

**INVESTIGATION OF TOPOLOGICAL NODAL
SEMIMETALS THROUGH ANGLE-RESOLVED
PHOTOEMISSION SPECTROSCOPY**



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To my dear wife, Rahel,
for all her love, care, and encouragement.

To my firstborn, Jeo,
for the smiles during the sleepless nights

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Abstract

Nodal semimetals host either degenerate points (Dirac/Weyl points) or lines whose band topology in Brillouin zone can be classified either as trivial (normal nodal semimetals) or non trivial (topological nodal semimetals). This thesis investigates the electronic structure of two different categories of topological nodal semimetals probed by angle-resolved photoemission spectroscopy (ARPES):

The first material is Indium Bismuth (InBi). InBi is a semimetal with simple tetragonal structure with $P4/nmm$ space group. This space group is predicted to host protected nodal lines along the perpendicular momentum direction at the high symmetry lines of the Brillouin zone boundary even under strong spin-orbit coupling (SOC) situation. As a semimetal with two heavy elements, InBi is a suitable candidate to test the prediction. The investigation by ARPES demonstrates not only that InBi hosts the nodal line in the presence of strong SOC, it also shows the signature of type-II Dirac crossing along the perpendicular momentum direction from the center of Brillouin zone. However, as the nodal line observed is trivial in nature, there is no exotic drumhead surface states observed in this material. This finding demonstrates that Dirac crossings can be protected in a non-symmorphic space group.

The second material is $NbIrTe_4$ which is a semimetal that breaks inversion symmetry predicted to host only four Weyl points. This simplest configuration is confirmed by the measurement from the top and bottom surface of $NbIrTe_4$ showing only a pair of Fermi

arcs each. Furthermore, it is found that the Fermi arc connectivity on the bottom surface experiences re-wiring as it evolves from Weyl points energy to the ARPES Fermi energy level. This change is attributed to the hybridisation between the surface and the bulk states as their projection lie within the vicinity of each other. The finding in this work demonstrates that although Fermi arcs are guaranteed in Weyl semimetals, their shape and connectivity are not protected and may be altered accordingly

Keywords:

Topological Nodal Line Semimetal, Topological Weyl Semimetal, Z_2 Invariant, Fermi arc, ARPES.

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Introduction

The search for new phases in material physics has been following the Landau theory of spontaneous symmetry breaking. However, the study of quantum Hall effect has opened up a new territory for studying phase change by investigating the topological order of material without any spontaneous symmetry breaking involved [1]. This new field called topological materials offers a plethora of exotic features with their unique bulk states relating to their intriguing surface states. This thesis describes the study on topological nodal semimetal investigated by using Angle-resolved Photoemission Spectroscopy (ARPES). This surface sensitive technique reveals the unique surface features simultaneously with the bulk features making it the suitable experimental tool for probing each material candidate.

1.1 Motivations for Research

Topological nodal line semimetal and topological Weyl semimetal are the two sub-categories of topological materials which have driven the research for this thesis. The start of this graduate study was marked by the discovery of these two sub-fields of topological materials, triggering an intense race to discover the materials that can satisfy these characteristics.

For the nodal line semimetal, the quest is to demonstrate the existence of nodal line, either Dirac/Weyl crossing, which maybe accompanied by the exotic “drumhead” surface states [2]. Apart from that, prediction on the existence of nodal line protected by crystalline symmetry has also fuelled the search from a different direction [3].

For topological Weyl semimetal, the discovery of the earlier generation has ignited further work on realising the ideal Weyl semimetal with minimum number of Weyl points [4]. This minimum Weyl semimetal with only four Weyl points (inversion breaking system) or two Weyl points (time reversal breaking system) will be the playing ground to investigate further the Fermi arc connectivity and the possibility to externally control it for further application.

1.2 Objectives of the Work

The objectives of this thesis are presented as follow:

1. To realise the nodal line protected by crystalline symmetry.
2. To realise the minimum Weyl semimetal in material with inversion symmetry breaking.
3. To investigate the Fermi arc in minimum Weyl semimetal.

1.3 Scope of the Work

With the objectives as outlined above, the scope of the thesis is described as follows.

Chapter 2 discusses a brief introduction to the ARPES technique. This chapter will establish the foundational knowledge necessary for the discussion in this thesis.

Chapter 3 provides the overview of the topological materials with their theoretical background. The historical development will be discussed to give the background of the

search towards the category of nodal line and Weyl semimetal.

Chapter 4 describes the project on InBi semimetal, which is found to host nodal line semimetal due to its non-symmorphic symmetry. Another exotic feature such as type-II Dirac points is also discussed.

Chapter 5 demonstrates the realisation of minimum Weyl semimetal within inversion symmetry breaking material. This chapter also describes how different surface leads to different surface states configuration. The Fermi arc connectivity is also discussed as it hybridises with the bulk states.

The thesis is closed in chapter 6 with the summary of the works done and several future projects are also suggested.

Angle-Resolved Photoemission Spectroscopy

Angle-resolved Photoemission Spectroscopy (ARPES) is a powerful experimental technique to directly visualise the dispersion relation of electrons in crystalline materials. Following the advancement in angular and energy resolution, ARPES has become the best technique to investigate the band structure of material via direct probing. This chapter presents a brief introduction of the ARPES technique that was used throughout the D.Phil study. Afterwards, it surveys the main parts of the setup in modern ARPES.

2.1 ARPES Intensity Theoretical Analysis

ARPES is based on photoelectric effect that was initially introduced by Hertz [5], Hallwachs [6], Lenard [7] and was explained theoretically by Einstein [8] which brought him a Nobel prize in 1921. In short, this effect describes the situation where electrons are emitted from a material after being illuminated by light. Einstein modelled the light to exist in quanta or packet of energy, which was then called photon, with each energy follows Planck's postulate as $E_n = nh\nu$. One photon will eject one electron out of the material

given sufficient photon energy by relation (see figure 2.7)

$$E_k = h\nu - \phi_m - |E_B|. \quad (2.1)$$

where E_k is the kinetic energy of the electron, $h\nu$ is the energy of one photon with frequency ν , ϕ_m is the work function of the material, and E_B is the binding energy of the electron while inside the material.

The electron itself is excited with a certain transition probability rate given by

$$\frac{dP_{i \rightarrow f}}{dt} = \frac{2\pi}{\hbar} \left| \langle \psi_f^N | H_{int} | \psi_i^N \rangle \right|^2 \delta(E_f^N - E_i^N - h\nu) \quad (2.2)$$

with $|\psi_i^N\rangle$ and $|\psi_f^N\rangle$ are initial and final (after light interaction with sample) N electrons ground state, E_i^N and E_f^N are the energy of N electrons initial and final, and H_{int} is the interaction Hamiltonian. Afterwards, the detector for ARPES will measure the intensity proportional to the overall transition probability rate i.e.

$$I_{\text{ARPES}} \propto \sum_{\text{all } i \rightarrow f \text{ possible}} \frac{dP_{i \rightarrow f}}{dt}. \quad (2.3)$$

Assuming the H_{int} only acts on one electron, we may treat the initial and the final state as the anti-symmetrised product (given with operator C) of the single electron state and the rest $N - 1$ electrons. Initially, the state comprises the single electron state at momentum number $\vec{k}$ and the remaining $N - 1$ electrons without wavenumber $\vec{k}$ given as $|\psi_i^N\rangle = C |\phi_{i,\vec{k}}\rangle |\psi_i^{N-1,\vec{k}}\rangle$. After excitation, we assume a **sudden approximation** so that the final state comprises the single free electron state at kinetic energy $E_{\vec{k}}$ and the remaining $N - 1$ electrons states given as $|\psi_f^N\rangle = C |\phi_{f,E_{\vec{k}}}\rangle |\psi_f^{N-1,\vec{k}}\rangle$. With this expression, we may re-write the equation 2.2 as

$$\frac{dP_{i \rightarrow f}}{dt} = \frac{2\pi}{\hbar} \left| \langle \phi_{f,E_{\vec{k}}} | H_{int} | \phi_{i,\vec{k}} \rangle \right|^2 \left| \langle \psi_f^{N-1,\vec{k}} | \psi_i^{N-1,\vec{k}} \rangle \right|^2 \delta(E_f^N - E_i^N - h\nu). \quad (2.4)$$

There are two components we need to tackle. First, the $\left| \left\langle \psi_f^{N-1, \vec{k}} \left| \psi_i^{N-1, \vec{k}} \right\rangle \right|^2$ which is related to the **spectral function** of the ARPES. This part describes the overall shape of our ARPES peaks and also the indication if the system is strongly or weakly correlating. Second, the $\left| \left\langle \phi_{f, E_{\vec{k}}} \left| H_{int} \left| \phi_{i, \vec{k}} \right\rangle \right|^2$ which is usually written as $|M_{f, i, \vec{k}}|^2$ or the **matrix element**. This section shows if the electron transition is even possible fundamentally or forbidden.

2.1.1 Spectral Function of ARPES

The $\left| \left\langle \psi_f^{N-1, \vec{k}} \left| \psi_i^{N-1, \vec{k}} \right\rangle \right|^2$ expression represents the overlap integral of the initial and the final state of the remaining $N - 1$ electrons. The simplest way to tackle this is to assume the **frozen state** assumption where $\left| \left\langle \psi_f^{N-1, \vec{k}} \left| \psi_i^{N-1, \vec{k}} \right\rangle \right|^2 = 1$ i.e. nothing is changed between the initial and the final state of the remaining $N - 1$ electron. This is a good approximation if the electrons in our system are weakly interacting. However, this may not be the case as we need to consider the reaction of the remaining $N - 1$ electrons after one electron vacates its place.

Following the calculation in ref. [9], we may assume that after one electron leaves, the remaining $N - 1$ electrons have s number of states to re-configure themselves. As a consequence, there are s number of probability rates that should be summed over i.e.

$$\frac{dP_{i \rightarrow f}}{dt} = \sum_s \frac{dP_{i \rightarrow s}}{dt} \propto \sum_s \left| \left\langle \psi_{f, s}^{N-1, \vec{k}} \left| \psi_i^{N-1, \vec{k}} \right\rangle \right|^2 = \sum_s |c_s|^2 \quad (2.5)$$

where we express the projection $\left\langle \psi_{f, s}^{N-1, \vec{k}} \left| \psi_i^{N-1, \vec{k}} \right\rangle = c_s$.

The **spectral function** of ARPES is defined as [10]

$$A_{\vec{k}, E} = \sum_s |c_s|^2 \delta(E_f^N - E_i^N - h\nu) = \sum_s |c_s|^2 \delta(E_{\vec{k}} + E_{f, s}^{N-1} - E_i^N - h\nu) \quad (2.6)$$

that is related to single particle Green's function with complex self-energy $\Sigma_{\vec{k}, E} = \Sigma'_{\vec{k}, E} + i\Sigma''_{\vec{k}, E}$

$$G_{\vec{k},E} = \frac{1}{E - \varepsilon_{\vec{k}} - \Sigma_{\vec{k},E}} \quad (2.7)$$

$$A_{\vec{k},E} = \frac{1}{\pi} \text{Im} G_{\vec{k},E} = \frac{1}{\pi} \frac{\Sigma''_{\vec{k},E}}{\left[E - \varepsilon_{\vec{k}} - \Sigma'_{\vec{k},E}\right]^2 + \left[\Sigma''_{\vec{k},E}\right]^2} \quad (2.8)$$

where $\varepsilon_{\vec{k}}$ is the electron band energy.

For a weakly interacting system, the self-energy is 0 leading to $A_{\vec{k},E} = \delta(E - \varepsilon_{\vec{k}})$. In this situation, ARPES will read purely the bandstructure of material as calculated from any Density Functional Theory (DFT) without taking electron correlation. However, equation 2.8 demonstrates that a more realistic ARPES spectra will have a dispersion shift by $\Sigma'_{\vec{k},E}$ and obtain peak broadening by $\Sigma''_{\vec{k},E}$. The **Lorentzian peak** broadening along energy dimension by $\Sigma''_{\vec{k},E}$ is related to the finite lifetime of the single particle state and other scattering rate due to electron-electron, electron-phonon, electron-magnon, etc [11]. The lifetime of the single particle state is proportional to $\varepsilon_{\vec{k}}^2$ measured from Fermi energy i.e. higher binding energy leads to a broader the signal [12, 13]. In relation to temperature, $\Sigma''_{\vec{k},E} \propto (\pi k_B T)^2 + (\varepsilon_{\vec{k}} - \mu)^2$ [14] indicates that the width is broadened as temperature rises. In real experiment, this Lorentzian broadening is even further convoluted with the Gaussian broadening from the detector limitation [15].

Meanwhile, the ARPES data for a strongly correlated system will show other satellite peak apart from the main peak discussed above as the consequence of the multiple excited states s that it has (see 2.6) and is manifested in *incoherent* part of the self-energy expression [10, 14, 16] (figure 2.1). However, *we will neglect this correlation effect for the discussion in this thesis* as we are still in the regime of weakly interacting system.

2.1.2 Matrix Element in ARPES

There are two approaches to calculate $|M_{f,i,\vec{k}}|^2$ up to the writing of this thesis which are **one step model** and **three steps model**. One step model may provide a more realistic

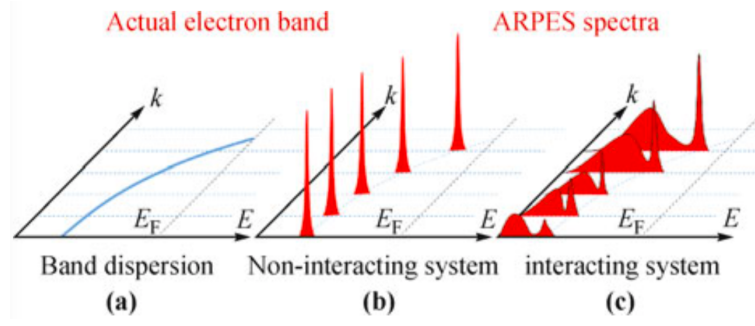


Figure 2.1: ARPES peaks reading show that a non-interacting system (b) will have a single peak reading with a finite width following the original dispersion curve (a). Meanwhile, the interacting system (c) shows a satellite peak following the original peak (a). Figure adapted from [16].

picture of the data as it may involve many body effects [17], self-energy correction [18, 19], relativistic correction [20–22], spin effect [19, 23, 24], etc. However, within the scope of this thesis, the most intuitive approach is the three steps model where we assume [10, 14, 25]:

1. The electron from a single particle Bloch ground state is excited to another final Bloch state within the crystal bulk. Thus, we approximate $|M_{f,i,\vec{k}}|^2$ to be the transition to the final state in the bulk and not the free electron state in vacuum. We may write it as $|\phi_{\vec{k}_f, \kappa_f}\rangle$ with momentum $\vec{k}_f$ and band index κ_f .
2. The excited electron travels towards the surface with a complex perpendicular wave-vector to simulate decays. The typical mean free path of excited electron inside material is shown in *universal curve* figure [2.2](#).
3. The electron escapes the surface to the vacuum and becomes a free electron state in vacuum. At this step, we require the $\vec{k}_{||, \text{inside}} = \vec{k}_{||, \text{outside}}$ as conservation of parallel momentum.

With the expression of H_{int} as an incoming photon (electromagnetic wave), we may write the matrix element in ARPES as

$$|M_{f,i,\vec{k}}|^2 = \left| \langle \phi_{f,E_{\vec{k}}} | H_{int} | \phi_{i,\vec{k}} \rangle \right|^2 = \left| \langle \phi_{f,E_{\vec{k}}} | \left(-\frac{eA_0}{m_e} e^{i\vec{k}_{hv} \cdot \vec{r}} \hat{\epsilon} \cdot \vec{p} \right) | \phi_{i,\vec{k}} \rangle \right|^2 \quad (2.9)$$

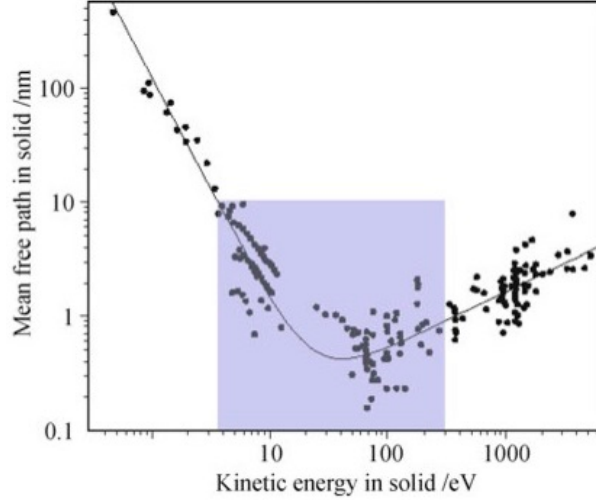


Figure 2.2: Universal curve of electron mean free path as it travels inside the material as the function of its kinetic energy. The purple box is the typical kinetic energy range for ARPES measurement. This curve implies that ARPES is more surface sensitive with longest penetration depth (decay length λ in equation 2.12) about 10 nm. Figure adapted from [16].

where we deliberately state $|\phi_{f,E_{\vec{k}}}\rangle$ as $|\phi_{\vec{k}_f,\kappa_f}\rangle$, and also $|\phi_{i,\vec{k}}\rangle$ as $|\phi_{\vec{k}_i,\kappa_i}\rangle$.

Following the argument by Moser in ref [26], we may start expressing item 1 by describing the initial bloch state inside the bulk as the inverse Fourier transform of the Wannier state $|\vec{R}, \kappa\rangle$

$$|\phi_{\vec{k}_i,\kappa_i}\rangle = \sum_{\vec{R}} e^{i\vec{k}_i \cdot \vec{R}} |\vec{R}, \kappa_i\rangle \quad (2.10)$$

while the final state is approximated as a free electron moving inside a periodic potential

$$|\phi_{\vec{k}_f,\kappa_f}\rangle = \sum_{\vec{G}} C_{\vec{k}_f - \vec{G}}^{\kappa_f} |\vec{k}_f - \vec{G}\rangle \quad (2.11)$$

where the $C_{\vec{k}_f - \vec{G}}^{\kappa_f}$ is the solution of the **central equation** with reciprocal lattice vector $\vec{G}$ [26].

Afterwards, the description of item 3 requires us to express the final free electron state as simply $|\vec{k}_f\rangle$. However, with decaying feature mentioned in step 2, we may modify the state as $|\vec{k}_f - \frac{i}{\lambda} \vec{e}_\perp\rangle$ to express the decaying wave (evanescent wave of the free electron

wave outside) with a phenomenological decay length λ as

$$\left\langle \vec{r} \left| \vec{k}_f - \frac{i}{\lambda} \hat{n}_\perp \right. \right\rangle = e^{i\vec{k} \cdot \vec{r}} e^{\frac{r_\perp}{\lambda}} \quad (2.12)$$

where $\hat{n}_\perp$ is the surface normal vector and λ describes the decay length measured from the surface towards the bulk material.

With those, we will have

$$C_{\vec{k}}^{\kappa_f} = \delta \left(\vec{k} - \vec{k}_f + \frac{i}{\lambda} \hat{n}_\perp \right) \quad (2.13)$$

and finally the expression of **Matrix element** becomes

$$\begin{aligned} M_{\vec{k}_f, \vec{k}} &\propto 2\pi \frac{N}{V} \underbrace{\hat{\epsilon} \cdot \left(i\vec{k}_f - \frac{1}{\lambda} \hat{n}_\perp \right)}_{\text{I}} \underbrace{\left\langle \vec{k}_f - \vec{k}_{h\nu} + \frac{i}{\lambda} \hat{n}_\perp \left| \vec{0}, \kappa \right. \right\rangle}_{\text{II}} \\ &\quad \times \underbrace{\delta \left(\vec{k}_\parallel - \vec{k}_{f,\parallel} + \vec{k}_{h\nu,\parallel} + \vec{G}_\parallel \right)}_{\text{III}} \\ &\quad \times \underbrace{\frac{1}{i(k_\perp - k_{f,\perp} + k_{h\nu,\perp}) + \frac{1}{\lambda}}}_{\text{IV}} \end{aligned} \quad (2.14)$$

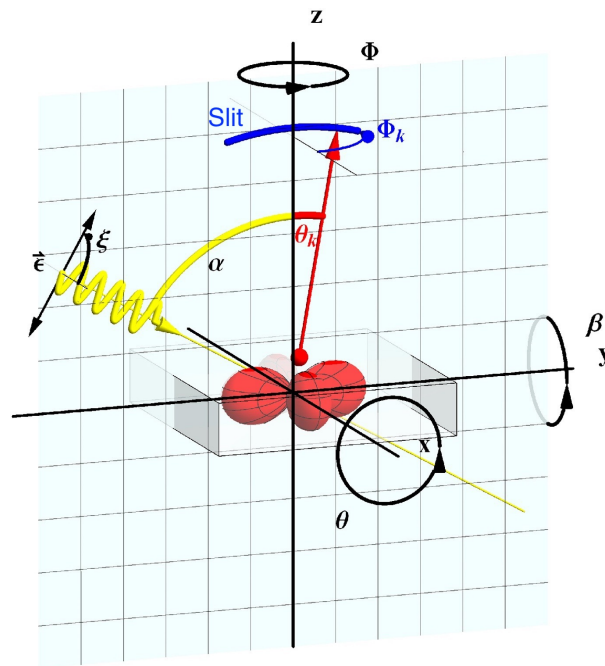
The explanations of each component are listed below:

1. Component I describes the effect of photon polarisation used in ARPES in relation to the outgoing electron momentum $\vec{k}_f$ and the vector normal to the sample surface $\hat{n}_\perp$. The vectorial expression of $\hat{\epsilon}$ following the configuration in figure 2.3 is given as

$$\vec{\epsilon} = \epsilon e^{i\eta} \begin{pmatrix} \cos \xi \\ e^{i\delta} \cos \alpha \sin \xi \\ e^{i\delta} \sin \alpha \sin \xi \end{pmatrix} \quad (2.15)$$

where η is the absolute phase of the light, ξ is the angle between the light polarisation and the x -axis as described in figure 2.3, α is the angle between photon direction and the detector slit, δ is the relative phase between the principal components.

For **linearly polarised**, the relative phase $\delta = 0$. Afterwards, there are two commonly used configurations which are p -polarised when $\xi = \pi/2$ (the polarisation is



on the scattering plane) or s -polarised when $\xi = 0$ (the polarisation is perpendicular to the scattering plane). We can calculate that for s -polarised light, the I component will be $\propto k_{f,x}^2$ which will vanish at $k_{f,x} = 0$. However, this suppression is less severe in real experiment since we have many plane waves at the final state. Meanwhile, the p -polarised light will give us matrix element $\propto k_{f,y}^2 + \frac{\sin^2 \alpha}{\lambda^2}$ which will give us more intensity in several direction as compared to s -polarised light. For **right/left circularly polarised light** (CR/CL), we have $\delta = \pm\pi/2$ with $\xi = \pi/4$ which will give us matrix element of $\propto \frac{\epsilon^2}{2} \left(k_{f,x}^2 + k_{f,y}^2 + \frac{\sin^2 \alpha}{\lambda^2} \right) \mp \epsilon^2 k_{f,x} \frac{\sin \alpha}{\lambda}$. This shows that the left and right circular light has a non-zero dichroism intensity i.e.

CL and CR will light either side of α accordingly. In short, component I demonstrates that different light polarisation may give us a different intensity result accordingly.

2. The term II can be approximated further by assuming that the photon momentum and the order of $\frac{i}{\lambda}$ are small compared to the final momentum $\vec{k}_f$. Thus we will have $\langle \vec{k}_f | \vec{0}, \kappa \rangle$ which describes the angular distribution of ARPES intensity originated from the orbital character of the material. The detailed discussion is available in ref. [26].
3. III describes that the final excited parallel momentum is related to the initial parallel momentum up to a reciprocal lattice vector parallel to the surface conservation i.e. $\vec{k}_{i,\parallel} - \vec{k}_{f,\parallel} + \vec{G}_{\parallel} = 0$. This is assuming that the photon momentum is small. This $\vec{k}_{f,\parallel}$ is what we called as $\vec{k}_{\parallel, \text{inside}}$ in the third step of three-steps model section 3 above.
4. The last component IV will give us a *pseudo* conservation of perpendicular momentum provided the λ term is very large. When $\lambda \rightarrow \infty$, we will have

$$\left| \frac{1}{i(k_{\perp} - k_{f,\perp} + k_{h\nu,\perp}) + \frac{1}{\lambda}} \right|^2 \rightarrow \pi \delta(k_{\perp} - k_{f,\perp} + k_{h\nu,\perp}) \quad (2.16)$$

i.e. $k_{\perp} = k_{f,\perp}$ is true only at large penetration depth in the bulk $\lambda \rightarrow \infty$. For typical ARPES data where λ is finite, we expect a severe broadening due to several $k_{f,\perp}$ contributing to the reading as a function of Lorentzian peak. As the full width half maximum of Lorentzian function is $\propto \frac{1}{\lambda}$, we expect more broadening from the data nearer to the surface (usually called k_z broadening). The universal curve of λ and the kinetic energy of electron is given in figure 2.2.

2.1.3 Further Comment on k_z Broadening

The effect of component IV above will limit the accuracy in perpendicular momentum measurement. This also affects the parallel momentum measurement since what we

measure with a given photon energy is the combination of several k_z components. Strokov has reported the simulation of this intrinsic k_z broadening as the function of $\frac{1}{\lambda}$ (in his calculation is called $\delta k_\perp$) in ref. [27]. The result is shown in figure 2.4. We may see that if the uncertainty is 0 or the $\lambda \rightarrow \infty$, the simulated peaks (dots) coincide with the calculated band structure (line) while the peaks themselves are broadened by the Lorentzian broadening as discussed in Spectral Function discussion above (2.8). As the uncertainty is bigger i.e. the λ is short, we may see the alteration of the observed peak from the calculated band structure. Interestingly, there is a value of uncertainty where we see a *shoulder* peak ($\delta k_\perp = 0.6\|\Gamma X\|$) even though there is no calculated band at that position. This is the signature of lost k_z information which is fully realised in the highest uncertainty simulation result on the right. It shows a non-dispersing ARPES result with broad peaks since ARPES has no information of the perpendicular momentum.

2.2 Parallel and Perpendicular Momentum Analysis in ARPES

Upon excitation by the photons, the electrons will hemi-spherically be excited out of the material. Since the surface does not perturb the translational symmetry along its plane, we may express the conservation of parallel momentum as stated before $\vec{k}_{||,f} = \vec{k}_{||,inside} = \vec{k}_{||,outside}$ in part 3 of three step model. From the calculation of component III in Matrix Element (3), we know that the momentum of the ejected electron parallel to the sample should be conserved up to reciprocal lattice vector.

$$\vec{k}_{||,outside} - \vec{k}_{||,i} = \vec{G}_{||} \quad (2.17)$$

We may calculate the outside momentum as given by

$$k_{outside} = \frac{\sqrt{2m_e E_k}}{\hbar}, \quad (2.18)$$

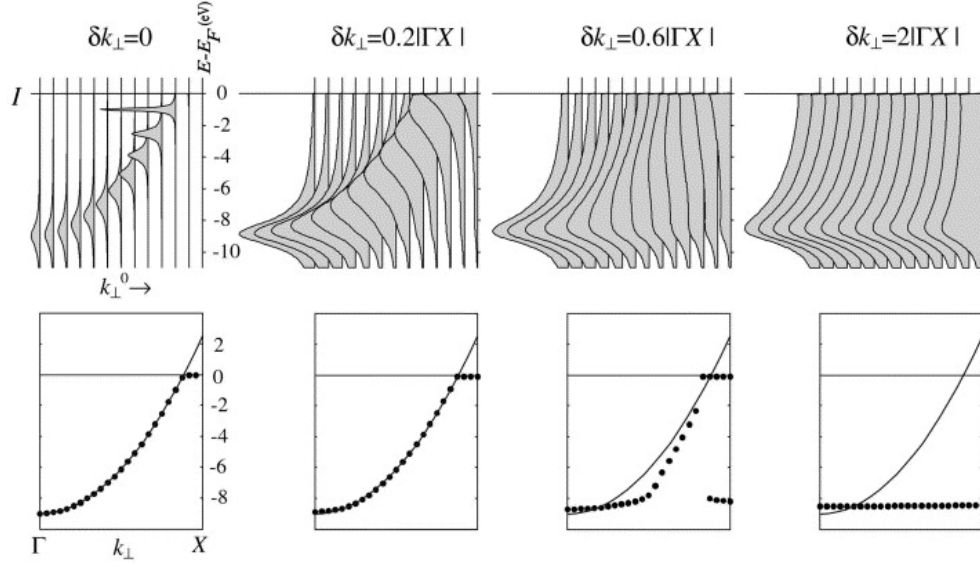


Figure 2.4: The simulated ARPES data along the perpendicular momentum with varying uncertainty in $k_{\perp}$. The simulated result with zero uncertainty $\delta k_{\perp} = 0$ shows that the simulated peaks of ARPES (dots) coincides with the calculated band structure (line). The broadening along the energy is the intrinsic broadening from the Spectral Function. As the $\delta k_{\perp}$ increases, the peaks broadening along the energy increases as the self-energy (2.1.1) part increases. Afterwards, the simulated ARPES peaks deviate from the band structure with further increment of $\delta k_{\perp}$ until the peaks lose the information of k_z dispersion at the largest simulated $\delta k_{\perp}$. Figure adapted from [27].

with the E_k defined in equation 2.1 which will give us the desired momentum for dispersion relation (see figure 2.5).

From here, we may express the parallel momentum outside in x and y coordinate as such

$$k_{||, \text{outside}} = \frac{\sqrt{2m_e E_k}}{\hbar} \sin \theta \quad (2.19)$$

$$k_x = k_{||, \text{outside}} \cos \phi = \frac{\sqrt{2m_e E_k}}{\hbar} \sin \theta \cos \phi \quad (2.20)$$

$$k_y = k_{||, \text{outside}} \sin \phi = \frac{\sqrt{2m_e E_k}}{\hbar} \sin \theta \sin \phi \quad (2.21)$$

The equation 2.20, 2.21, and 2.17 above imply that by collecting the ejected electrons angular positions and kinetic energy, we may map the $k_{||, i}$ of the material translated by

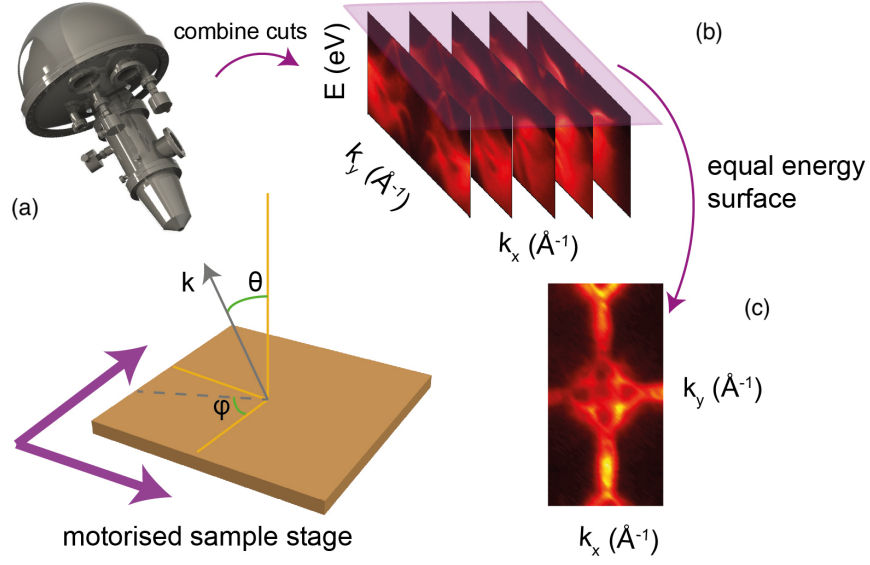


Figure 2.5: (a) Schematic of ARPES measurement. Motorised sample stage allows different spots of investigation. The two angles give two independent variables to decouple the momentum components. (b) Several cuts (k_y, E) from the analyser are group together to produce the 2D dispersion relation data (k_x, k_y, E). (c) Example of equal energy surface taken at Fermi energy position of the material.

certain $\vec{G}$. In other words, we will get multiple copies of the 2-Dimension (2D) dispersion relation (k_x, k_y, E) parallel to the surface of interest. Meanwhile, the perpendicular momentum at the outside can be calculated as

$$k_{\perp, \text{outside}} = \frac{\sqrt{2m_e E_k}}{\hbar} \cos \theta \quad (2.22)$$

This $k_{\perp, \text{outside}}$ cannot be equal to the $k_{\perp, \text{inside}}$ since the surface creates a discontinuity in potential, which can be modelled simplistically with a single potential barrier V_o called *inner potential*. Furthermore, following the equation [2.16](#), it is clear that the damping effect creates an intrinsic broadening along momentum (Lorentzian peak in nature) where several $k_{\perp, i}$ will contribute to the $k_{\perp, f}$ result (usually called k_z broadening) [27]. Meanwhile, the perpendicular momentum of ARPES can be modelled as

$$k_z = k_{\perp, \text{inside}} = \sqrt{\frac{2m_e^*}{\hbar^2}(E_k + V_o) - k_{\parallel}^2} \quad (2.23)$$

$$= \sqrt{\frac{2m_e^*}{\hbar^2}(E_k + V_o) - \frac{2m_e E_k}{\hbar^2} \sin^2 \theta} \quad (2.24)$$

where m_e^* is the effective mass of the electron inside the material and V_o is the inner potential that varies for different material. Thus, taking several **photon energies data** at a particular cut through the Γ point (see figure 2.6) will give us the k_z dependence of that particular cut direction. For example, we may get $X\Gamma X/RZR$ band structure in simple tetragonal structure if our surface is the (001) plane.

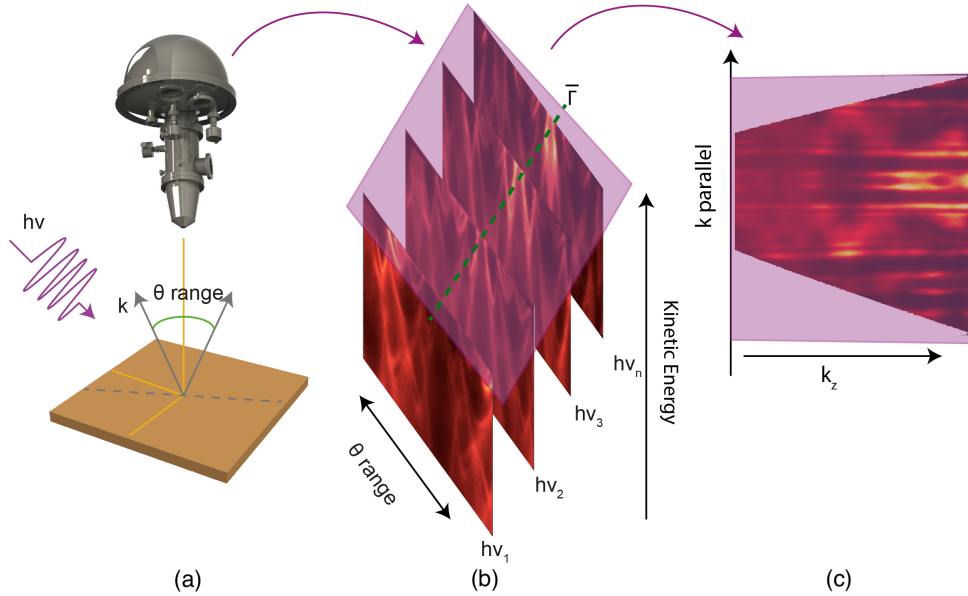


Figure 2.6: (a) Schematic of ARPES measurement when measuring k_z dependence. The analyser is positioned to cut the Γ point. (b) Several cuts from different photon energies group together before converted into $k_{\parallel}$ and k_z (c) Example of equal energy surface taken at Fermi Energy position of the material.

2.3 Energy Analysis in ARPES Analyser

The equation [2.1](#) tells us the relation of the kinetic energy with the variable of photon energy and the constants of binding energy and work function. During the experiment, we may get the work function of our system by taking the difference between the photon energy and the highest kinetic energy (zero binding energy) $\phi = E_k - h\nu$. However, it should be noted that *this work function is not the work function of the material but rather the work function of the detector*. The arguments are detailed below.

1. The photo-electron will be excited with a given kinetic energy as in equation [2.1](#)

$E_k = h\nu - \phi_{\text{sample}} - |E_B|$. This is the first step of ARPES (step [1](#) discussed before).

2. However, during the step [2](#) of ARPES, some electrons may suffer inelastic collisions which decreases the overall kinetic energy and creates a secondary peak. Thus, we will have the *primary electron* peaks which corresponds to the valence band and the core level of the material, and the *secondary electron* peaks which has a continuous energy spectrum (see figure [2.7](#)).

3. During experiment, the Fermi energy of the material should lie on the same level as the Fermi energy of the detector (or else there is an inequilibrium and particle/energy transfer). As the consequence, the detector will detect the kinetic energy that is shifted by the difference between the work function of analyser and the sample.

$$E_{k,\text{analyser}} = E_k + \phi_{\text{sample}} - \phi_{\text{analyser}} = h\nu - \phi_{\text{analyser}} - |E_B| \quad (2.25)$$

hence the work function that we read in the detector is the work function of the detector (not the material).

4. Eventually, we may calibrate our ARPES Fermi level as 0 position and express the energy in terms of their binding energy or simply express it as $E - E_F$.

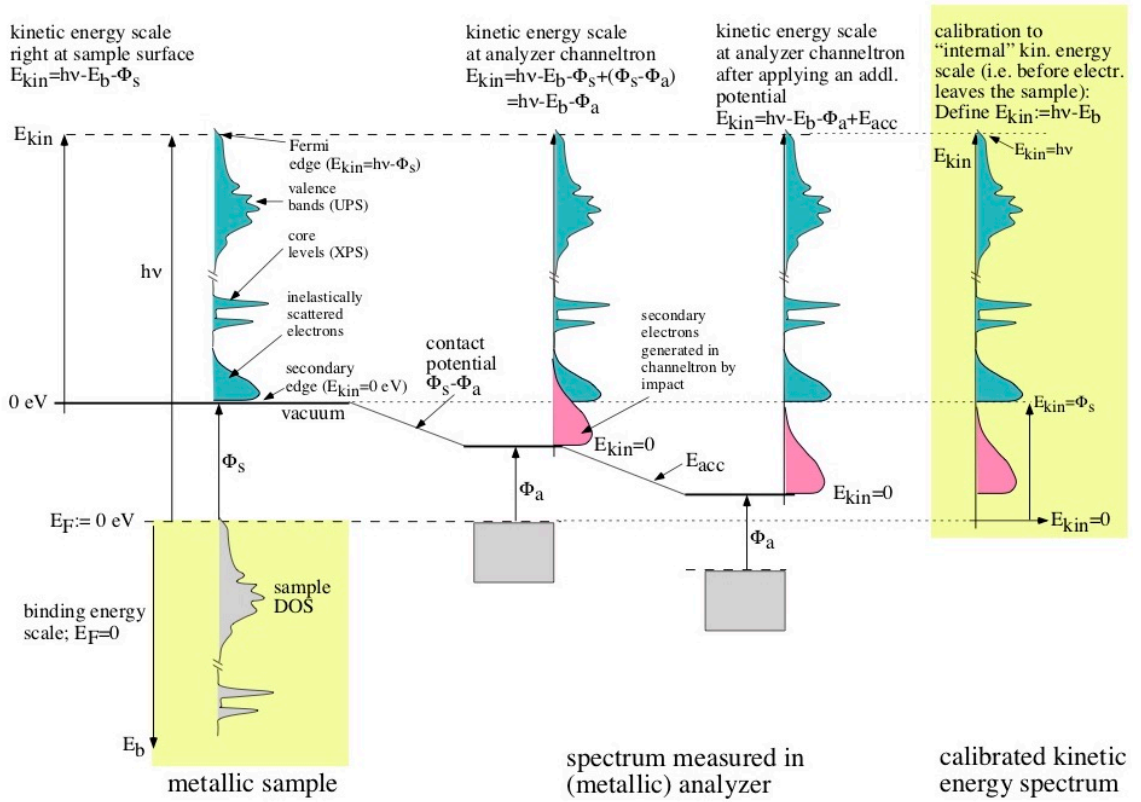


Figure 2.7: Initially the photon will eject the electron and each will have kinetic energy as shown in the left panel. As the sample and detector share the same vacuum, their Fermi level should equilibrate creating the contact potential difference of $\phi_{\text{sample}} - \phi_{\text{analyser}}$. The detector will then receive the electrons with their complete feature of primary and secondary electron peaks, and its own unique secondary electron peak generated in the channeltron. During the measurement, we may introduce an accelerating field to separate the channeltron secondary peak and the rest. The final energy axis is scaled from the Fermi level as 0 to express the binding energy of the electron inside the sample. Figure adapted from [28].

2.4 Experimental Setup of ARPES

The following section will discuss in brief the main parts in ARPES which are light source and the end station. Most of the work in this thesis were done in Diamond Light Source i05 HR ARPES end station which can be found in this reference [29]. Other works were also done in other synchrotron end station such as APE beamline in Elettra

Sincrotrone which can be found in detail here [30] and also Advanced Light Source BL4 [31] and BL10 [32].

2.4.1 Light Source

There are several light sources commonly used in PES measurement such as X-ray tube, gas discharge lamp, synchrotron radiation, and laser [33]. This section describes in brief the light source used by the author to do ARPES measurement which are from the synchrotron and the laser.

Synchrotron Light Source

By the late 19th century, it is generally known that an accelerated charged particle may radiate electromagnetic wave and thus losing its energy in what we call as *bremsstrahlung* radiation [34]. However, we may utilise this radiation as a source of X-ray for experiments. One way to utilise this is by **accelerating the charge particle perpendicularly by magnetic field while it is moving in a relativistic regime** whose radiation will be called **synchrotron radiation**. If the charged particle is moving classically, the radiation characteristic will be a symmetric dipole pattern. However, if it is moving nearer the speed of light, the radiation has a forward projection (see figure 2.8). This "unidirectional" radiation is the useful output as the light source for experiment.

This is realised in a synchrotron radiation facility where it has several main parts that will be discussed as follow (interactive simulation is available in this reference [35]):

1. **Electron Gun.** As the rate of loss in radiation is proportional to $B^2\gamma^2$ with $\gamma = \frac{1}{\sqrt{1-\frac{v^2}{c^2}}}$, it is more efficient to use electron as the charged particle than proton. With electron, we may get the same radiation output with less energy input (remember that energy is $E = \gamma mc^2$). This electron gun is basically the cathode ray tube that works with the same principle like the old TV tube [36].

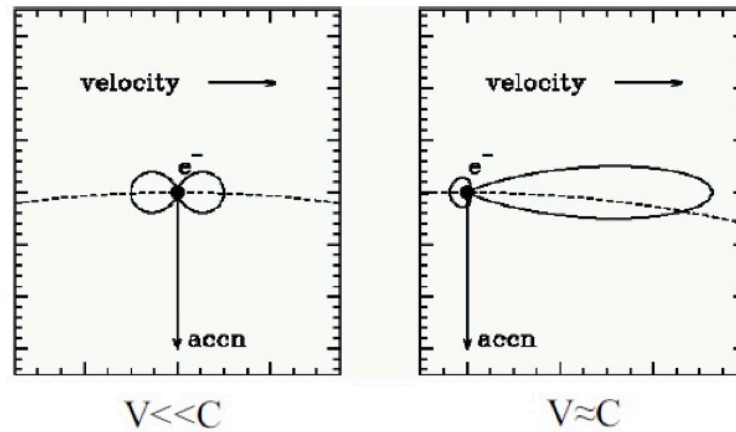


Figure 2.8: Charged particle accelerated perpendicularly emitting a radiation with characteristic shape shown. For a non-relativistic speed, the radiation characteristic is symmetric like a dipole while the relativistically moving charge will emit an X-ray to the front at a certain angle. Figure adapted from [33].

2. **The Linac.** The linear accelerator (Linac) is the place where the emitted electrons from the gun are accelerated via electric field before they are injected into the booster ring. In principle, the Linac has plates with alternating charge creating an always-positive charge in front of the electrons accelerating them forward.
3. **Dipole Magnet.** This part acts like a mirror as it will alter the direction of the electron beam through Lorentz force due to the magnetic field. The configuration of this dipole magnet will determine how sharp the electron beam will turn.
4. **The Booster Ring.** After the linear acceleration, electrons can be directed towards the booster ring (via the dipole magnet) for further acceleration. The shape of this ring is not a perfect circle as it is more like an N-polygon where each vertex has a dipole magnet to alter the electron movement. One side of the polygon has a **radio frequency (RF) cavity** that will accelerate the electron each time it makes a full “circle”. When the desired energy is reached (about $0.99999998c$, 3 GeV for Diamond Light Source [34]), the beam will be injected into the storage ring.

5. **The Storage Ring.** This is the main ring where the electrons are travelling to give out X-ray as it bends. Like the booster ring, the shape of this storage ring is like an N-polygon but now it is equipped with the undulator (wiggler, see figure 2.9) which will generate a more intense X-ray beam at the particular direction towards the beamline. As it travels, the electrons will lose energy and thus will be replaced by the new electrons from the booster ring. This process continues to give a constant light source for each beamline.
6. **Beamline.** This is the part where the X-ray is further manipulated to be used in the experiment (end-station). After the undulator, we may steer the intense light towards our sample by mirror accordingly. The important part along this line is the grating where we can choose the desired energy for the experiment. At the end of this line, we have the end-station where the experiment is conducted.

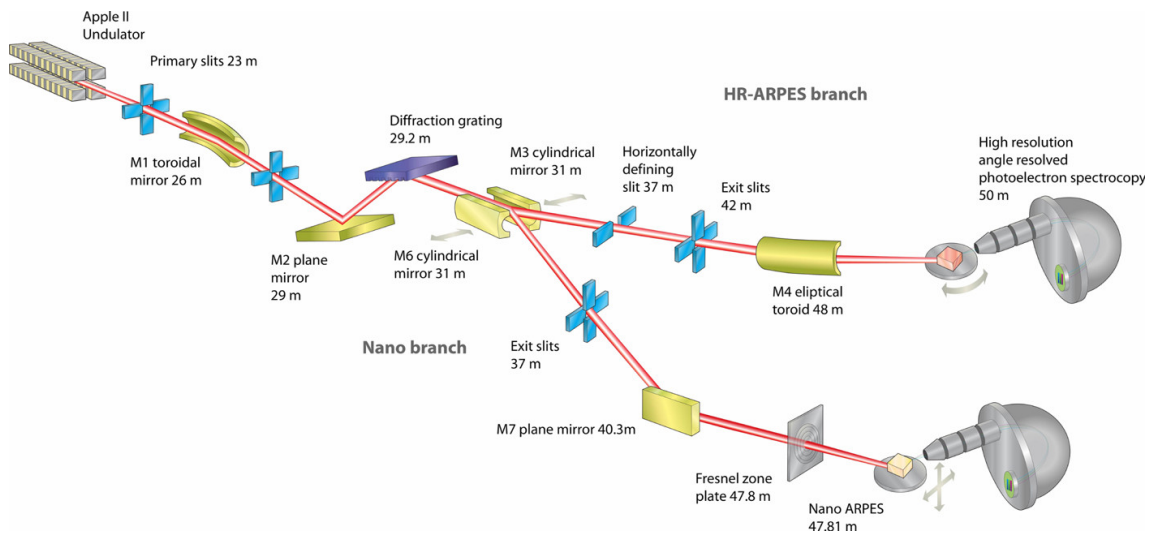


Figure 2.9: Typical layout of beamline at ARPES beamline station. Figure shown is i05 layout in Diamond Light Source [29]. It starts from the undulator to generate an intense X-ray by wiggling electrons. Afterwards the direction of the X-ray beam may be steered by magnetic mirror or plane mirror. Afterwards, the grating may select the desired energy for experiment for each end station towards the sample. Figure adapted from [29].

The advantages of using synchrotron as compared to other mentioned sources are the

high intensity it may give ($\sim 10^{12}$ photons/s) due to the undulator and the flexibility of energy tuning for experiment. With wide energy range to choose from 10s of eV to 1000s of eV, many surfaces and bulk characteristics can be unveiled (see the universal curve in figure 2.2).

Laser

Author's note: the technique described below will not be featured in the subsequent chapters and is only part of the graduate training to setup a laser input for an ARPES system.

Laser in deep UV range maybe used as the photon source for ARPES experiment since it has higher momentum & energy resolution, higher bulk sensitivity (see the universal curve 2.2), and easier electron spin manipulation [33]. With the typical work function of material (~ 4 eV) and the commercially available laser system, the 6 eV Fourth Harmonic Generation (FHG) laser was setup as part of this graduate training. Ultrafast laser system is used here as it may reach the necessary fluence per pulse to generate the second harmonic out of the non-linear crystal (in this case is Barium Borate or BBO crystal) [37]. The fundamental laser wavelength available from the oscillator (Tsunami model from Spectra-Physics) is in the range of 700 - 1000 nm with typical power up to 1 W, repetition rate of 80 MHz, and pulse width <100 fs. The oscillator itself is pumped by Millennia pump of continuous 532 nm from Spectra-Physics Lasers, Inc.

In this setup, the fundamental wavelength used is 824 nm since the maximum photon energy output of the FHG from a BBO is 206 nm for a type-I phase matching BBO [38]. Initially, the 824 nm laser is focused on BBO 1 to generate the Second Harmonic Generation (SHG) of 412 nm (see figure 2.10). This type-I phase matching BBO is relatively straight forward to use as it only requires a perpendicular input with the light polarisation matching the BBO axis (in our case the BBO axis is rotated to follow the

parallel polarisation of our laser). The SHG output from this type-I BBO will also travel in the same direction as the input but with a perpendicular polarisation output (output is s-polarised or *senkrecht*). Afterwards, the 206 nm is focused on the second BBO (also type-I phase matching BBO) to generate the SHG 206 nm out of it. Since we need the 206 nm output to be s-polarised, we rotate the 412 nm before the BBO 2 by using the Half-Wave Plate (HWP). The typical output of 206 nm is in the energy of 0.0005 nJ per pulse (50 μ W). This is three times smaller than the report from Dessau's group with 0.0015 nJ per pulse [39]. Subsequently, this FHG laser is guided through the UHV chamber to be used for ARPES experiment.

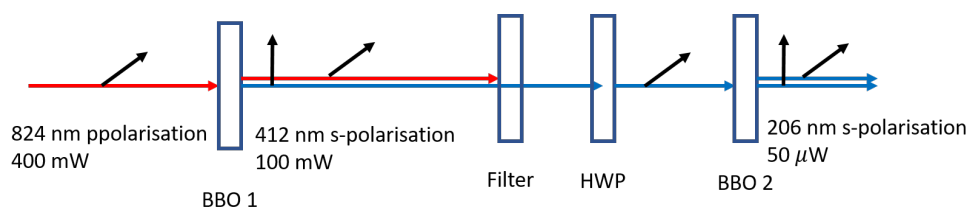


Figure 2.10: Fourth Harmonic Generation Schematic. The fundamental wavelength (824 nm) from the oscillator passes through the first BBO crystal generating a Second Harmonic Generation laser of 412 nm with perpendicular polarisation. This 412 nm light is used to shoot another BBO crystal to generate the Fourth Harmonic Generation of 206 nm out of it. This 206 nm light is used in the subsequent ARPES experiment.

2.4.2 End-station

In the typical ARPES measurement, the sample can be prepared *ex-situ* or *in-situ*. The important point is to prepare a clean surface for the measurement. The sample prepared *ex-situ* maybe cleaved inside the chamber to create a fresh cut of the surface. However, an Ultra High Vacuum (UHV) environment is needed to ensure the freshly cleaved surface is kept clean and relatively free from air molecules absorption. Apart from that, the UHV environment also ensures a sufficient mean free path for the ejected electrons towards the detector. Thus, the ARPES station is a carefully designed UHV chamber

equipped with the necessary elements for ARPES measurement (see figure 2.11) as will be discussed as followed:

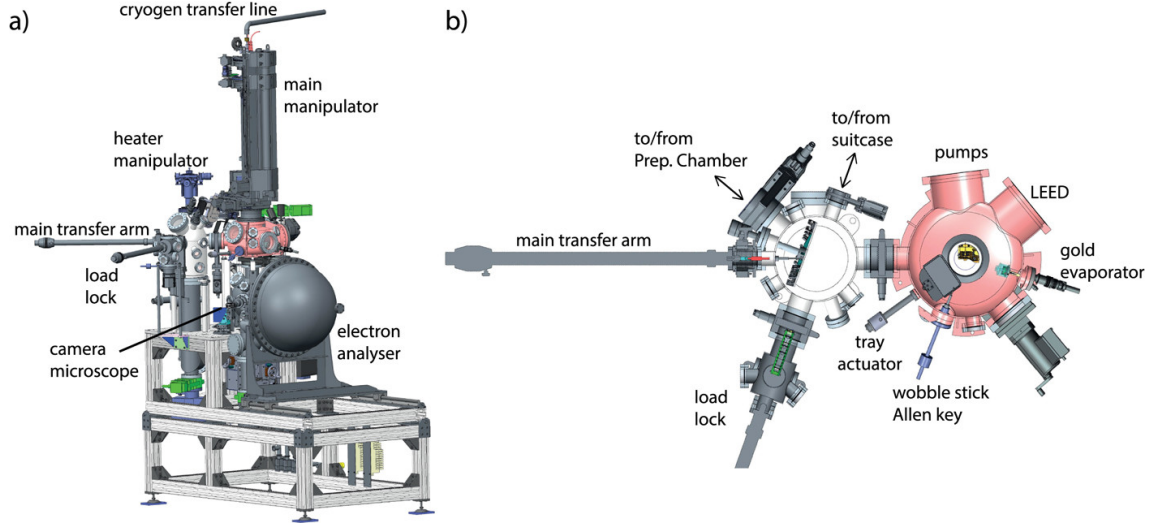


Figure 2.11: ARPES end-station at i05 beamline in Diamond Light Source as viewed from the side (a) and viewed from above (b).

1. **Vacuum System.** ARPES experiment requires a UHV system to support a clean environment to probe the sample's surface and let the ejected electrons have enough mean free path to travel towards the detector. The mean free path of electron is given as $\lambda = 0.007/P$ in cm unit where P is the pressure in mbar [40]. With this, we may see that a mere 10^{-5} mbar pressure has already given us a 7 m length which is longer than typical ARPES chamber. However, there is time t associated with the time to produce a layer of absorbed molecules on sample surface by $t = 3 \times 10^6/P$. With this in picture, at least a 10^{-10} mbar pressure is needed to get a decent ARPES measurement time without contaminating the surface with deposit of unwanted molecules. In typical ARPES experiment, there are several vacuum pumps needed to achieve the required pressure (differential pumping). The first one is the **rough pump**, usually a **scroll pump** which will roughly bring the pressure down from the atmospheric pressure to a 10^{-3} mbar pressure. Afterwards, a **turbo-molecular pump** is turned on to eject the remaining air molecules

out down to the desired 10^{-10} mbar. This pump works with a rotating blade to evacuate the air inside the chamber. Afterwards, **the ion pump** is needed to further maintain the pressure by ionising the existing molecules and deposit them on the surface of the wall. The combination of these pumps will give the ideal pressure to do ARPES measurement.

2. **Sample Manipulator.** In some ARPES stations, the beamline designer may choose to move the sample around a fixed light - detector configuration or choose to rotate the analyser while keeping the sample as fixed. In any case, we need the sample mount that is be able to move in 6-degrees of freedom: 3 translations and 3 rotations. This sample manipulator is also attached with a thermostat to read the temperature of the sample during the experiment. A sample shield can also be added to further reduce the temperature down to 10 K with liquid Helium.
3. **Electron Analyser.** This part is the last component to collect and read the ARPES data. After the electrons are ejected, they will travel across the chamber towards the opening slit of the analyser. With this slit, the analyser is taking the data according to the slice/cut direction along the opening slit. After the slit, the electrons enter the two concentric hemispheres acting like a hemispherical capacitor that will deflect the electrons to move inside its dome. There is a retarding parameter that will alter the kinetic energy value without altering the overall distribution of the energy. This important parameter called *pass energy* determines which central energy the analyser should read on. This retardation procedure will also enhance the energy reading resolution. The electrons will eventually hit the Multichannel Plate (MCP) at different position according to their kinetic energy and also their entry slit angle. The MCP works as a multiplier before the phosphor screen to be read by the CCD. Thus, in a single experiment cut, we may get the data readout of electron intensity with a particular kinetic energy (E_k) at a certain received angular position (θ). We may collect several cuts by rotating the sample position to

convert them into a 2D dispersion data as discussed in figure [2.5](#).

Topological Nodal Semimetal

A new era in physics has begun when new phases of matter are classified through their topological characteristic without resorting to Landau spontaneous symmetry breaking arguments [1]. This chapter gives a brief background on the properties of the topological material studied throughout the graduate training. The term nodal semimetal itself describes specifically the semimetal whose bandstructures intersect at point/s or line in the reciprocal lattice providing a plethora of exotic characteristics [2]. However, it is necessary to layout a broad background from the earliest topological material to set the proper context of the study.

3.1 Topology and Physics

The study of topology can be traced back to the work of Euler, Gauss, Kelvin, and Tait [41]. All of those are about the study of geometry where certain quantity is preserved under a continuous change of its property. One of Euler's early problem famously called **the bridges of Königsberg** describes if certain configuration of lands and rivers can be connected by the least number of bridges. Euler also worked on the famous topological invariant term called **Euler characteristic** $\chi = V - E + F$, where certain shaped can be grouped according to the number of Vertices (V), Edges (E), and Faces (F). If

the object is smooth, we may create a triangulation on it to show the number of V , E , and F of the object. For example, the Euler characteristic of a sphere is 2, while the Euler characteristic of any polyhedra (cube, tetrahedron, octahedron, etc.) is also 2. It describes that all of these forms belong to the same category according to this topological classification. We may imagine that we can triangulate the sphere and continuously deform the imaginary wires to form any polyhedra shape. Meanwhile, a doughnut belongs to a different topological classification as its Euler characteristic is 0. Consequently, deforming the imaginary wires from triangulating the torus or doughnut will not give us any sphere or polyhedra. However, we may deform it into circle, regular strip, Möbius strip, or Klein bottle as they have characteristic of 0 too. We may guess that this characteristic is closely related to the available holes in the object as further described in the Gauss-Bonnet theorem. This theorem states that

$$\chi = \frac{1}{2\pi} \int_S K dA \quad (3.1)$$

where K the Gaussian curvature is integrated over a given surface A . If it is a closed surface, the Gauss-Bonnet theorem will reproduce the Euler characteristic with simplicity $\chi = 2 - 2g$ where g is the genus or the number of holes on the object.

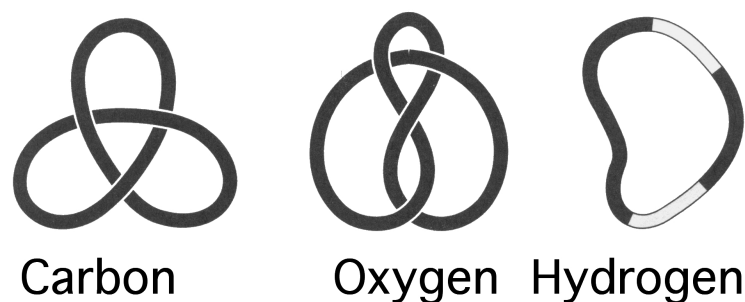


Figure 3.1: Theory of knots by Lord Kelvin and Peter Tait attempted to describe atom in terms of knots. Figure adapted from [42].

The known unsuccessful attempt to link chemistry/physics and topology came from the

work of Lord Kelvin and Peter Tait. After the classification of atoms into a periodic table, they (especially Tait) attempted to make a table of all possible knots and hoped to find the connection between their table and the known periodic table of atoms [41]. Although this idea may sound ludicrous nowadays, it was a daring attempt from them which eventually opened up a new branch of mathematics called **theory of knot**. The first successful work to describe physics phenomenon with topology came from the work of Kosterlitz and David J. Thouless where they described a phase transition with topological defect [43, 44]. Afterwards, we also have the famous work by Thouless, Kohmoto, Nightingale, and den Nijs (TKNN, 1982) where they successfully described the quantum Hall effect (QHE) or integer quantum Hall effect (IQHE) from the perspective of topological phase transition [45]. In 1983, Duncan Haldane also used concept in topology to his theory of spin chain [46, 47]. Most importantly, in his 1988 work, Haldane expanded the possibility of a QHE phenomenon without any external magnetic field which nowadays is called quantum anomalous Hall effect (QAHE) [48]. It should be noted that the theoretical prediction of QHE has been made earlier by T. Ando and Y. Uemura in 1974 (without resorting to topological explanation) [49], which was experimentally realised in 1980 by von Klitzing using high magnetic field on 2D semiconductor [50]. Thus, these breakthrough works describing topological phase transition by TKNN and Haldane was not well celebrated until the discovery of quantum spin Hall insulator called 2D topological insulator [51], 3D topological insulator [52–54], and other topological materials [55–59] about 30 years later. Kosterlitz, Thouless, and Haldane eventually shared their 2016 Nobel prize in Physics after their finding brought forth a new challenging branch in condensed matter called topological materials that holds many promises for future technology such as spintronics [60] and topological qubits for topological quantum computer [61, 62].

3.2 Berry Phase

Describing topological property in a material can be started from the idea of Berry phase. In introductory quantum mechanics course, we usually ignore the phase related to time evolution in our wavefunction called dynamical phase factor (we only care about the magnitude squared of our wavefunction). However, in 1984, Berry published a paper about another phase factor which arises from a cyclic evolution of the system under adiabatic condition that cannot be ignored [63]. This phase has a real contribution in physical system considering systems with different paths. In this section, we will visit this concept briefly to establish the idea of Berry phase and curvature that will be useful in further discussion of topological materials.

We may start by considering a simple system with two levels of energy which can be generalised into a solid state system with Bloch function. Consider a time dependent Hamiltonian

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H}(t) |\psi(t)\rangle \quad (3.2)$$

In adiabatic system, we assume that the Hamiltonian is changing slowly with time. In this manner, the system will have enough time to respond to the change. At each particular time, we may assume that the system always has a set of well-defined eigenstates and eigenenergies. For example, we may expand or shrink the width of an infinite square well system adiabatically and on each time, it has a well-defined eigenstates/energies. Lastly, if a particle starts at a certain energy level n , it will stay at that energy level during the adiabatic process with a certain probability to shift to another level.

In our two-level case, we may assume that the system has two eigenstates called $|\alpha(t)\rangle$ and $|\beta(t)\rangle$ that are dependent on time t , with eigenenergies $\varepsilon_\alpha(t)$ and $\varepsilon_\beta(t)$ accordingly. Let's start with the system to be at a particular state

$$|\psi(t)\rangle = a(t) |\alpha(t)\rangle + b(t) |\beta(t)\rangle \quad (3.3)$$

with both the eigenstates and the coefficient in front of them dependent on time. Following the Schrödinger equation, we may get that

$$\begin{aligned} i\hbar \left(\frac{\partial a(t)}{\partial t} |\alpha(t)\rangle + a(t) \frac{\partial}{\partial t} |\alpha(t)\rangle + \frac{\partial b(t)}{\partial t} |\beta(t)\rangle + b(t) \frac{\partial}{\partial t} |\beta(t)\rangle \right) \\ = a(t) \varepsilon_\alpha(t) |\alpha(t)\rangle + b(t) \varepsilon_\beta(t) |\beta(t)\rangle. \end{aligned} \quad (3.4)$$

If we take the inner product with $\langle \alpha(t) |$, we may get

$$i\hbar \left(\frac{\partial a(t)}{\partial t} + a(t) \langle \alpha(t) | \frac{\partial}{\partial t} |\alpha(t)\rangle + b(t) \langle \alpha(t) | \frac{\partial}{\partial t} |\beta(t)\rangle \right) = a(t) \varepsilon_\alpha(t). \quad (3.5)$$

We may get similar expression by doing inner product with $\langle \beta(t) |$. By a little rearrangement, we may express the equation as

$$\left(\frac{\partial}{\partial t} + \frac{i}{\hbar} \varepsilon_\alpha(t) \right) a(t) = -a(t) \langle \alpha(t) | \frac{\partial}{\partial t} |\alpha(t)\rangle - b(t) \langle \alpha(t) | \frac{\partial}{\partial t} |\beta(t)\rangle. \quad (3.6)$$

If we have non-changing eigenstates, the right-hand side can be taken as zero, and thus we get the usual expression

$$a(t) = a(0) e^{-\frac{i}{\hbar} \int_0^t \varepsilon_\alpha(t) dt} = a(0) e^{-i\phi} \quad (3.7)$$

where the ϕ is related to the dynamical phase.

However, returning to equation [3.6](#), we may investigate the situation when the starting wavefunction is at $|\alpha(t)\rangle$ and let the system evolve accordingly. Within first order approximation, we should include the first term in the right-hand side of equation [3.6](#) and neglect the second term. The result is

$$a(t) = a(0) e^{-\frac{i}{\hbar} \int_0^t \varepsilon_\alpha(t) dt} e^{i \int_0^t \langle \alpha(t) | \frac{\partial}{\partial t} |\alpha(t)\rangle dt} = a(0) e^{-i\phi} e^{i\gamma} \quad (3.8)$$

where we call the $\int_0^t \langle \alpha(t) | i \frac{\partial}{\partial t} | \alpha(t) \rangle dt = \gamma$ as **Berry phase** and this phase depends on which path we take as the system evolves.

This can be seen if we parametrise the t with a multi-dimensional variables (say three dimensional momentum space for a crystal structure) called $\vec{R}(t)$, we may re-write the Berry phase as

$$\gamma = \int \langle \alpha(\vec{R}) | i \nabla_{\vec{R}} | \alpha(\vec{R}) \rangle \cdot d\vec{R} = \int \vec{A} \cdot d\vec{R} \quad (3.9)$$

where we have defined **Berry connection** $\vec{A}$ which is **analogous to Vector Potential** of a magnetic field. Then, if we do a cyclic movement in circuit C where $\vec{R}(0) = \vec{R}(t)$, the Berry phase is expressed as

$$\gamma = \oint_C \vec{A} \cdot d\vec{R} = \iint_{\vec{S}} \nabla \times \vec{A} \cdot d\vec{S} \quad (3.10)$$

where we have used Stoke's theorem to relate the closed line integral with an integral on an area $\vec{S}$. We can see the analogous expression to the magnetic field vector potential by relating **Berry curvature** $\vec{\Omega} = \nabla \times \vec{A}$ to the magnetic field $\vec{B}$. It should be noted also that the Berry phase calculation expression can be generalised into any states that we have in the system.

3.3 Chern Insulator

3.3.1 Integer Quantum Hall Effect

The form of the equation [3.10](#) is similar to what Gauss used to define his topological characterisation in equation [3.1](#). In fact, this idea of Berry curvature is used to define if a certain two-dimensional material is trivial or non-trivial Chern insulator. This property was used to differentiate between trivial insulator and a QHE in the work of TKNN [45]. The topological classification is done by calculating the first Chern number defined as

$$c_1 = \frac{1}{2\pi} \iint_{BZ} \vec{\Omega} \cdot d^2\vec{k} \quad (3.11)$$

where we integrate the top-most filled band (in the form of Bloch eigenstate) over the Brillouin Zone (BZ) [64]. TKNN found out that the expression of the Chern number is related to the Hall conductivity by

$$\sigma_{xy} = c_1 \frac{e^2}{h}. \quad (3.12)$$

We can see that trivial Chern insulator has c_1 value of 0 describing the situation where normal insulating phase occurs. Increasing the magnetic field, we start to see the Landau levels appearing. In the first Landau level, the σ_{xy} is quantised as $1 \times \frac{e^2}{h}$ describing a situation of insulating bulk in the middle yet with a chiral conducting edge states. As we increase the magnetic field further, we may reach another Landau level with different quantisation of σ_{xy} . Although the physical appearances are similar (insulating bulk and conducting edge), different Landau levels are categorised differently according to the topological classification/Chern number. We may imagine as if different Landau levels represent different physical objects with different number of holes/genus on it.

3.3.2 Haldane's Model

The work in QHE/IQHE above was expanded further by the work of Haldane with his proposal of realising the conducting edge state without requiring any high magnetic field (thus, without Landau level) [48]. His work involves a honeycomb lattice like graphene but with different hopping parameter from site a to b thus breaking inversion symmetry. Afterwards, he introduced segmented magnetic fluxes (to lift up the time reversal symmetry/invariant (TRI)) within one unit cell with vanishing sum (see figure 3.2). These fluxes replace the need of external magnetic field to create the QHE effect.

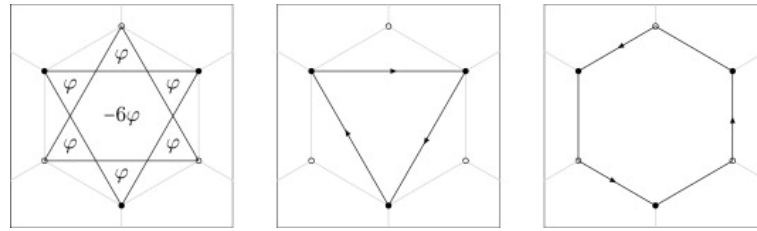


Figure 3.2: The Haldane's model is a 2D model like graphene but with a different atom on each site *black* and *white*. He introduced segmented small fluxes as shown on the left with net flux of zero. These fluxes lift up the time reversal invariant and replace the need of external magnetic field to realise QHE. The hopping parameter of nearest neighbour and next nearest neighbour are different breaking the inversion symmetry. Figure adapted from [64].

3.4 Topological Insulator

Topological Insulator (TI) is a phase of insulator where the surface has a protected gapless conducting state while the bulk is fully gapped [1, 54, 65]. The development of it starts with Mele and Kane in 2005 who published an article called quantum spin Hall effect (QSHE) in graphene [66]. They expanded Haldane's idea by replacing the need of flux with a Spin Orbit Coupling (SOC) within the material itself (thus keeping the time reversal (TR) symmetry intact) [66]. The first realisation of this QSHE material or 2D TI is from the suggestion of Bernevig et.al. on HgTe quantum well system [67] and confirmed by the work from König et.al. [51]. Afterwards, the discovery of 3D TI also followed promptly by the works of Chen, Hasan, and others [1, 52–54, 68].

The result of this strong SOC interaction in 2D material is a fully gapped bulk and a two conducting edge channels like in QAHE. These two channels are distinct for each current carries spin-polarised electrons while the opposite current carries the spin-flipped version of the it (see figure 3.4) and thus called as quantum spin Hall effect. These two channels form a Dirac crossing that is protected with TR symmetry ensuring the topological nature of it.

3.4.1 Band Inversion in Topological Insulator

Before we go into the topological classification of it, we may introduce an intuitive picture on how to differentiate between the topologically trivial or non-trivial insulator (Normal insulator (NI) or TI). It should be noted that both NI and TI have a gapped bulk, and both may have conducting surface states too. However, the difference between them is in the position of the bands forming the bandgap. When the bands are formed, they retain some characteristic related to orbital composing them. If it has an inversion symmetry, we may even talk about the parity of the bands forming the gap. In either case, the bands' orbital characteristic is flipped in TI case as compared to the NI (see figure 3.3).

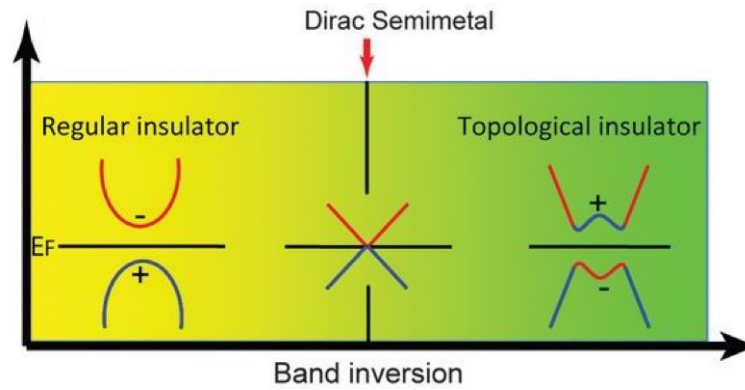


Figure 3.3: The configuration of TI bandgap has a flipped band configuration as compared to the NI. This can be done in by tuning the SOC of the material until the bandgap closes thus creating a Dirac semimetal and eventually flipped over. Figure adapted from [69].

We may introduce this swapping in band orbital by tuning the sample continuously such as changing the width of the quantum well in HgTe, 2D case [51] or changing the stoichiometry of the sample like in $\text{Bi}_{1-x}\text{Se}_x$, 3D case [68]. In either case, the act of tuning changes the topological property of the material.

The consequence of this band inversion in TI is that the bands should be re-flipped again at the surface to maintain the continuity of band topology towards the vacuum [1]. This

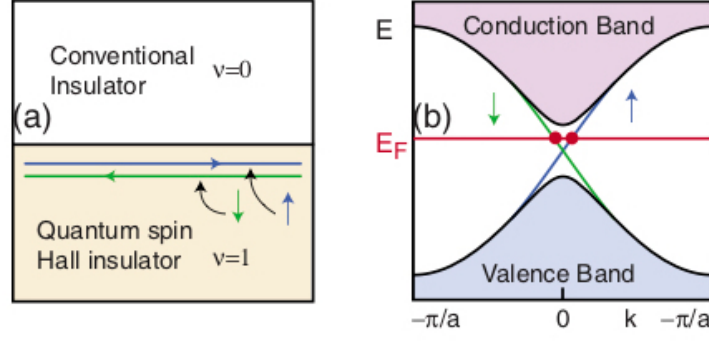


Figure 3.4: (a) Edge states of Mele-Kane insulator can host spin polarised currents with direction of currents are tied with the direction of spin (opposite current host opposite electron spin). (b) Bandstructure of such insulator host a metallic edge that is protected due to time-reversal invariant (TRI) symmetry. The Dirac crossing is robust and can only be undone by breaking either the TRI or I symmetry. Figure adapted from [1].

effect demands a band-crossing on the surface that is protected due to this topological configuration. Thus, the surface/edge of TI possess the special protected metallic surface which can conduct electricity although the bulk is fully gapped (see figure 3.4).

3.4.2 Z_2 Invariant

The topological invariant related to the TI system is called Z_2 invariant as introduced in the subsequent paper from Kane in the reference [70]. There are also other mathematical formulations of Z_2 which lead to the same conclusion by Moore and Balents [71], Qi, Hughes, and Zhang [72], and others. Detailed discussion on the derivation can be read further from the work of Ando in reference [73]. In short, Z_2 invariant can only take either value 0 (trivial) or 1 (non-trivial/topological) and is defined in the following way. Define a TR operator $\mathcal{T}$ which will make $\mathcal{T} \hat{H}(\vec{k}) \mathcal{T}^{-1} = \hat{H}(-\vec{k})$. For a spin- $\frac{1}{2}$ electron, $\mathcal{T}^2 = -1$ as you get a -1 factor after flipping the electron spin by 360 degrees. Similar like TKNN calculation, we take the occupied Bloch state $|u_m(\vec{k})\rangle$ label m and define a matrix $w_{mn}(\vec{k}) = \langle u_m(\vec{k}) | \mathcal{T} | u_n(-\vec{k}) \rangle$. Note that there are 4 points of time

reversal invariant momentum (TRIM) in 2D that will make $\vec{k} = -\vec{k}$ (8 points in 3D case). The Z_2 invariant called ν is defined as

$$(-1)^\nu = \prod_{a=1}^4 \delta_a \quad (3.13)$$

where

$$\delta_a = \frac{\text{Pf}[w(\Lambda_a)]}{\sqrt{\text{Det}[w(\Lambda_a)]}}, \quad (3.14)$$

Pf is pfaffian, and Λ_a is the TRIM- a momentum position. The value of ν can only be 0 or 1 indicating the trivial/non-trivial phase.

Z_2 Invariant with Inversion Symmetry

A short-cut can be used to calculate the Z_2 invariant **if the system has inversion symmetry** by using the parity of the Bloch states. We may define the parity eigenvalue at TRIM $\zeta_m(\Lambda_a) = \pm 1$ and re-define the δ_a as

$$\delta_a = \prod_m \zeta_m(\Lambda_a). \quad (3.15)$$

For a 3D case, we get Z_2 invariant calculated from 8 TRIM points as

$$(-1)^\nu = \prod_{a=1}^8 \delta_a = \prod_{a=1}^8 \prod_m \zeta_m(\Lambda_a). \quad (3.16)$$

It is called as the **strong topological invariant** since we have other three **weak topological invariants** defined as [74]

$$(-1)^{\nu_k} = \prod_{n_k=1; n_j \neq k=0,1} \delta_{i=(n_1, n_2, n_3)} \quad (3.17)$$

where $\nu_k = \nu_1, \nu_2, \nu_3$ and n_1, n_2, n_3 represents which surface we are looking. The equation [3.17](#) basically says that to calculate the weak indices, we first need a well-defined

surface (describing which ν_k), then we multiply the four δ_i s available on that surface, and lastly get the value of ν_k accordingly.

In practice, the TI indices for 3D material are written as

$$(\nu; \nu_1, \nu_2, \nu_3) \quad (3.18)$$

where $\nu = 1$ means a strong topological insulator regardless of what the other indices are. If this happens, the material is fully gapped in the bulk and it will host spin-polarised currents on all surfaces whose bandstructure is a Dirac cone. The existence of the Dirac cone (in 2D or 3D case) can be understood from the requirement of the symmetry as follows:

1. The $\mathcal{T}$ will ensure the existence of two eigenstates called Kramer's pair. This can be proved by contradiction. If a time reversal invariant Hamiltonian only has non-degenerate eigenstate called $|\phi\rangle$ such that $\hat{H}|\phi\rangle = \varepsilon_\phi|\phi\rangle$, acting the $\mathcal{T}$ on the eigenstate will give $\mathcal{T}|\phi\rangle = e^{i\alpha}|\phi\rangle$ where α is some phase obtained. Acting the $\mathcal{T}$ twice will give us $\mathcal{T}^2|\phi\rangle = \mathcal{T}e^{i\alpha}|\phi\rangle = e^{-i\alpha}\mathcal{T}|\phi\rangle = e^{-i\alpha}e^{i\alpha}|\phi\rangle = 1$. This contradicts with the fact that $\mathcal{T}^2 = -1$. Therefore, $\mathcal{T}|\phi\rangle = |\theta\rangle$ where $|\theta\rangle$ is a different eigenstate of the Hamiltonian where both $|\phi\rangle$ and $|\theta\rangle$ are called Kramer's pair. It should be noted that they may or may not form a degenerate point depending on their location.
2. In a crystal structure, the operator $\mathcal{T}$ will transfer Bloch state $|\phi_{m,\vec{k},\sigma}\rangle$ into its Kramer's pair $|\phi_{m,-\vec{k},-\sigma}\rangle$. If the surface Hamiltonian also neglects the spin e.g. no SOC, the $|\phi_{m,\vec{k},\sigma}\rangle$ will share the same energy with $|\phi_{m,\vec{k},-\sigma}\rangle$ making the band degenerate. From here, we see that $|\phi_{m,\vec{k}}\rangle$ and $|\phi_{m,-\vec{k}}\rangle$ are doubly degenerate Kramer's pair. However, since SOC is turned on in TI surface, this condition will lift up this spin-up spin-down degeneracy on the surface.
3. However, there are special points at TRIM, at $\vec{k} = 0$ or at BZ boundary TRIM,

where $\mathcal{T}$ will transfer the band into its own copy, yet a distinct eigenstate. This will ensure that at those high symmetry TRIM points, we will have a Dirac crossing by the surface states involved.

4. There are two possibilities of these Kramer's pair connection at the TRIMs, either they cross pair-wise or they cross by swapping pairs as shown in figure 3.5. The Z_2 topology in the bulk will ensure the Kramer's pair will swap pair at the surface's TRIM i.e. the Fermi level will always cut the surface states odd times, as compared to even times like in NI. It is clear that the surface state of NI can be pushed around such that the the Fermi level does not cut any surface state. Meanwhile, the TI surface state will always have at least one surface state cut by the Fermi level no matter how we distort the configuration of the states. Thus, this Dirac cone is robust against perturbation and cannot be gapped unless the TRI is broken.

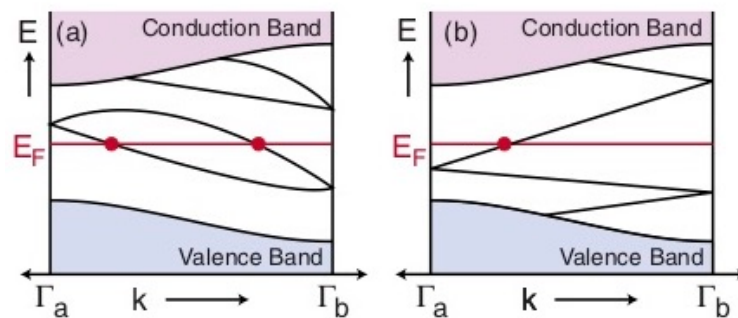


Figure 3.5: Time reversal invariant ensures that there are two bands called Kramer's pair sharing the same energy. However, at TRIM those pair coincide creating a protected crossing. (a) display the connection of Kramer's pair on the surface of trivial insulator/normal insulator. In principle, we may push around the surface state so that our Fermi level does not cut any surface state (thus not conducting). (b) displays the swapping Kramer's pair connection in topological insulator. This setting ensures that the Fermi level will always cut a surface state at least once (and odd number afterwards) thus creating a metallic state on the surface that cannot be destroyed. Figure adapted from [1].

However, if the $\nu = 0$, we may still get a weak topological insulator if either one of the weak indices is 1. Trivial insulator is only when all of the indices are 0. To connect this with our previous understanding, the weak topological insulator can be seen as a stacking of several layers of 2D material with QSHE. There may be conducting surface following the original conducting edge and no conducting surface on the side whose index is 0. However, this surface states on surface with weak index 1 are not robust against localisation or disorder, thus the name is weak indices [74].

Z_2 Invariant without Inversion Symmetry

In a system without inversion symmetry, there is no parity of band to calculate Z_2 invariant with. However, the Z_2 invariant can still be calculated by introducing the Wannier center evolution along real space position e.g. z position along the layer direction as a function of the high symmetry line e.g. $(k_x, k_y, k_z) = (0, k_y, 0), (k_x, 0, 0)$, etc [75–77]. Afterwards, we calculate how many times the Wannier centres cross an reference line. If the Wannier centres do not cross the line or cross it even times, that plane has trivial Z_2 number. However, if the Wannier centres cross the line odd times, there are non-trivial Z_2 invariant along the high symmetry line. As the consequence, a non-trivial surface state is expected to cut through the perpendicular momentum axis from the line e.g. non-trivial Z_2 invariant at line $(k_x, k_y, k_z) = (0, k_y, 0)$ demands a non-trivial surface state crossing the k_y axis.

This concept of Z_2 invariant is proven to be powerful to classify phase of matter; it even has its own routine package for physicist to use called Z_2 -pack [77]. As long as the material has a local gap with band inversion occuring, a Z_2 invariant can be calculated to determine the topology of the particular gap. In fact, the material itself may not be an insulator and even be a semimetal like in LaBi [78] and XIrTe_4 , $\text{X} = \text{Ta, Nb}$ (will be discussed later), but they have a non-trivial Z_2 invariant at the band inversion and also host the exotic Dirac crossing surface/edge states.

3.5 Topological Weyl and Dirac Semimetal

Weyl/Dirac semimetal is a semimetal that possesses bulk band crossing/s whose low energy Hamiltonian follows the equation of Weyl/Dirac i.e. linear dispersion relation within the vicinity of the point [79–82]. In 1928, P.A.M. Dirac successfully combined special relativity and quantum mechanics in his famous Dirac equation which have shed the light to uncover anti-particle matter. His equation is written as shown below

$$i\hbar \frac{\partial}{\partial t} \psi = (c\vec{\alpha} \cdot \vec{p} + \beta mc^2) \psi \quad (3.19)$$

where c is speed of light, $\vec{\alpha}$ and β are 4×4 matrices, $\vec{p}$ and m are the particle momentum and rest mass. One possible solution to describe movement of electrons in free space can be written as

$$i\hbar \frac{\partial}{\partial t} \psi = \left(c\vec{\sigma} \cdot \vec{p} + \begin{pmatrix} I & 0 \\ 0 & I \end{pmatrix} mc^2 \right) \psi \quad (3.20)$$

where $\vec{\sigma}$ is the Pauli matrices and I is the 2×2 identity matrix. It is clear that the equation naturally requires the wavefunction to have four components which are interpreted as spin-up and spin-down for each of the particle and its anti-particle. For a massless system, the equation reduces into a particle with linear dispersion relation as

$$i\hbar \frac{\partial}{\partial t} \psi = \begin{pmatrix} 0 & c\vec{\sigma} \cdot \vec{p} \\ c\vec{\sigma} \cdot \vec{p} & 0 \end{pmatrix} \psi \quad (3.21)$$

In this form, the equation can be decoupled into 2×2 to give the Weyl equation as below

$$i\hbar \frac{\partial}{\partial t} \chi_{\pm} = \pm c\vec{\sigma} \cdot \vec{p} \chi_{\pm} \quad (3.22)$$

where $\chi_{\pm}$ is the 2×1 wavefunction with different chirality describing the Weyl particle which is still elusive until the writing of this thesis.

3.5.1 Weyl/Dirac Equation Counterpart in Material

In condensed matter physics, we may get the counterpart of massless Weyl/Dirac equation when the Hamiltonian has a similar form as in equation [3.22](#). The band dispersion

will be a linear line/cone within the vicinity of a point called Weyl/Dirac point. Weyl or Dirac points can be differentiated from the number of degenerate bands where Dirac equation requires four eigenstates while Weyl has only two eigenstates [82]. This can be realised by doing an expansion of the Hamiltonian within the vicinity of the band crossing. For example, the low energy Hamiltonian in 2D system may take the form as shown below (Weyl Semimetal)

$$\hat{H}(\vec{k}) = v(k_x\sigma_x + k_y\sigma_y + \lambda\sigma_z) \quad (3.23)$$

which is the modified form of the Weyl/Dirac equation due to the λ term. The eigenenergy of the equation [3.23](#) is given below as

$$E^2 = \lambda^2 + k_x^2 + k_y^2 \quad (3.24)$$

which is a gapped "cone". It will be a pure conical shape when the term λ vanishes. In other words, any interaction involving perpendicular direction z in 2D system will open a gap of the Weyl/Dirac point. Graphene is the famous 2D system to host Dirac points at K and K' point where the points are easily gapped upon introducing impurities on its surface [83]. Thus, this Weyl/Dirac point is not robust and protected like the Dirac cone on the surface of topological insulator.

However, this problem does not exist in 3D material as the form of the Hamiltonian can be written in similar fashion as equation [3.22](#)

$$\hat{H}(\vec{k}) = \sum_{\substack{i=1,2,3 \\ j=0,x,y,z}} v_{ij}k_i\sigma_j \quad (3.25)$$

where $\sigma_0 = I$, $\sigma_{1,2,3}$ are the Pauli matrices, v_{ij} is the Fermi velocity tensor on ij component, and $k_{1,2,3}$ are the crystal momentum component $k_{x,y,z}$. The equation above gives eigenenergy as below

$$E = \sum_{i=1,2,3} v_{i0}k_i \mp \sqrt{(v_{iz}k_i)^2 + (v_{ix}k_i)^2 + (v_{iy}k_i)^2} = T(\vec{k}) \mp U(\vec{k}) \quad (3.26)$$

where the $T(\vec{k})$ is called as the kinetic term and the $U(\vec{k})$ is called as the potential term. If we first ignore the kinetic term, the energy dispersion will be in the shape of 4D gapless cone (E, k_x, k_y, k_z) which cannot be visualised fully in our 3D world. However, projecting the energy E with any 2 momentum components will reveal the conical shape, as found in the 2D case. Furthermore, there is no perturbing term reacting with the momentum component that will open up the Weyl/Dirac point. Any extra term will only change the value of the effective Fermi velocity on each direction. By this explanation, we already get a sense of “topological” protection as found in TI Dirac cone.

Re-introducing the kinetic term $T(\vec{k})$ will introduce a tilt to the cone which will give an interesting dispersion relation (see figure 3.6). Since the upright cone obeys the Lorentz invariance relation ($E^2 - p^2 c^2 = \text{const}$), this tilted cone is said to be Lorentz invariance violating dispersion; this kind of Weyl/Dirac point is also called type-II Weyl-Dirac point (see figure 3.6 c & d) [84].

3.5.2 Topological Classification of Weyl/Dirac Semimetal

The realisation of Weyl/Dirac crossing starts from introducing the band-inversion as mentioned in topological insulator before. However, without turning on the SOC, the crossing band will stay intact creating a (closed) line that we call as **nodal line** (see figure 3.6). After turning on the SOC, the nodal line will be gapped leaving a conduction and a valence band with inverted characteristic similar to the TI (figure 3.6.a). However, given the system with I and TRI symmetry, we may have some Dirac points intact due to the protection from the crystal symmetry. For example, the first two 3D Dirac materials to be found, Cd_3As_2 with space group $I4_1/acd$ [69] and Nb_3Bi with space group $P6_3/mmc$ [59], both have C_4 and C_6 that supports multiple irreducible representation for Dirac points to occur in pair along the ΓZ direction [79] (see figure 3.6.b). While those materials own upright Dirac cone, there are also other material with type-II Dirac cone that has been predicted and confirmed to host the pair of protected Dirac points like

in PtSe₂ [85] and InBi [86]. In spite of their gapless situation, Dirac semimetal topology can still be calculated at their $k_z = 0$, comparing with their $k_z = \pi/c$ or BZ boundary position. For example, the two Dirac points in Cd₃As₂ are non trivial in their mirror Chern number calculation ($n_M = \pm 1$), while the Nb₃Bi, PtSe₂, and InBi's Dirac points are non-trivial in their 2D Z_2 invariant (like in 2D TI) [85–87]. Thus we can see that the topological phase transition occurs from non-trivial at $k_z = 0$ and trivial at $k_z = \pi/c$.

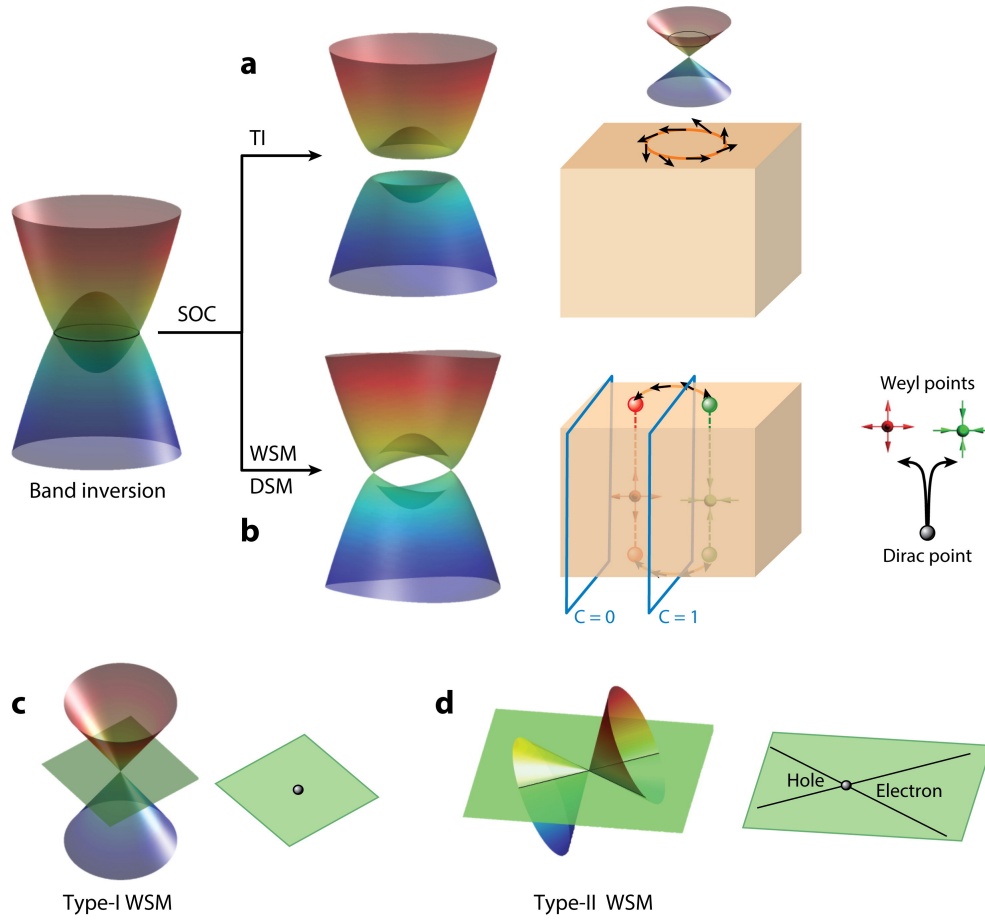


Figure 3.6: (a & b). Certain crystal configuration may force the conduction and the valence band to cross each other creating a band inverted region (most left figure). After turning on the SOC, the degenerate line may be lifted up leaving behind a topological insulator phase. Topological insulator phase has a unique robust Dirac cone on the surface with helical spin as shown. However, due to additional protection from crystal symmetry, some points may be left intact creating a Weyl/Dirac point depending on the degeneracies on the point. Consequently, a unique Fermi arc exists on the surface connecting two points with different monopole charge. Dirac point can be split into two oppositely charged Weyl points by either breaking the inversion symmetry or the time reversal symmetry. (c) Weyl/Dirac point with a vertical cone dispersion called Type-I Weyl/Dirac point. (d) Weyl/Dirac point may disobey Lorentz Invariance rule and exhibit a tilted cone called as Type-II Weyl/Dirac point. Figure adapted from [81].

By breaking either the I or the TRI , the Dirac points formed may be split into two Weyl

points with opposite chirality [56, 58, 88–92]. Furthermore, the Berry curvature $\vec{\Omega} = \nabla \times \vec{A}$ calculation shows that the Weyl points are acting like monopole or source/sink for the Berry curvature. Weyl points with positive chirality act like a source of Berry curvature while the Weyl point with negative chirality acts like a sink. Thus, in the early discovery, Weyl points are called the synthetic magnetic monopole in condensed matter physics (see figure 3.6.b and 3.7) [80]. Furthermore, collapsing opposite Weyl points in BZ may annihilate them preserving the total number of monopole.

The minimum configuration of Weyl semimetal can be realised by breaking the Time reversal invariant with only a pair of Weyl points. This configuration is also the toy model to understand the fundamental interest in Weyl semimetal [93]. Other minimum configuration of Weyl semimetal from breaking the inversion symmetry is to have four Weyl points distributed symmetrically in the BZ. In any configuration, the topological characteristic of Weyl semimetal can be calculated from the Chern number between the Weyl points as shown in figure 3.6.b. It can be seen that between the Weyl points of opposite chirality, the Chern number is non-trivial while the Chern number outside that region is trivial. Thus, we should expect a unique surface states occur in between those Weyl points manifested from the non-trivial topology of the bulk.

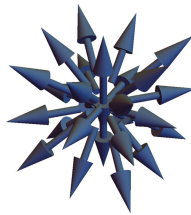


Figure 3.7: Berry curvature around the Weyl point is acting as if the point is a source/sink of it analogous to a magnetic monopole with positive/negative sign indicating the chirality of the point. Figure shown is the Berry curvature from a Weyl point with positive chirality. Figure adapted from [80].

3.5.3 Fermi Arc on Topological Weyl/Dirac Semimetal

Due to the non-trivial topology as discussed previously in 3.5.2, Weyl semimetal hosts a unique surface state called Fermi arc that connects the surface projection of Weyl points with opposite chirality (see figure 3.6.b) [79–82]. The connectivity is in such a way that Weyl semimetal host a chiral edge state on the surface where the topology is non-trivial (similar to IQHE). Thus, opposite surfaces host Fermi arc at different momentum direction, where the combined projection (top and bottom surface) forms a closed loop. With this kind of Fermi arc, Weyl semimetal exhibits a giant anomalous Hall effect that depends on the separation of the Weyl points in the form of $\sigma_{xy} = \frac{e^2}{2\pi h}(k_+ - k_-)$ ($k_{\pm}$ is the positive/negative Weyl points) [82]. Apart from that, Weyl semimetal also shows a Chiral anomaly after applying $\vec{B}$ field perpendicular to it [82]. As can be seen in figure 3.8, the perpendicular $\vec{B}$ forces the electron to move in circular motion following the Lorentz force. However, as the Fermi arc is broken at certain momentum direction, the electrons on one surface cannot form a full circle. The electrons on the opposite surface also experience the same obstacle but in opposite momentum direction. With this constraint, the electrons eventually find a way to form a closed circular motion by tunnelling through the bulk and appear on the opposite surface to complete the full circular orbit (and continue to tunnel back and forth moving in "circular" motion). This creates the chiral anomaly where the moving charges are not "conserved" due to the disappearing, tunnelling, and reappearing processes. In other words, we may say that the Fermi arc in this case acts like the first Landau level with chirality (see figure 3.8).

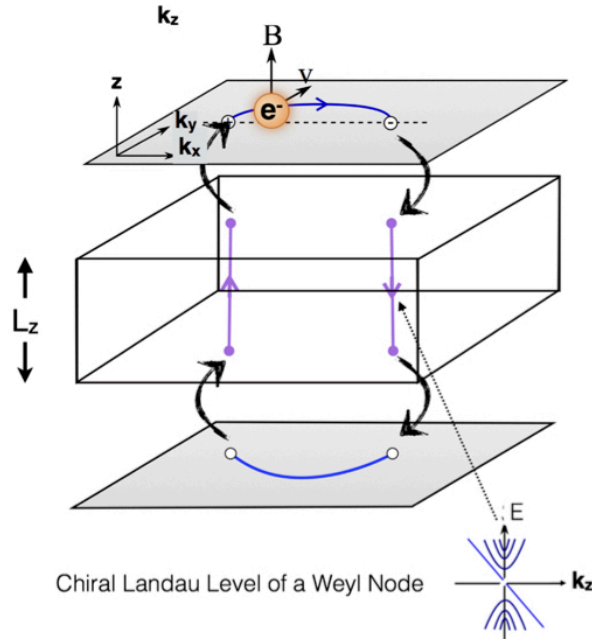


Figure 3.8: Upon introducing perpendicular magnetic field to Weyl semimetal, the electron on the surface moves in circle due to the Lorentz force. However, the broken nature of the arc forbids a full circle of movement of the electron. This situation forces the electron to tunnel through the bulk and appear on the other surface to continue the circular movement. This is called the anomalous chirality phenomena. Figure adapted from [79].

Although Fermi arc is predicted and does appear on the surface of topologically non-trivial Weyl semimetal, its existence does not guarantee the topology of the bulk itself. This is shown in the work Bruno et.al. where they investigated the Fermi arc on WTe_2 [94]. They calculated that the Fermi surface of WTe_2 at temperature where Weyl points exist (non-trivial) versus the higher temperature when they vanish (trivial), show a similar form. In other word, the bands attributed as Fermi arc persist even though there are no more Weyl points in the bulk of WTe_2 . This work indicates that we should exclude all trivial topology scenario in the assignment of the Fermi arc. This is even more important if the distance of Weyl points with opposite chirality is relatively close to each other (easier to annihilate each other).

Fermi arc also appears on the surface of Dirac semimetal although it looks like a closed surface (see figure 3.9). We may imagine that the Dirac point is the result from two Weyl points stabilised to co-exists together [79]. In this scenario, it is natural to expect a combined Fermi arcs forming a closed loop as shown in 3.9. However, upon tuning a perturbation term that respects the symmetry, the Fermi arcs can be detached from the position of Dirac point and form a loop. Although that surface state itself cannot be destroyed by perturbation (topologically protected by the non-triviality of the $k_z = 0$ position), the Fermi arcs are not protected to always connect the Dirac points. This shows that the Fermi arc is of different nature than the Fermi arcs found in Weyl semimetal [57].

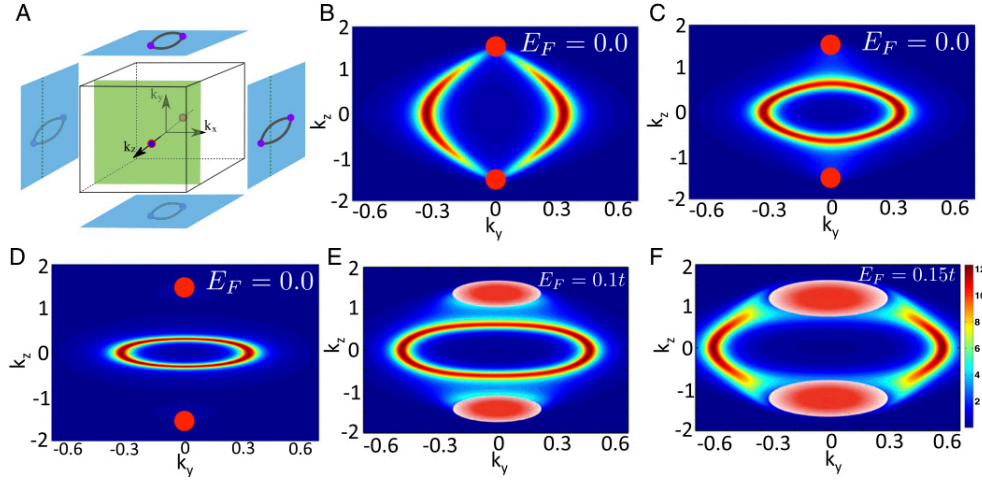


Figure 3.9: (A) Dirac semimetal host a closed loop surface state which is originally called Fermi arc like in Weyl semimetal. Upon tuning the perturbation term that preserves the symmetry (B) - (F), the Fermi arc shape can be detached from the Dirac point position and forms a closed loop as shown in (E). This show that the Fermi arc in Dirac semimetal is of different nature (also not topologically protected) than the Fermi arc in Weyl semimetal. Figure adapted from [57].

3.6 Topological Nodal Line Semimetal

Nodal line semimetal hosts a Weyl/Dirac line crossing forming a continuous line throughout the BZ [86,95,96], a closed loop [97–99], an arc [100], or even a chain of rings [101].

The straightforward model comes from the previous discussion in 3.5.2 where the closed nodal loop is formed by simply inverting the bands before turning on the SOC (see figure 3.6) [99, 102–105]; The line crossing formed can be in the type-I shape or in type-II shape [105]. After turning on the SOC, there are several paths that the system can take as listed in the figure 3.10.

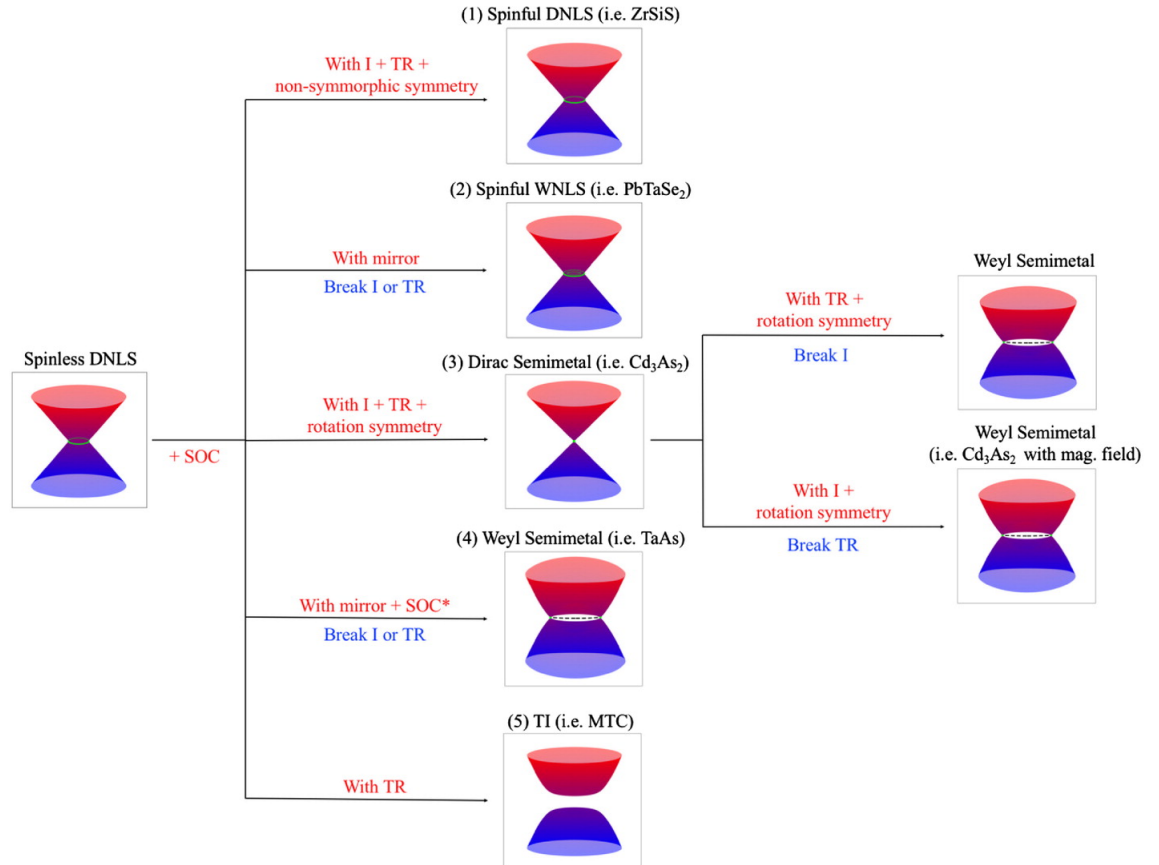


Figure 3.10: After turning on SOC, there are several path the nodal line can evolve. In principle, SOC will gap the nodal line and become TI (case (5)). With certain symmetry imposed, there are Weyl/Dirac points intact at finite points reflecting the symmetry protection (case (3) and (4)). Up to the writing of the thesis, only two kinds of evolutions reported to preserve the nodal line like in case (1) and (2). Case (1) is shown to be trivial in topology while case (2) is reported to be topological although the reported drumhead surface states are not dispersionless. Figure adapted from [102].

3.6.1 Topological Classification of Nodal Line Semimetal

The nodal line itself can be classified topologically in two independent Z_2 invariants called ζ_1 and ζ_2 . The first topological invariant ζ_1 comes from calculating the Berry phase by integrating the Berry connection $\vec{A}$ on the closed loop circling the nodal line (see figure 3.11) as

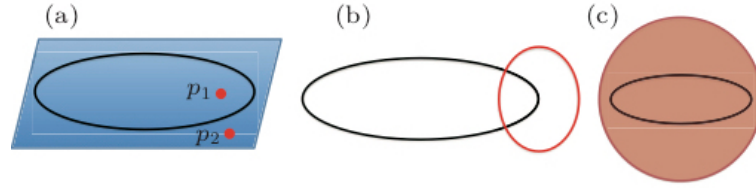


Figure 3.11: (a) The topology of nodal ring can be defined in two different areas: p_1 inside and p_2 outside. (b) To calculate the first topological invariant ζ_1 is by integrating the Berry connection $\vec{A}$ along the closed loop in red circling the nodal loop. (c) The second topological classification of nodal line is by calculating the 2D Z_2 invariant where the Berry connection is calculated on the surface enclosing the nodal ring. Figure adapted from [106].

$$(-1)^{\zeta_1} = \oint d\vec{k} \vec{A}(\vec{k}) \cdot d\vec{k} \quad (3.27)$$

where $\zeta_1 = 0$ means a trivial topology as the nodal line can easily be gapped by small perturbation that respects symmetry, while $\zeta_1 = 1$ is a non-trivial topology that protects the nodal line intact.

The second topological invariant calculation is in principle equivalent to calculating the 2D Z_2 invariant on a spherical surface enclosing the nodal line. If the $\zeta_2 = 0$, although the nodal line is protected in $zeta_1$, this nodal line can disappear by tuning the Hamiltonian adiabatically (thus making it trivial in both invariant classification) [106]. The effective Hamiltonian can be written with equation below

$$H(\vec{k}) = (m - k_x^2 - k_y^2)\sigma_x + k_y\sigma_y, \quad (3.28)$$

where we may tune the parameter m to make the nodal ring ($m > 0$) disappear at $m < 0$ [106].

If the ζ_2 invariant is non-trivial, the nodal ring cannot be destroyed even with adiabatic tuning of the Hamiltonian. The effective Hamiltonian can be written as below

$$H(\vec{k}) = q_x s_x + q_y \tau_y s_y + q_z s_z + m \tau_x s_x, \quad (3.29)$$

where the resulting nodal line is protected by Z_2 invariant and cannot disappear at any number of m [106]. The schematic of topological protection can be seen in figure 3.12.

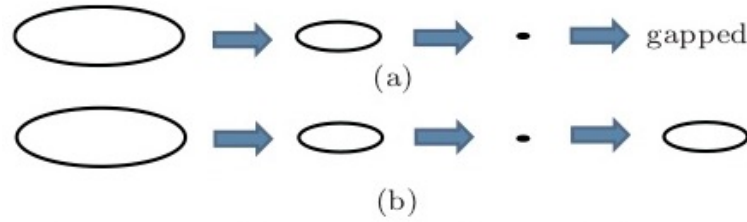


Figure 3.12: (a) Evolution of the ζ_2 trivial nodal ring as we tune the parameter m in equation 3.28. There will be a critical value of m where the nodal line shrinks into a point and will disappear beyond that value. (b) Evolution of the ζ_2 non-trivial nodal ring as a function of m in equation 3.29. The topological protection ensures that the nodal ring exists in any value of m . The critical value of m will only shrink the nodal line into a small loop without vanishing it. Figure adapted from [106].

3.6.2 Drumhead Surface States in Nodal Line Semimetal

The exotic surface states reported for this topological nodal line semimetal is called the drumhead surface state as it covers the surface projection of the nodal ring [99, 100, 107–110]. However, it should be noted that most of the early reports come from a calculation without imposing SOC. Thus, the reported nodal lines are not protected from SOC as it is ubiquitous in real material. Even if the materials have small SOC as

in HfSiS/ZrSiS, ARPES results have shown no drumhead like surface states on $\bar{\Gamma}\bar{X}\bar{M}$ plane indicating that the nodal line may not survive without further crystal protection [95,96,98]. Thus, several attempts has been reported where SOC interaction is included such as in Cu₂Si [109], TlTaSe₂ [108], and Ca₃P₂ [107]. However, there is only one attempt to demonstrate the drumhead surface states by using ARPES in reference [99] up to the writing of this thesis.

Investigation of Nodal Line in Topological Semimetal InBi

This chapter describes the ARPES work in InBi which demonstrates that InBi hosts nodal lines along the XX and the AM line in the Brillouin Zone (BZ). These nodal lines are found to be a topologically trivial yet robust due to protection of non-symmorphic symmetry (glide and screw axis symmetry). Apart from that, InBi also hosts a pair of topologically non-trivial type-II Dirac points along the ΓZ line. The associated Fermi arc connecting these Dirac points are not visible for ARPES on the natural cleavage along (001) direction. The main contributions from the author in this work are in ARPES experiment, analysis, and data presentation, bulk band calculation, and protection arguments from crystal symmetry. The contributions from collaborators involved sample supplies by Sasagawa, et. al. from Tokyo Institute of Technology, ab-initio calculation for surface states by Yan, et. al. from Max Planck Institute. The majority of the works presented here have been published by the author in this reference [86].

4.1 Background Study of InBi

Reader who is interested in the theoretical background for nodal line material should consult chapter 3 for details.

The quest for discovering and confirming new topological phases of matter has been started since the finding of topological insulator (TI) state in Bi_2Se_3 [111] and Bi_2Te_3 [52]. Afterwards, various kinds of topological materials have been discovered following TI such as topological Dirac semimetal (Nb_3Bi [59], Cd_3As_2 [69], ZrTe_5 [112], etc.), topological Weyl semimetal (TaAs [58], NbAs [90], MoTe_2 [91, 92], WTe_2 [94], etc.) and topological nodal line semimetal (Cu_3PdN [113], PbTaSe_2 [99], Ca_3P_2 [107], $\text{ZrSiS}/\text{HfSiS}$ [95], etc). All these materials host a special nodal points/line (see figure 4.1) which may bring interesting phenomena, such as unusually high carrier mobility [114], giant diamagnetism [115], etc.

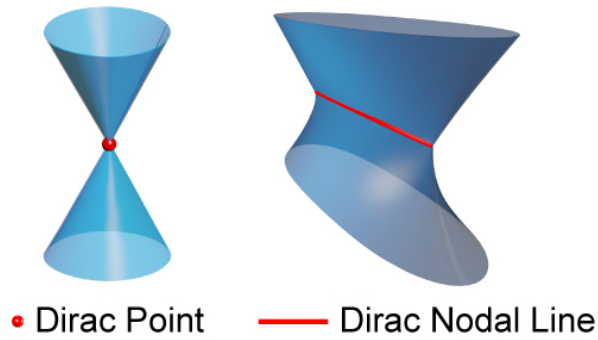


Figure 4.1: Nodal point is a Weyl/Dirac point where the bandstructure disperses linearly within the vicinity of the point (left panel). Meanwhile, the nodal line is when that point is extended into a line (right panel).

The background of InBi study in this thesis started from realising that both Indium and Bismuth are heavy elements with strong spin-orbit coupling (SOC) [116]. With strong SOC, there is a higher possibility for it to host inverted band gap which causes a different

topology in the band. Meanwhile, a less complex material (binary compound) is desirable as a gateway to understand the vast field of topological materials. Furthermore, a flat layered material is an excellent practice ground to harness the experimental skill in ARPES for the author. Thus, one of the available layered binary compounds with relatively heavy elements and a simple tetragonal structure called Indium Bismuth (InBi) was chosen.

4.2 Crystal Structure of InBi

The crystal structure of InBi has been known to be a simple tetragonal structure similar to PbO structure [117–121]. This structure is different from other Indium-V family which has a zinc blend crystal structure [122–124]). Our single crystal XRD (supernova) results in figure 4.2 confirm that the InBi crystal structure has $P4/nmm$ (129) space group with lattice constants $a = b = 5.014 \pm 0.002 \text{ \AA}$ and $c = 4.784 \pm 0.003 \text{ \AA}$. InBi is also a relatively flat layered sample excellent for ARPES measurement, as shown in figure 4.2

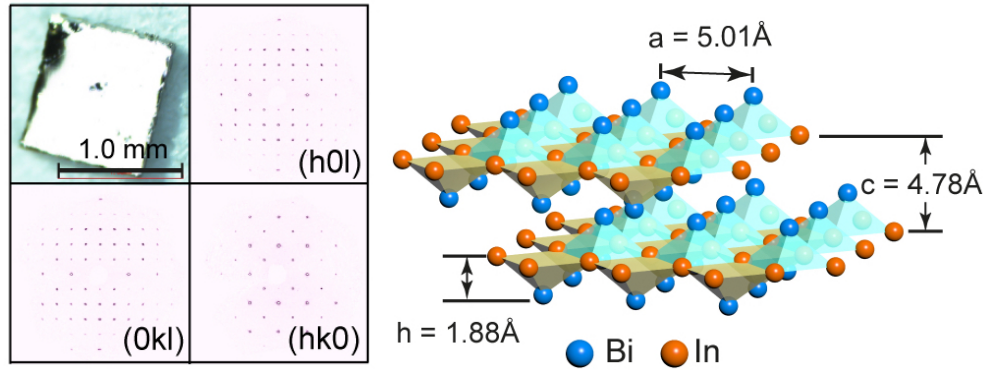


Figure 4.2: Photo of InBi sample (top left panel) shows a relatively flat surface excellent for ARPES measurement. Unwarped XRD patterns on three main surface projections of InBi are shown (h0l), (0kl), (hk0). The observed Bragg peaks agree with the known value of InBi crystal structure ($P4/nmm$ space group) and lattice constants ($a = b = 5.014 \pm 0.002 \text{ \AA}$ and $c = 4.784 \pm 0.003 \text{ \AA}$). Right panel shows crystal structure of InBi with $P4/nmm$ space group

The crystal structure of InBi can be seen in right panel of figure 4.2 to show that the $P4/nmm$ hosts both glide plane and screw axis symmetry which will be shown in section 4.3 to be responsible for protecting the nodal line in any $P4/nmm$ structures. As shown in figure 4.2, the crystal has a layered structure with natural cleaving plane along the [001] direction due to its relatively weak bonding between the sublayer of Bismuth [125].

4.3 Non-Symmorphic Symmetry Protection on Nodal Line

Within the $P4/nmm$ space group, there are two non-symmorphic symmetries protecting the degeneracies of Dirac nodal line, which are glide symmetry and screw axis symmetry (also assuming time reversal symmetry). In 3D BZ as shown in figure 4.3, without SOC, there are several nodal lines observed as shown in figure 4.4. The nodal lines lie on the red plane are protected by C_{2v} symmetry as discussed in reference [126]. It is found that these nodal lines are not protected under SOC as the crossings are made of two bands with different irreducible representation and may hybridise with SOC lifting the degeneracy. Several ARPES attempts have confirmed the corresponding energy splitting and showed that there is no drumhead surface states inside the loop along (001) direction made by this red nodal line; even in materials with small SOC such as in ZrSiS/HfSiS [95, 96, 126]. Afterwards, there are also nodal lines found and marked with green plane in figure 4.4 along the MXRA plane. Without SOC, this nodal plane is also protected by C_{2v} symmetry [102]. After turning on the SOC, only the XRX and the AMA nodal lines survive as they are protected further by the non-symmorphic symmetry, as discussed in reference [127, 128]. The pictorial explanation of this protection has been discussed by Yang, et. al. in [102]. In the following, we will consider the protection explanation from the symmetry operator point of view. The spinless case for each symmetry will be discussed and followed by the case including spin to see the effect on SOC for each nodal lines.

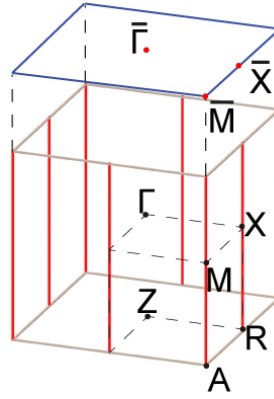


Figure 4.3: Brillouin zone of simple tetragonal structure, $P4/nmm$ space group with projected surface Brillouin zone along the (001) direction. The solid red lines along XX and AA indicate the protected nodal line due to the non-symmorphic symmetry.

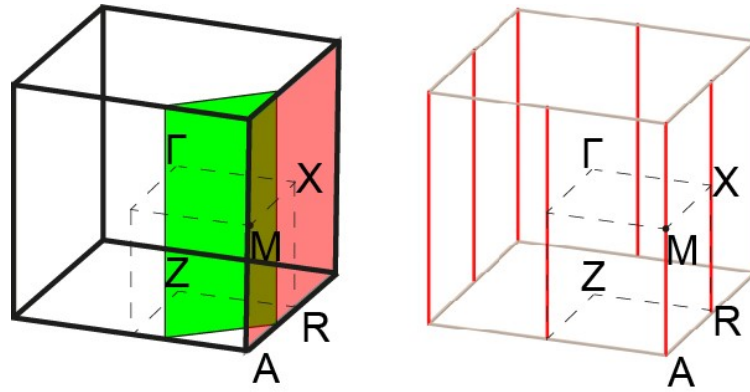


Figure 4.4: Before SOC, there are plane of nodal line found as indicated by the green and red plane both protected by C_{2v} symmetry. However, after SOC is turned on, only the nodal lines along XX and AA remain as they are further protected by the non-symmorphic symmetry (glide plane and screw axis).

4.3.1 Glide Symmetry

First protection come from the glide symmetry with xy plane as glide mirror which can be expressed with the operator below

$$G; (x, y, z, t) \rightarrow (x + 1/2, y + 1/2, -z, t). \quad (4.1)$$

Define a new composite operator with inversion symmetry I called Θ_G where

$$\Theta_G = I * G; (x, y, z, t) \rightarrow (-x - 1/2, -y - 1/2, z, t) \quad (4.2)$$

which will transfer momentum

$$(k_x, k_y, k_z) \rightarrow (-k_x, -k_y, k_z). \quad (4.3)$$

Thus, the operator Θ_G has invariant momentum at RXR, AMA, and ZTZ line. Afterwards, it should be noted that applying Θ_G twice is invariant as

$$\Theta_G^2 = (I * G)^2; (x, y, z, t) \rightarrow (x, y, z, t) \quad (4.4)$$

so $\Theta_G = \pm 1$ where the eigenstates will be called $|\phi_{\Theta_G}^{\pm}(\vec{k})\rangle$.

Afterwards, we will define an operator that has invariant momentum everywhere from composite of I and time reversal invariant T as

$$\Theta_T = I * T; (x, y, z, t) \rightarrow (-x, -y, -z, -t) \quad (4.5)$$

which will transfer $(k_x, k_y, k_z) \rightarrow (k_x, k_y, k_z)$ to itself.

The next step is to examine the effect of Θ_T on the eigenstates of Θ_G . To do this, we investigate the composite operator below

$$\Theta_T \Theta_G; (x, y, z, t) \rightarrow (x + 1/2, y + 1/2, -z, -t) \quad (4.6)$$

$$\Theta_G \Theta_T; (x, y, z, t) \rightarrow (x - 1/2, y - 1/2, -z, -t) \quad (4.7)$$

and realise that

$$\Theta_G \Theta_T |\phi_{\Theta_G}^{\pm}(\vec{k})\rangle = e^{-ik_x a - ik_y b} \Theta_T \Theta_G |\phi_{\Theta_G}^{\pm}(\vec{k})\rangle = \pm e^{-ik_x a - ik_y b} \Theta_T |\phi_{\Theta_G}^{\pm}(\vec{k})\rangle. \quad (4.8)$$

The expression above describes that at certain momentum $-k_x a - k_y b = \pm\pi$, the operator Θ_T switches the label of eigenstates of Θ_G to have

$$\Theta_G \Theta_T \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle = \mp \Theta_T \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle. \quad (4.9)$$

Combining the fact of equation 4.9 and equation 4.3, we have come to conclusion that Θ_G guarantees a degenerate line at XRX position.

However, this may not be so in the case with SOC. If the SOC is turned on, the first thing to realise is that $\Theta_G^2 = -1$ as we flip the spin of electron twice. Therefore, the eigenvalue of $\Theta_G = \pm i$. In this case, we can show that equation 4.9 will be

$$\begin{aligned} \Theta_G \Theta_T \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle &= -\Theta_T (\pm i) \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle \\ &= \pm i \Theta_T \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle \end{aligned} \quad (4.10)$$

where we have used the relation $Ti = -iT$. Equation 4.10 shows that after turning on the SOC, the Θ_T only relates the eigenstate with same label. However, there is symmetry M_{xy} which should have been taken into consideration that will fix this issue in SOC calculation. Before that, we need to confirm that M_{xy} will not disturb the result from the calculation without-SOC. We can start by showing that

$$\Theta_T \Theta_G M_{xy}; (x, y, z, t) \rightarrow (y + 1/2, x + 1/2, -z, -t) \quad (4.11)$$

$$\Theta_G \Theta_T M_{xy}; (x, y, z, t) \rightarrow (y - 1/2, x - 1/2, -z, -t). \quad (4.12)$$

Thus, the relation in 4.8 still holds with $\left| \phi_{\Theta_G}^{\pm} (\vec{k}) \right\rangle$ now is written as $M_{xy} \left| \phi_{\Theta_G}^{\pm} (\vec{k}) \right\rangle$. Afterwards, notice that M_{xy} and Θ_G share the same eigenstates if spin is ignored, or $\Theta_G M_{xy} = M_{xy} \Theta_G$.

$$\Theta_G M_{xy}; (x, y, z, t) \rightarrow (-y - 1/2, -x - 1/2, z, t) \quad (4.13)$$

$$M_{xy} \Theta_G; (x, y, z, t) \rightarrow (-y - 1/2, -x - 1/2, z, t). \quad (4.14)$$

Hence, we can safely write

$$\begin{aligned} \Theta_G \Theta_T M_{xy} \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle &= -\Theta_T \Theta_G M_{xy} \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle \\ &= \mp \Theta_T M_{xy} \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle \end{aligned} \quad (4.15)$$

which shows that the Θ_T still relates the eigenstate of Θ_G with opposite label at XRX line in no-SOC case.

Now, after turning on SOC, realise that M_{xy} anticommutes with Θ_G which will fix the equation [4.10](#) as

$$\begin{aligned} \Theta_G \Theta_T M_{xy} \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle &= -\Theta_T \Theta_G M_{xy} \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle \\ &= \Theta_T M_{xy} \Theta_G \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle \\ &= \mp i \Theta_T M_{xy} \left| \phi_{\Theta_G}^{\pm} (-k_x a - k_y b = \pm\pi) \right\rangle. \end{aligned} \quad (4.16)$$

It is clear that the glide symmetry in $P4/nmm$ guarantees nodal line along the XRX made from eigenstates of glide symmetry in both without and with SOC case.

4.3.2 Screw Axis Symmetry

The second symmetry protection comes from the screw axis symmetry which can be expressed as

$$S_{2x}; (x, y, z, t) \rightarrow (x + 1/2, -y, -z, t). \quad (4.17)$$

Following the similar argument in glide symmetry section [4.3.1](#), we may express a composite operator with inversion symmetry as

$$\Theta_{S_{2x}} = I * S_{2x}; (x, y, z, t) \rightarrow (-x - 1/2, y, z, t) \quad (4.18)$$

which will transfer momentum $(k_x, k_y, k_z) \rightarrow (-k_x, k_y, k_z)$; invariant plane is $k_x = 0, \pm\pi/a$ plane. It can also be shown that $\Theta_{S_{2x}}^2 = 1$ which will give new eigenstates called $|\phi_{\Theta_{S_{2x}}}^{\pm}(\vec{k})\rangle$ with eigenvalue ± 1 . The result of the operator Θ_T acting on these eigenstates is shown below

$$\Theta_T \Theta_{S_{2x}}; (x, y, z, t) \rightarrow (x + 1/2, -y, -z, -t) \quad (4.19)$$

$$\Theta_{S_{2x}} \Theta_T; (x, y, z, t) \rightarrow (x - 1/2, -y, -z, -t) \quad (4.20)$$

$$\Theta_{S_{2x}} \Theta_T |\phi_{\Theta_{S_{2x}}}^{\pm}(\vec{k})\rangle = \pm e^{ik_x a} \Theta_T |\phi_{\Theta_{S_{2x}}}^{\pm}(\vec{k})\rangle \quad (4.21)$$

where at $k_x = \pm\pi/a$ we will get

$$\Theta_{S_{2x}} \Theta_T |\phi_{\Theta_{S_{2x}}}^{\pm}(k_x = \pm\pi/a)\rangle = \mp \Theta_T |\phi_{\Theta_{S_{2x}}}^{\pm}(k_x = \pm\pi/a)\rangle. \quad (4.22)$$

The result confirms that on the plane of MXRA, the operator Θ_T relates the eigenstates of $\Theta_{S_{2x}}$ with opposite label guaranteeing the nodal lines.

However, after the SOC is turned on, this will not be the case as most of the nodal lines on it will be gapped. This can be shown in the following arguments. First, notice that $\Theta_{S_{2x}}^2 = -1$ as we flip the electron spin twice and thus the eigenvalues are $\Theta_{S_{2x}} = \pm i$. Overall, this will make the equation [4.21](#) become

$$\Theta_{S_{2x}} \Theta_T |\phi_{\Theta_{S_{2x}}}^{\pm}(\vec{k})\rangle = \mp i e^{ik_x a} \Theta_T |\phi_{\Theta_{S_{2x}}}^{\pm}(\vec{k})\rangle \quad (4.23)$$

where we have used the fact that $Ti = -iT$. It is clear that at $k_x = \pm\pi/a$, the equation above will be

$$\Theta_{S_{2x}} \Theta_T \left| \phi_{\Theta_{S_{2x}}}^{\pm} (k_x = \pm\pi/a) \right\rangle = \pm i \Theta_T \left| \phi_{\Theta_{S_{2x}}}^{\pm} (k_x = \pm\pi/a) \right\rangle. \quad (4.24)$$

The equation 4.24 describes that the nodal plane has been gapped as Θ_T relates the eigenstates with the same label.

However, we may introduce another symmetry in $P4/nmm$ that may fix the situation in this SOC calculation. In this screw axis section, we introduce the symmetry operator V as shown below

$$V = \mathcal{T}_{0\frac{1}{2}0} M_y; (x, y, z, t) \rightarrow (x, 1/2 - y, z, t) \quad (4.25)$$

which shares the same eigenstates with $\Theta_{S_{2x}}$. The new operator combined with $\Theta_{S_{2x}}$ will make the invariant momentum to be only in XRX, AMA, and Z Γ Z. Afterwards, notice that the operator V anticommutes with $\Theta_{S_{2x}}$ as both of them contain mirror operation. Next, we calculate that

$$\Theta_T \Theta_{S_{2x}} V; (x, y, z, t) \rightarrow (x + 1/2, y - 1/2, -z, -t) \quad (4.26)$$

$$\Theta_{S_{2x}} \Theta_T V; (x, y, z, t) \rightarrow (x - 1/2, y - 1/2, -z, -t) \quad (4.27)$$

and show that after SOC is turned on, the equation 4.23 can be modified as

$$\begin{aligned} \Theta_{S_{2x}} \Theta_T V \left| \phi_{\Theta_{S_{2x}}}^{\pm} (\vec{k}) \right\rangle &= e^{ik_x a} \Theta_T \Theta_{S_{2x}} V \left| \phi_{\Theta_{S_{2x}}}^{\pm} (\vec{k}) \right\rangle \\ &= -e^{ik_x a} \Theta_T V \Theta_{S_{2x}} \left| \phi_{\Theta_{S_{2x}}}^{\pm} (\vec{k}) \right\rangle \\ &= -e^{ik_x a} \Theta_T V (\pm i) \left| \phi_{\Theta_{S_{2x}}}^{\pm} (\vec{k}) \right\rangle \\ &= \pm i e^{ik_x a} \Theta_T V \left| \phi_{\Theta_{S_{2x}}}^{\pm} (\vec{k}) \right\rangle \end{aligned} \quad (4.28)$$

where we have utilised $Ti = -iT$. It is clear that at $k_x = \pi/a$, we can get back

$$\Theta_{S_{2x}} \Theta_T V \left| \phi_{\Theta_{S_{2x}}}^{\pm} (k_x = \pm\pi/a) \right\rangle = \mp i \Theta_T V \left| \phi_{\Theta_{S_{2x}}}^{\pm} (k_x = \pm\pi/a) \right\rangle \quad (4.29)$$

which shows that the Θ_T relates the eigenstate of $\Theta_{S_{2x}}$ of opposite value, and guarantees degeneracy along the XRX and AMA line.

It has been shown that both glide and screw axis symmetry protects the degeneracy along the XRX and AMA line even in the presence of SOC. Both of these nodal lines are considered as topologically trivial within the classification mentioned in chapter 3.6 since the Berry phase calculation around them gives a trivial value [3, 86, 104].

4.4 Band Structure Calculation of InBi

The bulk band reported below was calculated by the author using Wien2k under close supervision of our collaborator. In this section, the feature of the band structure will be discussed such as the nodal line feature in XRX and AMA, and also the type-II topological Dirac point along the $Z\Gamma Z$ line.

4.4.1 Calculated Nodal Line in InBi

The bulk band calculation is shown in figure 4.5 which confirms the existence of nodal points/lines marked with red and green circles in the without-SOC case. These nodal lines are consistent with our discussion before and they are gapped after SOC as predicted. Since Indium and Bismuth are relatively heavy atoms, their SOC is relatively stronger than other reported $P4/nmm$ materials. It can be seen from the gap opened on the previously nodal line marked with green. However, the nodal lines along the XRX and AMA survive as they are further protected by the non-symmorphic symmetry as discussed in section 4.3. Furthermore, since these lines are quadruply degenerated (from calculation), they are called Dirac nodal lines in contrast to Weyl nodal lines with doubly

degenerated lines. We shall call nodal/Dirac interchangeably to the rest of the chapter. A closer look on the orbital characters along the line of interest is shown in figure 4.6 where the nodal lines along the XRX and AMA are made from different bands with different orbital characters.

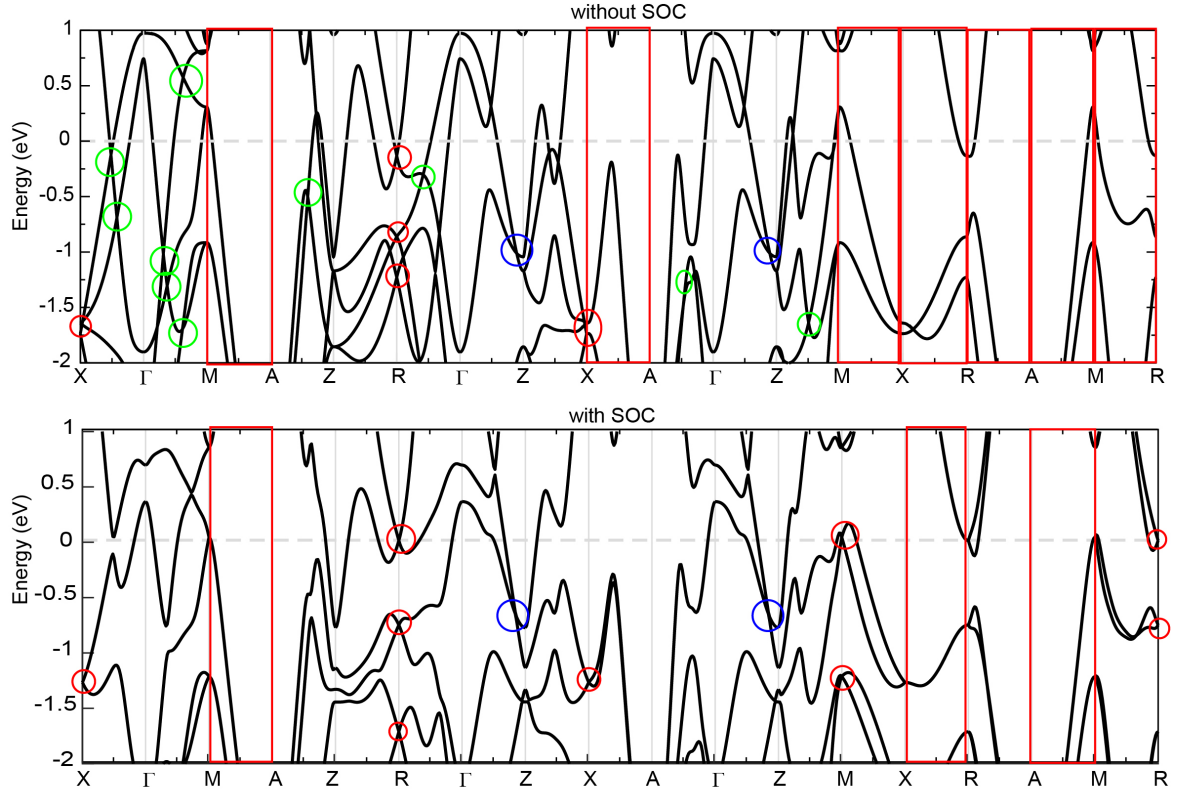


Figure 4.5: Bulk band calculation of InBi without (top panel) and with SOC (bottom panel) show that some nodal lines are gapped after turning on SOC (green colour) while the nodal line along XRX and AMA survive (red colour) as predicted from the non-symmorphic symmetry arguments. There is also a type-II Dirac point along the Z Γ line (blue colour) which is protected after turning on SOC.

4.4.2 Protected Dirac Crossings by C_4 Symmetry

Apart from the nodal line along the XRX and AMA, $P4/nmm$ space group allows the formation of protected Dirac crossing along the high symmetry line Z Γ Z due to the C_4

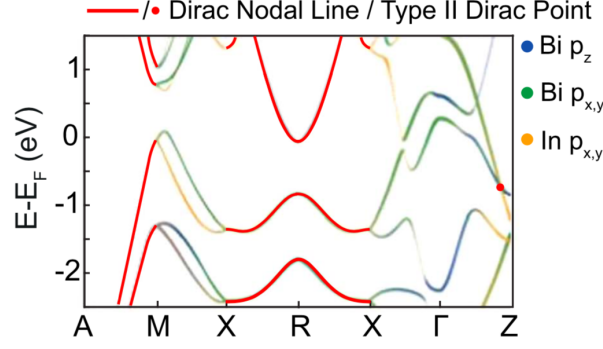


Figure 4.6: Nodal line in XRX and AMA line is formed by bands from different orbital characters and they are protected by the non-symmorphic symmetry. There is a type-II protected Dirac point along the ΓZ line which shows a band inversion between Bi p_z and Bi $p_{x,y}$, In $p_{x,y}$.

symmetry similar to the previously reported topological Dirac semimetal in Cd_3As_2 and Na_3Bi [59, 69] (discussed in chapter 3.5.2). It can be seen in figure 4.6 along the ΓZ line where we have a band inversion crossing between Bi p_z and Bi $p_{x,y}$, In $p_{x,y}$. Our collaborator confirmed further that this crossing has non-trivial topology from the evolution of Wannier charge centres using non-Abelian Berry connection [75, 129]. This protected Dirac crossing also exists in other $P4/nmm$ materials where the tilting of the cone depends on the type of the material. For example, it is reported that $P4/nmm$ material called AMgBi (A=K, Rb, Cs) has a Dirac cone tilted in critical position between type-II and type-I cone [130].

4.4.3 Surface States Calculation of InBi

In this section, the surface states of InBi is simulated by our collaborator using a slab technique calculation with the top layer exposing the Bismuth layer termination along the (001) direction. The detailed technical information is reported in reference [86]. For the purpose of this thesis, it is sufficient to understand the following points:

1. The slab is a semi infinite crystal structure with finite layers along the direction of

cleaving and infinite plane in other direction. For example, this InBi calculation used 36 layers of InBi single layer. As more layer is added to the calculation, the resulting calculation is approximately closer to the bulk calculation.

2. The resulting band structure is the band structure on the projected surface without any information of perpendicular momentum. In our case it will be the projected bandstructure along the $\bar{X}\bar{\Gamma}\bar{M}$ (001) plane.
3. Each band has a projection intensity indicating how many percent of the wavefunction resides on the projected layers. For example, if the bands are calculated and projected onto the first two layers, the intensity indicates how much of the wavefunction resides on these top two layers. This is a good indication if a certain band originates from the surface or more from the bulk. In this InBi work, we used projection onto the first 3 layers of InBi.

4.5 ARPES Measurements of InBi

After the crystal was cleaved inside the ARPES UHV chamber, a flat and shiny (001) surface is exposed for further ARPES measurement. From the core level measurement, the elements of the material is further confirmed to have Indium and Bismuth peaks as shown in figure [4.7](#) revealing the characteristic $4d_{5/2}$ and $4d_{3/2}$ peaks for Indium and $5d_{5/2}$ and $5d_{3/2}$ peaks for Bismuth. Detailed technique on sample growing by our collaborator has been reported in reference [86].

The broad Fermi surface (FS) map was measured to show the square BZ with four-fold symmetry (figure [4.8](#)), confirming the tetragonal crystal structure at (001) cleavage plane, and demonstrating the high quality of the sample and sample surface.

In the following, we systematically display the band structure of InBi and the slab calculation comparison to show the agreement between the measured and calculated band

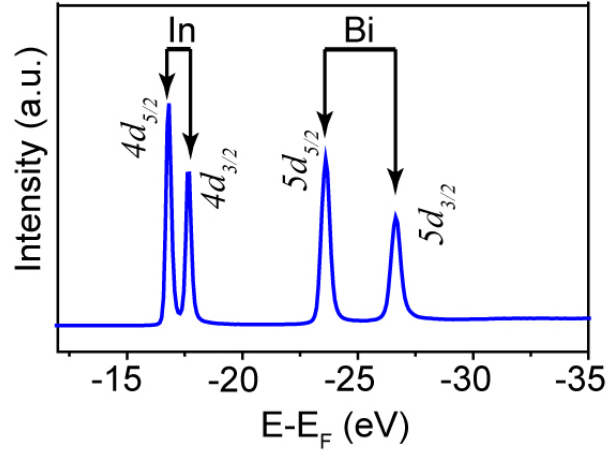


Figure 4.7: Core level data of InBi reveals the characteristic of $4d_{5/2}$ and $4d_{3/2}$ peaks for Indium and $5d_{5/2}$ and $5d_{3/2}$ peaks for Bismuth confirming the elemental composition.

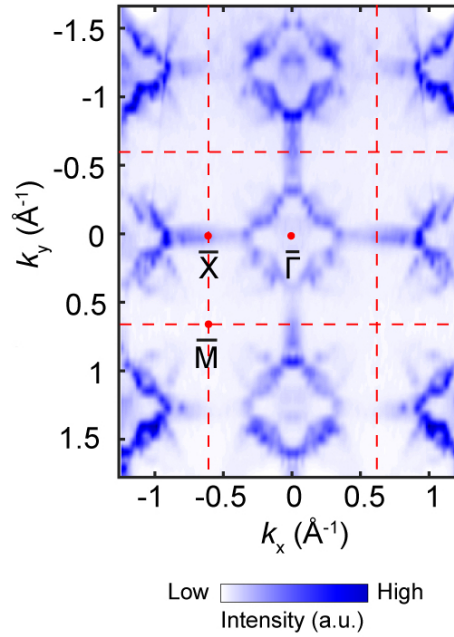


Figure 4.8: Fermi surface map of InBi along the (001) plane. It shows a tetragonal crystal structure demonstrating the high quality of sample surface.

structure. Figure 4.10(a) demonstrates the 3D volume plot of the electronic band structure, showing both the Fermi surface and the band dispersions along high symmetry directions. The result shows more bands than the result from the bulk band calculation

(see the 3D Fermi surface in figure 4.9). This indicates that most of the InBi bands come from the surface. Thus, the slab calculation is performed to investigate both bulk and surface electronic states. The corresponding high symmetry cuts calculations at $\bar{X}\bar{\Gamma}\bar{X}$, $\bar{M}\bar{\Gamma}\bar{M}$, and $\bar{M}\bar{X}\bar{M}$ in figure 4.10 (b), (c) and (d), respectively, show a good agreement with the measured dispersions and supporting that the majority of the photoemission intensity on InBi come from the surface. The seemingly Dirac crossing at $\bar{X}$ around -0.5 eV is not a topological surface states since in principle they can be moved around up or down in energy to leave no state within the energy range. The evolution of constant energy surfaces and several energy levels are shown in figure 4.10 (e) and (f) showing most of the rich features comes not from the surface but more of the projection of several k_z positions. A closer investigation on it reveals that they are the calculated states at $\bar{X}$ around $-0.71 \text{ eV} \sim -1.26 \text{ eV}$. As this range coincides with the position of the nodal line that will be investigated, a higher photon energy is needed to minimise the surface states and resolves more of the bulk nodal line observed in 4.6.

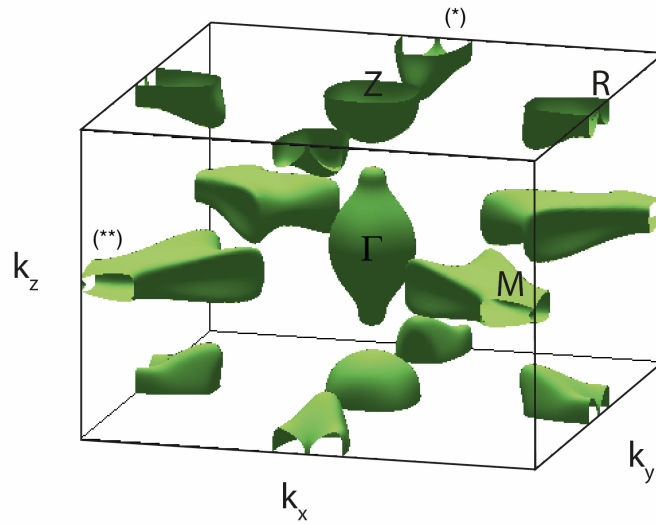


Figure 4.9: Calculated 3D Fermi surface of InBi. The cross/bridge shape (*) lies at Z position while the Γ position has a band like flower petals (**) stretching to the M direction. Both of these features can be seen generally in ARPES measurement.

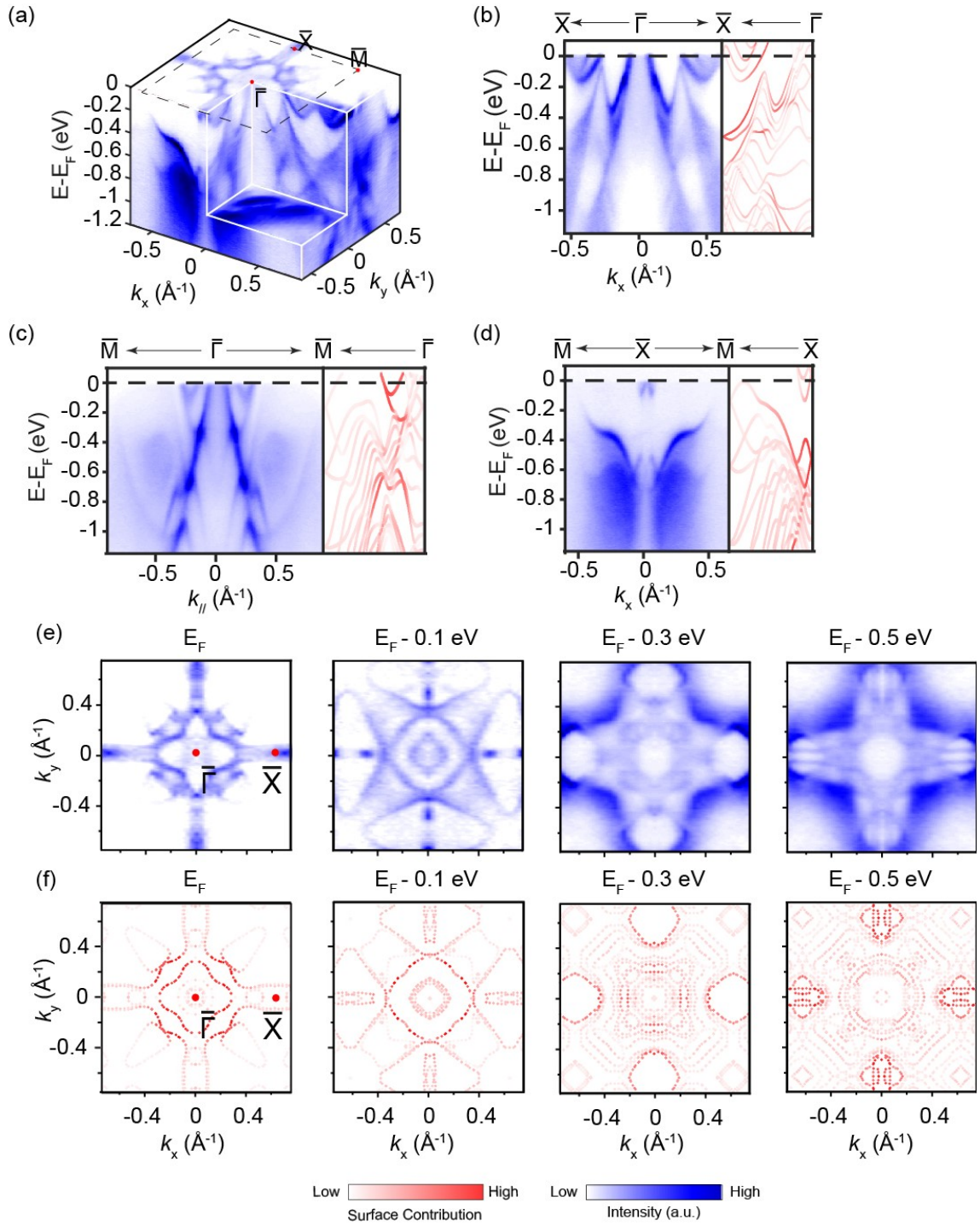


Figure 4.10: (a) General 3D reconstruction of InBi ARPES data at 65 eV photon energy with several high symmetry cuts shown. (b), (c), & (d) High symmetry cut ($\bar{X}\bar{\Gamma}\bar{X}$, $\bar{M}\bar{\Gamma}\bar{M}$, and $\bar{M}\bar{X}\bar{M}$) ARPES data with calculated surface states which agree well. The surface projection strength is indicated from low (white) to high (red). The ARPES intensity strength is indicated from low (white) to high (blue).

Several photon energies are used to further distinguish the bulk bands from the surface. As shown in figure 4.11, several photon energies from 19 eV - 100 eV has been used to map the fermi surface of InBi. From the result, we could always identify a “flower” shape feature near the $\bar{\Gamma}$ point (labeled with SS or surface state) originates mostly from the surface states which is further proved by the *ab-initio* calculations. In addition, some other features on the Fermi surface, including the circle around $\bar{\Gamma}$, the flower petal-like shape towards $\bar{M}$, and the cross/bridge shape along $\bar{\Gamma} - \bar{X}$ (labeled with BS or bulk states) change in the shape and intensity at different photon energies, suggesting their bulk nature. It can be compared with the figure 4.9 that the cross/bridge shape lies on $k_z = \pi/c$ plane while the flower petal-like shape lies on $k_z = 0$ shape.

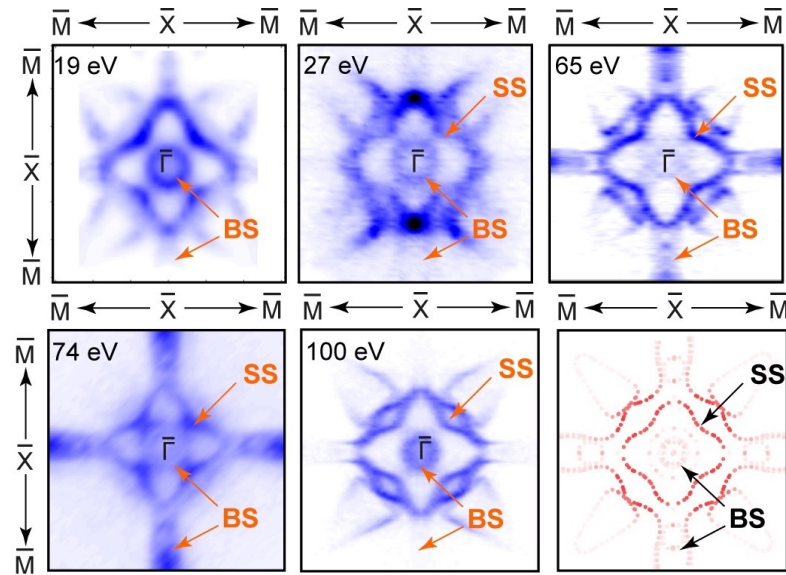


Figure 4.11: Fermi surfaces of InBi at different photon energies to demonstrate the surface states (SS) and the bulk states (BS). The calculated surface states on Fermi surface are also shown for comparison (bottom right panel). It is clear from the ARPES result that the cross/bridge towards X and the flower petal-like feature towards the M vary as photon energy changes indicating their bulk origin (labelled with BS).

4.5.1 k_z -Dependent Measurement on InBi

Photon energy dependent measurements were performed on the $\bar{X}\bar{\Gamma}\bar{X}$ cut to demonstrate the existence of the nodal line along the XX line. Photon energy from 30 eV - 240 eV was used to probe different k_z position and the constant energy surface (plane ΓXRZ) at Fermi energy and binding energy 0.75 eV are shown in figure 4.12. The respective BZ position is shown on the side. From the constant energy maps, we could identify two straight lines in the middle of Γ and X. These two lines come from the “flower” shape in figure 4.11 and the lack of k_z variation proves their surface nature. In contrast, the feature around X (corresponding to the bridge/cross shape in figure 4.11) is dispersive along k_z and agrees nicely with the calculated bulk bands overlaid on top of it in magenta. From the result, we may also see that starting around 100 eV above, the surface contribution is relatively suppressed which can be a good candidate range to demonstrate the existence of nodal line.

4.6 Nodal Line in InBi

The ARPES result from 100 eV is shown in figure 4.13. It can be seen that at this higher mean free path (higher photon energy, see figure 2.2), the surface states are relatively suppressed more and it has better cross section with the bulk [131]. The Energy Distribution Curve (EDC) and the Momentum Distribution Curve (MDC) show clearly the Dirac point at X which lies around 1.30 ± 0.05 eV binding energy. The reconstruction of the Dirac point at X point is also shown in figure 4.13 where the bulk states prediction (in magenta) is nicely overlapped on top of the ARPES data. Then, the equal energy contour was extracted out to demonstrate the point-like feature of Dirac points. The bulk states predictions are placed on top of it where we can clearly observe the existence of SS which is not predicted by the bulk states calculation.

The photon dependent data along the XX line are shown in figure 4.14 to demonstrate

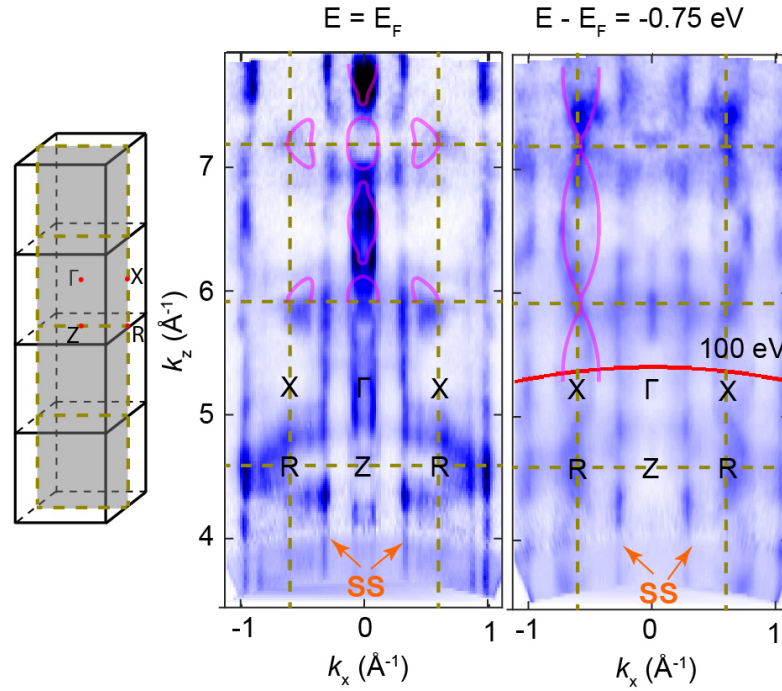


Figure 4.12: Fermi Surface data and constant energy surface at higher binding energy (0.75 eV) along the Γ XRZ plane confirm surface state and bulk state features along k_z direction. The SS features relatively disappear at higher photon energy ($k_z > 5 \text{ \AA}^{-1}$). The calculated BS in magenta are overlapped to indicate the bulk contribution. Photon energy 100 eV which cuts through the X point is indicated.

the nodal line peak evolution along k_z . The experimental dispersion generally agrees with the calculated band but is severely broadened due to the k_z broadening effect as discussed in chapter 2.1.3. To further illustrate the Dirac points evolution, the nodal line nearer to the Fermi level is investigated. This is due to the other broadening effect at higher binding energy nodal line as discussed in section 2.1.1 e.g. nodal line at AMA line reaches up to 2 eV at half BZ.

The cut at several k_z positions (from Γ X Γ to ZRZ) are shown in figure 4.15 with the overlapped calculation results from Γ X Γ to ZRZ is also shown. The cuts demonstrate well the movement of the peak from X position to the R position as further shown by the

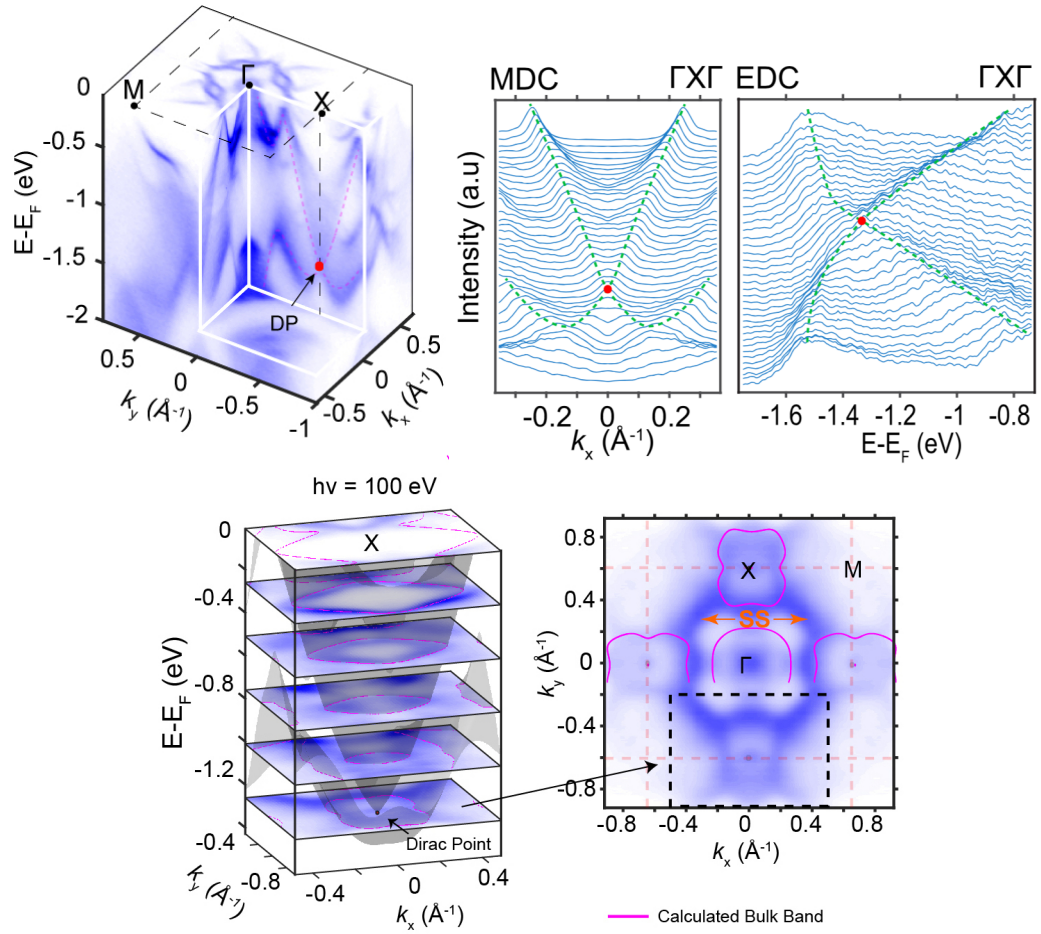


Figure 4.13: (Top left panel) ARPES data from 100 eV measurement shows a Dirac point (DP) on X buried at higher binding energy. (Top right panels) This is further confirmed from the Energy Distribution Curve (EDC) and the Momentum Distribution Curve (MDC) where they show peak of intensity at the Dirac point. (Bottom left panel) A reconstruction of the Dirac point at X from 100 eV ARPES data and calculated BS overlapped to each other. (Bottom right panel) Constant energy surface at the Dirac points position shows clearly the dots and also reveals the surface states as the bulk calculation does not predict it. The 3D data representation shows that the surface states are relatively suppressed at 100 eV although some still survive.

EDC and also the extracted peak in figure 4.15. Apart from that, the cuts also demonstrate that at each photon energy, the data probed comprises several k_z positions from the k_z broadening effect discussed in chapter 2.1.3. From the EDC data, the shoulder

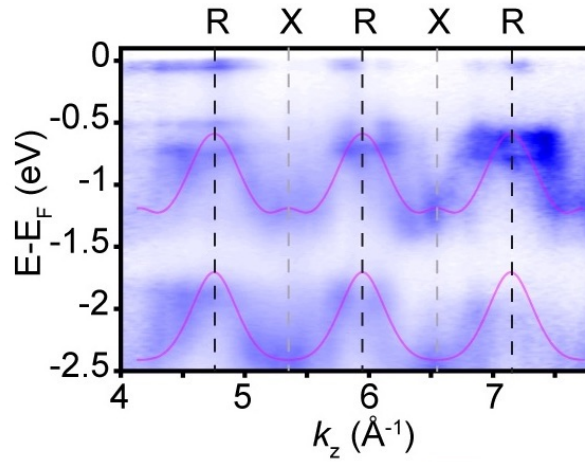


Figure 4.14: k_z measurement along XRX line reveals the dispersion of Dirac nodal line. The nodal line at higher binding energy is severely broadened as inherent effect of ARPES measurement. The nodal line result is also broadened in momentum due to the k_z broadening effect inherent to ARPES. Bulk band calculation in magenta is overlapped to show a good agreement of the nodal line shape.

peak discussed in figure 2.4 is also observed confirming the mixture of spectral weight from other k_z momentum. Within the limitation of ARPES, this data has confirmed the existence of nodal line in XRX and also confirmed the protection of non-symmorphic symmetry in InBi in the presence of strong SOC.

4.6.1 Further comment on InBi k_z Broadening

As discussed in chapter 2.1.3, the result of photon dependent data comes from convoluting the Lorentzian peak from all possible momenta. In the following, the calculated nodal line along the XRX is broadened with artificial Lorentzian and Gaussian functions to simulate the inherent ARPES spectral function and the instrumental error. Afterwards, the resulting simulated ARPES data is convoluted with the Lorentzian broadening from k_z measurement to simulate our ARPES XRX result. In figure 4.16, the comparison shows a fair agreement that the ARPES data is indeed a broadened version of the original

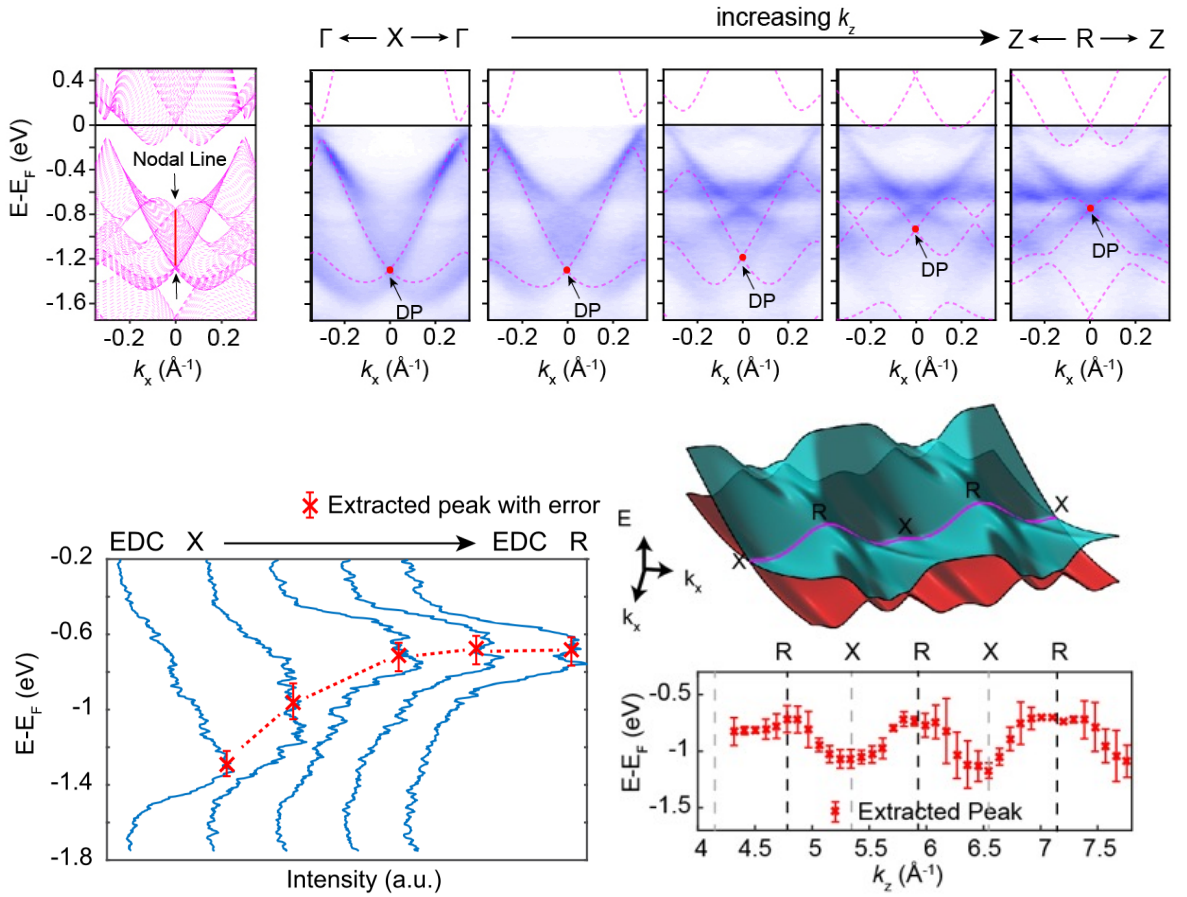


Figure 4.15: (Top panels) Several cuts from X to R positions are shown where the nodal peak movement agrees relatively well with the predicted band structure (top left panel). (Top panels, magenta lines) The overlapped calculated result from X to R is also shown to demonstrate that the resulting cut from ARPES is severely broadened as each cut contains the contribution from several k_z positions. (Bottom left panel) The extracted Dirac peaks along the energy distribution curve (EDC) is shown to further justify the peak movement. (Bottom right panel) The overall peaks from X to R are also extracted with errors indicated. (Bottom right) The reconstructed nodal line from the calculation is also shown for reference.

nodal line shape. The shoulder peak from neighbouring k_z momentum is also observed especially at the position where the dispersion gradient is high. The broadening effect also explains why the lower part of the observed nodal line are relatively flat albeit the little dispersive curve found in the calculation. However, the k_z broadening effect does

not explain the flatness of the upper part of the nodal line, which is attributed to the uncertainty from the k_x momentum.

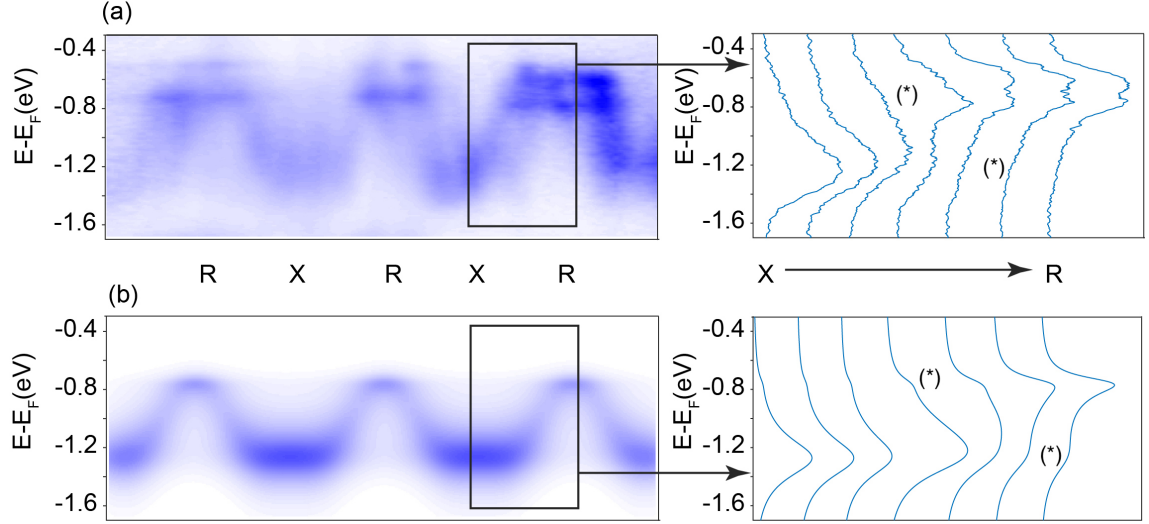


Figure 4.16: The simulated k_z broadening effect along XRX (Bottom panels) agrees fairly with the ARPES data along the XRX cut (Top panels). It also shows the shoulder peak (*) from the neighbouring k_z momentum indicating the broadening effect as mentioned in [\[2.1.3\]](#).

4.7 Type-II Dirac Points in InBi

The ARPES result along the $\Gamma\Gamma Z$ direction is also reported here where the type-II Dirac points are predicted (figure [4.17](#)). With the linear horizontal (LH) polarisation, the resulting data is relatively convoluted with both surface and bulk states burying the shape of the type-II data. Thus, another measurement is carried out with linear vertical (LV) polarisation (90 degree from LH) to suppress some bands. The result shows a fair agreement with the prediction although the Dirac points are not clearly resolved. The author argues the k_z broadening buries the Dirac point especially with the little k_z momentum window of the Dirac point. The reconstruction of the type-II and the constant energy surface at $\Gamma\Gamma ZR$ crossing the Dirac point from the calculation are also shown for reference.

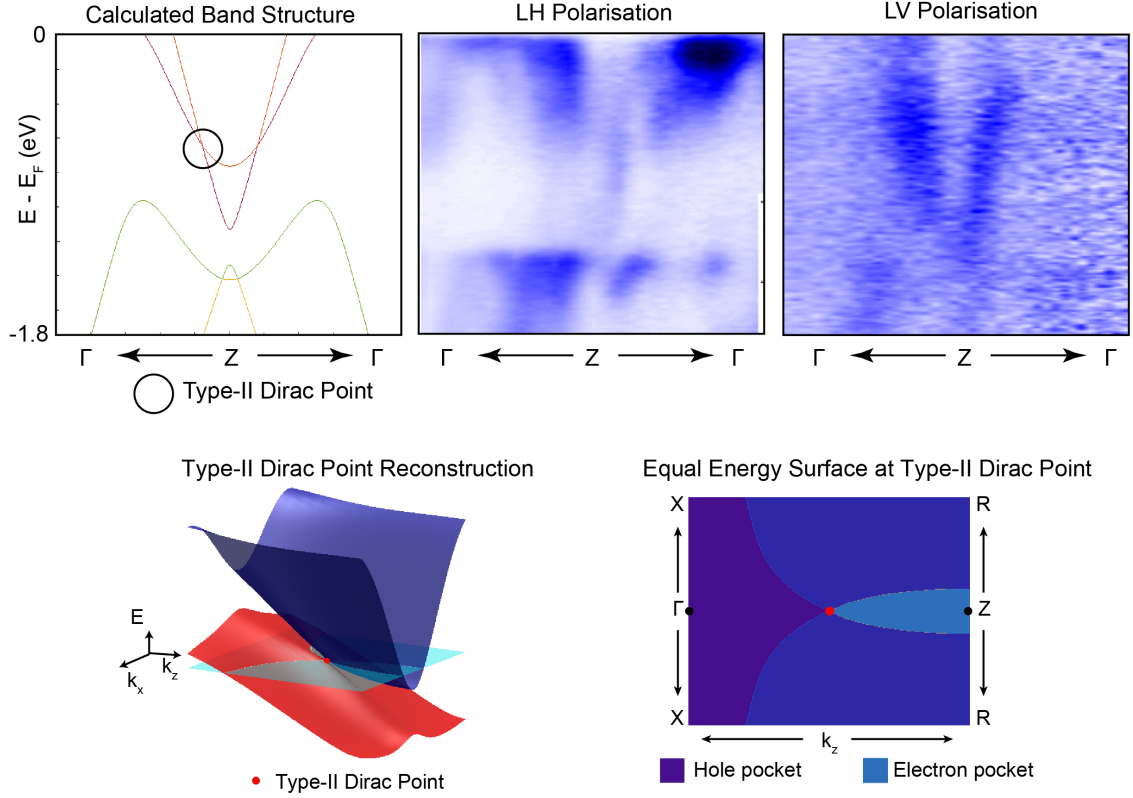


Figure 4.17: (Top middle and right panels) ARPES attempts to show the type-II Dirac point in InBi. The linear horizontal polarisation shows a convoluted signal from surface and bulk bands burying the type-II signal. The linear vertical polarisation is used to suppress those signal resulting in a fair shape agreeing with the shape of the type-II Dirac point (Top left panel) although the point itself is not resolved. The reconstruction of type-II and the constant energy surface are also shown for reference (Bottom panels).

It should be noted that from the (001) surface, our ARPES data does not show the existence of Fermi arc connecting these two Dirac points as they are projected onto the same momentum. Thus, a measurement along the side surface (100)/(010) is needed to confirm this. However, due to the high difficulty in cleaving the side surface, the author has not

succeeded to measure it up to the writing of this thesis. This difficulty can be visualised by a thick pile of paper. It is relatively easy to separate the pile (InBi) paper by paper (layer by layer) as compared to cutting through the side of the pile creating a flat surface.

4.8 Perspectives and Summary

As discussed in section 4.3, the protection arguments do not assume any atomic composition. In fact, two $P4/nmm$ nodal line materials have been reported in semimetal ZrSiS/HfSiS [95] and even semiconductor $\text{Bi}_2\text{O}_2\text{Se}$ [132]. However, none of the known $P4/nmm$ samples host the nodal line near to the Fermi surface. This greatly hinders the further study, e.g. transport measurement, to investigate the effect of this nodal line. Thus, other $P4/nmm$ candidate with nodal line near the Fermi level is highly desirable. The same argument also applies to the type-II Dirac crossing that its effect on physical measurement can be tested if it lies somewhere near the Fermi level.

In summary, this chapter shows the existence of nodal line in InBi which sits on the XRX line in momentum space. With strong SOC in InBi, the persistence of this nodal line demonstrates the robust protection from the non-symmorphic symmetry of the crystal structure. Our ARPES data also shows a signature of type-II Dirac point, as predicted from the calculation.

Investigation of Minimum Topological Weyl Semimetal NbIrTe₄ with Inversion Symmetry Breaking

This chapter describes the work in topological Weyl semimetal NbIrTe₄ where it demonstrates that NbIrTe₄ hosts a type-II Weyl points (WPs). It also shows that as inversion symmetry is broken, the atomic configuration of NbIrTe₄ allows the minimum number of WPs, which is four points. ARPES data from NbIrTe₄ also shows that it has the exotic Fermi arc with different connectivity between the top surface and the bottom surface. Furthermore, we demonstrate that the connectivity of the Fermi arc may change due to hybridisation with the bulk band, as shown from the bottom surface. The main contributions from the author in this work are the ARPES experiment, analysis, and data presentation. The contributions from collaborators involved sample supplies by Sasagawa, et. al. from Tokyo Institute of Technology, ab-initio calculation for surface states by Yan, et. al. from Max Planck Institute.

5.1 Background Study of NbIrTe₄

Topological Weyl semimetal (TWS) is an intriguing topological material which harbors composite massless Weyl fermions [2, 82, 84]. According to the “no-go theorem” [133], WPs always appear in pairs of opposite chirality [2, 58, 82, 134] which act like the source and sink of Berry curvature [135]. Thus, in the early days of its discovery, these type of materials are given a buzz-name “synthetic magnetic monopole” material for its analogous mathematical expression [80, 135]. Apart from the Weyl crossing of opposite chirality, another exotic feature about this material is the broken surface state called Fermi arc (FA) whose projection connects the WPs of opposite chirality. The term surface arc (SA) and Fermi arc (FA) will be used interchangeably in this thesis to describe this arc and its evolution at any energy level (Weyl point energy, Fermi level, and other). These special electronic structures correlate to various interesting transport properties, including birefringence [136], anomalous Hall effect [137], high carrier mobility [138], giant magnetoresistance [139], negative magnetoresistance [140, 141], oscillating quantum spin Hall effect [142], etc.

This TWS was just widely investigated during the start of this NbIrTe₄ study within the material with inversion breaking symmetry. In this framework, the minimum number of Weyl points allowed are four points where the Weyl points pair have their own time reversal counterpart. However, most of the early studied materials such as in (Ta, Nb)(As, P) [4, 134], (W, Mo)Te₂ [91, 92, 143–146], LaAlGe [147], and XAuTe (X = Na, K, Rb) [148] harbour more than four WPs with short arc. Thus, it is of fundamental interest to find the Weyl semimetal with minimum number of Weyl points and long Fermi arc to understand the exotic properties deeper. This minimum Weyl semimetal can also unravel the property of the Fermi arc as different surface conditions may alter its connectivity, as reported in the reference [149] while overall maintaining the surface chiral velocity [150].

The ternary transition metal chalcogenides MM'Te₄ (M=Nb/Ta, M'=Ir/Rh) are good candidates for this study, as reported in the work of Liu et al. [151]. Their predecessors such as WTe₂ and MoTe₂ have also been shown to have fewer number of Weyl points with detectable Fermi arcs. Furthermore, they all are in layered form making it more desirable for device studies. Especially for MM'Te₄, their ternary nature allows tuning the chemical potential (e.g. to reach the WPs energy) via changing the stoichiometry feasible [52, 152, 153].

Similar to the predecessors, MM'Te₄ have been proposed to host type-II Weyl crossing while their single layer form is predicted to be a quantum spin Hall insulator (see figure 5.1) [151].

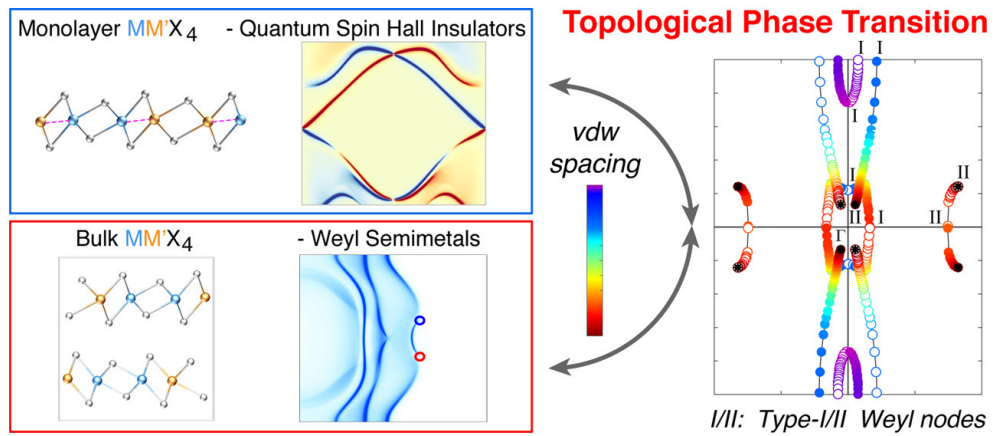


Figure 5.1: (Left panels) MM'Te₄ monolayer is predicted as quantum spin Hall insulator while the bulk phase host Weyl points. Depending on the van der Waals spacing, the WPs may be generated and separated further as shown on right panel. Figure adapted from [151].

Focusing on the bulk variations, one member of them, which is the NbIrTe₄, is predicted to host only four WPs sitting at the same energy at $k_z = 0$ (see figure 5.2) [151].

However, other report contradicts this value with 16 WPs reported [154]. The TaIrTe₄ result of Liu et al. with 8 WPs (see figure 5.28) is also in direct conflict with the work of Koepnick et al. [155] which claims that TaIrTe₄ has 4 WPs. A follow up ARPES

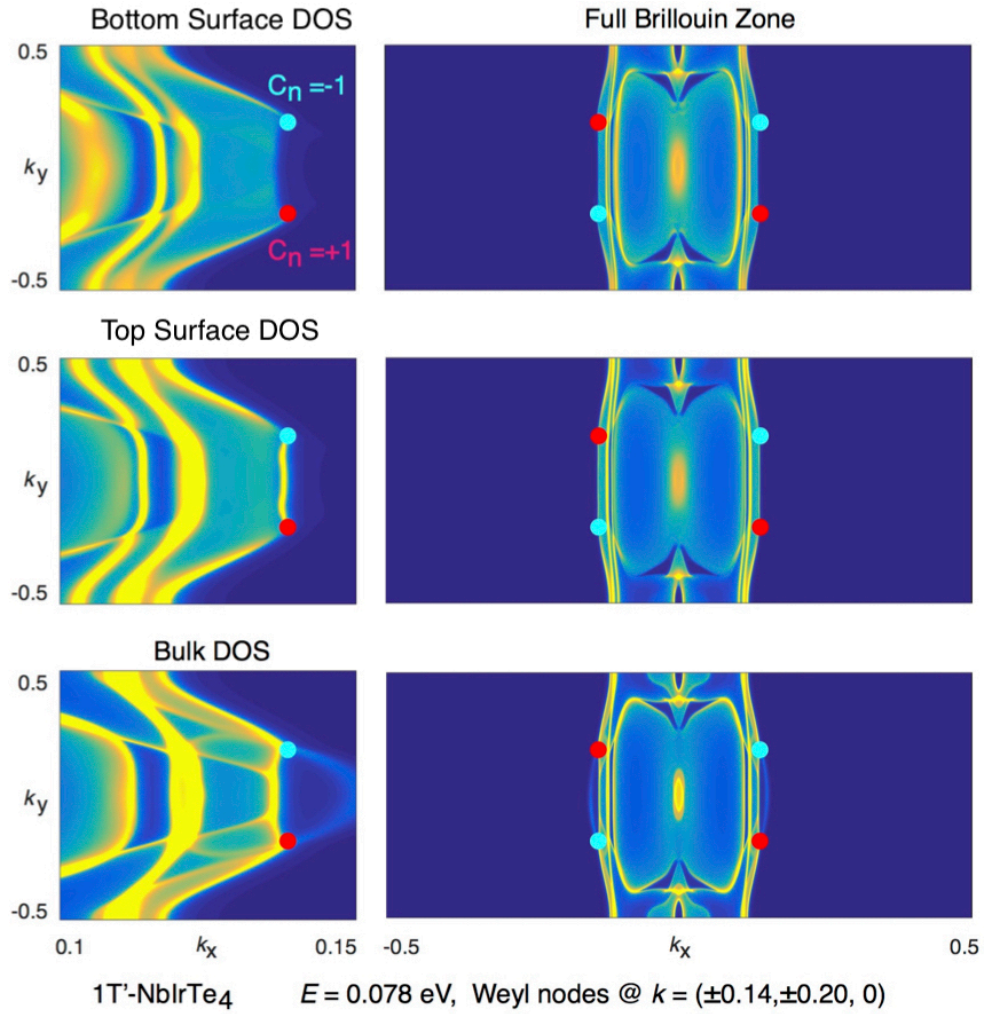


Figure 5.2: NbIrTe₄ is predicted to only host 4 WPs. Surface DOS for both surfaces are shown to display the Fermi arcs. The straight line along k_y on the top is assigned as Fermi arc since it does not exist on bottom surface and it connects the WPs position. While the bottom surface Fermi arc is assigned to the band extending out to outer BZ along k_y direction. Figure adapted from [151].

work on Koepernik's work by Haubold et. al. in reference [156] is also not conclusive to support that TaIrTe₄ only has 4 WPs as they have found the arc corresponding to the WPs in figure 5.3 while the ARPES data near Γ is blurred. The result still leaves the WPs near Γ claimed by Liu unproven, although it does not positively confirm that TaIrTe₄ has only 4 WPs. At most, it agrees that TaIrTe₄ has at least 4 WPs as indicated by the arc.

Another work by Belopolski et al. also attempted to demonstrate TaIrTe₄ band structure near the WPs position which is above the Fermi level by using laser-pumped ARPES. Yet, their claim of TaIrTe₄ has 4 WPs is still premature as the WPs near the Γ are also not discussed.

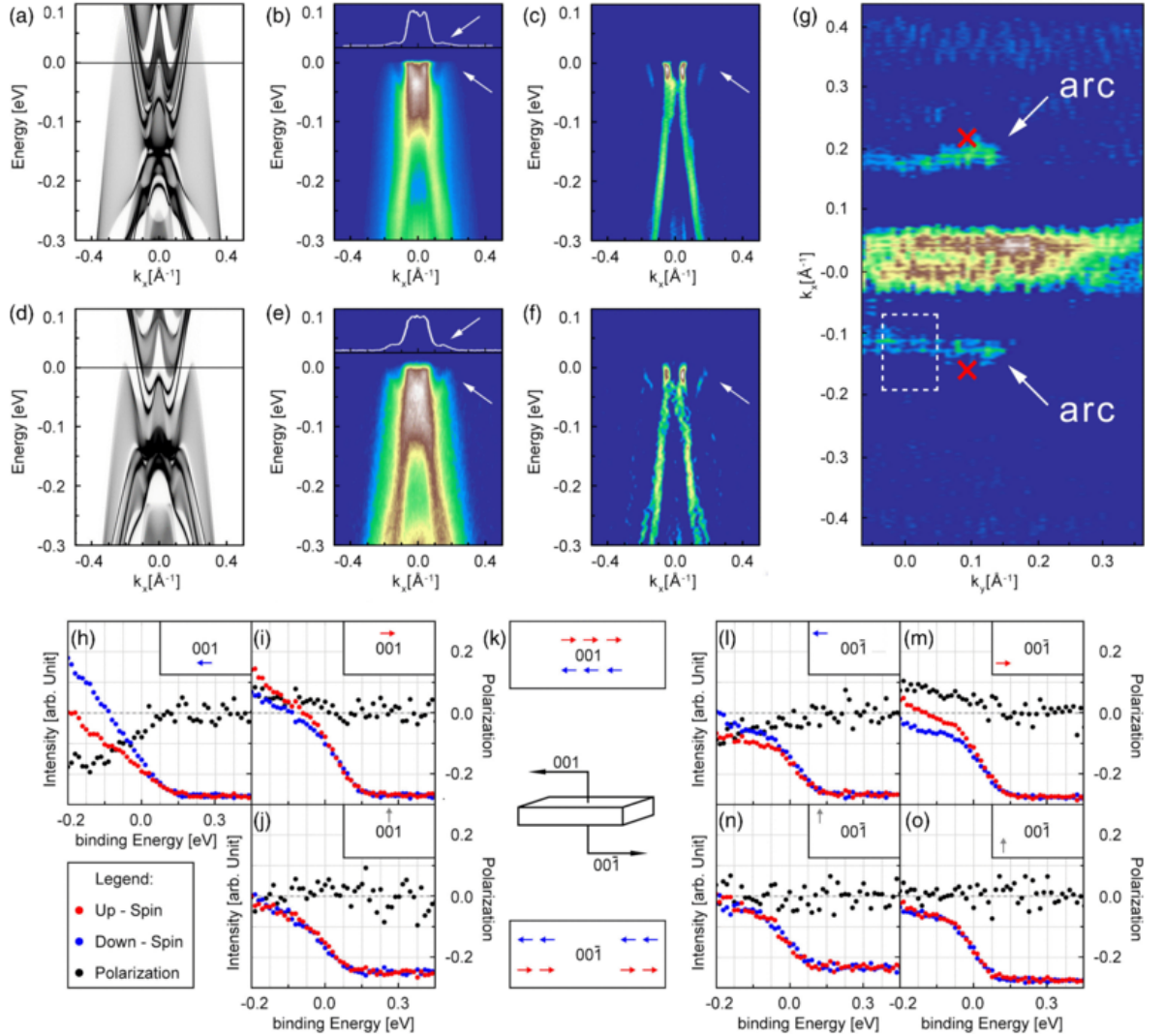


Figure 5.3: TaIrTe₄ reported in the work of Haubold et. al. [156] is predicted to host only 4 WPs. (a),(b),(c) Calculated dispersion, ARPES result, and second derivative analysis of ARPES result to visualise the Fermi arc dispersion (white arrows) are shown for $\bar{X}\bar{\Gamma}\bar{X}$ at (a),(b),(c) and for $\bar{S}\bar{Y}\bar{S}$ at (d),(e),(f). (g) Fermi surface of ARPES showing arc signature. However, this Fermi surface is not conclusive to describe any feature near the $\bar{\Gamma}$ as the detailed structure is not well resolved. Figure adapted from [156].

In this context, the work of NbIrTe₄ may shed a new insight on the existence of Weyl semimetal with 4 WPs. It is understood that the number of WPs may be sensitive to the properties of the material e.g. straining one lattice constant may shift the WPs pair to annihilate each other [82]. Hence, ARPES observation on the pristine material may settle the disputed WPs number by observing how the arcs are connecting at the Fermi level. Observation on two different surfaces of NbIrTe₄ (call them S₁ and S₂) may also give insights on how different surface connects the WPs differently.

5.2 Crystal Structure of NbIrTe₄

NbIrTe₄ has a non-centrosymmetric crystal structure as shown in figure 5.4 that has space group of Pmn21. Our 3D XRD measurement confirms this space group with lattice constants $a = 3.77 \pm 0.01 \text{ \AA}$, $b = 12.51 \pm 0.01 \text{ \AA}$, and $c = 13.12 \pm 0.01 \text{ \AA}$ and also confirms the good quality of our sample (figure 5.5). In principle, NbIrTe₄ can be viewed as the doubled WTe₂ and MoTe₂ in T_d phase (holding two Te-(Nb,Ir)-Te layers within one unit cell) where we have Peierls distortion along b direction on the Te atom sheet. From the lattice constant, it can be inferred that NbIrTe₄ has a belt/needle like feature as one lattice is significantly shorter than the other. This direction also dictates which orientation to mount the sample during the ARPES measurement as the longest dimension should be aligned to the analyser slit orientation. Afterwards, a closer look on the top layer and the bottom layer reveals that the top layer can be transformed into the bottom layer by glide symmetry (mirrored on xz plane and translated). This situation creates two types of exposed surfaces after cleaving namely S₁ (top surface) and S₂ (bottom surface) on which ARPES measurement can be performed (see figure 5.4).

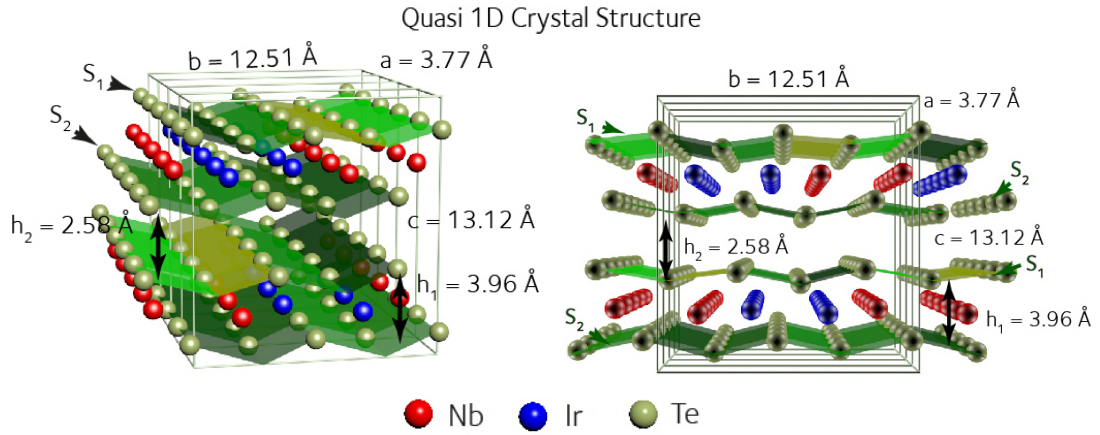


Figure 5.4: NbIrTe₄ shows a quasi 1D structure with inversion symmetry breaking as requirement to realise Weyl semimetal.

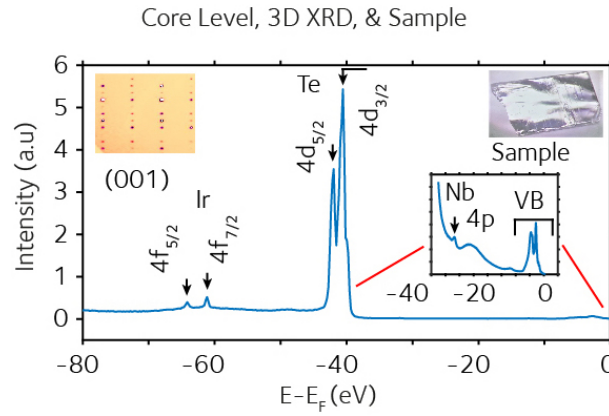


Figure 5.5: NbIrTe₄ used is shown in the picture where it shows a good quality crystal structure. The elemental composition is also confirmed with core level measurement.

5.3 Band Structure Calculation of NbIrTe₄

The technical details of band structure calculations are beyond the scope of this thesis. In principle, they are calculated based on density functional theory (DFT) with the projected augmented wave (PAW) potential as implemented in the Vienna Ab initio Simulation Package (VASP) [157]. The exchange-correlation energy was considered in the generalized gradient approximation (GGA) level with a Perdew-Burke-Ernzerhof (PBE) functional [158]. The tight binding matrix was constructed by projecting the Bloch

wave functions onto maximally localized Wannier functions (MLWFs) [159]. Based on the tight binding model Hamiltonian, our collaborator has calculated the surface states by half infinite boundary conditions using the iterative Green's function method [160]. The k-dependent local density of states (LDOS) are projected from the half-infinite bulk to the outermost surface unit cell in the (001) direction for both top and bottom surfaces.

The main information for the experimentalist like the author to read and interpret the calculations are listed below:

1. The bulk calculation produces the band calculation assuming the material is infinite in size. Any band from ARPES that does not appear in the bulk calculation most likely comes from the surface.
2. Each of the bulk band has orbital character originating from the composing atomic orbital. This characteristic can be used to investigate any band inversion occurring in the material.
3. The surface states from Green's function calculation differs in technique as compared to the slab calculation (section 4.4.3). In Green's function calculation, the material is assumed to be semi-infinite with one finite boundary represents the ARPES cleaving surface. Then, in Green's function calculation, we are calculating the Density of State (DOS) instead of "following" the band as in the slab calculation. Thus, projecting the DOS on the outermost layer will differentiate the surface states as opposed to bulk states from the intensity of it.
4. However, slab calculation has its own merit by giving the information of each bands involved in the calculation e.g. how they evolve from one energy to another and how they evolve as more layers are added into the calculation. After all, the real sample is not semi-infinite but finite slabs albeit relatively many (not in order of 10 like in routine slab calculation). Therefore, each technique can complement each other to give a better understanding on the band structure.

5.4 Weyl Points in NbIrTe₄

The summary of bulk band structure calculation by using lattice constant from experiment can be seen in figure 5.6 along several high symmetry cuts. With the given lattice

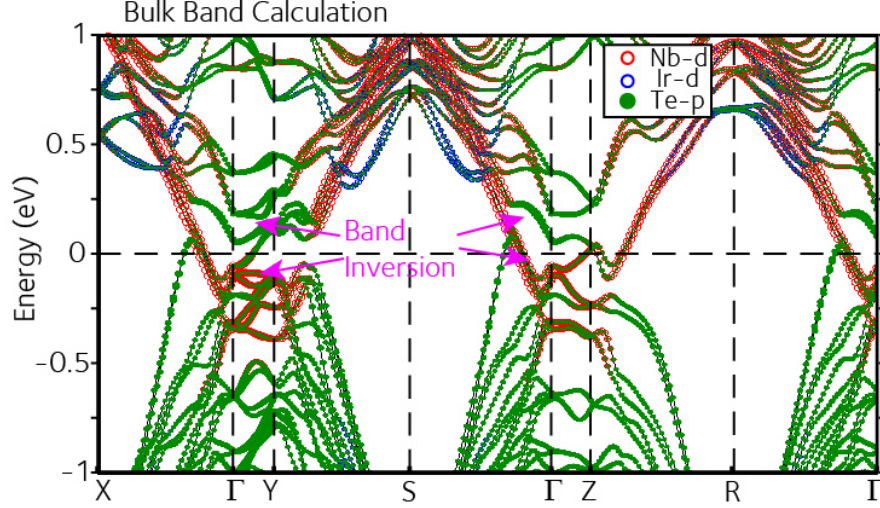


Figure 5.6: NbIrTe₄ bulk band calculation along high symmetry cuts. It prominently shows that there is band inversion around Γ point.

constant from experiment, the calculation managed to reproduce NbIrTe₄ harbouring four type-II linear crossings at high symmetry cut (figure 5.7). First of all, the WPs positions are pinned at $k_z = 0$ due to symmetry $T * M_x * G_y$ inherent to MM'Te₄ [151]. Next, the four WPs are found at $(k_x, k_y) = (\pm 0.1492\pi/a, \pm 0.1332\pi/b) = (\pm 0.248, \pm 0.067)\text{\AA}^{-1}$ above the Fermi level ($E = 0.131$ eV) similar to its family TaIrTe₄ in Koepernik et al. work (see figure 5.6(b)&(c)) [155]. The confirmation was further done by calculating the Berry curvature around the suggested WPs positions. It can be seen in figure 5.8 that the Berry curvature acts as if there are sources/sinks around the crossing points suggesting they are indeed a pair of WPs of opposite chirality. Chern number calculation around those points also reconfirms the sign of the monopole accordingly. Furthermore, a thorough calculation also confirms that there are no additional Weyl points near the Γ points as reported for TaIrTe₄ case in reference [151] and also

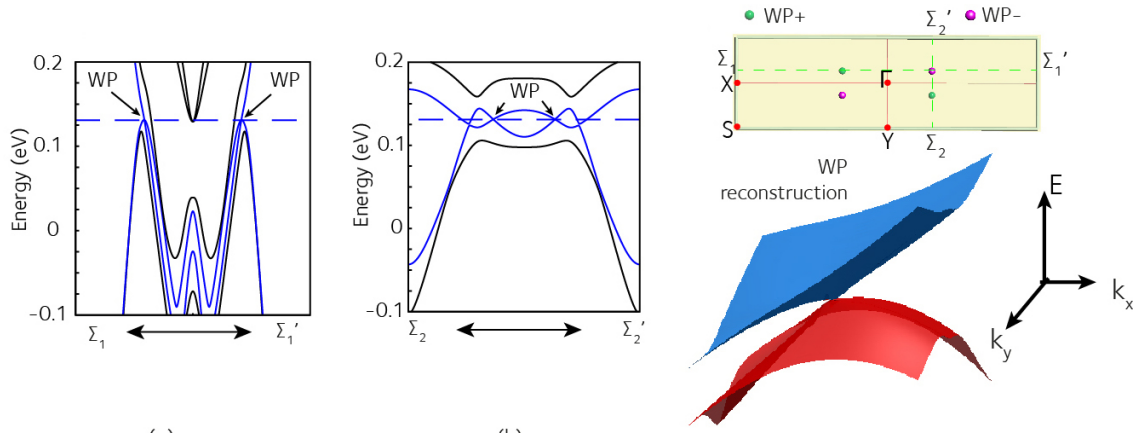


Figure 5.7: Bulk band calculation along the Weyl points showing the Weyl crossing accordingly. Location of Weyl points are pinned on $k_z = 0$ due to symmetry requirement. The 3D reconstruction is also shown.

other Weyl points in NbIrTe₄ as reported in reference [154]. Thus, the theoretical calculation provides a solid ground to investigate the ARPES data within the four WPs framework.

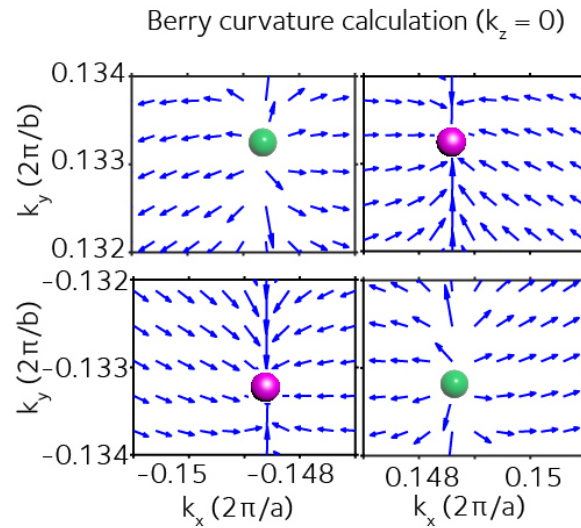


Figure 5.8: The Berry curvature calculation shows that at those four points it acts as if there is source and sink indicating Weyl points existence.

The type-II nature of the points are also confirmed from the constant energy surface

plot in figure 5.9 where the evolution of the band towards the WPs point are shown. At $E = 0.131$ eV, the zoomed in of WP energy contour is shown confirming the type-II crossing: electron pocket like, hole pocket like, and the WP crossing.

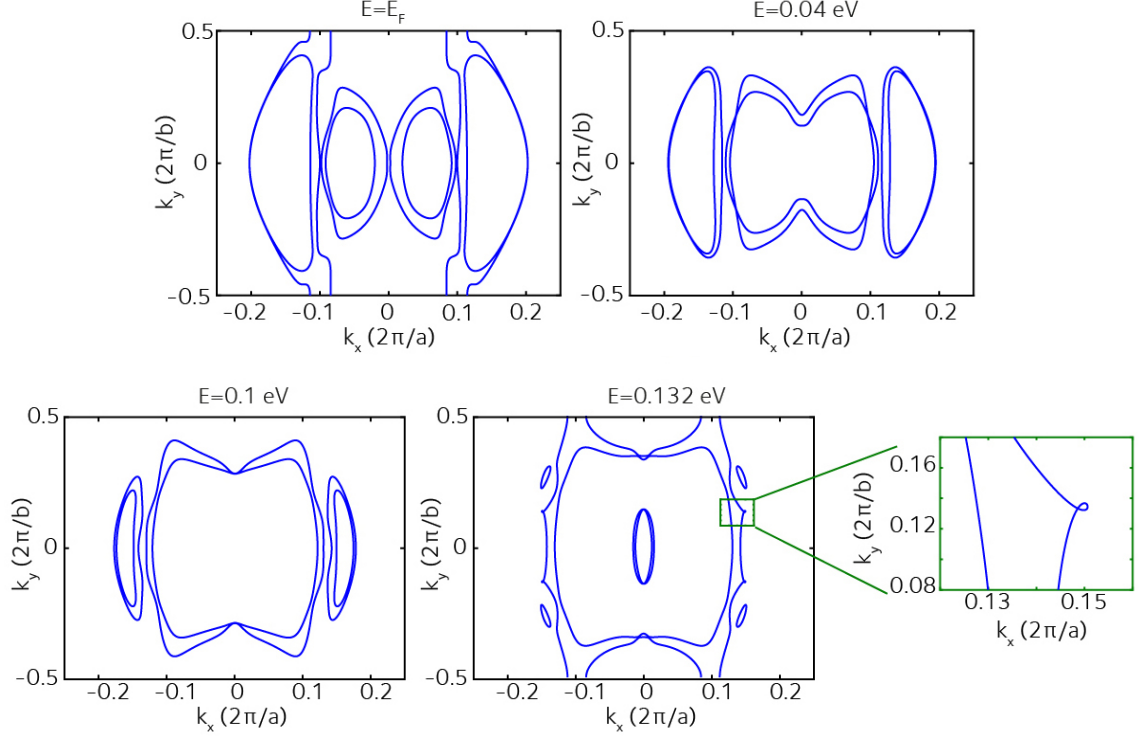


Figure 5.9: Constant energy surfaces of bulk calculation from ARPES Fermi energy level (E_F) towards Weyl points energy at higher energy ($E = 0.132$ eV), with the zoomed-in picture of around Weyl point showing the type-II nature of the point.

5.5 Z_2 Invariant in NbIrTe₄

Finally, a clear band inversion around Γ point is also observed in figure 5.6 (Te-p and Nb-d) indicating a topological nature similar to any Z_2 material. Thus, the Z_2 topological invariants was calculated in the time reversal invariant planes without including zero band gaps inside. As have been discussed in section 3.4.2, the Z_2 invariant in the inversion symmetry breaking system can be obtained by the Wannier center evolutions.

As shown in figure 5.10, the loops of Wannier centers change partners at time reversal invariant point in $k_x = 0$ plane, hence cutting the reference line odd times. Meanwhile, the evolutions of Wannier centers cut the reference lines zero or even times in the other three planes. Therefore, the nontrivial Z_2 invariant exists in $k_x = 0$ plane, and non-trivial topological Fermi arcs are expected to cross k_y -axis.

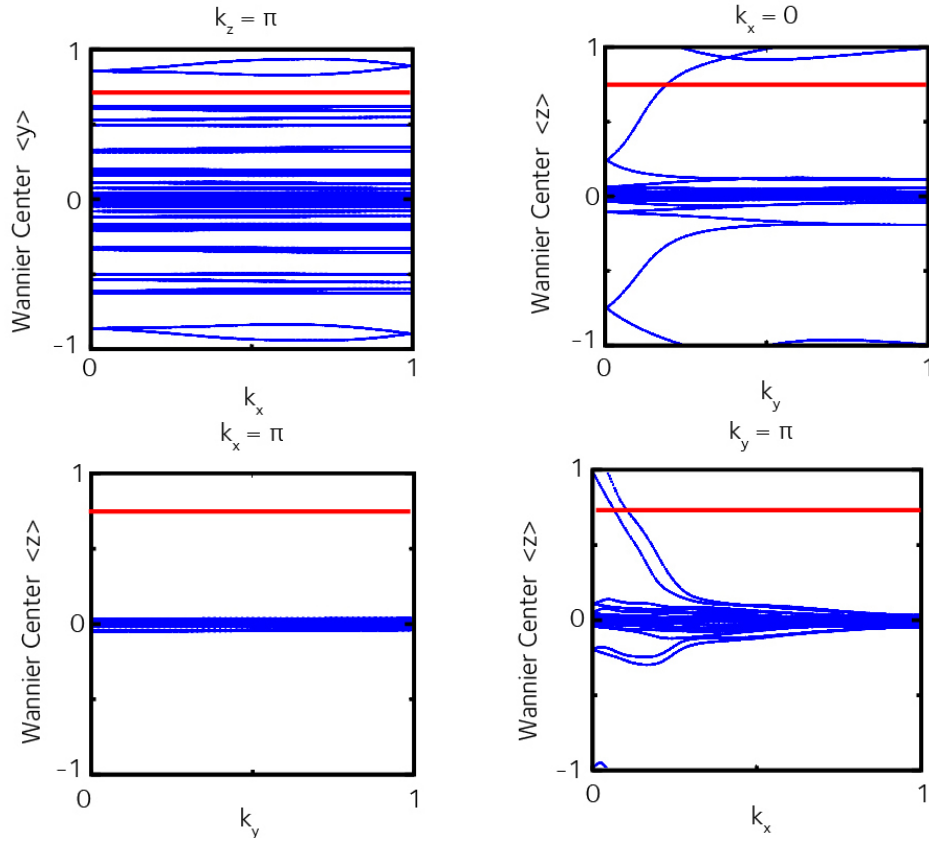


Figure 5.10: Wannier centre evolution along the high symmetry plane. Only at $k_x = 0$ along the k_y axis that we have odd number of red line (reference line) crossing indicating non-trivial Z_2 number.

5.6 Assignment of Fermi Arc in NbIrTe₄

With the existence of Weyl point at $k_z = 0$ plane, Fermi arcs are expected to appear in the cleavable (001) surface with different connection configurations due to the different

surface termination S_1 and S_2 . Calculation from Liu et al. has confirmed this feature as shown in figure 5.2. Although the overall feature looks similar, a zoomed-in figure reveals some state missing between the top S_1 and bottom S_2 surface. From the figure 5.2, it is suggested that the Fermi arc on the top surface connects the WPs along k_y as that state does not appear on bottom surface. However, assigning Fermi arc on Bottom surface can be tricky as the remaining surface looks similar to the rest of the panel (no unique states appear). Thus, following the general occurrence that Fermi arc originates from the WPs position, the Fermi arc on Bottom surface is assigned to the state such that it connects the WPs along k_y to another BZ. The schematic of Fermi arc connection is shown in figure 5.11.

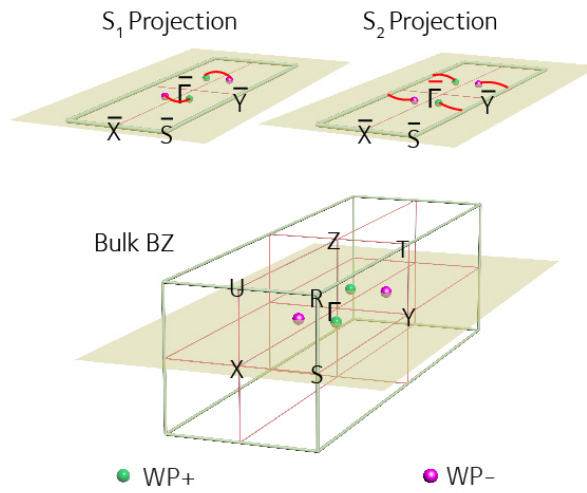


Figure 5.11: Schematic of Fermi arc connection for both top S_1 and bottom S_2 surfaces. The arc on the top connects the oppositely charged WPs within the same BZ along the k_y direction while the bottom arc connects the WP at neighbouring BZ along the same direction of k_y .

5.7 General ARPES Results of NbIrTe₄

In the following discussion, the ARPES results will be shown side by side with the calculated Green's function as comparison.

The NbIrTe₄ sample for ARPES measurement was cleaved in-situ to expose a fresh surface for experiment. The typical surface of NbIrTe₄ is shown in the inset of figure 5.5 where it shows the shiny part of it suitable for ARPES measurement. To confirm the composition of the sample, the core level was measured where it shows the peak from Te $4d_{5/2}$ and $4d_{3/2}$ as the strongest, followed by Ir peaks $4f_{5/2}$ and $4f_{7/2}$. However, the Nb peak was not detected although we zoomed in into the predicted peak position. This is due to the small cross section of the used photon energy (100 eV) to the Nb atom. The trick used was to change the photon energy with a lower one and focus around the peak energy itself. Eventually, the Nb $4p$ peak was found to finally complete the composition confirmation during the ARPES measurement.

The general feature of ARPES measurement is shown in figure 5.12 where it confirms the quasi 1D nature of NbIrTe₄. The rectangular symmetry of (001) surface is also shown from the figure. Overall, there are two big hole pockets on each BZ with interesting states near the center to be further investigated. Afterwards, exposing the two surfaces can be done easily by cutting the sample into two and flip one sample to expose two different surfaces together (see figure 5.13). This will guarantee the two surfaces are available for each ARPES measurement although we may not know which one is top or bottom until measured.

5.7.1 Bulk Bands from Top and Bottom Surfaces

The top and bottom surfaces ARPES summary are displayed in figure 5.16 and 5.18. Some bands share common features describing their bulk origin and surface independent nature. For example, the two big hole pockets, labelled as Bulk Valence Band (BVB), on the side from $\bar{\Gamma}$ towards the $\bar{X}$ direction agreeing the bulk band calculation in figure 5.9. The photon dependence measurement on one particular cut through $\bar{\Gamma}$ and the k_z dependence Fermi surface are also shown in figure 5.14 and 5.15 to further confirm the bulk nature. Apart from the two hole pockets, the features near the $\bar{\Gamma}$ is surface dependent

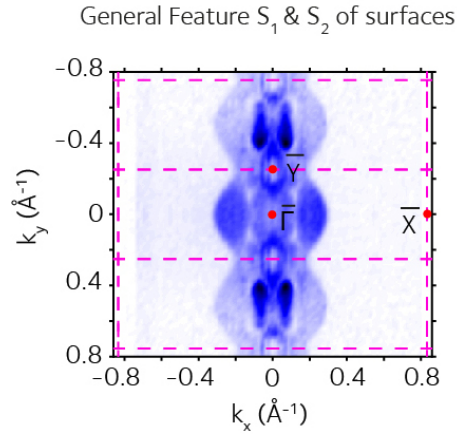


Figure 5.12: General ARPES Fermi surface from top and bottom surface showing a quasi 1D chain structure with prominent two hole pockets and interesting surface states in the middle.

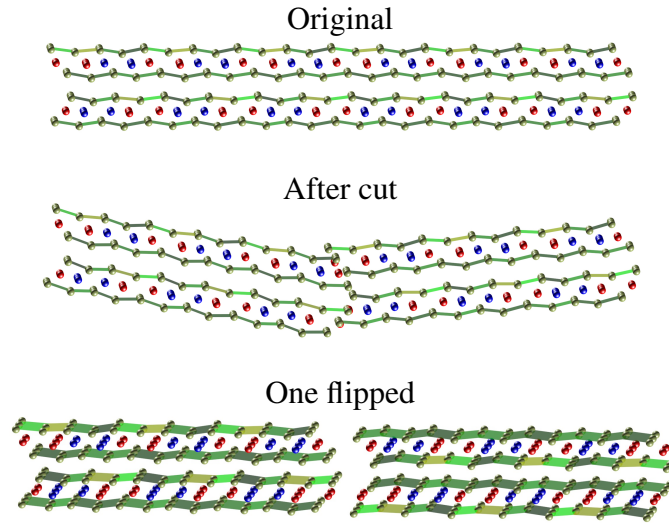


Figure 5.13: The two surfaces can be measured with ARPES by exposing them together after cutting and flipping one piece to show both surfaces upward.

which will be discussed afterwards. It should be noted that the ARPES Fermi level is about 0.132 eV lower than the WPs position. Thus, the pristine ARPES result will not be able to show the Weyl crossing. However, the bands that originates from the surface shown on the ARPES Fermi level may tell the story of the arc connection at the WPs energy position.

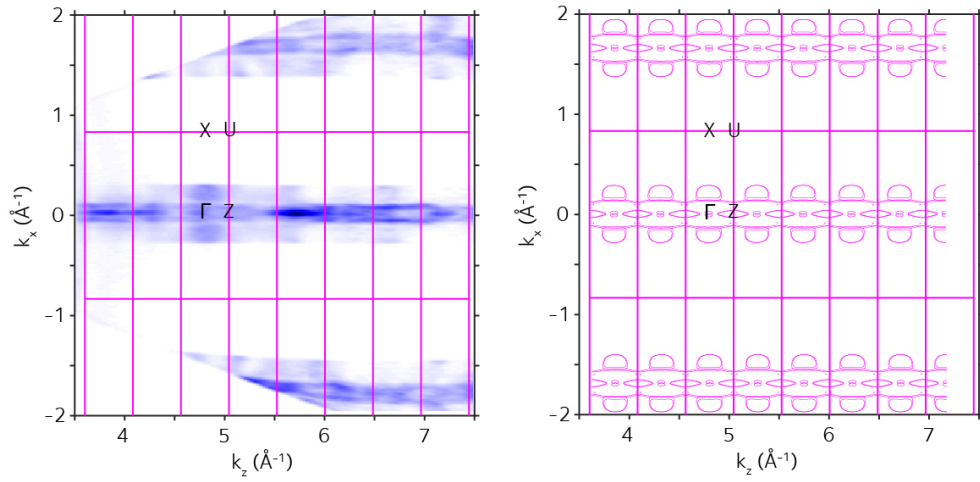


Figure 5.14: The resulting k_z dependent Fermi surface is shown agreeing in general with the bulk calculation as shown.

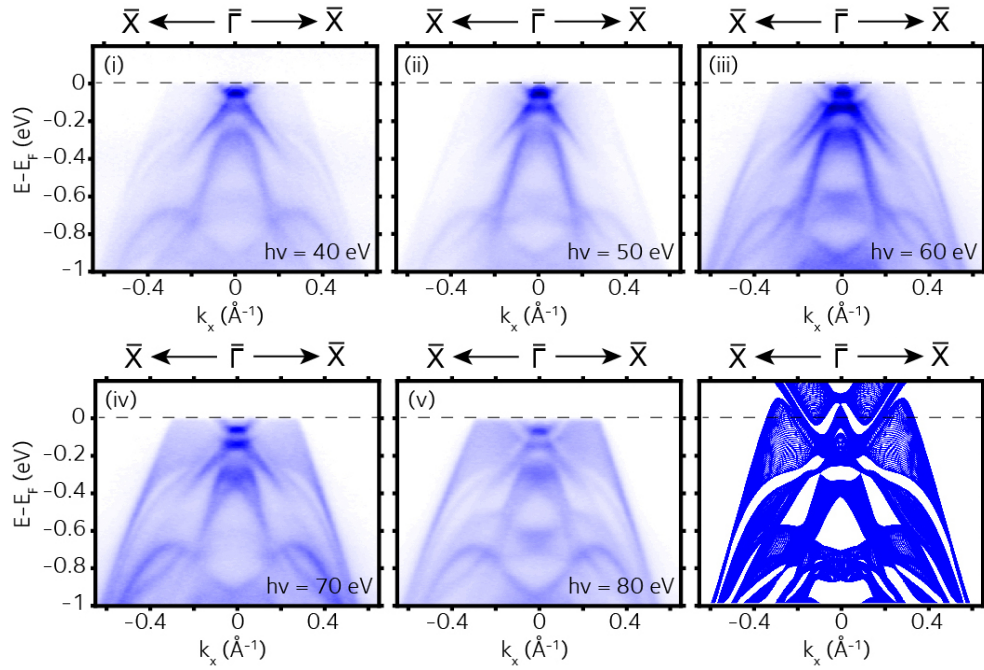


Figure 5.15: The cuts at several photon energy are shown to demonstrate that the two hole pockets originate from the bulk. The overlapped calculated data from Γ to Z is also shown on the lower right panel in blue.

5.7.2 The Electronic Structure of NbIrTe₄ Top Surface

The ARPES measurement on the top surface S_1 shows a consistent agreement with the predicted surface states calculation in general as can be seen in figure 5.16. The surface related features are the elliptical hole pocket and several “broken” arcs observed which can be compared directly to the calculation (figure 5.16(b),(c)). The seemingly broken arcs near the $\bar{Y}$ are of trivial nature as the calculation suggests they should be connected towards near the $\bar{\Gamma}$ position (figure 5.16(c)). The broken feature is attributed to the hybridisation with the bulk and ARPES cross section thus the remaining states are not visible; not that they do not exist. Therefore, they are labelled as Surface States (SS) for the purpose of the discussion. However, the observed arc near the bulk hole pockets lies on the calculated Fermi arc position (figure 5.16(c)). Thus, this arc is called the Surface Arc (SA) in this discussion as this state is the evolution from the Fermi arc (FA) state at the WPs position. It can be seen that the arc direction agrees with the connectivity of the FA from the calculation discussed before in section 5.6. Apart from the SA, the surface state crossing along $\bar{Y}\bar{\Gamma}\bar{Y}$ is also observed confirming the Z_2 non-trivial topology in NbIrTe₄. The crossing can be seen more clearly on the bottom surface result (figure 5.19(e)(3)).

The SS found on S_1 surface may suggest an interpretation of more than 4 WPs to reside in NbIrTe₄. However, this can be refuted by investigating the surface states belonging to the bottom S_2 surface.

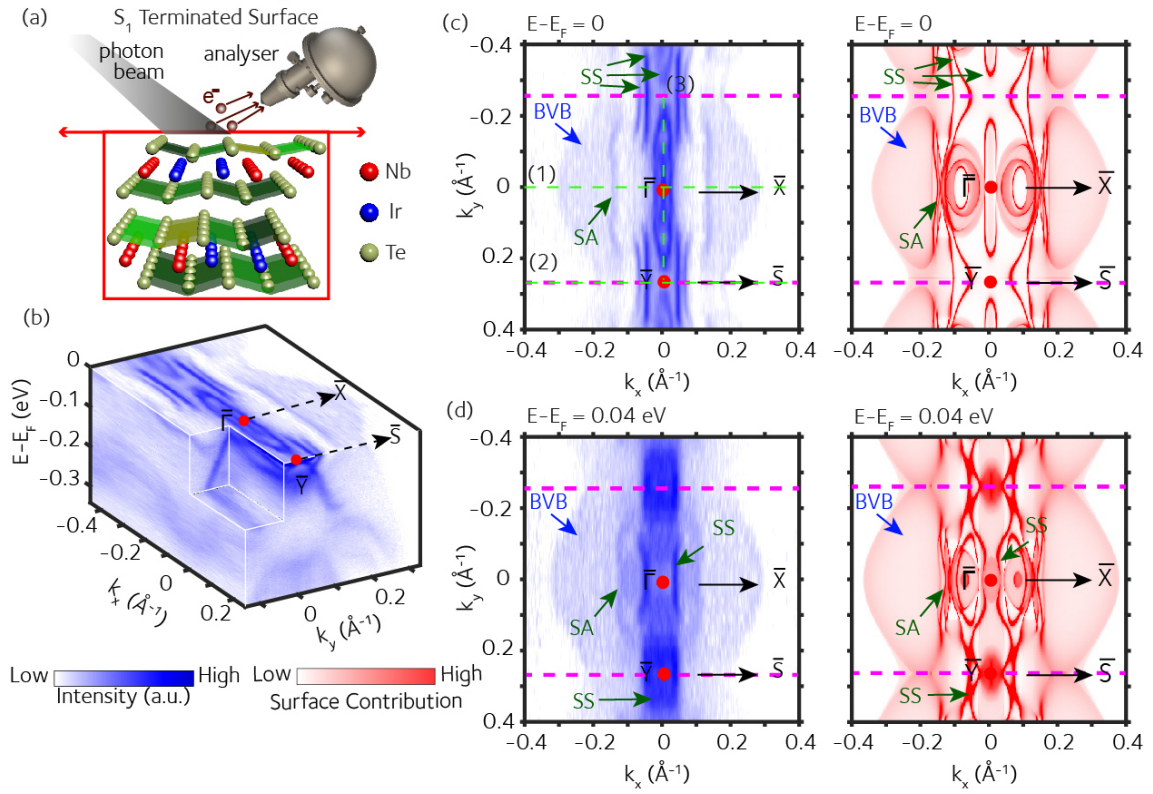


Figure 5.16: ARPES result for top surface agrees well with the predicted Green's function calculation. (a) Illustration of taking data from top surface. (b) The 3D-volume ARPES data reconstruction. (c) and (d) Constant energy surface at ARPES Fermi energy and at 0.04 eV binding energy are shown and compared to the Green's function calculation. The state labelled as surface arc (SA) is the evolution of the Fermi arc at the WPs position at higher binding energy. The seemingly broken arc states labelled as normal surface states (SS) are the trivial SS which hybridised with the bulk and it looks broken in ARPES measurement. The Bulk Valence Band (BVB) is the two hole pockets which are the bulk states at $k_z = 0$ plane.

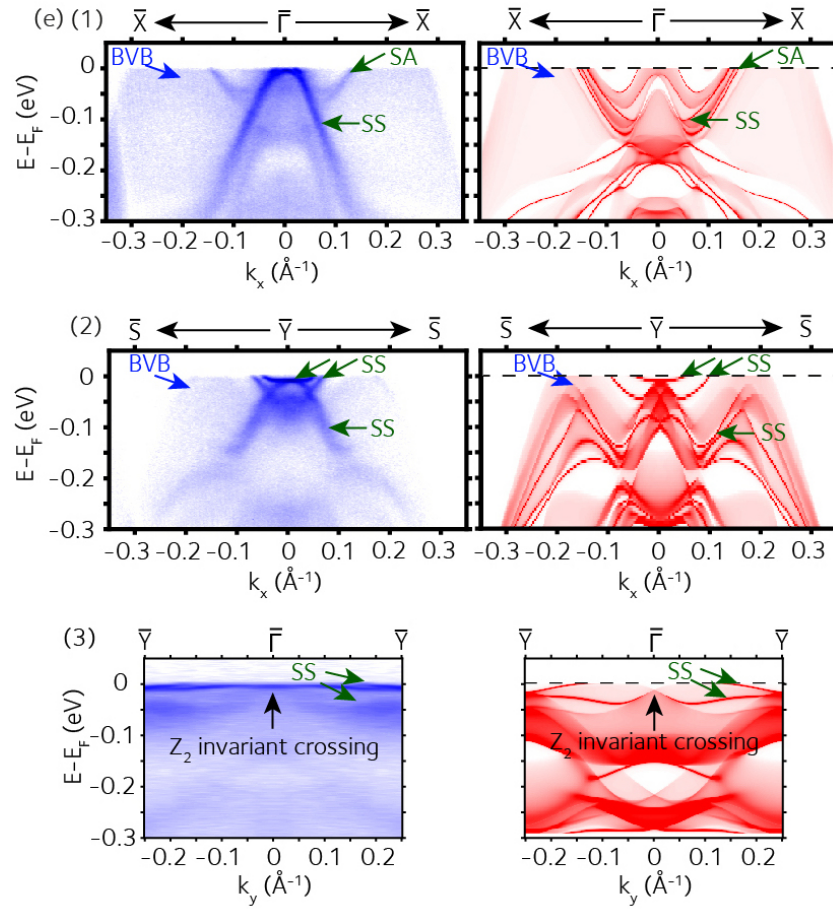


Figure 5.17: The ARPES cuts from high symmetry line $\bar{X}\bar{\Gamma}\bar{X}$ (e)(1), $\bar{S}\bar{Y}\bar{S}$ (e)(2), $\bar{Y}\bar{\Gamma}\bar{Y}$ (e)(3) are shown and compared with the Green's function calculations. They show a good agreement between ARPES and calculation. Apart from the SA and the SS mentioned in figure 5.16, there is also surface state crossing which is related to the Z_2 non-trivial nature of the sample on panel (e)(3).

5.7.3 The Electronic Structure of NbIrTe₄ Bottom Surface

The ARPES measurement on the bottom surface S_2 also shows a consistent agreement with the predicted surface states calculation in figure 5.18. The surface related features differ significantly from the S_1 surface confirming that top and bottom surfaces are not equivalent. Instead of the elliptical hole pocket, S_2 surface host an interesting hour glass shape which is broken near the bulk hole pocket (labeled with SA in figure 5.18(c)).

Afterwards, instead of several “broken” arcs near $\bar{Y}$, S_2 surface hosts a double eye shape which will be called inner and outer eye for the discussion (marked with (*)) in figure 5.18(c)). A closer investigation reveals that the inner eye is actually connected to the hour glass feature (see the 3D reconstruction in figure 5.18(b) and also 5.19(e)(3)). First, it should be noticed that the only broken feature shown are the hour glass feature and the broken position is also near to the projected WPs momentum position. Thus we attribute this hour glass to the Surface Arc (SA) while the eye shape both inner and outer are called SS for the discussion (although it is shown before that the inner eye SS evolves into the hour glass SA). The cut along $\bar{Y}\bar{\Gamma}\bar{Y}$ (figure 5.19(e)(3)) shows how the inner and outer eye evolve accordingly especially how the inner eye evolve into a Z_2 crossing, which eventually become the hour glass feature.

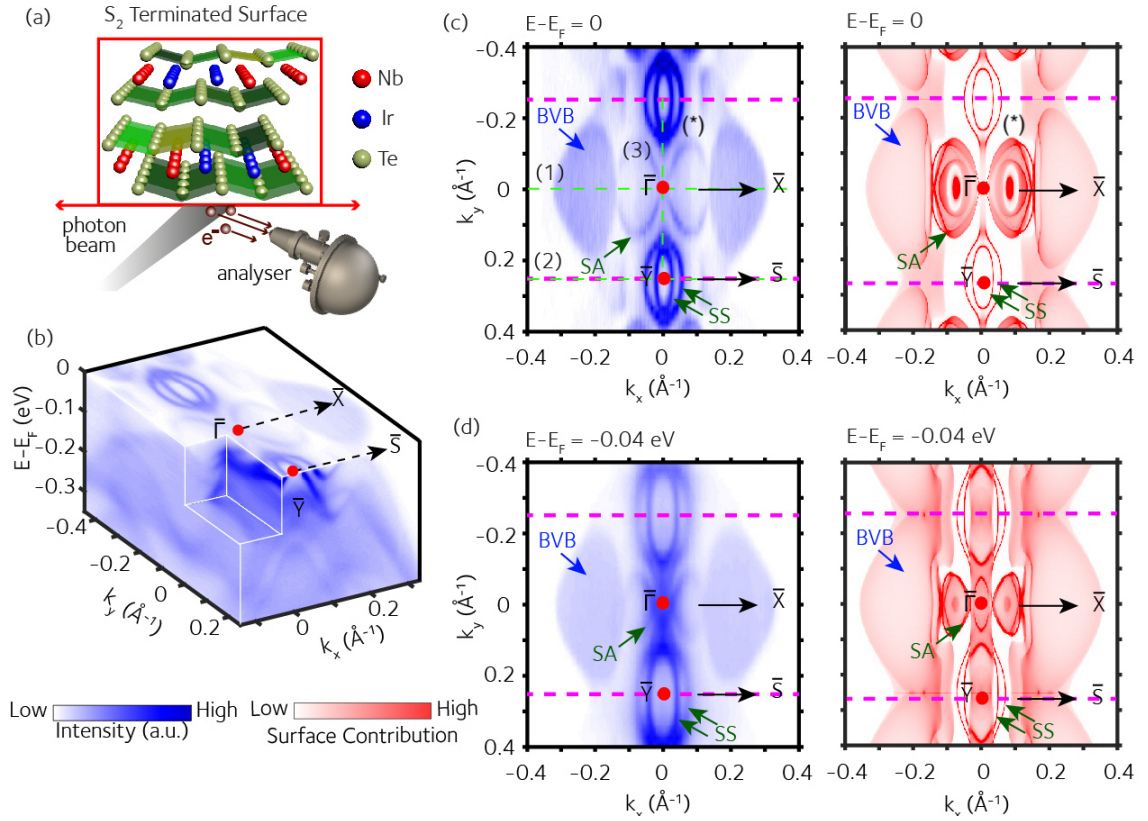


Figure 5.18: ARPES result for bottom surface agrees well with the predicted Green's function calculation. (a) Illustration of taking data from top surface. (b) The 3D-volume ARPES data reconstruction. (c) and (d) Constant energy surface at ARPES Fermi energy and at 0.04 eV binding energy are shown and compared to the Green's function calculation. The hour glass state labelled as surface arc is the evolution of the Fermi arc at the WPs position at higher binding energy. The eye feature near the $\bar{Y}$ consists of two concentric eye shape (*) labelled outer and inner eye (marked with SS). The Bulk Valence Band (BVB) is the two hole pockets which are the bulk states at $k_z = 0$ plane.

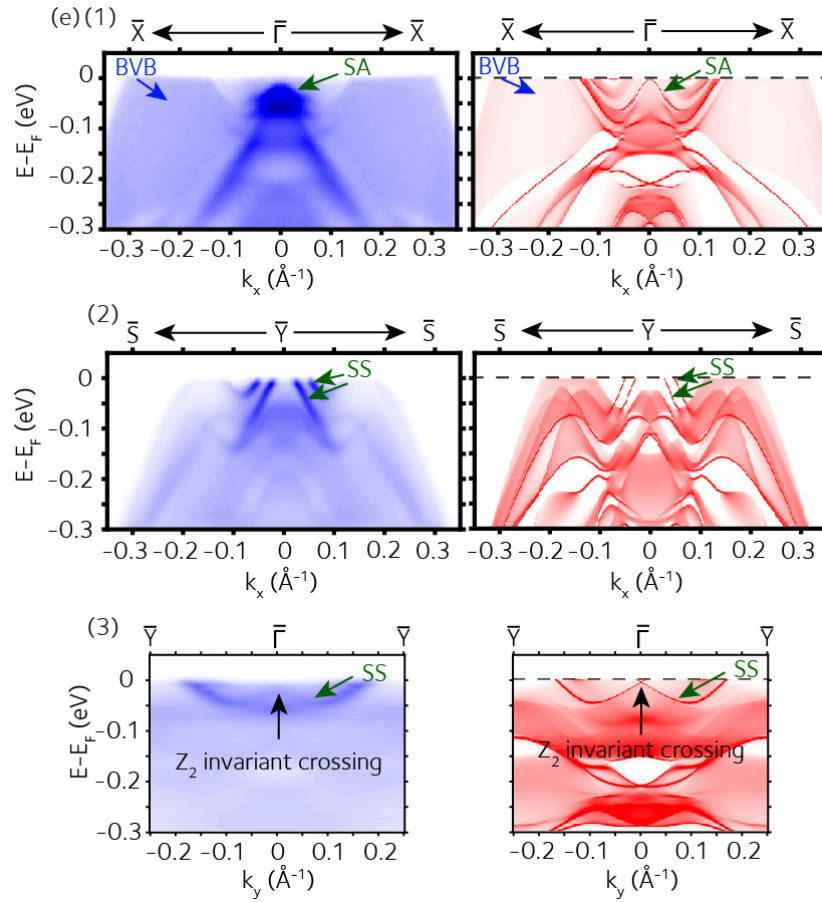


Figure 5.19: The ARPES cuts from high symmetry line $\bar{X}\bar{\Gamma}\bar{X}$ (e)(1), $\bar{S}\bar{Y}\bar{S}$ (e)(2), $\bar{Y}\bar{\Gamma}\bar{Y}$ (e)(3) are shown and compared with the Green's function calculations. They show a good agreement between ARPES and calculation. Apart from the SA and the SS mentioned, there is also surface state crossing, which is related to the Z_2 non-trivial nature of the sample on panel (e)(3).

Fermi Arc Rewiring on Bottom Surface

The surface states connection on the bottom surface is rather interesting where the Z_2 surface state related is also connected to the SA of the WPs. Furthermore, the assignment of the hour glass as arc is in direct conflict with the assignment of arc previously from the calculation in figure [5.2](#) reference [151]; the hourglass connects WPs projection along the k_x direction within the BZ while the assigned arc at WPs position connects along k_y direction to neighbouring BZ. This finding has not been reported before that a Fermi arc

connection changes at different binding energy. To investigate the band evolution, the figure 5.20 shows the evolution of calculated constant energy surface from WP position towards the ARPES Fermi level. It can be seen that the assigned SA at WPs position lies so closely near the bulk band electron pocket near $\bar{Y}$ position. This close proximity may hybridise the surface state with the bulk state dissolving the arc following the evolution of the bulk band. Afterwards, it evolves following the bulk band movement becoming the hour glass shape which has strong surface component. In the figure 5.20, we also label the transition energy level between (X1, 0.06 eV) and (X2, 0.05 eV) indicating when the connection changes toward k_x within the BZ. At ARPES Fermi energy, the SA is already connected to the hourglass feature which is the Z_2 surface state origin. The cartoon in figure 5.21 visualises the change of arc connectivity between different binding energy. This is also the reason this thesis call it SA and not purely FA as it is a hybridisation result of bulk and surface band.

Meanwhile, the top surface state evolution shows no significant change for the assigned Fermi arc as shown in figure 5.22.

5.8 Reaching the Weyl Point Energy

The explanation offered in section 5.7.3 can be tested further by raising the Fermi level of ARPES towards the position of the WPs. There are several ways to do this such as: pump probe ARPES, in situ K dosing, atomic doping / stoichiometry change, increasing Te vacancies, etc. In the following, we will comment on the K-dosing technique that has been done.

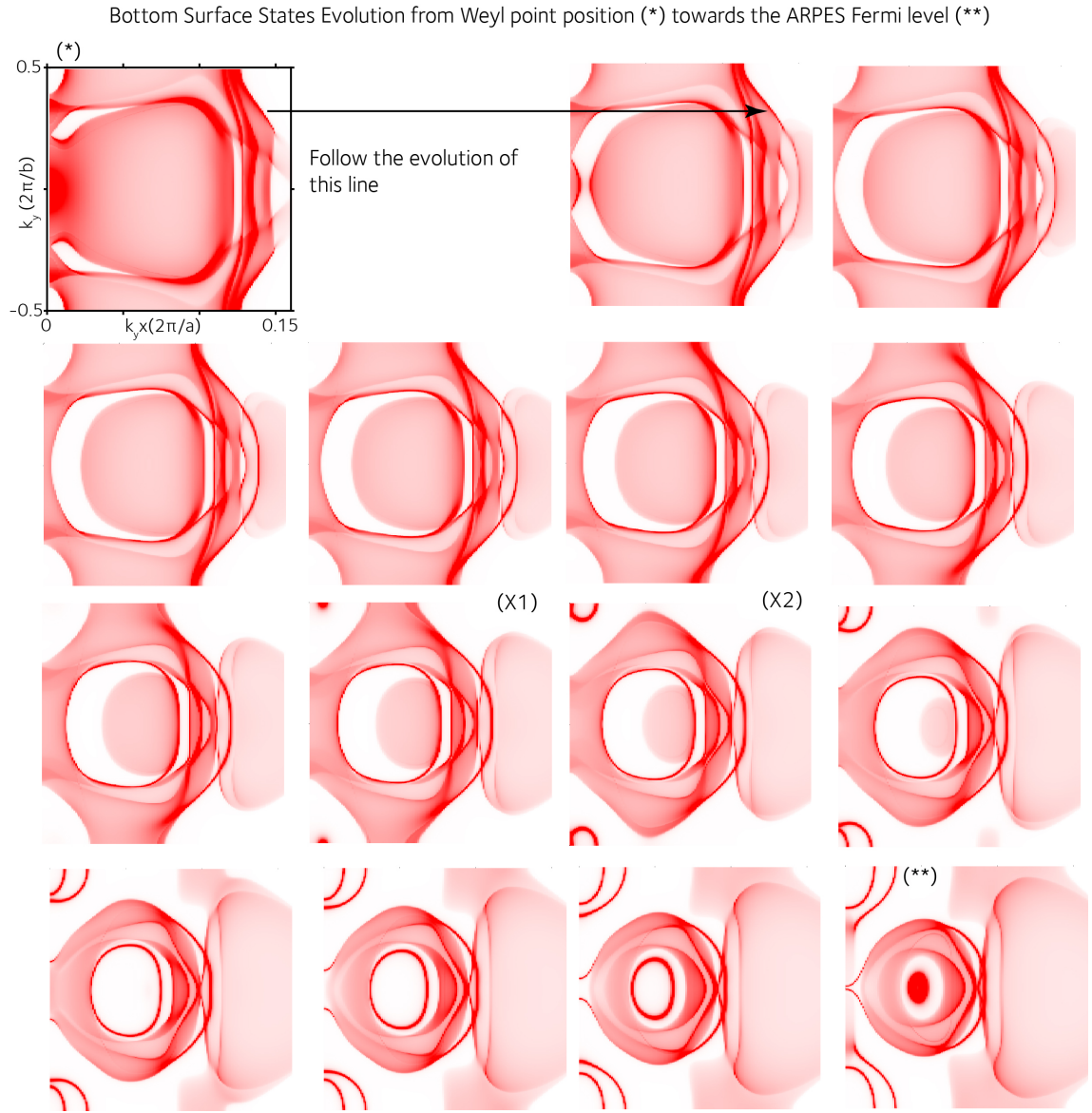


Figure 5.20: The evolution of calculated constant energy surface from Weyl point position (*, 0.132 eV) towards the ARPES Fermi level (**). Each panel is 0.01 eV apart. The assigned Fermi arc from the WPs position evolves following the movement of the bulk states towards the ARPES Fermi level. From level (X1, 0.06 eV) to level (X2, 0.05 eV), there is change in connectivity direction from k_y direction towards neighbouring BZ to the k_x direction within the same BZ. This arc eventually is connected to the hour glass crossing which is the Z_2 crossing (**).

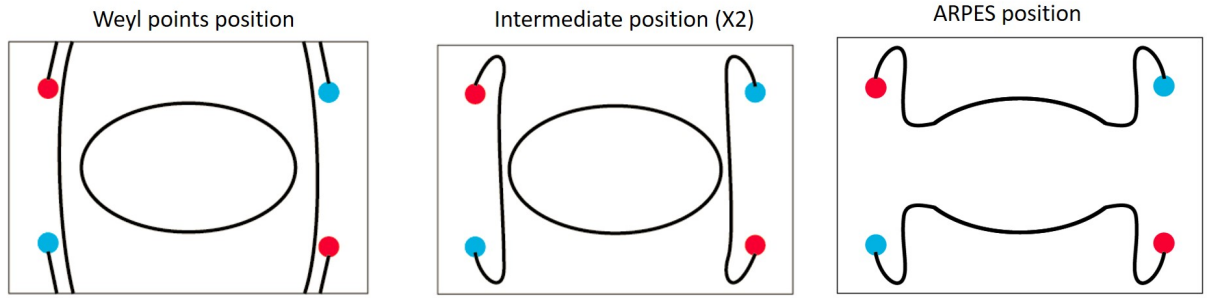


Figure 5.21: With the initial connection to the neighbouring BZ, eventually the arc hybridise with the nearby surface/bulk states leaving the intermediate state which is equivalent to the (X2) position in figure 5.20. Afterwards, another hybridisation takes place to connect the surface arc across the k_x .

5.8.1 K Dosing on NbIrTe₄

As the predicted WP energy is ~ 132 meV above E_F , attaching K atoms through sputtering onto the sample surface may raise the Fermi level in-situ during the ARPES measurement. This is done to reach a higher Fermi level with the hope of reaching the WPs position before the sample is completely destroyed. As K atom is inert, the K layer on the surface in principle only acts as an electron donor to the system investigated, thus raising the Fermi level [69, 161, 162]. This technique is destructive in nature as it covers the sample surface with random K atom. Although the X-ray may reach the sample through the K layer/s, the photo-electrons need to travel further distance to reach the vacuum. Thus, there will be a situation when the K layers are thick enough that the sample ARPES result cannot be seen anymore. Meanwhile, this technique has also been reported to alter the surface state configuration [161, 162] (not the bulk) due to its nature of re-dressing the surface. Therefore, a careful investigation is needed to interpret the result of surface states configuration after K-dosing.

After K-dosing both surfaces, the energy raised was about 0.05 eV with error about

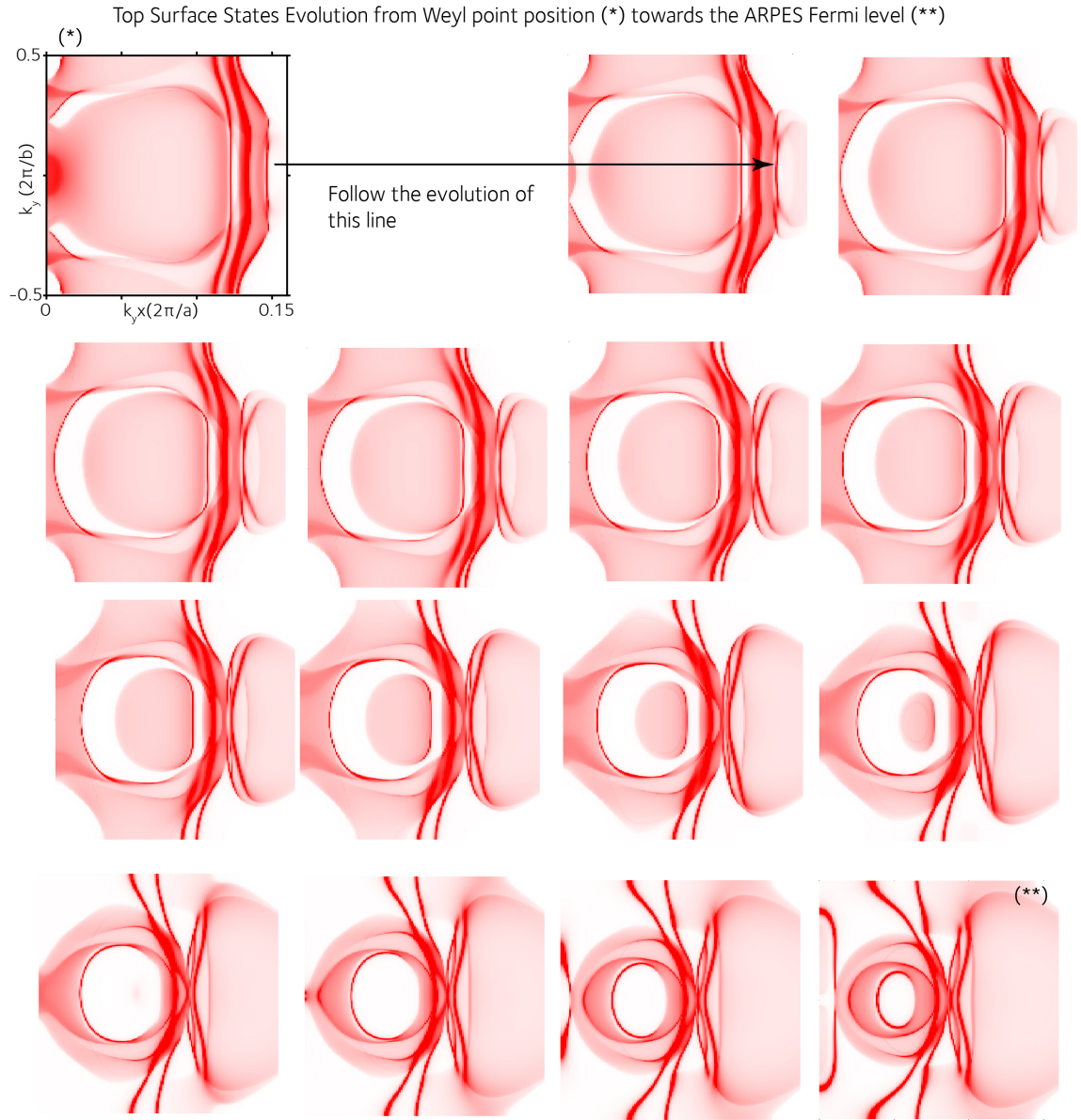


Figure 5.22: The evolution of constant energy surface from Weyl point position (*) towards the ARPES Fermi level (**). The assigned Fermi arc from the WPs position does not change significantly towards the ARPES Fermi level maintaining the same connectivity along k_y direction.

0.01 eV. The Fermi level could not be raised further up to the Weyl points energy position for the signal was lost after second attempt dosing. Figure 5.23 demonstrates the evolution of the SAs from WPs energy position to the pristine ARPES energy position. Figure 5.23(a),(b)(i) describes the calculated data which show a general agreement

with the ARPES result both pristine and K-dosed (figure 5.23(a),(b)(ii)). It can be seen that the SA for the S_1 evolves smoothly maintaining the original connection while the SA at S_2 changes connectivity at different binding energy (see the schematic in figure 5.23(a),(b)(iii)).

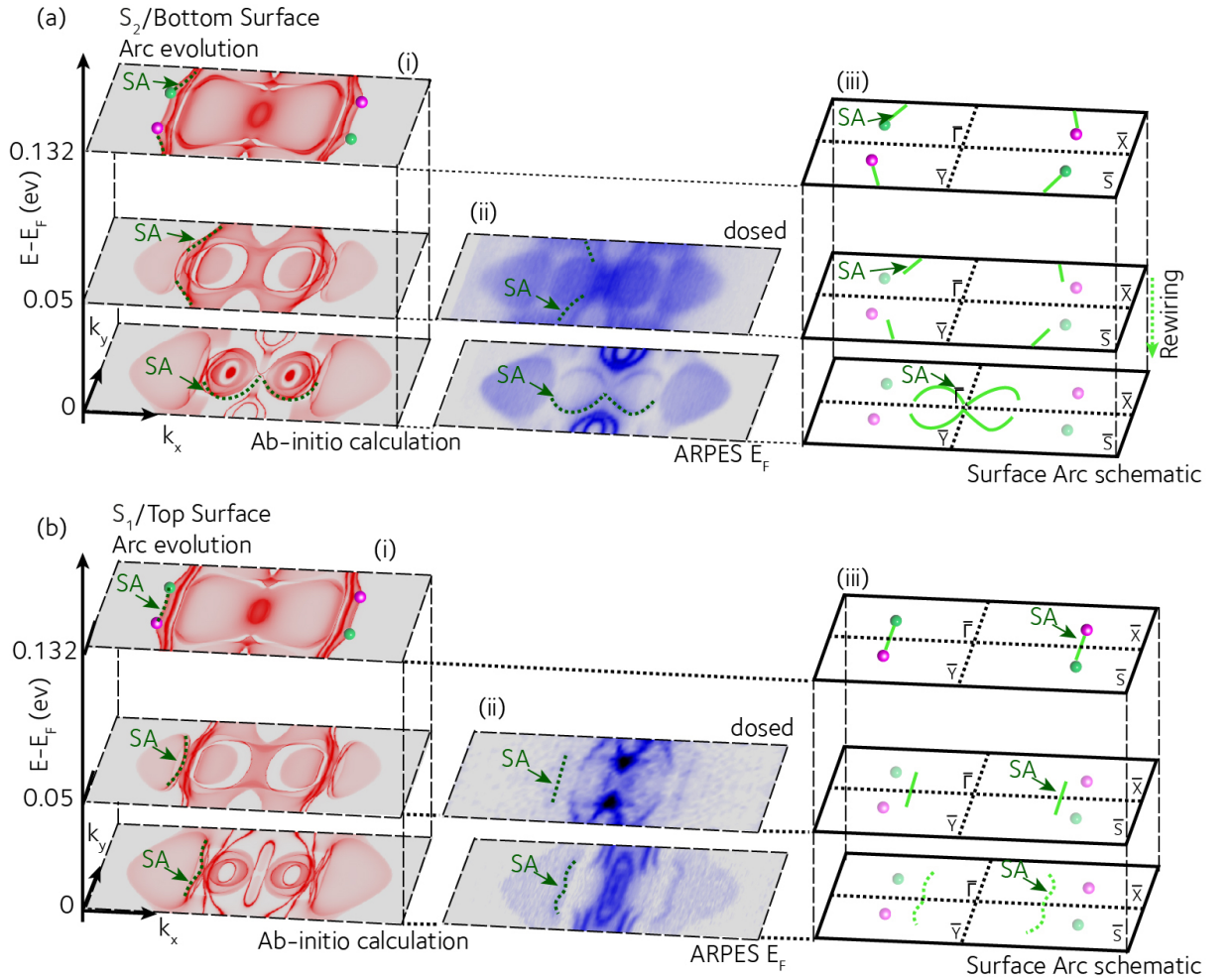


Figure 5.23: (a)&(b) Comparison of calculated data on panel (i) and ARPES result on panel (ii) (pristine and K-dosed) demonstrating the agreement of SAs evolutions on both S_2 (a) and S_1 (b) surface. Panel (iii) describes schematically the SAs from the WPs position at ($E=0.132$ eV) to the Fermi energy level of the ARPES measurement. The S_2 surface shows a re-wiring of SAs at different binding energy which is attributed to the hybridization between surface and bulk states.

However, a closer investigation on the bottom surface K-dosed result shows that the positioning of the assigned arc is attached onto a different side of the middle two electron holes near $\bar{\Gamma}$; the calculation shows that it is attached to the outside while the ARPES data shows it is attached to the inside. Meanwhile, it is tempting to say that the two fine states found after K-dosing are just the same inner/outer eyes from the pristine ARPES. However, this statement can be refuted as their Fermi area differs. Figure 5.24 also reveals how the two new surface states evolve in 3D which is different from the inner/outer eye evolution in figure 5.18. This difference between K-dosed and calculation at the corresponding energy level signals that the K-atoms does not only donor electrons, but also alter the surface states connection. However, it is sufficient to show that the Fermi arc at the higher energy than the pristine ARPES Fermi level shows a different connectivity. To visualize it in 3D picture, the SA band from WP position towards the ARPES data position is shown in figure 5.25 and 5.26. Despite of the rewiring, at each energy level, the projected SA from both surfaces still connect a different pair of oppositely charged WPs and thus consistent with the electronic structure of a relatively simple type-II Weyl semimetal (4 WPs and 2 Fermi arcs connecting them).

5.9 Perspectives and Summary

In conclusion, we have measured the band structure of the type-II TWS in NbIrTe₄ with the ARPES technique and found a good agreement with our ab-initio calculation. We have shown that the NbIrTe₄ has two different surface terminations each having rich SS features and SA features connecting different pairs of WPs. Furthermore, the ARPES data show that the SA feature on one surface may rewire at different binding energy which is attributed to the hybridization with the bulk band. This work may give further insight on how the exotic Fermi arc evolves at different terminations within the same material and provide understanding for possible future application especially in utilising the Fermi arc connection.

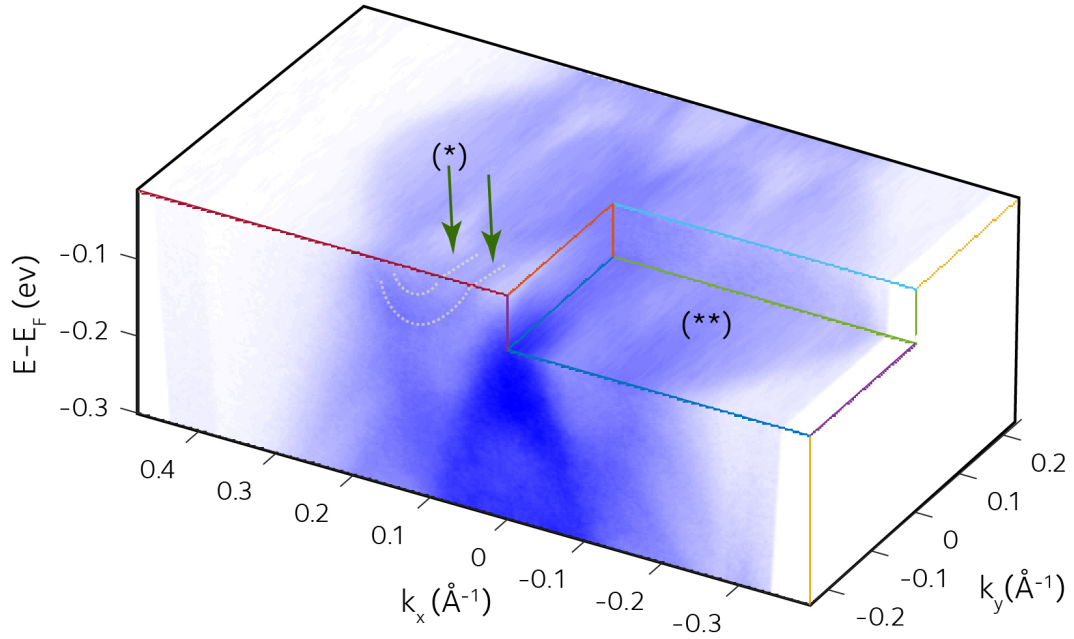


Figure 5.24: There are two new surface states after K-dosing which evolve into electron pockets as shown by the two green arrows and traced by the dashed lines. The (*) marks the assigned SA at that energy position after K-dosing connecting to the neighbouring BZ. The pristine ARPES Fermi level is marked with (**) showing that the surface states, including the original outer/inner eye and the hour glass are blurred after K-dosing.

Further works can be done for this NbIrTe_4 system to understand how the Fermi arc can be rewired by creating more Te vacancies. This treatment will add more free electrons to move, thus raising the Fermi level. However, it should be noted that the resulting surface states may be altered due to this surface restructuring. Furthermore, pump probe may also be used to probe the higher Fermi level without changing the sample intrinsically, although it may introduce another laser-induced phenomena such as optical Stark effect and Floquet-driven chiral edge state along the boundary of the laser-exposed region [163]. Investigating the other $\text{MM}'\text{Te}_4$ cousins can also shed light on the understanding of the Fermi arc connection. Up to the writing of this thesis, our collaborator has not managed to synthesise other than TaIrTe_4 and NbIrTe_4 samples. The TaIrTe_4

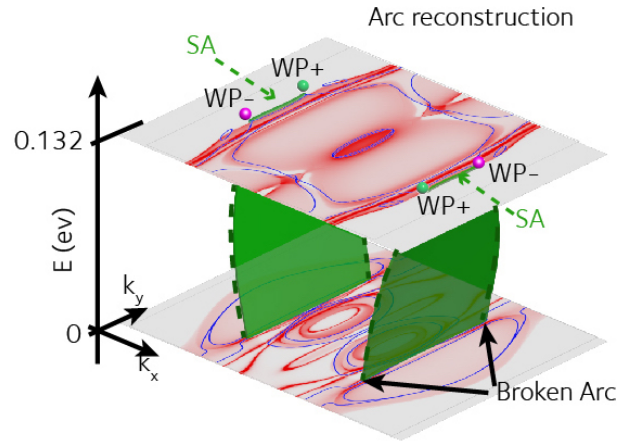


Figure 5.25: The suggested SAs evolution in 3D picture (green surface) for top surface. The connectivity does not change from WPs position towards the pristine ARPES Fermi level. The constant energy contour at 0.132 eV above E_F and at E_F shows the overlapped plot of the DFT calculation (blue solid lines, where the Weyl fermion and WPs are clearly seen) and surface slab calculations (red intensities, where the bulk continuum and the Fermi arcs are clearly seen).

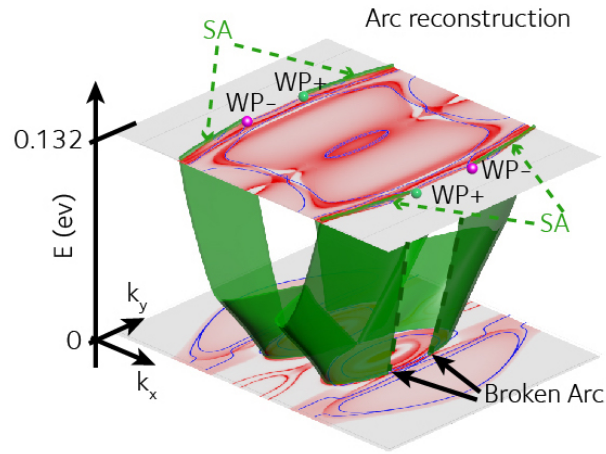


Figure 5.26: The suggested SAs evolution in 3D picture (green surface) for bottom surface. There is a change of connectivity from the WPs towards the pristine ARPES Fermi level. The constant energy contour at 0.132 eV above E_F and at E_F shows the overlapped plot of the DFT calculation (blue solid lines, where the Weyl fermion and WPs are clearly seen) and surface slab calculations (red intensities, where the bulk continuum and the Fermi arcs are clearly seen).

itself has been measured with ARPES by the author and showed that it is a p-type sample, thus no fine surface states observed (5.27). This probably explains why previous publication in TaIrTe₄ did not show the detailed ARPES Fermi surface [156].

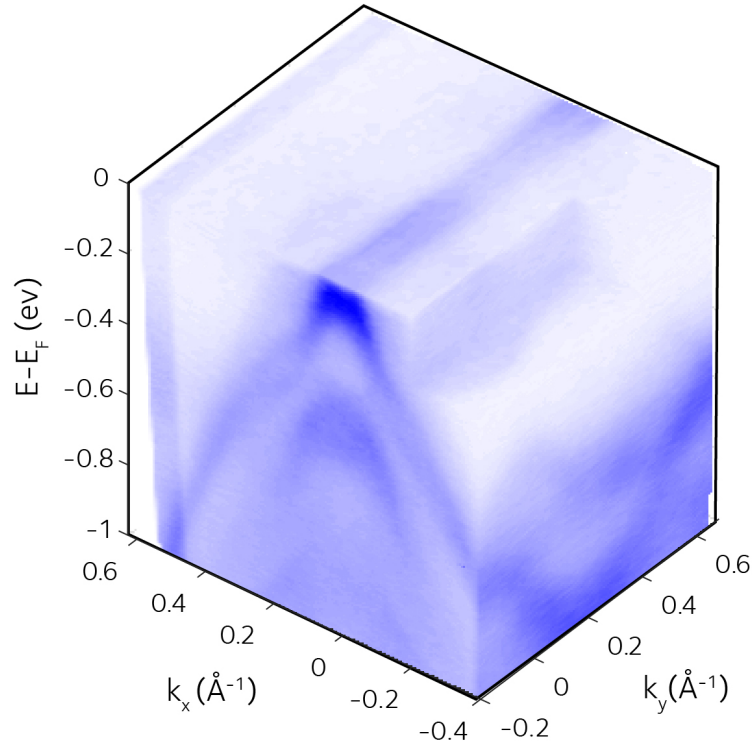


Figure 5.27: TaIrTe₄ made so far reveals that it is a p-type material with even lower ARPES Fermi level than the NbIrTe₄, thus it has no fine surface states observed.

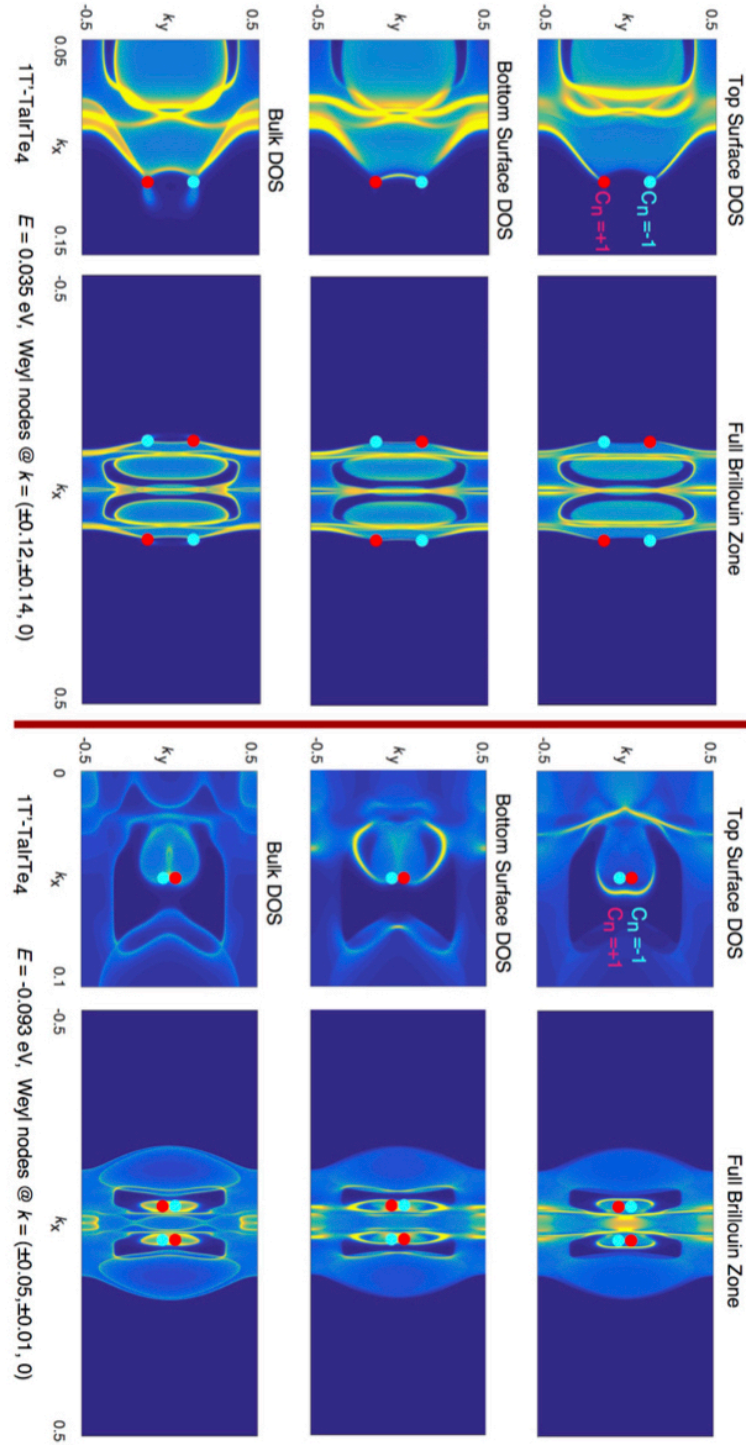


Figure 5.28: TaIrTe₄ is predicted to have only 8 WPs. Surface DOS for both surfaces and both WPs energy position are shown to investigate the Fermi arc. The predicted Fermi arc on the WPs pair at higher energy ($E = 0.035$ eV panels) is similar to the one predicted in NbIrTe₄. The WPs found at lower energy ($E = -0.093$ eV panels) are not found in NbIrTe₄. The respective Fermi arc configurations are displayed. Figure adapted from [151].

Summary and Future Works

6.1 Summary

This thesis has described the experimental works during the D.Phil study. Each of the experimental accomplishments have expanded the current knowledge about the topological material field in general and particularly in topological nodal line semimetal through the work in InBi and topological Weyl semimetal through the work in NbIrTe₄.

The first chapter has laid the introduction, the scope, and the objectives for the thesis. The two main objectives within the scope of this thesis were the observation of nodal line in non-symmorphic material and the investigation of Fermi arc connectivity in Weyl semimetal.

The second chapter has described a brief foundation on the experimental technique used which is ARPES. This technique is a surface sensitive technique that may reveal the bandstructure of materials in-situ and it is non-destructive. The inherent limitation on the perpendicular momentum measurement has also been discussed.

The third chapter explored the development of topological material field starting from the Chern number in quantum Hall effect. The concept of topology here is applied to

classify a phase of material without involving any symmetry-breaking argument. The list of materials that have been discussed are:

1. Topological insulator with Z_2 invariant which has a protected Dirac crossing on the surface of it, yet a fully gapped system in the bulk.
2. Topological Dirac semimetal which has protected Dirac points with non-trivial topological property.
3. Topological Weyl semimetal which hosts pairs of Weyl points with opposite chirality. The unique Fermi arc states which connect Weyl points of opposite chirality have also been discussed.
4. Topological nodal line semimetal which hosts a line/loop of Dirac/Weyl crossing with the predicted drumhead surface state.

The fourth chapter discussed the observation of protected nodal line in topological semimetal InBi. This chapter showed that the protection of nodal line comes from the non-symmorphic symmetry even under strong SOC. The nodal line existence has been verified experimentally by tracing the Dirac point on each photon energy in ARPES measurement. The intrinsic k_z broadening of ARPES is also shown in the InBi measurement that explains the broadened nodal line as seen from the experiment. As the future works of this project, we may search another candidate of material with similar space group $P4/nmm$ that has nodal line near the Fermi energy. With this condition, further work such as transport measurement can be done on it to get the signature of the nodal line from its contribution to the transport signal.

The fifth chapter demonstrated that NbIrTe₄ hosts four Weyl points which is the minimum number an inversion symmetry breaking system may host. The ARPES measurement has confirmed the number of Weyl points as it shows a unique pair of Fermi arcs on both side of the terminations. This chapter also showed that the Fermi arc on the

bottom termination changes connectivity at different binding energy due to hybridisation with the bulk states. As the future work of this project, we may pursue spin-ARPES measurement on both sides to confirm the nature of the Fermi arcs. It is well known that Fermi arc has a chiral spin texture that may be observed by spin-ARPES measurement [92, 134]. As a preliminary work, the spin-ARPES measurement has been done on the top surface with a promising result as shown in figure 6.1(a). It demonstrates that along the Fermi arc, there is a chiral net spin pointing along the y direction (the direction of the arc). The future works from here is to show the spin texture on the bottom side 6.1(b) and (c) if it also has the chiral structure or not.

In the following, several the future projects will be discussed. The first section will discuss the possible project about the infinitely adaptive series of $\text{Bi}_2/\text{Bi}_2\text{Se}_3$ and $\text{Bi}_2/\text{Bi}_2\text{Te}_3$ compounds with varying ratio between the thin film of Bi_2 and the quintuple block of Bi_2Se_3 or Bi_2Te_3 . Afterwards, other infinitely adaptive series material $\text{GeTe}/\text{Sb}_2\text{Te}_3$ is also discussed. Other possible works are also discussed as other future project.

6.2 Future Works

6.2.1 Infinitely Adaptive Series of $\text{Bi}_2/\text{Bi}_2\text{Se}_3$ and $\text{Bi}_2/\text{Bi}_2\text{Te}_3$

The early generation of 3D topological insulator (TI) which are Bi_2Se_3 and Bi_2Te_3 have been heavily studied [1, 52, 54, 111, 164–166]. As the early generation of material to confirm the strong type of TI, it is natural to pursue the search to the weak TI counterpart. Previous works have tried to predict and claim the discovery of weak TI [1, 167, 168]. However, there is no decisive evidence of its existence up to this report writing. Therefore, utilising the idea available from the theory [1, 168], the weak TI maybe realised through manipulating the bismuth thin film and the quintuple of Bi_2Se_3 and Bi_2Te_3 .

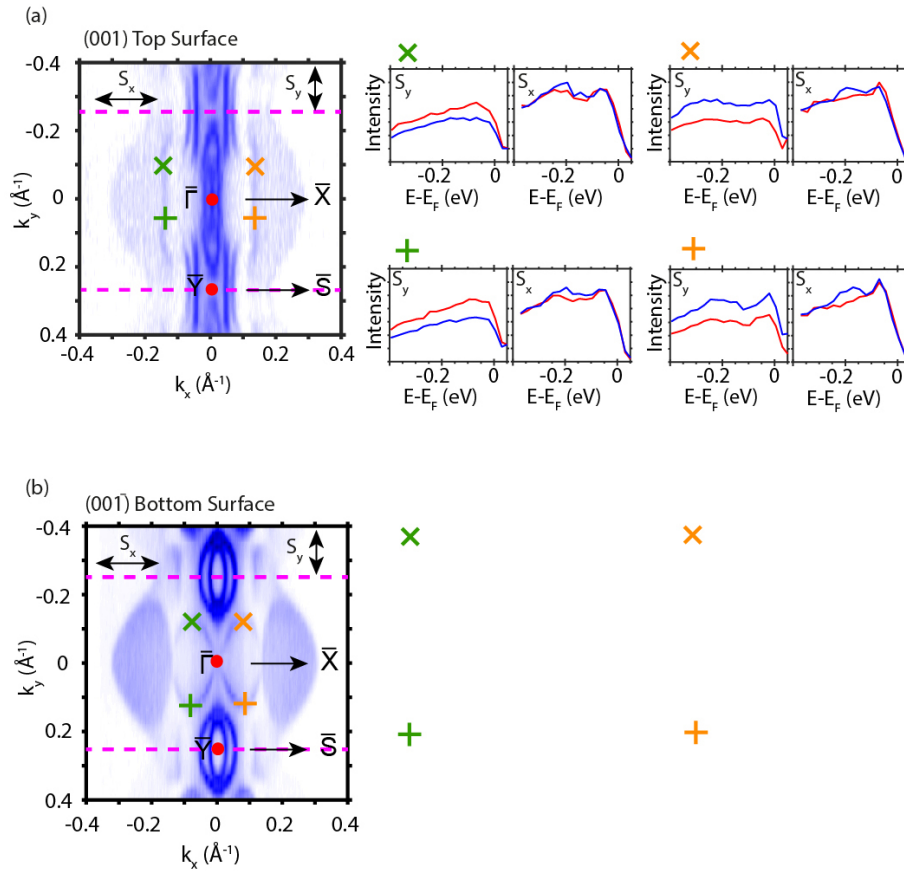


Figure 6.1: (a) spin-ARPES result on top surface reveals a chiral spin structure along y direction as the dominant spin flips color from the green $\times$ and $+$ sign (dominated by red color) to the orange $\times$ and $+$ sign (dominated by blue color); where blue and green represent spin-up or down respectively. Meanwhile, the spin along x direction show an equal contribution (no spin texture). (b) is the future work to be done on bottom surface to further confirm if it has chiral structure as the signature of Fermi arc.

Sample Growth

The works about infinitely adaptive series of $\text{Bi}_2/\text{Bi}_2\text{Se}_3$ and $\text{Bi}_2/\text{Bi}_2\text{Te}_3$ have been reported before [55, 169–171]. In short, infinitely adaptive series is the combination of several layers (m layers) of Bismuth thin film (111) and several quintuples (n quintuples) of Bi_2Se_3 or Bi_2Te_3 . Subsequently, they will be called by the ratio of the layers/quintuple as $m : n$. Both of the alloys are easily grown via solid state reaction within a very narrow temperature window [169, 170, 172]. At the point of writing, the

author has tried to grow the 1 : 1 ratio and managed to grow small sized crystals. However, this crystal is not a good sample for conventional ARPES measurement (see figure 6.2). Therefore, a good quality sample is needed to continue this project.

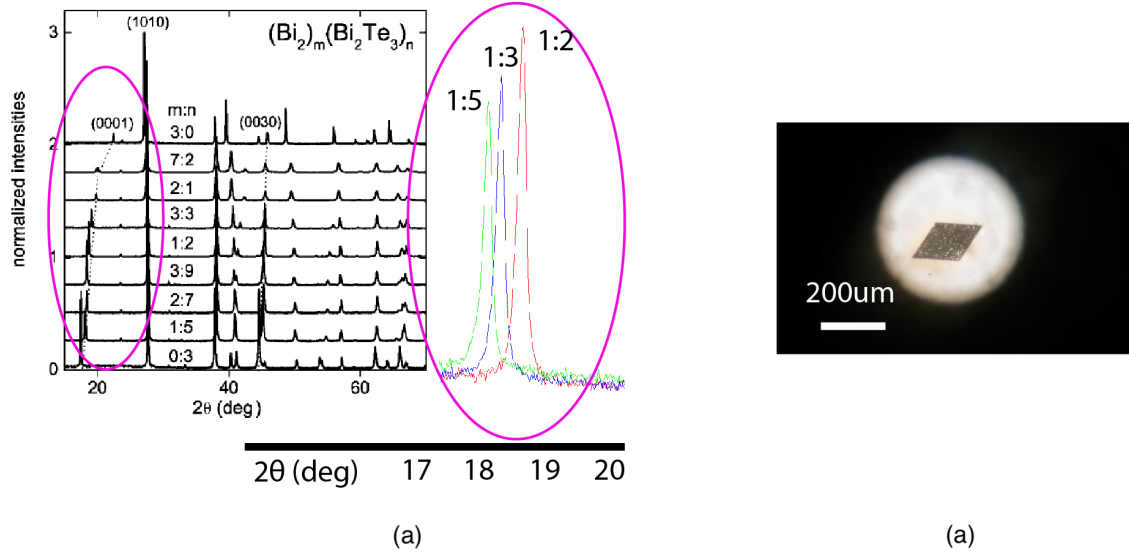


Figure 6.2: Home grown 1:5, 1:3, 1:2 ratio are confirmed through the XRD peak measurement. However, the typical sample size is small as shown above in the order of the X-ray spot size, not suitable for conventional ARPES measurement.

ARPES Measurement on 1:1

Meanwhile, preliminary ARPES measurement on 1 : 1 ratio for both of $\text{Bi}_2/\text{Bi}_2\text{Se}_3$ and $\text{Bi}_2/\text{Bi}_2\text{Te}_3$ have been done and presented briefly in figure 6.3(c) and (d) (samples are from collaborator). The schematic of the materials are presented in a way to incorporate the three unique layers for each parents compound [169, 170]. The result for the $\text{Bi}_2/\text{Bi}_2\text{Se}_3$ agrees well with the previous report by Valla et.al [55] while none has reported the $\text{Bi}_2/\text{Bi}_2\text{Te}_3$ counterpart.

Up to this result, the project shows a promising direction as future works. The ratio of m:n maybe varied to investigate the evolution of the surface state. The current result only

Varying m and n

Subsequently, the number of Bismuth layer (m) and Bi_2Se_3 or Bi_2Te_3 quintuple layers (n) (see figure 6.4) may be varied. The main goal is to find the right ratio so that the surface states on the top (bottom) layers are not communicating with each other any further [168], thus the surface state may disappear at the right ratio. The disappearance of the surface state will be a direct proof of weak TI and can be further confirmed by STM measurement to scan the edge state.

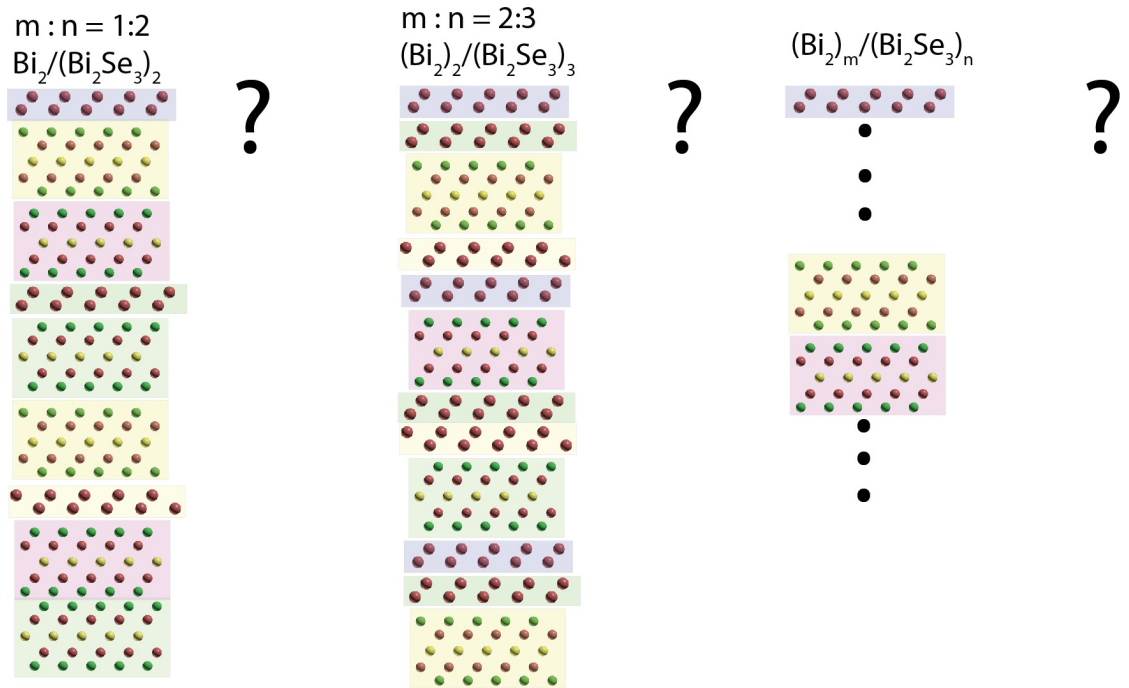


Figure 6.4: The goal is to find the right ratio of m and n to create the weak TI.

6.2.2 Infinitely Adaptive Series of GeTe/Sb₂Te₃

Similar to the system with Bi_2Se_3 , another early generation of 3D TI can be used which is Sb_2Te_3 . The quintuple layer will be filled with GeTe layer instead of Bismuth. It has been reported before that the pristine 1:1 ratio is a semimetal that has Z_2 crossing at the $\bar{\Gamma}$ point, thus still maintains the TI characteristic [173]. It will be another proof

of concept if the ratio variation may induce a weak TI phase along the (001) surface or another phase.

6.2.3 Mn-doping on the Infinitely Adaptive Series Candidates

Afterwards, the layered systems mentioned above maybe doped with Mn atom to induce a magnetic impurity. Inducing a time-reversal breaking may induce the phase transition into Weyl semimetal or a massive topological insulator; only experiment may tell which path will be realised.

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