition of the FS described above [9, 19].
4.4. STANDARD SHUBNIKOV-DE HAAS OSCILLATION ANALYSIS

Figure 4.2: (a) OFS SdH oscillations of S2 at various temperatures after subtracting the background. (b) Temperature dependence of the OFS oscillation amplitude of S2. Fitting with the thermal damping factor yields the effective mass \( m^* \). (c) LL fan diagram used to obtain the oscillation frequencies, \( F \), and the phase factors of the OFSs for Samples S1-S7. The solid symbols denote LL indices for the minima and maxima of the SdH oscillations. The solid lines are the linear fits to the experimental data. The values of the intercepts of the fitting lines with the LL index axis are shown in the inset. The error bars in the inset indicate the standard deviation of the fitting errors. (d) OFS SdH oscillations of S2 fitted by the LK formula, which yields the Dingle temperature.

4.4 Standard Shubnikov-de Haas oscillation analysis

To deduce the electronic structure via standard SdH oscillation analysis, the Lifshitz-Kosovich (LK) formula is used as follows [26, 27, 29]:

\[
\rho \rho_0 = \frac{5}{2} \left( \frac{B}{2F} \right)^{\frac{1}{2}} \frac{2\pi^2 k_B T m^*/\hbar B}{\sinh(2\pi^2 k_B T m^*/\hbar B)} e^{-\frac{2\pi^2 k_B T m^*/\hbar B}{\hbar e B}} \cos 2\pi \left( \frac{F}{B} + 1 + \frac{\phi_B}{2\pi} + \delta \right) \tag{4.2}
\]

where \( F \) is the oscillation frequency, \( k_B \) the Boltzmann constant, \( e \) the elementary charge, \( T \) the temperature, \( T_D \) the Dingle temperature, \( \phi_B \) the Berry phase, and \( \delta \) the phase
shift determined by the dimensionality. Figure 4.2(a) shows the OFS SdH oscillations of S2 at various temperatures after subtracting the background. Fitting the temperature dependence of the OFS oscillation amplitudes of S2 around 11.65 T with the thermal damping factor, \( \frac{2\pi^2 k_B T m^* / \hbar e B}{\sinh(2\pi^2 k_B T m^* / \hbar e B)} \), from Equation 4.2, as shown in Fig. 4.2(b), yields the effective mass, \( m^* = 0.191 \pm 0.005 m_e \), where \( m_e \) is the free electron mass. Because \( \rho_{xx} < \rho_{xy} \), as shown in Figs. 4.1(b) and 4.1(c), the minima and maxima of the SdH oscillations are assigned as integer \((n)\) and half integer \((n + 1/2)\) LL indices, respectively.

Linear fits of the LL indices vs. \( 1/B \) of S1 to S7 in the LL fan diagram of Fig. 4.2(c) yield the oscillation frequency \( F \) (slopes of the fit lines) and the phase factor, \( -\frac{\phi_B}{2\pi} \) (intercepts with the LL index axis), for each sample. Taking the value \( \delta = \pm 1/8 \) for our three-dimensional (3D) system [26, 27, 29], the range of the intercepts from 0.375 to 0.625 indicates a nontrivial \( \pi \) Berry phase. The inset of Fig. 4.2(c) shows the Berry phases for S1 to S7, and nearly all of them are located in the range from 0.375 to 0.625. After obtaining \( m^* \), \( F \), and the phase factor, we fit the OFS SdH oscillation data of S2 with Equation (4.2)to obtain the Dingle temperature \( T_D \). As shown in Fig. 4.2(d), the LK formula fits well with the experimental data, resulting in \( T_D = 17.6 \pm 0.12 \text{ K} \). The same analysis process was applied to sample S1 and samples S3 to S6 (see Subsection 4.8.2). Only the oscillation frequency was obtained for S7, however. All of the fitting parameters, \( F \), \( m^* \), and \( T_D \), are tabulated in Table 1.

Figures 4.3(a) and 4.3(b) shows \(-d^2 R_{xx}/dB^2\) as a function of \( B \) for S5 and S7, the maxima and minima of which correspond to the oscillation maxima and minima. Besides the high frequency oscillations from the OFS in high field, low frequency oscillations from the IFS can be observed in low field, as indicated by the blue arrows. Fig. 4.3(c) shows the LL fan diagram for the IFS. Because the SdH oscillations from the IFS for S5 and S7 are very close to the regime of \( \rho_{xx} \approx \rho_{xy} \), we carefully assigned the LL integer \( n \), as discussed
4.4. STANDARD SHUBNIKOV-DE HAAS OSCILLATION ANALYSIS

Figure 4.3: $-d_R^{R}/dB^2$ as a function of $B$ for (a) S5 and (b) S7. The blue arrows indicate the positions of the integer and half integer LLs. (c) LL fan diagram for IFS of S5 and S7. The inset shows the values of the intercepts of the fitting lines with the LL index axis. The error bars in the inset indicate the standard deviation of the fitting errors. (d) The energy-momentum dispersion determined by the Rashba parameters from the experimental results. The blue and red curves represent two spin-split bands with opposite spin direction. The solid lines are the Fermi levels for S1-S7 calculated by the Rashba model.

in Appendix E Subsection 4.8.5. For S5, the LL integer $n$ is assigned to the maxima of the SdH oscillations, and in the low field part for S7, the LL integer $n$ is assigned to the maxima of the SdH oscillations, while in the high field part, the LL integer $n$ is assigned to the minima of the SdH oscillations. The linear fittings yield the frequencies $2.81 \pm 0.10$ and $5.93 \pm 0.01$ T, respectively, and the intercepts with the LL index axis are at $0.756 \pm 0.048$ and $0.700 \pm 0.003$, respectively, which are very close to the region from 0.375 to 0.625 and indicate that the IFS also has a non-trivial $\pi$ Berry phase. The non-trivial $\pi$ Berry phase in the OFS and IFS is consistent with the pure bulk Rashba effect, which was first
Table 4.1: Parameters determined from SdH oscillations and the Rahsba model for samples from S1 to S7. $m^\text{OFS}$ is the effective mass of the OFS. $F^\text{OFS}$ and $F^\text{IFS}$ are oscillation frequencies from the OFS and IFS which yield $k^\text{OFS}_F$ and $k^\text{IFS}_F$, via the Onsager relation. $T^\text{OFS}_D$ is the Dingle temperature of the OFS. $E_F$ is calculated by the Rashba model. The carrier density $n$ is calculated with the 3D model, $(1/3\pi^2)(2eF/\hbar)^{3/2}$. $\mu$ is carrier mobility calculated by $e\hbar/2m^*k_BT_D$.

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<th></th>
<th>$m^*$</th>
<th>$F^\text{OFS}$</th>
<th>$T^\text{OFS}_D$</th>
<th>$k^\text{OFS}_F$</th>
<th>$\mu^\text{OFS}$</th>
<th>$F^\text{IFS}$</th>
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<td>S1</td>
<td>0.203</td>
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<td>458.5</td>
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<td>65.69</td>
<td>640.2</td>
<td>23.61</td>
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<td>20</td>
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<td>537.4</td>
<td>27.61</td>
<td>10.88</td>
<td></td>
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</tr>
<tr>
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<td>162.1</td>
<td>20.5</td>
<td>70.20</td>
<td>537.8</td>
<td>30.11</td>
<td>11.69</td>
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<tr>
<td>S5</td>
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<td>172.3</td>
<td>21.05</td>
<td>72.37</td>
<td>522.9</td>
<td>2.81</td>
<td>9.24</td>
<td>33.52</td>
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reported in BiTeI [18].

4.5 Determination of Rashba parameters and Fermi levels

We now determine the Rashba parameters and then calculate the Fermi levels of the seven samples from the Rashba model. According to the Onsager-Lifshitz equation, $F = (\hbar/2\pi e)A_F$, where $A_F$ is the extremal area of the cross section of the FS perpendicular to the $B$ direction. With $A_F = \pi kF^2$, the Fermi wave vector is obtained, $k_F = \sqrt{2eF/\hbar}$, as given in Table 1. Substituting the IFS wave vector $k^\text{IFS}_F$ and the OFS wave vector $k^\text{OFS}_F$ of S5 and S7 into Equation (1) yields $k_0 = 0.03158$ and $0.03006$ Å$^{-1}$, respectively; the similar values indicate self-consistency of the model. Then, the Rashba energy, $E_R = h^2k_0^2/2m^* = 18.45$ meV, and the Rashba constant, $\alpha_R = 2E_R/k_0 = 1.20eV\AA$, are obtained with the average of the two $k_0$ and the average effective mass of S1-S6, which agree with the theoretical values [31, 32]. Substituting the $k_F$ of S1-S7 into Equation (1) 4.7 yields the corresponding EF given in Table 1. With $k_0$ and $m^*$ determined, the dispersion relation is plotted in Fig. 4.3(d), and the solid lines are the calculated Fermi
4.6. RESOLUTION OF A 3D FERMI SURFACE

levels for the seven samples. When the SdH oscillation with a single frequency exhibits a non-trivial $\pi$ Berry phase, it is easy to relate the oscillation to the topological surface state in BiTeCl, which was recently observed by angle-resolved photoelectron spectroscopy (ARPES) [33]. The emergence of two sets of oscillations, however, rules out this possibility in this measurement. Furthermore, as tabulated in Table 4.1, the carrier densities calculated from the SdH oscillations with the 3D model $n = (1/3\pi^2)(2eF/\hbar)^{3/2}$ are consistent with the Hall effect measurements on the typical sample S4, $8.87 \times 10^{18}$ cm$^{-3}$, which also indicates the bulk origin of the oscillation.

4.6 Resolution of a 3D Fermi surface

To resolve the 3D FS topology, the SdH oscillations were measured over an extended range of angles with the measurement configuration shown in Figure 4.4(a). The oscillations exhibit symmetry in $\pm \theta$ [Fig. 4.4(b)], which corresponds to the symmetry of the FS. With increasing tilt angle $|\theta|$, the number of observed oscillation periods becomes less, and the amplitude diminishes, which is similar to the behaviour of a two-dimensional (2D) electronic system. Fig. 4.4(c) plots the oscillations as a function of $1/\cos \theta$ from $0^\circ$ to $52^\circ$. From $0^\circ$ to $12^\circ$, the oscillation can be reasonably described by a 2D FS, in which the period of oscillation depends on $1/B \cos \theta$, but as the tilt angle increases further, the oscillations deviate from the expectation for a 2D FS. While the oscillation signal cannot be extracted for angles between $56^\circ$ and $82^\circ$, clear oscillations are again visible for angles around $90^\circ$ with a spherical FS character, depending on $1/B$ rather than $1/B \cos \theta$, however, with amplitude much smaller than those around $0^\circ$ [Fig. 4.4(d)].

Now we propose a quantitative 3D FS topology which captures the above feature of the oscillation. Fig. 4.4(e) shows the angle-dependent oscillation frequency. The experimental data (black solid circles) deviate from the cylindrical FS for the 2D electronic system represented by the blue solid line ($F_\theta \propto 1/\cos \theta$), but the data can be fitted well by a
Figure 4.4: (a) Measurement configuration for angle-dependent SdH oscillations at 2.5 K. The electric current and rotation axis are parallel to the x direction, and the $B$ is along the z direction. $\theta$ is defined as the angle between $B$ and the z axis. The OFS SdH oscillations of $S_2$ measured from $-34^\circ$ to $40^\circ$ (b) and from $0^\circ$ to $52^\circ$ (c) are plotted as functions of $B$ and $1/B \cos \theta$. The oscillations are obtained after removing the polynomial background and have been vertically shifted for clarity. The dashed lines indicate the oscillation period at $0^\circ$ on the scale with $1/B$, which is consistent with the Landau quantization. (d) The OFS SdH oscillations of $S_2$ around $90^\circ$ reveal its spherical nature. (e) Tilt angle dependence of $F$ fitted with cylindrical and prolate spheroid FS. (f) Vertical cross-sectional view of the 3D FS cut along the $k_z$ direction for $S_2$. The blue rectangle denotes the cylindrical FS of a 2D electronic system, and the red ellipse denotes a prolate spheroid FS. The black and purple solids represent the OFS and IFS, which are proposed to explain the observations in Fig. 4(b)–(e). The dashed line indicates the extremal cross-section of the FS perpendicular to $B$.

The spherical FS behaviour around $90^\circ$ may be caused by the hollow shape of the OFS near zero momentum, which makes the extremal cross-sectional area constant around $90^\circ$. The half-height of the OFS, $a \approx 34.5 \times 10^{-3} \AA^{-1}$, is estimated by treating the extremal cross section of the OFS as a rectangle. The vertical cross-sectional view of the 3D FS is prolate spheroid FS (red solid line) when $\theta < 52^\circ$, $F = \frac{\hbar^2}{2e} \sqrt{\left(\frac{a}{b}\right)^2 \sin^2 \theta + \cos^2 \theta}$, see Subsection 4.8.3) with a major axis $a = 119.6 \times 10^{-3} \AA^{-1}$ and a minor axis $b = 65.69 \times 10^{-3} \AA^{-1}$, located on the $k_z$ axis and the $k_\parallel$ plane of the momentum space, respectively.
shown in Fig. 4.4(f).

4.7 Conclusion

In this work, we studied the SdH oscillations from the bulk Rashba spin-split conduction band of BiTeCl. The transition from two-frequency to single-frequency oscillation reveals the topological transition from a spindle-torus to a ring-torus FS. The momentum offset, Rashba energy, and Rashba coupling constant have been determined for giant Rashba spin splitting in BiTeCl. Both the inner and the outer Fermi surfaces have a non-trivial $\pi$ Berry phase. Angle-dependent oscillation measurements reveal the three-dimensional FS topology when the Fermi level lies in the vicinity of the Dirac point.

Notes added. (1) Initially, we observed quantum oscillations in BiTeCl with a single frequency and non-trivial Berry phase, and attributed this oscillation to a topological surface state in an earlier report [34]. In this work, by combining the Hall measurements, the Fermi surface tuning, and more extensive angle-dependent SdH measurements, we find that the oscillations originate from the bulk and that the previous observation of an SdH oscillation with a single frequency corresponds to the extremal case when the Fermi level is located in the vicinity of the Dirac point, where the oscillation from the IFS disappears. When preparing this manuscript, we became aware of another two works which also conclude that SdH oscillations in BiTeCl originate from the bulk [35, 36]. Our work is different from Ref. [35] and [36], however, as we observe oscillations from both the IFS and the OFS in lower magnetic field, the topological transition of the FS by tuning the carrier density with the self-doping effect, and the non-trivial $\pi$ Berry phase of both the IFS and OFS. Furthermore we have used angle-dependent measurements to resolve the 3D Fermi surface. (2) A topological transition of the FS was also observed in BiTeI, but the relative position of the Fermi level and the band-crossing point were tuned by pressure, which modifies the band structure [37]. Very recently, we have become aware of
4.8 Supplementary materials

4.8.1 Typical SdH oscillations without background subtraction

Figures 4.5(a) and 4.5(b) show two typical Shubnikov-de Haas oscillations without background subtraction observed in measurements. In Fig. 4.5(a) clear SdH oscillations can only be observed in high magnetic field, as indicated by the blue arrow, while in Fig. 4.5(b), weak SdH oscillations can be observed in both low and high magnetic field, as indicated by the blue and red arrows, respectively.

4.8.2 Standard SdH oscillation analysis with LK formula of more samples

In addition to the standard SdH oscillation analysis with the LK formula for quantum oscillations from the OFS of S2 in Fig. 4.2(a), 4.2(b), and 4.2(d), the same analysis method used in the main text was used for the other samples, except for S7, as shown in Figs. 4.6-4.8. In combination with the LL fan diagram, the effective mass $m^*$, oscillation frequency, $F$, and Dingle temperature, $T_D$, can be extracted, as shown in Table 1 in the main text.
4.8.3 Angle-dependent SdH oscillation frequency of a prolate spheroid FS

According to the angle-dependent SdH oscillation in Fig. 4.4(e), the FS deviates from the cylindrical shape for a two-dimensional electronic system. To describe the 3D FS in BiTeCl, several FS geometries were tried, and it was found that a prolate spheroid based FS can fit the angle-dependent oscillation frequency reasonably well when $\theta \leq 52^\circ$ (See Fig. 4.9 ). The equation of the prolate spheroid, in which two semiaxes with length, $b$, in the $k_\parallel$ plane and one semiaxis, $a$, in the $k_z$ direction can be expressed as:

$$\frac{x^2 + y^2}{b^2} + \frac{z^2}{a^2} = 1, \quad (a > b) \quad (4.3)$$

If the extremal cross section of the FS perpendicular to the magnetic field is an ellipse ($\theta > 0$) or a circle ($\theta = 0$), where $\theta$ is the tilt angle, its equation can be expressed as:

$$\frac{x^2}{b^2} + \frac{y^2}{a^2 \sin^2 \theta + b^2 \cos^2 \theta} = 1 \quad (4.4)$$

Therefore, the extremal cross-sectional area of the FS perpendicular the magnetic field is

$$A_F = \pi b^2 \sqrt{\left(\frac{a}{b}\right)^2 \sin^2 \theta + \cos^2 \theta} \quad (4.5)$$
Figure 4.7: (a)–(f) Temperature dependence of the oscillation amplitude for S1–S6. The red solid lines are the fitting with the thermal damping factor, $\frac{2\pi^2 k_B T m^*}{\hbar eB} \sinh(2\pi^2 k_B T m^*/\hbar eB)$, which yields the effective mass.

Figure 4.8: (a–f) LK fitting of SdH oscillations at 2.5 K for S1–S6, which yields the Dingle temperature.
Figure 4.9: Vertical cross-sectional view of the 3D FS cut along the $k_z$ direction for S2. The blue rectangle denotes the cylindrical FS of a 2D electronic system, and the red ellipse denotes a prolate spheroid FS with major axis $a = 119.6 \times 10^{-3} \text{Å}^{-1}$ and minor axis $b = 65.69 \times 10^{-3} \text{Å}^{-1}$, respectively. The black and purple solids represent the OFS and IFS, which is proposed to explain the observations in Fig. 4.4(b)-4.4(e). The dashed line indicates the extremal cross-section of the FS perpendicular to the magnetic field.

Because $F = (\hbar/2\pi e)A_F$, $F$ as a function of $\theta$ can be expressed as

$$F = \frac{\hbar b^2}{2e} \sqrt{(\frac{a}{b})^2 \sin^2 \theta + \cos^2 \theta} \quad (4.6)$$

### 4.8.4 Angle-dependence of SdH oscillation from S4

Besides the angular dependence of the SdH oscillation analysis in sample S2, similar measurements were also carried out on sample S4. Fig. 4.10(a) shows the quantum oscillations from $-6^\circ$ to $46^\circ$, in which the number of observed oscillation periods becomes less as the tilt angle increases and the oscillation amplitude diminishes, in a similar way to S2. Fig. 4.10(b) shows the same quantum oscillations as Fig. 4.10(a) on the $1/B$ scale. The dashed lines in Fig. 4.10(b) indicate the period of oscillations at $0^\circ$. It can be seen more clearly that the oscillations from the OFS of S4 exhibit a stronger two-dimensional feature compared with those of S2, which agrees with the topological transition of the FS. Because the Fermi level of S4 is higher than that of S2, the Fermi surface is more like the spindle-torus shape, and the OFS is more cylindrical in shape.
 assignment of Landau level index and determination of Berry phase

The measurements of both longitudinal resistivity and Hall resistivity are important not only for calculating the carrier density and Hall mobility, but also for assigning the Landau level (LL) index and determining the Berry phase. Because of $\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{xy}^2}$, while for $\rho_{xx} \gg \rho_{xy}$, the minima and maxima of the oscillations in the longitudinal conductivity $\sigma_{xx}$ are out of phase with those in the longitudinal $\rho_{xx}$, the LL integer $n$ is assigned to the oscillatory maxima of $\rho_{xx}$; for the case of $\rho_{xx} \ll \rho_{xy}$, the minima and maxima of the oscillations in $\sigma_{xx}$ are in phase with those in $\rho_{xx}$, and the LL integer $n$ is assigned to oscillatory minima of $\rho_{xx}$. How the phase factor shifts when $\rho_{xx} \approx \rho_{xy}$ is still unclear, however. To answer this question, we establish a simple model to estimate the phase shift window. Assumption 1: $\rho_{xx} = \Delta \rho_{xx} + \rho_{xx}^{\text{const}}$, $\Delta \rho_{xx} \ll \rho_{xx}^{\text{const}}$, where $\Delta \rho_{xx}$ is the oscillatory part of $\rho_{xx}$, and $\rho_{xx}^{\text{const}}$ is the background and assumed to be a constant for simplicity. (In our case as shown in Fig. B3, $\frac{\Delta \rho_{xx}}{\rho_{xx}} \approx \frac{\Delta \rho_{xx}}{\rho_{xx}} < \frac{1}{1000}$)

Assumption 2: The oscillations in the experiment come from $\Delta \rho_{xx}$.

Now when $\rho_{xx} \ll \rho_{xy}$, which is always the case in a one-band model when SdH oscil-
Figure 4.11: (a)–(l) Longitudinal conductivity, $\sigma_{xx}$, as a function of magnetic field on the reciprocal scale is plotted for various $\rho_{xy}$. Among them, $\rho_{xy} = 5000$ and 2 correspond to $\rho_{xx} \ll \rho_{xy}$ and $\rho_{xx} \gg \rho_{xy}$, respectively.
CHAPTER 4. OBSERVATION OF TOPOLOGICAL TRANSITION OF FERMI SURFACE IN BULK RASHBA SEMICONDUCTOR BITECL

...ation is observed \( \rho_{xy} = \rho_{xx} \mu B \), with \( \mu B \gg 1 \) in order to have SdH oscillations, then we can write:

\[
\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{xy}^2} \approx \frac{\rho_{xx}^{\text{const}}}{\rho_{xy}^2} + \frac{\Delta \rho_{xx}}{\rho_{xy}^2} \tag{4.7}
\]

So \( \sigma_{xx} \) is in phase with \( \rho_{xx} \).

When \( \rho_{xx} \gg \rho_{xy} \) (which is possible in a multiband case where there is a dominant low mobility band present), then we can write:

\[
\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{xy}^2} \approx \frac{1}{\rho_{xx}^2} \tag{4.8}
\]

So \( \sigma_{xx} \) is out of phase with \( \rho_{xx} \).

In the case of \( \rho_{xx} \approx \rho_{xy} \), because of \( \frac{\Delta \rho_{xx}}{\rho_{xx}^2} < \frac{1}{1000} \) as shown in Fig. 4.8, \( \rho_{xx} \) can be written approximately as \( \rho_{xx} = 1000 \cos(50/\mu B) \), where the oscillation amplitude is assume to be 1 for simplicity and the constant part is set to 1000. As \( \rho_{xy} \) is varied from 2 to 50000, \( \sigma_{xx} \) is plotted as a function of magnetic field on the reciprocal scale, as shown in the Fig. 4.11. For \( \rho_{xx} \ll \rho_{xy} \), i.e., \( \rho_{xy} = 5000 \rho_{xx} \) (see (l) of Fig. 4.11), and \( \rho_{xx} \gg \rho_{xy} \), i.e., \( \rho_{xy} = 2 \rho_{xx} \) (see (a) of 4.11), the phase factors in \( \sigma_{xx} \) differ by 180°. When \( \rho_{xx} \approx \rho_{xy} \), it was found the phase only changes in a very narrow window. The change in \( \rho_{xy} \) is on the order of \( 2 \Delta \rho_{xx} \), which equals \( 2 \cos(50/\mu B) \approx 2 \), and in this case, will shift the phase by 180°. When \( 999 \rho_{xx} \leq \rho_{xy} \leq 1001 \rho_{xx} \), the period of oscillation becomes halved.

As in the experimental data shown in Figs. 4.1(b) and 4.1(c) the regime of \( \rho_{xx} \approx \rho_{xy} \) is around 3–5 T. For the SdH oscillations from the OFS of S1 to S7, \( \rho_{xx} \ll \rho_{xy} \), so the LL integer \( n \) is assigned to the minima of SdH oscillations. The SdH oscillations from the IFS of S5 can be categorized into the regime of \( \rho_{xx} > \rho_{xy} \), so the LL integer \( n \) is assigned to the maxima of the SdH oscillations, as shown in Fig. 4.12(a). For the SdH oscillations from the IFS of S7, because the oscillations extend from the low field, around 1.5 T, to...
4.8. SUPPLEMENTARY MATERIALS

Figure 4.12: $-d^2 R_{xx}/dB^2$ as a function of $1/B$ for samples S5 and S7. The dashed-dotted lines mark the minima and maxima of the SdH oscillations, indicating the oscillatory periods on the $1/B$ scale.

High field, around 8 T, in the low field part the LL integer $n$ is assigned to the minima of the SdH oscillations, and in the high field part, the LL integer $n$ is assigned to the maxima of the SdH oscillations, as shown in Fig. 4.12(b). The dashed-dotted lines indicate the minima and maxima of oscillations and also indicate that the oscillatory periods are on the $1/B$ scale, which agrees with the Landau quantization.

Figure 4.13: Fast Fourier transform spectra of SdH oscillation frequency for samples S5 (a) and S7 (b).
CHAPTER 4. OBSERVATION OF TOPOLOGICAL TRANSITION OF FERMI SURFACE IN BULK RASHBA SEMICONDUCTOR BITECL

4.8.6 Extraction of SdH oscillation frequency with fast Fourier transform

Figure 4.13 shows the SdH oscillation frequencies for S5 and S7 yielded by the respective fast Fourier transforms (FFTs). They are quite close to the oscillation frequencies extracted from Landau level fan diagram analysis, 2.81 T and 5.93 T for S5 and S7, respectively.

4.9 References

4.9. REFERENCES


Chapter 5

Multiple Fermi pockets revealed by Shubnikov-de Haas oscillations in WTe$_2$

Abstract

The recently discovered non-saturating and parabolic magnetoresistance and the pressure-induced superconductivity in low temperature in WTe$_2$ imply its rich electronic structure and possible practical applications. Here we use magneto-transport measurements to investigate the electronic structure of WTe$_2$ single crystals. A non-saturating and parabolic magnetoresistance is observed from low temperature to high temperature up to 200 K with magnetic fields up to 8 T. Shubnikov–de Haas (SdH) oscillations with beating patterns are observed, the fast Fourier transform of which reveals three oscillation frequencies, corresponding to three pairs of Fermi pockets with comparable effective masses, $m^* \sim 0.31m_e$. By fitting the Hall resistivity, we infer they can be attributed to one pair of electron pockets and two pairs of hole pockets, together with nearly perfect compensation of the electron-hole carrier concentration. These magneto-transport measurements reveal the complex electronic structure in WTe$_2$, explaining the non-saturating magnetoresistance.

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CHAPTER 5. MULTIPLE FERMI POCKETS REVEALED BY SHUBNIKOV-DE HAAS OSCILLATIONS IN WTe$_2$

5.1 Introduction

The peculiar magnetoresistance of the ditelluride WTe$_2$ has attracted intensive research. Extremely large magnetoresistance (XMR) has been measured [1], suggesting possible applications at low temperatures in high magnetic field and a new avenue for magnetoresistivity, as the giant magnetoresistance which has been commerilized now was 50% when it was discoverd [2]. While XMR has also been observed in bismuth [3] and graphite [4], the magnetoresistance in these materials saturates with increasing field and deviates from a parabolic magnetoresistance (MR) behaviour [4, 5]. In addition to XMR, angle dependent studies revealed that WTe$_2$ also has a large longitudinal linear magnetoresistance [6]. The demonstration of pressure-induced superconductivity in WTe$_2$ [7, 8], further highlight the rich electronic structure that makes this material so interesting.

First-principles calculations suggest the presence of small electron and hole pockets along the $\Gamma-X$ direction in the Brillouin zone, such that WTe$_2$ is a semimetal [1]. The nearly perfect electron-hole ($n$-$p$) compensation with large carrier mobility in WTe$_2$ has consequently been put forward as the origin of the extremely large and perfectly parabolic MR [1]. A recent angle-resolved photoemission spectroscopy experiment has revealed approximately same-sized electron and hole pockets along the $\Gamma-X$ direction at low temperature, which supports the idea that the carrier compensation leads to the XMR [9]. In both works, only two pairs of Fermi pockets are reported. We note, however, that the first-principles calculations show that the valence band along the $\Gamma-X$ direction consists of multiple bands, which may result in multiple hole pockets [1, 10]. In addition, a potential second set of electron and hole pockets may form along the $Z-U$ direction, which is parallel to the $\Gamma-X$ direction but with different $k_z$ [1]. Therefore it is very crucial to investigate the details of the electronic structure and discern whether extra Fermi pockets are present, and then determine whether the extra electron and hole pockets would affect
5.2. LARGE AND NON-SATURATING MAGNETORESISTANCE

the $n$-$p$ compensation in relation to the non-saturating parabolic MR.

Next to angle-resolved photoemission spectroscopy (ARPES), quantum oscillations form another powerful method to investigate the electronic structure, which has advantages such as very high $k$-space resolution in all three crystallographic directions and high energy resolution. Quantum oscillations has been extensively used in understanding the band structure of metals [11], revealing the origin of high temperature superconductivity [12], and probing topological surface states [13–16], bulk Rashba materials [17, 18], and Dirac semimetals [19, 20].

In this work, we have performed magneto-transport measurements on WTe$_2$ single crystals at various temperatures and magnetic fields. In addition to the observation of large and non-saturating MR in the temperature range between 2.5 and 200 K and in the magnetic field up to 8 T, we observed Shubnikov–de Haas (SdH) oscillations accompanied by beating patterns, indicative of multiple states. The analysis of the SdH oscillations reveals three pairs of Fermi pockets, all having an effective mass around 0.31$m_e$. The fit of the low temperature Hall data indicates that the Fermi pockets can be attributed to one electron band and one hole band, which consist of two pairs of hole pockets, although the electrons and holes are nearly perfectly compensated in WTe$_2$.

5.2 Large and non-saturating magnetoresistance

The WTe$_2$ single crystals used in this work have needle-like shapes with the $c$-axis perpendicular to the surface. The magnetoresistance measurements were performed in a 9 T physical properties measurement system (PPMS) using the four probe method. The Hall resistance was measured using the six probe method. All electrical contacts were prepared at room temperature with silver paste. The magnetic field was perpendicular to the $ab$-plane in the magnetotransport measurements. The sample dimensions for these MR and Hall measurements were $3.83 \times 0.26 \times 0.11 \ mm^3$. 

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Figure 5.1: Temperature dependence of the resistance from 2.5 to 150 K in various magnetic fields. Inset: magnetic field dependence of the “turn-on” temperature of the metal-insulator-like transition, with the red solid line showing a linear fitting with slope of 6.5 K/T.

Figure 5.1 shows the temperature dependence of the resistance from 2.5 to 150 K in various magnetic fields, with the resistance plotted in log scale. The resistance shows a strong response to the magnetic field and we find an increment by more than one order of magnitude at low temperatures and applying a field of 8 T. Interestingly, the corresponding magnetoresistance at high temperature is quite small. While the temperature-dependent resistance at 0 and 2 T magnetic field exhibits metallic behaviour, it has an insulating dependence at low temperature in fields larger than 4 T. The “turn on” temperatures of the magnetic-field-driven metal-insulator-like transition (defined as the temperature where the first derivative of the magnetoresistance with respect to the temperature equals zero) are given in the inset of Fig. 5.1, which shows a linear dependence on the magnetic field and a slope of 6.5 K/T.

Figure 5.2(a) shows the magnetoresistance at various temperatures, defined by MR = ($R_B - R_0$)/$R_0$ × 100%, which shows no sign of saturation up to 8 T. The MR reaches around 1850% at a temperature of 2.5 K in a field of 8 T, which is consistent with
5.3. IDENTIFY MULTIPLY FERMI POCKETS BY SDH OSCILLATIONS

Fig. 5.1. Below 10 K, the MR decreases slightly with increasing temperature. Above 10 K, the MR decreases dramatically with increasing temperature. The MR is less than 100% above 75 K. Clear SdH oscillations are observed at 2.5 K, indicating a large carrier mobility. Figure 5.2(b) presents a log-log plot of the MR at various temperatures. The linear dependence in Fig. 5.2(b) indicates that parabolic MR behaviour is in accordance with what is reported in Ref. [1], and our results show that it can persist up to 200 K.

Figure 5.2: (a) Magnetoresistance up to ±8 T from 2.5 to 200 K. (b) Log-log plot of corresponding MR in Fig. 2(a). The data from 2.5 to 10 K almost overlaps, which is indicated by the black circle.
5.3 Identify multiply Fermi pockets by SdH oscillations

Now, we use the SdH oscillations to analyze the electronic structure of the WTe$_2$ used in this experiment. In contrast to the SdH oscillations in other systems with a single Fermi pocket, the SdH oscillations in WTe$_2$ exhibit a beating pattern as shown in Fig. 5.3(a). This indicates that there are two or more Fermi pockets of similar size which are involved in the SdH oscillations. Figure 5.3(b) shows an oscillation phase shift caused by the multiple Fermi pockets. Since each band with sufficient mobility will give rise to SdH oscillations that oscillate cosinusoidally as a function of $1/B$ [18], each oscillation peak
in Fig. 5.3(a) can be assigned an integer number \( n \) which corresponds to an oscillation period. The difference between intercepts on the \( n \) axis of two linear fits with same slope represented by two solid red lines reveals a phase shift of the oscillations through the beating node which locates between 0.148 T\(^{-1}\) and 0.159 T\(^{-1}\).

To resolve how many Fermi pockets are involved, we have carried out a fast Fourier transform (FFT) analysis on the SdH oscillations. The results are shown in in Fig. 5.3(c). We can identify three peaks: \( F_1 \approx 70.1 \) T, \( F_2 \approx 98.1 \) T, and \( F_3 \approx 154.2 \) T. The Fermi pockets with frequencies \( F_1, F_2, \) and \( F_3 \) are defined as the \( \beta, \alpha, \) and \( \gamma \) Fermi pockets, which are indicated by red, blue, and green dashed lines, respectively. Figure 5.3(d) shows the second derivative, \(-d^2 R_{xx}/dB^2\), as a function of magnetic field on the reciprocal scale. The period of the oscillations is visualized by the dashed-dotted lines and the solid lines. It can be seen that the period between two solid lines is different from the period between two successive dashed-dotted lines. This suggests that the regime between the two solid lines is the node position of the beating pattern. The solid red line is a qualitative fit of the Lifshitz-Kosovich (LK) formula with one electron band and one hole band, as discussed in the two-band model below.

According to the LK formula, the effective mass of carriers can be obtained by fitting the temperature dependence of the normalized FFT amplitudes with a thermal damping factor, \( R_T = \frac{2\pi^2 k_B T m^*/\hbar eB}{\sinh(2\pi^2 k_B T m^*/\hbar eB)} \), where \( k_B \) is the Boltzmann constant, \( T \) the temperature, \( m^* \) the effective mass, \( \hbar \) the reduced Planck’s constant, and \( e \) the elementary charge. The results are shown in Fig. 5.3(e). Since the oscillations observed in the measurement are in the interval from 5 to 8 T, the value of the magnetic field \( B \) is set to 6.5 T. The effective masses for the \( \alpha, \beta \) and \( \gamma \) Fermi pockets yielded by the fits are 0.304, 0.322, and 0.313 \( m_e \), respectively.
5.4 Infer possible nature of Fermi pockets by two-band model

Now, we discuss the possible origin of the three pairs of Fermi pockets. According to the first-principles calculations, WTe$_2$ is a semimetal with a pair of small electron and hole pockets along the $\Gamma-X$ direction in the Brillouin zone, and a potential second set of electron and hole pockets that may form along the $Z-U$ direction, which is parallel to the $\Gamma-X$ direction but with different $k_z$ [1]. We also note that the valence band along the $\Gamma-X$ direction consists of multiple bands [1, 10], which may result in multiple hole pockets. In our SdH oscillation measurements, the sizes of the Fermi pockets which are calculated using $A_F = \pi k_F^2 = 2eF/\hbar$, $A^\alpha_F = 0.00953 \text{ Å}^{-2}$, $A^\beta_F = 0.00664 \text{ Å}^{-2}$, and $A^\gamma_F = 0.00953 \text{ Å}^{-2}$, respectively. Here, $F$ is the frequency of the SdH oscillations, $k_F$ is the Fermi wave vector, and $A_F$ is the cross-sectional area of the Fermi pocket. The small size of the Fermi pockets is consistent with the features of a semimetal and agrees with the ARPES results.

To identify the carrier types of the Fermi pockets, the Hall resistivity ($\rho_{xy}$) was measured up to 8 T from low temperature to room temperature, as shown in Fig. 5.4(a). The negative and linear $\rho_{xy}$ above 200 K indicates that the dominant carrier is of $n$-type. This is in agreement with the fact that at high temperature, the electron pockets dominate the conduction according to the ARPES experiments [9]. The $\rho_{xy}$ is non-linear at low temperature, however, which indicates that at least two types of carriers are at play. We fit $\rho_{xy}$ at 5 K with using a two-band model as shown in Fig. 5.4(b),

$$\rho_{xy} = \frac{B[(\mu_1 n_1 + \mu_2 n_2) + (\mu_1 \mu_2 B)^2 (n_1 + n_2)]}{c[(\mu_1 n_1 + \mu_2 n_2)^2 + (\mu_1 \mu_2 B)^2 (n_1 + n_2)^2]}.$$  

Here, $n_1$ and $n_2$ are the carrier densities, and $\mu_1$ and $\mu_2$ are the carrier mobilities for band 1 and band 2, as described below. We have substituted the carrier density calculated from the SdH oscillation, $n = (1/3\pi^2)(2eF/\hbar)^{3/2}$ and found one hole band (band 1) with carriers from the $\alpha$ and $\beta$ pockets ($n_1 = n_\alpha + n_\beta = 1.79 \times 10^{19} \text{ cm}^{-3}$, where $n_\alpha = 1.132 \times 10^{19} \text{ cm}^{-3}$ and
5.4. INFER POSSIBLE NATURE OF FERMI POCKETS BY TWO-BAND MODEL

Figure 5.4: Two-band model analysis: (a) $\rho_{xy}$ at various temperatures from the low temperature of 5 K to room temperature at 300 K. (b) $\rho_{xy}$ data at 5 K fit with the two-band model. (c) Schematic band structure near the Fermi level along the $\Gamma-\Xi$ direction. $\gamma$ represents an electron pocket, and $\alpha$ and $\beta$ represents two hole pockets. (d) Schematic diagram of the location of the Fermi pockets.

$n_\beta = 0.658 \times 10^{19}$ cm$^{-3}$, respectively), and one electron band (band 2) with carriers from the $\gamma$ pocket, $n_2 = n_\gamma = -2.42 \times 10^{19}$ cm$^{-3}$, which can give the best fit of the Hall data, yielding $\mu_1 = 1164.5$ cm$^2$V$^{-1}$s$^{-1}$ and $\mu_2 = 1045.5$ cm$^2$V$^{-1}$s$^{-1}$, respectively. The mobility is very close to the threshold value for observation of SdH oscillations: $\mu B \approx 1$ for a magnetic field of 5 to 10T. Therefore, the band structure near the Fermi level can be represented as in Fig. 5.4(c), and the three pairs Fermi pockets are identified as one pair of electron pockets and two pairs of hole pockets. Moreover, the quantum oscillation signal can be qualitatively fit by the LK formula with two oscillation frequencies, one corresponding to the electron pockets, $F_e = F_3$ and the other one corresponding to the
two pairs of hole pockets, \( F_h \approx (F_1^2 + F_2^2)^{1/2} \), as shown by the solid red line in Fig. 5.3(d). Therefore, the band structure near the Fermi level for the WTe\(_2\) measured in this work can be schematically shown in Fig. 5.4(c). The Fermi pockets are schematically represented in Fig. 5.4(d).

Our FFT analysis of SdH oscillations reveals three pairs of Fermi pockets in our samples, instead of the two pairs of pockets reported in previous works [1, 9]. Our observations on the multiple Fermi pockets agree with the multiple valence bands obtained by first-principles calculations [1, 10]. The fit of the Hall resistivity indicates that one of the three pairs of Fermi pockets consists of electron pockets, while the other two consist of hole pockets, and the carrier densities of electrons and holes are nearly perfectly compensated.

Our work suggests that the electronic structure of WTe\(_2\) could be even more complicated than the two pairs of electron and hole pockets of approximately the same size, but as long as the electrons and holes are compensated the non-saturating parabolic MR will still persist.

Note added: Three recent works have also revealed multiple Fermi pockets, two from quantum oscillation experiment and one from ARPES experiment [21–23]. However the number of Fermi pockets is different in each work including this one, which further indicates the complexity of the electronic structure of WTe\(_2\). This may be because the number of Fermi pockets is sensitive to the Fermi level. Future electric gating work may be helpful to clearly clarify the cause.

5.5 References


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CHAPTER 5. MULTIPLE FERMI POCKETS REVEALED BY SHUBNIKOV-DE HAAS OSCILLATIONS IN WTe$_2$


Chapter 6

Change of electronic structure in WTe$_2$ thin film

Abstract

We use quantum oscillations from magneto-transport measurement to study the electronic structure of WTe$_2$ thin film with different thickness. The angle dependent quantum oscillations reveal a crossover from a three-dimensional to two-dimensional electronic system when the sample thickness is below 15 nm. The fast Fourier transform spectrum of quantum oscillations further shows the Fermi pockets get smaller when samples become thinner, suggesting the overlap between conduction band and valence band are getting smaller. We also use a back-gate to tune the carrier density of the thin film and to distinguish the electron and hole pockets. Our results support the potential nontrivial topological state in thinner samples and explain the carrier density decrease when thin film thickness is reduced in references.
CHAPTER 6. CHANGE OF ELECTRONIC STRUCTURE IN WTE₂ THIN FILM

6.1 Introduction

Tungsten ditelluride, one of transition metal dichalcogenides, has attracted a lot of attention recently. For bulk WTe₂, it exhibits unsaturated and extremely large magnetoresistance (MR) [1], which is believed due to its nearly equal amount of electrons and holes [1–6]. Surprisingly, although WTe₂ is a layered material, it is a three-dimensional (3D) electronic system with mass anisotropy as low as 2, instead of two-dimensional (2D) electronic system [7]. Bulk WTe₂ is also predicted to be a type-II Weyl semimetal, in which Lorenz invariance is absent and the Weyl point appears at the boundary of electron and hole pockets [8]. This triggers new interests on this material [9–14].

Furthermore, monolayer WTe₂ is predicted to be a nontrivial semimetal where both topological metallic edge state and 2D metallic bulk state are present, but applying small strain could lift overlap of conduction and valence band and turn it into a 2D topological insulator [15], where only the topological edge state is metallic but the 2D bulk state is insulating [16–22]. Very recently, one work reports a signature of possible band gap opening in monolayer sample from optical and transport measurement in thin film samples with thickness 9 to 11.7 nm and supported by band structure calculation which includes many body effect [23], meanwhile another experiment work observed semi-metallic monolayer samples become insulating in 2D bulk with topological nontrivial metallic state on their edge when temperature is below around 100 K [24]. On the other hand, monolayer WTe₂ has also been proposed as a 2D Dirac semimetal which is protected by nonsymmorphic space group symmetries [25, 26]. In addition, the interest on unusual MR of bulk WTe₂ has been extended to thin film samples [27–30]. Electron and hole compensation is found in samples down to thickness around 10 nm, but the MR of thin film is suppressed significantly due to the surface scattering from amorphous surface oxides [28, 29, 31, 32]. However, the decrease of carrier density as the sample thickness reduced is unexpected.
Therefore, to understand the rich phase diagram of 2D WTe$_2$ and to explain why the carrier density decreases as sample thickness is reduced, it is necessary to study the electronic structure of the WTe$_2$ thin film samples when sample thickness is approaching monolayer thickness.

Quantum oscillations due to Landau quantization are a powerful method to study band structure and Fermi surface of materials [33–36]. Here we use the quantum oscillations observed in magneto-transport to study the thickness dependent electronic structure of WTe$_2$ thin films. Angle dependent quantum oscillations reveal a 3D-to-2D crossover when the sample thickness is below 15 nm. The fast Fourier transform of quantum oscillations further shows the size of Fermi pocket is getting smaller when sample thickness is reduced, indicating the overlap between conduction band minimum and valence band maximum of the semi-metallic WTe$_2$ thin film becomes smaller. This explains the decrease of carrier density as the sample thickness is reduced in recent reports and support the band gap opening in monolayer samples. We also use back-gate to tune the Fermi level and found the Fermi pocket corresponding to the dominant quantum oscillation frequency is from electron pockets.

6.2 Device fabrication and magnetotransport measurement method

WTe$_2$ thin films with different thickness are cleaved from bulk WTe$_2$ single crystal to 285 nm SiO$_2$/Si substrate with alignment markers by scotch-tape method. E-beam lithography are used to fabricate the alignment makers, electrodes, and bonding pads. Before depositing Ti/Au electrodes with typical thickness 10nm/60nm, contact areas are treated with Ar plasma to remove native oxides. To further reduce the contact resistance, the devices are annealed in furnace with N$_2$ gas at 200 °C for 2 hours. To reduce the oxidization
CHAPTER 6. CHANGE OF ELECTRONIC STRUCTURE IN WTe$_2$ THIN FILM

of the sample surface, after cleaving, the thin films are only exposed to air before the contact area patterning with EBL and during the bonding of the devices to the chip carrier. In other time, the thin films are always covered by PMMA and stored in a vacuum desiccator or a N$_2$ glove box. The accurate thickness is measured by atomic force microscope (AFM) after the magneto-transport measurement. The magneto-transport is measured in Oxford dilution fridge up to 10 T using standard low frequency lock-in technique. Unless otherwise stated magneto-transport measurements are performed at $T = 30$ mK.

6.3 Crossover to a two-dimensional system

Figure 6.1: (a) Optical images of thick (right, S33) and thin (left, S54) samples. (b) Schematic diagram of angle dependent measurement configuration. Magnetic field is parallel with $z$ direction, the rotation axis of substrate and current direction are parallel with $x$ axis, the theta is defined as an angle between $z$ axis and the normal of sample surface. (c) Quantum oscillations $\Delta R_{xx}$ vs. $1/B_\perp$ for S33, the data traces at different angles are vertically translated for clarity. $B_\perp$ is perpendicular component of magnetic field, $B_\perp = B \sin \theta$. The black dash dot lines indicate the minima of $\Delta R_{xx}$ of $\theta = 90^\circ$. (d, e) and (f, g) are the quantum oscillations $\Delta R_{xx}$ vs $1/B_\perp$ and $\Delta R_{xy}$ vs. $1/B_\perp$ for S31 and S54, respectively. The black dash dot lines indicate the minima of $\Delta R_{xx}$ and $\Delta R_{xy}$, and the black solid lines indicate the node position of beat pattern. All the quantum oscillations $\Delta R_{xx}$ and $\Delta R_{xy}$ are obtained by subtracting polynomial background from $R_{xx}$ and $R_{xy}$ and are low pass filtered in $1/B$ scale to remove high frequency noise.

First, we show the WTe$_2$ thin film below 15 nm is a 2D system, contrasting the previous
6.4. THICKNESS DEPENDENT FERMI POCKET SIZE

hypothesis which regards it as 3D bulk system [28, 31]. Figure 6.1(a) shows optical images of two typical devices we fabricate, S31 (blue color) and S54 (green color). Figure 6.1(b) shows a schematic diagram of the measurement configuration for angle dependent magneto-transport measurement. The current is driven through the $ab$ plane of the WTe$_2$ crystal and when the magnetic field is rotated from out of plane to in-plane, it is always perpendicular to the current.

We observe quantum oscillations related to the Landau quantization both in $R_{xx}$ and $R_{xy}$. Clear quantum oscillation signals are obtained from $R_{xx}$ and $R_{xy}$ after subtracting the polynomial background as shown in Fig. 6.1(c)-6.1(g). In the bulk WTe$_2$, quantum oscillations have been observed when magnetic field is parallel to its all three crystal-axes, which corresponding to a Fermi surface of a 3D system [3, 37]. This is consistent with the low mass anisotropy measured by reference [7].

In our angle-dependent magneto-transport measurement of thin film samples, for the thicker one, device S33 (26 nm) in Fig. 6.1(c), shows bulk behavior, since quantum oscillations $\Delta R_{xx}$ not depend on perpendicular component of magnetic field, $B_\perp = B \sin \theta$, to the surface as the sample is tilted in applied field. For example, the oscillations between 0.15 T$^{-1}$ to 0.2 T$^{-1}$ observed in the 90° cannot be observed in 75° and 60° and the oscillation period at different angles are not the same. For thin samples with thickness below 15 nm, devices S31 (15nm), and S54 (11nm), however, both the period and amplitude of the quantum oscillations from $R_{xx}$ and $R_{xy}$ as functions of $1/B_\perp$ at different angles are the same, as shown in Fig. 6.1(d)-6.1(e) and Fig. 6.1(f)-6.1(g). This indicates there is a crossover from 3D to 2D electronic system when the sample thickness is below 26 nm.

6.4 Thickness dependent Fermi pocket size

Now we show another aspect of electronic change in WTe$_2$ thin film, the change of Fermi pocket size in WTe$_2$ thin films. Figure 6.2(a) shows a fast Fourier transform spectrum of
Figure 6.2: (a) Fast Fourier transform (FFT) spectrum of quantum oscillations, $\Delta R_{xx}$, of WTe$_2$ thin film samples with different thickness and bulk reference sample [5]. (b) The FFT frequency vs. sample thickness, the thickness of bulk from references [3–5, 37] is set as infinite compared with thin film samples. The solid lines are the guide lines which show the shift of frequency as thickness is reduced. (c) Schematic diagrams showing the change of Fermi surfaces in half of Brillouin zone (top panels) and the band structure near Fermi surface along $\Gamma - X$ direction (bottom panels) as thickness is reduced (from right to left).

quantum oscillations from $\Delta R_{xx}$ of bulk to thin film samples. The FFT of bulk reference obtained from our previous work at 2.5 K [5] shows three frequency peaks, 86.3 T, 130.2 T and 140.1 T, the frequency around 162 T reported in [3, 4, 37] was not observed in our 3D bulk sample which may be due to relative high measurement temperature and low mobility of that band.

In order to resolve quantum oscillations from low mobility bands, all thin film samples are measured at millikelvin temperature and magnetic field up to 10 T. The FFT of the magneto-transport in the thick sample, device S33 (26 nm), is very close to bulk sample,
which is consistent with angle dependent measurement where S33 shows bulk behavior. In thinner samples S28 (16 nm) and S54 (15 nm), the FFT peaks shift to lower frequency. We note that the quantum oscillation signals from the WTe2 thin films are relative weak, reducing the signal to noise ratio in the FFT spectrum. However, in the highest signal to noise ratio sample, S28, we can clearly see four frequencies as indicated by the squares and circles in Fig. 6.2(a). In S31 and S54, the signal to noise ratio is not as good as S28, but four corresponding frequencies can still be found. In S33, two frequencies are observed, the other two frequencies are absent due to lower mobility of that sample.

To better illustrate the shift of frequency as the thickness is reduced, we plot frequency vs thickness as shown in Fig. 6.2(b). The frequencies of bulk samples are from reference [3–5, 37] and their thickness are set as infinite compared with the thin film samples. The solid lines are guides to the eye showing how each frequency shifts as the sample thickness is reduced. The frequencies $F_1$, $F_2$, $F_3$ and $F_4$ correspond to the frequency peaks indicated by solid circle, solid square, open square and open circle in the Fig. 6.2(a), respectively. It can be seen that there is a trend that the frequency become smaller when the sample thickness is reduced.

The frequency of quantum oscillations is related to the extremal cross-section area of Fermi surface perpendicular to the magnetic field. The lower frequency means smaller size of Fermi pockets. The change of Fermi pocket size could be the shift of Fermi level. However, if the shift of frequency is because of the change of Fermi level, the frequency from hole and electron pockets will change in opposite way. This is not the case here. The other possibility is the change of band structure as illustrated in the Fig. 6.2(c) which shows schematic diagrams how the change of band structure could decrease the size of both electron and hole pockets. The top and bottom panels of Fig. 6.2(c) are Fermi surface and band structure. As the thickness of sample is reduced from right to left, the
conduction band minima and valence band maxima are getting away from each other, bottom panel of Fig. 6.2(c), which will reduce the size of both electron and hole pocket as illustrated in top panel. This result is consistent with two recent works on the band gap opening in monolayer samples [23, 24].

Because the carrier density is proportional to the size of Fermi pocket, the decrease of Fermi pocket size also means the decrease of carrier density. We calculate the 2D carrier density from quantum oscillation frequencies in our high signal to noise ratio sample S28 by \( n = g_v g_s e F/h \), is \( 4.03 \times 10^{13} \text{ cm}^{-2} \) where \( g_s = 2 \) and \( g_v = 2 \) are spin and valley degeneracy, \( e \) is electron charge, \( h \) is Plank constant and \( F \) is the sum of \( F_1 = 77.3 \text{ T}, F_2 = 97.6 \text{ T}, F_3 = 113.9 \text{ T} \) and \( F_4 = 125.1 \text{ T} \). This is corresponding to 3D carrier density \( 2.69 \times 10^{19} \text{ cm}^{-3} \), very close to \( 3 \times 10^{19} \text{ cm}^{-3} \) from the 13 nm sample of reference [29], and to \( 7.5 \times 10^{19} \text{ cm}^{-3} \) from 15.6 nm sample of reference [28]. Therefore, the change of Fermi pocket size explains the unexpected reduction of carrier density obtained from two-band model fitting in reference decrease as the sample become thinner [28, 29].

### 6.5 Gate tunable SdH oscillations

To explore whether electron and hole are still compensated in thin film samples, it is necessary to measure the carrier density directly, instead of fitting of \( R_{xx} \) and \( R_{xy} \) by two-band model. The total carrier density can be calculated from frequency of quantum oscillations, but the electron and hole pockets cannot be distinguished. As we mentioned previously, the shift of Fermi level will change the size of electron and hole pockets in opposite way, which will be manifested in the change of quantum oscillation frequency. Therefore, we attempt to identify the nature of the Fermi pocket by using the back-gate voltage on sample S31 (15 nm) to change the carrier density and tune the Fermi level.

As we seen in Fig. 6.1(d)-6.1(e), the quantum oscillations are both observed in \( R_{xx} \) and \( R_{xy} \). Figure 6.3(a) shows the quantum oscillations \( \Delta R_{xy} \) at back-gate voltage from -70 V
6.5. GATE TUNABLE SDH OSCILLATIONS

Figure 6.3: (a) Quantum oscillations from $R_{xy}$ of S31 at different back-gate voltages. The oscillation traces are vertically offset for clarity. The -70 V trace has been divided into two parts, one is from 0.1 to 0.2 T$^{-1}$. The other part is from 0.2 to 0.255 T$^{-1}$, the amplitude of oscillations in this part has multiplied by a factor of 5. The dash dot lines indicate the oscillation period, and the black solid lines indicate the position of the node of beat patterns. (b) FFT of quantum oscillations in Fig. 6.3(a). the dash dot lines indicate the peak position of -70 V. (c) Fits of quantum oscillations $\Delta R_{xy}$ at different back-gate voltages. The open circles are the raw data and solid lines are fitting lines. (d) The oscillation frequency yield by the fit in Fig. 6.3(c).

Figure 6.3: (a) Quantum oscillations from $R_{xy}$ of S31 at different back-gate voltages. The oscillation traces are vertically offset for clarity. The -70 V trace has been divided into two parts, one is from 0.1 to 0.2 T$^{-1}$. The other part is from 0.2 to 0.255 T$^{-1}$, the amplitude of oscillations in this part has multiplied by a factor of 5. The dash dot lines indicate the oscillation period, and the black solid lines indicate the position of the node of beat patterns. (b) FFT of quantum oscillations in Fig. 6.3(a). the dash dot lines indicate the peak position of -70 V. (c) Fits of quantum oscillations $\Delta R_{xy}$ at different back-gate voltages. The open circles are the raw data and solid lines are fitting lines. (d) The oscillation frequency yield by the fit in Fig. 6.3(c).

to 70 V. The quantum oscillations at -70 V have largest amplitude and can be observed for $B > 4$ T. It also exhibits clear beat patterns, consistent with a nature of oscillations with multiple close frequencies. When the gate voltage is changed to 70 V, the oscillation amplitude is depressed, which is also observed in [28, 31].

What’s more, we observe small shift of quantum oscillations from both $R_{xx}$ (Supp. Mater.) and $R_{xy}$ (see Fig. 6.3(a)) as the back-gate voltage changes, indicating the change of oscillation frequency. The FFT of $\Delta R_{xx}$ show four frequency as shown in Fig. 6.2(a),
while FFT of $R_{xy}$ shows two frequency around 114 T and 122 T as shown in Fig. 6.3(b), which corresponding to $F_3$ and $F_4$ in Fig. 6.2(c) and $F_1$ and $F_2$ could not be observed in FFT of $\Delta R_{xy}$. Therefore, we use the LK formula to fit the quantum oscillations from $R_{xx}$ and $R_{xy}$. We find four frequencies observed in $\Delta R_{xx}$ make the fitting not converged but the Lifshitz-Kosevich formula fitting of $R_{xy}$ can be converged due to less fitting parameter. The fitting curves of $\Delta R_{xy}$ at different back-gate voltages are shown in Fig. 6.3(c). The LK fitting of $R_{xy}$ shows the $F_3$ increase as the back-gate voltage is changed from -70 V to 70 V and $F_4$ does not change much, as shown in Fig. 6.3(d). When the back-gate voltage changes from -70 V to 70 V, total electrons in the sample should increase and total holes should decease. The increase of frequency $F_3$ as the back-gate voltage changed from -70 V to 70 V suggests this frequency is from an electron pocket.

### 6.6 Conclusion

In summary, we observed the electronic structure change in WTe$_2$ thin film from the quantum oscillations of magneto-transport measurement. One finding is a crossover from 3D to 2D electronic system when sample thickness is less than 15 nm, which is unexpected in previous studies. The other find is that the size of Fermi pocket become smaller in the thin film sample compared with bulk samples, indicating the overlap between conduction band minimum and valence band maximum become smaller. This explain why the carrier density getting smaller when the sample thickness is reduced and support the band gap opening in further thinner samples. We also use the back-gate to tune the Fermi level and found the Fermi pocket corresponding to the dominant quantum oscillation frequency is electron pocket. With further thin sample, the back-gate could be more efficient to identify the nature of all Fermi pockets.
6.7 References


Chapter 7

General conclusion and prospect

The discovery of topological matter is by studying their peculiar electronic structure and properties [ref]. In this thesis, the quantum transport measurement is used to study electronic structure and properties of the topological matter candidates such as the 3D topological insulator BiSbTe$_3$, inversion asymmetric topological insulator BiTeCl and 3D Weyl semimetal WTe$_2$. To that end, the high quality single crystals such as BiSbTe$_3$ and BiTeCl are grown and the WTe$_2$ nano-devices are fabricated for the quantum transport measurement.

In Chapter 3, high quality 3D topological insulator BiSbTe$_3$ single crystals were grown, in which the bulk carrier density is suppressed and the Fermi level is tuned into bulk gap. Firstly, the topological surface state is verified by angle-dependent SdH oscillations and the weak anti-localization. Besides that, a crossover from the weak anti-localization to weak localization (WL) with increasing magnetic field is observed, which is temperature dependent and exhibits two-dimensional features. This behavior is consistent with the two-dimensional electron gas observed on the surfaces of topological insulators from angle-resolved photo emission spectroscopy [ref].

In Chapter 4, a polar semiconductor BiTeCl is studied, which is the first inversion asymmetric topological insulator candidate. Due to its inversion asymmetric crystal structure, the bulk band exhibits giant Rashba spin splitting. In the quantum transport measure-
ment, although the topological surface state is not detected in the transport measurement, a topological transition of the bulk Fermi surface from spindle-torus to torus was, for the first time, revealed in the transport experiment by varying the carrier density. In the Landau level fan diagram, both the inner and outer Fermi surfaces exhibit the expected non-trivial Berry phase from the Rashba spin splitting systems. Angle-dependent oscillation measurements further reveal the three-dimensional Fermi surface topology of BiTeCl when the Fermi level lies in the vicinity of the Dirac point.

In Chapter 5, the quantum transport measurements are performed on bulk WTe$_2$, a type II Weyl semimetal candidate, to understand its extremely large and non-saturated magnetoresistance. The SdH oscillations reveal multiple Fermi pockets, which indicates the electronic structure is more complex than the physical picture with simple one electron and one hole Fermi pockets. The effective mass from temperature-dependent SdH oscillations is measured and carrier densities are extracted from the SdH oscillation frequencies. The two-band model is attempted to fit the Hall resistance to extract the carrier mobility.

In Chapter 6, we studied the thickness-dependent electronic structure of WTe$_2$ thin films, to understand the transition from the 3D Weyl semimetal in bulk samples to the 2D topological insulator in the monolayer limit. Firstly, we used the angle-dependent SdH oscillations to reveal that there is a crossover from 3D to 2D electronic system as samples are made thinner. Secondly, we identified the nature of the Fermi pockets in the 12 nm sample. Thirdly, we traced the evolution of the size of Fermi pockets, which indicates the overlap between the conduction and valence bands are getting smaller as WTe$_2$ samples are made thinner.

The recent few years have seen the significant progress on the topological matter from quantum spin Hall insulators, to 3D topological insulators, to 3D Dirac and Weyl semimetals and so on, [ref.]. In addition, the sample quality has been improved a lot, which
allows the study of the intrinsic physical properties. For example, the Ref. [] reported that in 3D topological insulator BiSbTeSe$_2$, the topological surface state dominates the conduction and the quantum Hall effect is observed from the topological surface state.

Meanwhile, there are still many interesting physics can be explored in the material system studied in this thesis. For the BiSbTe$_3$ topological insulator, it is possible to further reduce the bulk carrier density by optimize the single crystal growth condition and partially substitute the Te with Se. The presence of a conventional two-dimensional electron gas at the sample surface suggests that protection of the sample surfaces from degradation by encapsulating or depositing a cap layer such as h-BN is necessary. For the BiTeCl, to probe the surface state, it is also necessarily to reduce the carrier density. Furthermore, to isolate the single termination of the surface may be also helpful since the Te-termination and Cl-termination have different charge polarity. Since the bulk WTe$_2$ is predicted as the type-II Weyl semimetal, it is of great interest to explore the chiral anomalous by measuring the longitudinal magnetoresistance. It’s also of great interest to fabricate the monolayer WTe$_2$ which could be tuned into two-dimensional topological insulator and could be further fabricated into topological field effect transistors when they are stacked into hBN-WTe$_2$-hBN… hBN-WTe$_2$-hBN multiple van de Vaas heterostructures.