Symmetry Enforced Topological Phases: Topological Insulators and Topological Semimetals

Ph.D. Thesis

By

Chiranjit Mondal



Department of Metallurgy Engineering and Materials Science INDIAN INSTITUTE OF TECHNOLOGY INDORE August 2020

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Chiranjit Mondal



Department of Metallurgy Engineering and Materials Science INDIAN INSTITUTE OF TECHNOLOGY INDORE August 2020



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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled Symmetry Enforced Topological Phases: Topological Insulators and Topological Semimetals in the partial fulfilment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the Department of Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from May 2016 to August 2020 under the supervision of Dr. Biswarup Pathak, Associate Professor, Department of Metallurgy Engineering and Materials Science, IIT Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

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(Chiranjit Mondal)

Dedicated

to My

Family and Friends

ABSTRACT

Symmetry protected nontrivial band topology has become an area of paramount research interest for unraveling novel dimensions in condensed matter physics (CMP). The time reversal invariant topological insulator (TI) has stimulated intense interest due to their intriguing properties, such as gapless boundary states, unconventional spin texture and so on. The recent years have witnessed a series of theoretical developments which have enabled us to classify the Z_2 non-magnetic band insulators. For example, the Z_2 even (ordinary) and Z_2 odd (topological) states are separated by a topological phase transition, where the bulk gap diminishes during the adiabatic deformation between these two states. In two-dimensional (2D) system, Z_2 odd class can be distinguished by the odd number of Kramer's pairs of counter propagating helical edge states, whereas in three-dimensional (3D) system, it can be characterized by the odd number of Fermi loops on the surface that enclose certain high symmetry points in the Brillouin zones (BZs). Soon after the experimental realization of quantum spin hall effect in 2D HgTe quantum wall, a number of 2D and 3D TIs have been theoretically predicted and experimentally verified. In fact, the search for new TI has been extended to zintl compounds, antiperovskites, and heavy fermion f-electron Kondo type systems. With the conceptual developments in the topological field, research on topological material has been extended from insulators to semimetals and metals. In topological semimetals, symmetry protected band crossing or accidental band touching leads to a nontrivial band topology in 3D momentum space. The topological properties of such semimetals mainly depend on the degeneracy of the bands at the crossing/touching point. A zero dimensional band crossing with two and four fold band degeneracy defines the Dirac and Weyl semimetals, respectively, which are quasi-particle counterparts of Dirac and Weyl fermions in high energy physics. Low energy Dirac fermions in condensed matter are essentially protected by time reversal symmetry (TRS), inversion symmetry (IS) and certain crystal symmetry. Quasi-particle Weyl fermion state can be realized by breaking either space inversion or time reversal of the crystal. In case of nodal line semimetal (NLS), the conduction and valance band touches along a line to form a one dimensional close loop. All the topological semimetals show some exotic phenomena, such as quantum magneto-resistance, chiral anomaly and so on.

In chapter 1, we have extensively discussed the topological band theory in CMP. We have discussed the general notion of topology in geometrical system and then we extend the discussion into the CMP through Berry phase formalism. We have started with quantum Hall effect in 2D electron gas where we discuss the non-trivial topological quantum Hall physics with external magnetic field. Then we generalize it to the quantum spin Hall (QSH) effect by using Kane-Mele Model in spin-orbit graphene. SQH effect is the first topological phenomena in that does not require an external magnetic field like quantum Hall case. In QSH effect, SOC of the crystal takes similar part as external magnetic field in quantum Hall effect. We have then discussed the 3D topological insulators and computation of Z_2 topological index, surface states, adiabatic continuation approach etc. We finally extended our discussion in gapless systems such as Dirac semimetal (DSM), triple point semimetal (TSM), nodal line semimetal (NLS), and Weyl semimetal (WSM). The importance of symmetry (both crystalline and TRS) on the semimetalic systems has been extensively discussed using toy models and symmetry based arguments. For the completeness of the discussions, we have also provided the detail of Berry phase, time reversal symmetry, model analysis for type-II DSM, description of the chiral anomaly for Weyl and Dirac metals and so on.

Density Functional Theory(DFT) has been emerged as a versatile tool to study the structural, electronic, optical properties of molecular and material based systems with a crux idea of replacing high dimensional wavefunction with electron density drastically reducing the complexity of many body Schrödinger equation. In this chapter 2, we have discussed the computational formalism of DFT which includes many-body Problem, Kohn-Sham equations, exchange-correlation functional etc. We have also provider the tight binding formalism based on localized Wannier orbital. We have used tight binding formalism for the computations of Fermi surfaces, surface states, topological index and so on.

In chapter 3, we predict the emergence of non-trivial band topology in the family of XX'Bi compounds having $P\overline{6}2m$ (# 189) space group. Using *first principle* calculations within hybrid functional framework, we demonstrate that NaSrBi and NaCaBi are strong topological insulator under controlled band engineering. Here, we propose three different ways to engineer the band topology to get a non-trivial order: (i) hydrostatic pressure, (ii) biaxial strain (due to epitaxial mismatch), and (iii) doping. Non-triviality is confirmed by investigating bulk band inversion, topological Z_2 invariant, surface dispersion and spin texture. Interestingly, some of these compounds also show a three dimensional topological nodal line semi-metal (NLS) state in the absence of spin orbit coupling (SOC). In these NLS phases, the closed loop of band degeneracy in the Brillouin zone lie close to the Fermi level. Moreover, a drumhead like flat surface state is observed on projecting the bulk state on the [001] surface. The inclusion of SOC opens up a small band gap making them behave like a topological insulator.

In chapter 4, we predict three full Heusler compounds $XInPd_2$ (X = Zr, Hf and Ti) to be potential candidates for type-II Dirac semimetals. The crystal symmetry of these compounds have appropriate chemical environment with a unique interplay of inversion, time reversal and mirror symmetry. These symmetries help to give six pairs of type-II Dirac nodes on the C₄ rotation axis, closely located at/near the Fermi level. Using *first principle* calculations, symmetry arguments and crystal field splitting analysis, we illustrate the occurrence of such Dirac nodes in these compounds. Bulk Fermi surfaces have been studied to understand the Lorentz symmetry breaking and Lifshitz transition (LT) of Fermi surfaces. By analyzing the evolution of arcs with changing chemical potential, we prove the fragile nature and the absence of topological protection of the Dirac arcs.

Noble metal surfaces (Au, Ag and Cu etc.) have been extensively

studied for the Shockley type surface states (SSs). Very recently, some of these Shockley SSs have been understood from the topological consideration, with the knowledge of global properties of electronic structure. In chapter 5, we show the existence of Dirac like excitations in the elemental noble metal Ru, Re and Os based on symmetry analysis and *first principle* calculations. The unique SSs driven Fermi arcs have been investigated in details for these metals. Our calculated SSs and Fermi arcs are consistent with the previous transport and photoemission results. We attribute these Dirac excitation mediated Fermi arc topology to be the possible reasons behind several existing transport anomalies, such as large non-saturating magneto resistance, anomalous Nernst electromotive force and its giant oscillations, magnetic breakdown etc. We further show that the Dirac like excitations in these elemental metal can further be tuned to three component Fermionic excitations, using symmetry allowed alloy mechanism.

In chapter 6, we show the occurrence of Dirac, Triple point, Weyl semimetal and topological insulating phase in a single ternary compound using specific symmetry preserving perturbations. Based on first principle calculations, **k**.**p** model and symmetry analysis, we show that alloying induced precise symmetry breaking in SrAgAs (space group $P6_3/mmc$) leads to tune various low energy excitonic phases transforming from Dirac to topological insulating via intermediate triple point and Weyl semimetal phase. We also consider the effect of external magnetic field, causing time reversal symmetry (TRS) breaking, and analyze the effect of TRS towards the realization of Weyl state. Importantly, in this material, the Fermi level lies extremely close to the nodal point with no extra Fermi pockets which further, make this compound as an ideal platform for topological study. The multi fold band degeneracies in these topological phases are analyzed based on point group representation theory. Topological insulating phase is further confirmed by calculating Z_2 index. Furthermore, the topologically protected surface states and Fermi arcs are investigated in some detail.

Composite quantum compounds (CQCs) have become an important avenue for the investigation of inter-correlation between two apparently distinct phenomenon in physics. Topological superconductors, axion insulators etc. are few such CQCs which have recently drawn tremendous attention in the community. Topological nontriviality and Rashba spin physics are seemingly two incompatible quantum phenomena but can be intertwined within a CQC platform. In chapter 7, we present a general symmetry based mechanism, supported by *ab-initio* calculations to achieve intertwined giant Rashba splitting and topological non-trivial states simultaneously in a single crystalline system. Such co-existent properties can further be tuned to achieve other rich phenomenon. We have achieved Rashba splitting energy (ΔE) and Rashba coefficient (α) values as large as 161 meV and 4.87 eVÅ respectively in conjunction with Weyl semimetal phase in $KSnSb_{0.625}Bi_{0.375}$. Interestingly, these values are even larger than the values reported for widely studied topologically trivial Rashba semiconductor BiTeI. The advantage of our present analysis is that one can achieve various topological phases without compromising the Rashba parameters, within this CQC platform.

In chapter 8, I present the conclusive remarks and the outcome of my research work. I also briefly discuss my future plans here.

PUBLICATIONS

<u>List of Publications</u>:

- Chiranjit Mondal, C K Barman, Sourabh Kumar, Aftab Alam and B Pathak, (2019) Emergence of Topological insulator and Nodal line semi-metal states in XX'Bi (X=Na, K, Rb, Cs; X'=Ca, Sr), Scientific Reports 9, 527, [DOI:10.1038/s41598-018-36869-0]
- Chiranjit Mondal*, Chanchal K Barman*, B Pathak and Aftab Alam, (2019) Type-II Dirac states in full Heusler compounds XInPd₂ (X = Ti, Zr and Hf), Phys. Rev. B 100, 245151, [DOI:https://doi.org/10.1103/PhysRevB.100.245151]
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- 4. Chiranjit Mondal^{*}, Chanchal K Barman^{*}, Aftab Alam and B Pathak, (2019) Broken symmetry driven phase transitions from a topological semimetal to a gapped topological phase in SrAgAs, Phys. Rev. B 99, 205112. [DOI:https://doi.org/10.1103/ Phys-RevB.99.205112]
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- C K Barman^{*}, Chiranjit Mondal^{*}, B Pathak and A Alam, (2020) Symmetry driven topological phases in XAgBi (X=Ba,Sr): An Abinitio hybrid functional calculations, Phys. Rev. Materials 4, 084201, [DOI:https://doi.org/10.1103/PhysRevMaterials.4.084201].

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- L. Ngamwongwan, P. Moontragoon, W. Jarernboon, Chiranjit Mondal, Biswarup Pathak, T. Kaewmaraya, (2020) Novel BCN-Phosphorene Bilayer: Dependence of Carbon Doping on Band Offsets for Potential Photovoltaic Applications, Applied Surface Sicence, 132, 2, [DOI:https://doi.org/10.1016/j.apsusc.2019.144327]
- C K Barman^{*}, Chiranjit Mondal^{*}, Sumiran Pujari, B Pathak and A Alam, Symmetry protection and giant Fermi arcs from higher-fold fermions in binary, ternary and quaternary compounds, Phys. Rev. B 102, 155147, [DOI:https://doi.org/10.1103/PhysRevB.102.155147]
- Chiranjit Mondal, C K Barman, Aftab Alam and Biswarup Pathak, (2020) Intertwined non-trivial band topology and giant Rashba spin splitting, (under review in Phys. Rev. Lett.).
 - (* Equal author contributions)

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Chapter 1

Topological Order In Condensed Matter Physics

Broken symmetry is a key concept in physics. We define new interactions, fundamental forces, and particles based on spontaneous broken symmetries based on Landau's theory of broken symmetry. In condensed matter physics (CMP), we deal with distinct phases of matter and their phase transitions such as, solid to liquid or liquid to gas. For a solid to liquid or liquid to gas phase transition, the translation symmetry need to be spontaneously broken. Similarly, in a magnetic material, spin rotation symmetry has to be spontaneously broken for magnetic phase transition. Gauge symmetry is broken in a super-conducting phase transition. Over the last few years, some paradigm shifting developments happened in CMP, that made possible to have a phase of matter which does not necessarily involve with any broken symmetry. One such example of this phase is topological phase of matter. In CMP, there is no standard model as it is in particle physics, where we often ask the questions what is beyond the standard model. In contrast, our queries in CMP rather involve with a set of questions whether there are any physics beyond the standard paradigm which mostly developed from observations, such as, quantum Hall effect, superconductivity, superfluidity, magnetism and so on. One such paradigm shifting question on the quantum Hall physics is the possibility of quantum Hall like phase without external magnetic field. Another way to ask this question is,

whether there is a topological phase beyond the quantum Hall state. Most importantly, it has become an important question, whether we can use these topological phases for some technological applications, such as room temperature superconductor, fault tolerant high speed quantum computing and so on.

The discovery of topological insulator (TI) [1-6] definitely gears up the study of topology as a means of sharply distinguish electronic phases, which has been classified as a new quantum state of matter. Initially, the classification schemes were developed based on the topological structure of ground state wave function for insulating systems; such as TI, topological crystalline insulator (TCI) [7] which later on extended to gapless systems, semimetals and metals [8-29, 37-45]. The fundamental properties of gaped system are the presence of gapless conducting states at interfaces with the trivial insulator or vacuum, i.e, where the topological index jumps from non-trivial to trivial value. In a two-dimensional (2D) quantum spin Hall insulator, the boundary state is one-dimensional (1D) helical edge state whereas it is 2D surface state for 3D TI. Both cases, time reversal symmetry (TRS) is the fundamental symmetry of the system and intrinsic spin-orbit coupling (SOC) plays the crucial role to define the topological structure of the wave functions. In contrast, topological semimetals (TSMs) are characterized by Fermi arcs surface states (SSs) which originate from a crossing of energy bands in momentum space. Such band crossing can be associated with a topological number which further leads to the topologically stable Fermi arcs on the surfaces. The nodal degeneracy, which are not associated with a topological index, may also provide Fermi arcs on the boundary but that arcs are not necessarily to be topologically protected. Hence, their appearance are fragile in nature. Symmetry plays the most important role for such band degeneracies and corresponding Fermi arcs for which the topological index are absent.

As the theoretical developments of topology in CMP are rel-

atively new and experimental realization of novel materials are restricted within handful of number, in this thesis, I will start from the basic development of the subject to the more deeper understanding in a pedagogical way. We will discuss the importance of topology in CMP through Berry phase formalism, topological band theory, Z_2 topological insulator and symmetry protected topological semimetal states in the subsequent sections.

1.1 Geometry and Topology

Topology is a mathematical properties of a geometrical structure which remain invariant with the smooth deformation of shape or size of the geometry. It is a global character that can not be affected by the local deformation of the system. In a more rigorous mathematical way, we can think of topology in the terms of Gaussian and geodesic curvature of a geometry. For instance, the topological index which defines the unique topological nature of the geometry can be computed by integrating the Gaussian curvature over the surface of that geometry. The Gauss-Bonnet theorem states that the integral of the Gaussian curvature over a closed surface is a quantized topological invariant, and its value is related to genus (g). The mathematical form of the theorem is give by,

$$g = \frac{1}{2\pi} \left[\int_M K dA + \int_{\partial M} k_g ds \right]$$
(1.1)

The first and second terms in the right hand side of the above equation are Gaussian and geodesic curvatures. g is the topological index which defines the number of holes in a geometric structure. If the values of g are different for two different geometry, they are distinct in topology, and can not be smoothly deformed one to other without changing the topological index g. For example, In Fig. 1.1,



Figure 1.1: Geometrical objects which differ in their genus (g). Objects with g=0 to 3 are different topological states and they can not be smoothly deformed. Two surfaces with same g (say, a torus and a coffee mug) can be deformed to each other as they are topologically equivalent.

sphere, torus and a double torus are topologically distinct as the topological index g (the number of holes) of these geometrical objects are zero, one and two respectively. Here the integer value of g can not be smoothly changed one to another without closing or opening a hole. In contrast, the torus can be deformed into a coffee mug without changing the topological number. Hence, they are topologically equivalent.

Now the question is, how the concept of this topology for the geometrical surfaces apply to the electronic structure of materials? The underlying mind set is to think of the Fourier space of electronic states of solid state material as a set of manifold. Then it is possible to define some set of invariant similar to classical definition of topology through Berry phase formalism or electronic motion over the close manifold. For instance, for a 2D system, a topological index for gaped electronic manifold is Z_2 topological index which can be expressed in a general form as [46],
$$Z_2 = \frac{1}{2\pi} \left[\oint_{\partial \tau} A(\mathbf{k}) dl - \int_{\tau} F(\mathbf{k}) d\tau \right] \mod 2 \tag{1.2}$$

where $A(\mathbf{k}) = i \sum_{n=1}^{N} \langle u_n(k) | \nabla_k | u_n(k) \rangle$ is the Berry connection over the occupied bands, and $F(\mathbf{k}) = \nabla_k \times A(\mathbf{k})$ is the corresponding Berry curvature. The surface integral is over half of the 2D Brillouin zone (BZ) surface τ and the line integral is over its boundary $\partial \tau$. The manifestation of topology in CMP will be further discussed in the subsequent section, topological band theory.

1.2 Topological Band Theory

Crystal is an arrangement of atoms where translation is the symmetry of the system. If the crystal is translational invariant along certain direction, crystal moment \mathbf{k} is the good quantum number along that direction which defines the periodic BZ. According to Bloch theorem, we can project the electronic states as a function of crystal momentum k. The Bloch states, $|u_m\rangle$ are the eigenstates of Bloch Hamiltonian in a unit cell. The eigenvalues of this Hamiltonian over the BZ collectively form the band structure of the crystal. The electronic state of a material can be defined whether it is insulator, semiconductor or metal, based on the knowledge of band structure. If the band structure have a relatively large energy gap, we call it an insulator. If the conduction and valence bands are overlapped, it is metal and if the band gap is moderate, it is semiconductor. Among these electronic states, insulator is the most fundamental state of matter. The simplest way to think of the insulating state is to consider the strong covalent bonding between atoms and crystal electrons. Though the insulating gap of an ordinary insulator is much lesser than an atomic insulator, such as solid argon, there is a sense in which both the insulating gap are same.

Actually, both the energy gaps are topologically trivial and can be connected to each other without topological phase transition. One way to imagine this to tune the band gap so as to interpolate between two insulating gaps continuously without closing and reopening the band gap. As such, if the two states are possible to connect through smooth deformation of its Hamiltonian without the gap closing, they are topologically equivalent. An ordinary insulator or atomic insulator can be topologically connected to vacuum which is trivial state according to relativistic quantum theory. Now the question is whether all the electronic states are topologically equivalent to a vacuum state or not. The answer lies in the great physics of band theory of topological sate of matter.

1.2.1 Berry Phase

If the Hamiltonian of a system evolve adiabatically in a parameter space, the wave function of the system gains an additional quantum mechanical phase on the top of the usual dynamical phase. This extra phase is called Berry phase which is gauge independent and hence, it is a measurable quantity. Let's consider a Hamiltonian $H(\mathbf{R})$ that evolve adiabatically in a parameter space \mathbf{R} . Assume \mathbf{R} changes through time evolution and makes a closed loop through its evolution, i.e, $\mathbf{R} \to \mathbf{R}(t)$. The parameter \mathbf{R} can be an external magnetic field for a two level system or a lattice momentum vector for crystal. Consider an instantaneous orthogonal eigen basis $|u_n(\mathbf{R})\rangle$ of the Hamiltonian $H(\mathbf{R})$ at an instant t. It satisfies the following equation at every instant of time as the parameter \mathbf{R} changes with time on the closed loop. The equation is,

$$H(\mathbf{R})|u_n(\mathbf{R})\rangle = \epsilon_n(\mathbf{R})|u_n(\mathbf{R})\rangle.$$
(1.3)

Because of the uncertainty on the phase, the above equation can not determine the state $|u_n(\mathbf{R})\rangle$ completely. The basis function supposed to be single valued and smooth on the closed loop when it is evolved in the parameter space. The time evolution of this quantum state is given by the time-dependent Schrödinger equation as,

$$i\hbar\partial_t |\phi(t)\rangle = H(\mathbf{R})|\phi(t)\rangle.$$
 (1.4)

If the time evolution of the Hamiltonian through the closed loop in the parameter space is smooth and adiabatic, the timedependent state $|\phi(t)\rangle$ can be expressed as,

$$|\phi(t)\rangle = \exp^{i\gamma_c} \exp\left[-\frac{i}{\hbar} \int_0^t dt' \epsilon_n \mathbf{R} |u_n(\mathbf{R})\rangle\right].$$
 (1.5)

where $\partial_t \gamma_c(t) = i \langle u_n(t) | \partial_t | u_n(t) \rangle$.

The phase factor in the above equations is the Berry phase which can be expressed as an integral over the close path C as,

$$\gamma_c = \int_C d\mathbf{R} \cdot \mathbf{A}_n(\mathbf{R}). \tag{1.6}$$

Where $\mathbf{A}_n(\mathbf{R})$ is the Berry vector potential or Berry connection.

We can use the Stock's theorem to rewrite the above path integral as a surface integral over the surface S (S is enclosed by the close loop C) in terms of the Berry curvature or Berry field strength as,

$$F_n(\mathbf{R}) = \nabla_R \times \mathbf{A}_n(\mathbf{R}). \tag{1.7}$$

Where $F_n(\mathbf{R})$ is the Berry curvature.

For a lattice where the parameter of the Hamiltonian is momentum vector \mathbf{k} , the Berry curvature can be expressed as,

$$F_n(\mathbf{k}) = \nabla_k \times \langle u_n(\mathbf{k}) | i \nabla_k | u_n(\mathbf{k}) \rangle.$$
(1.8)

Where $|u_n(\mathbf{k})\rangle$ is the Bloch eigen state.

Now, the point in BZ can be mapped to the same point in a periodic lattice by the reciprocal lattice vector \mathbf{K} , i.e, $\mathbf{k} + \mathbf{K} \to \mathbf{k}$. So, the \mathbf{k} vector forms a close loop when it sweeps over the full BZ. Then, the Berry phase takes the form

$$\gamma_c = \int_{BZ} d\mathbf{k} \langle u_n(\mathbf{k}) | i \nabla_k | u_n(\mathbf{k}) \rangle.$$
(1.9)

The notion of Berry phase is very important in topological physics and it will often be appeared in various context in the subsequent discussions.

1.2.2 Quantization of The Hall Conductance and First Chern Number

The Hall conductance can be express in terms of surface integration of Berry curvature over the BZ as,



Figure 1.2: The equivalence between a 2D BZ and a torus. (a) A rectangular 2D BZ with periodic boundary conditions. (b) The 2D BZ can be rolled around the k_x axis into a tube using the boundary conditions along k_y . (c) The tube can further be rolled into a torus. Adapted from Reference [50].

$$\sigma_{xy} = \frac{e^2}{2\pi h} \int_0^{2\pi} dk_x \int_0^{2\pi} dk_y [\nabla_{\mathbf{k}} \times \mathbf{A}(k_x, k_y)].$$
(1.10)

We can use the Stokes' theorem to evaluate the above integration. Considering the fact that the surface is smooth and simply connected, we can construct a torus from the 2D BZ with the periodic boundary conditions (see Fig. 1.2). This is how the concept of topology of BZ comes into the quantum Hall physics. Now, the above surface integral in terms of line integral around the first BZ;

$$\sigma_{xy} = \frac{e^2}{2\pi h} \int_0^{2\pi} dk_x \int_0^{2\pi} dk_y [\partial_{k_x} \mathbf{A}_y(k_x, k_y) - \partial_{k_y} \mathbf{A}_x(k_x, k_y)] = \frac{e^2}{2\pi h} \int_0^{2\pi} dk_y [\mathbf{A}_y(2\pi, k_y) - \mathbf{A}_y(0, k_y)] - \frac{e^2}{2\pi h} \int_0^{2\pi} dk_x [\mathbf{A}_x(k_x, 2\pi,) - \mathbf{A}_x(k_x, 0)].$$
(1.11)

Recalling that the states $|u(k_x, 0)\rangle$ and $|u(k_x, 2\pi)\rangle$ are same because of the periodic boundary condition in BZ. These two states can only be differ by an extra phase factor, i.e, $|u(k_x, 2\pi)\rangle =$ $\exp[i\theta_x(k_x)]|u(k_x, 0)\rangle$.

So, we can write the Berry connection as,

$$\mathbf{A}_{x}(k_{x}, 2\pi) = \langle u(k_{x}, 2\pi) | i\partial_{k_{x}} | u(k_{x}, 2\pi) \rangle$$
$$= -\partial_{k_{x}}\theta_{x}(k_{x}) + \mathbf{A}_{x}(k_{x}, 0).$$
(1.12)

Similarly, using $|u(2\pi, k_y)\rangle = \exp[i\theta_y(k_y)]|u(0, k_y)\rangle$, we have

$$\mathbf{A}_{y}(2\pi, k_{y}) = \langle u(2\pi, k_{y}) | i \partial_{k_{x}} | u(2\pi, k_{y}) \rangle$$
$$= -\partial_{k_{y}} \theta_{y}(k_{y}) + \mathbf{A}_{y}(0, k_{y}).$$
(1.13)

 $\theta_x(k_x)$ and $\theta_y(k_y)$ are two smooth functions. Using Eq. 1.12 and Eq. 1.13, we get the expression for quantum conductance as

$$\sigma_{xy} = \frac{e^2}{2\pi h} \int_0^{2\pi} dk_y [-\partial_{k_y} \theta_y(k_y)] + \frac{e^2}{2\pi h} \int_0^{2\pi} dk_x [\partial_{k_x} \theta_x(k_x)] = \frac{e^2}{2\pi h} [\theta_y(0) - \theta_y(2\pi) + \theta_x(2\pi) - \theta_x(0)].$$
(1.14)

All the four states $|u(0,0)\rangle$, $|u(0,2\pi)\rangle$, $|u(2\pi,0)\rangle$ and $|u(2\pi,2\pi)\rangle$ are the same states on the torus as shown in Fig. 1.2 (c). Hence, we can write the phase relations among these states as,

$$e^{i\theta_x(0)}|u(0,2\pi)\rangle = |u(0,0)\rangle,$$

$$e^{i\theta_x(2\pi)}|u(2\pi,2\pi)\rangle = |u(2\pi,0)\rangle,$$

$$e^{i\theta_y(0)}|u(2\pi,0)\rangle = |u(0,0)\rangle,$$

$$e^{i\theta_y(2\pi)}|u(2\pi,2\pi)\rangle = |u(0,2\pi)\rangle.$$

Which gives $|u(0,0)\rangle = e^{[\theta_x(0) + \theta_y(2\pi) - \theta_x(2\pi) - \theta_y(0)]} |u(0,0)\rangle.$

The single valuedness of state $|u(0,0)\rangle$ provides the condition

$$\theta_x(0) + \theta_y(2\pi) - \theta_x(2\pi) - \theta_y(0) = 2\pi C.$$
(1.15)

C is an integer which is called first Chern number or Thouless-Kohmoto-Nightingale-Nijs (TKNN) [47] topological index. This topological index ensure the quantization in Hall conductance and introduce the mathematical concept concept of topology into the quantum Hall physics. The Hall conductance is given by

$$\sigma_{xy} = C \frac{e^2}{h}.\tag{1.16}$$

1.2.3 Integer Quantum Hall Effect: Laughlin's Argument

The generalization of quantization of Hall conductance which had been experimentally established by Klitzing, Dorda, and Pepper, comes with the Laughlin's arguments [48]. Laughlin argued that the Hall conductance quantization is a consequence of the existence of the bulk mobility gap and gauge invariance. Also the transverse quantized Hall current inevitably introduce the edge state at the boundary. How can that be possible? The answer comes through the Laughlin's argument. For instance, for a 2D system having edges, the transport of Hall current upon a flux insertion is only possible if and only if there are some states at the edges to donate or receive the carriers. So, the bulk for such system is insulator (i.e, the Fermi level resides inside the mobility gap) but edges form the Fermi liquid state.



Figure 1.3: A schematic diagram for Laughlin's experiment for the integer quantum Hall effect. Adapted from Ref. [50].

Consider a 2D electron gas (2DEG) system with an external magnetic field applied perpendicular to it as shown in Fig. 1.3. The y-direction has the periodic boundary condition with the periodicity L_y and edges are there on the both sides of the sample along x-direction. Because of the periodic boundary condition, the 2DEG can be wrapped in y-direction to make a cylinder having the circumference L_y . The length of the cylinder is L_x . For each value of L_x along the axis of cylinder, \mathbf{k}_y is a good quantum number. The applied magnetic field in the 2D quantum Hall system is directed radially w.r.t to the axis of the cylinder. Laughlin then imagined a fictitious magnetic flux $\delta \Phi(t)$ (similar to an Aharonov-Bohm flux) along the axis of the cylinder. Note that, this flux does not originate from the radial magnetic field B, applied to the system. This is a flux that control and change the \mathbf{k}_y momentum, i.e $\delta \Phi(t)$ creates an electric field $\delta \mathbf{E}(t)$ along y-direction. Together this $\delta \mathbf{E}(t)$ and **B** generate a force on charges to move from one edge to another edge. This is equivalent to creating a potential difference between the edges.

Now, the vector potential generated by the flux is, $\delta \mathbf{A}(t) = (0, \frac{\delta \Phi(t)}{L_y}, 0)$, as one can verify from, $\oint \delta \mathbf{A} \cdot \mathbf{dl} = \oint dy \frac{\delta \Phi(t)}{L_y} = \delta \Phi(t)$.

The flux $\delta \Phi(t)$ generates an electric field

$$\delta \mathbf{E}(t) = -\frac{1}{c} \frac{\partial}{\partial t} \delta \mathbf{A}(t) = -\hat{y} \frac{1}{cL_u} \frac{\partial}{\partial t} \delta \Phi(t).$$

The source to drain current induced by this electric field is

$$\delta j_x(t) = \sigma_{xy}(t) \delta E_y(t)$$

Accordingly, the charge transported from source to drain is

$$\delta Q = L_y \int_0^\tau dt \frac{\partial}{\partial t} \delta \Phi(t)$$

= $-\frac{\sigma_{xy}}{c} [\delta \Phi(\tau) - \delta \Phi(0)].$ (1.17)

Let's choose $\delta \Phi(\tau) - \delta \Phi(0)$ is a single flux quantum, i.e,

$$\delta\Phi(\tau) - \delta\Phi(0) = -\Phi_0 = -\frac{hc}{e}.$$

We know that the Aharonov-Bohm flux has a periodicity of Φ_0 , namely the Hamiltonian of the 2DEG is periodic in the inserted flux with a period Φ_0 . Now for a many body system δQ is *ne. n* is an integer which actually quantized the Hall conductance and can be determined from the topology of band structure of the system.

So, the quantum hall Hall conductivity is $\sigma_{xy} = \frac{e^2}{h}n$.

This integer *n* carries the same physics as the first Chern number *C* as discussed previously in the derivation of σ_{xy} using Kubo formula.

1.2.4 Spin Quantum Hall Effect

Spin quantum Hall effect is the spin version of the integer quantum Hall effect. Intrinsic SOC of the system generates external magnetic field like effect and possesses two helical edge states at the boundary. Though, both orbital and spin change their sign under the TRS, SOC respect the TRS in quantum spin Hall system. It is a remarkable result in a sense that the presence of quantum spin Hall state without breaking of TRS. We can start with the Haldane model that describes a nontrivial Chern insulator with finite Hall conductance under the TRS breaking condition [49]. More than a decade later, it had been realized that a TRS intact system can also lead to equally interesting phenomenon as TRS broken integer quantum Hall physics. It was a great realization of a new topological phase by doubling the Haldane version through adding the SOC into the problem in Kane and Mele's work on spinfull graphene [51]. Kane and Male model shows the presence of gapless helical edge states on the boundary of graphene without breaking the TRS. Unlike integer quantum Hall phase, a spin dependent Chern number can not be used to define the topological Hall phase. Instead, a new topological invariant, called Z_2 index is required which was introduced by Kane and Mele in their pioneering work [52]. The discovery of topological phase in HgTe-CdTe quantum wall [53] was first experimental confirmation of quantum spin Hall phase in a real system which further stimulated the research of topology in condensed matter physics.

1.3 Z₂ Topological Insulator

After the discovery of QSH state in HgTe-CdTe quantum wall, in 2006, the generalization of QSH phase from 2D to 3D had been introduced independently by Moore and Balents [54], Fu, Kane, and Mele [55]. This new insulating electronic phase of matter in 3D had been named as "topological insulator". Fu, Kane and Mele proposed the bulk-boundary correspondence for TI phase of material where the topological non-trivial order of bulk electronic structure ensure the robust Dirac like conducting surface states (SSs) on its boundary. Soon after the theoretical prediction of TI phase in α -Sn and strained HgTe, in 2009, the second-generation TIs had been theoretically predicted and then experimentally verified in Bi₂Se₃ [2, 5]. Immediate after this material realization, several topological properties which have been predicted so far, have been experimentally verified in Bi₂Se₃ [57–63]. Then numerous number of TI have been predicted and verified in several material class using both *first-principle* DFT calculation and photoemission experiments [64–80].

1.3.1 Computation of Z_2 Topological Invariants

There are several formula to compute the Z_2 invariants [51, 52] of a material to check the topological phase. The parity counting method proposed by Fu and Kane is very simple and extensively used to compute Z_2 index in inversion symmetric crystal [81]. However, the system which does not possess inversion center, a method involved with adiabatic spin pumping by time-reversal polarization is particularly applicable which is the generalization of parity counting method in non-centrosymmetric system, proposed by Fu and Kane [82].

Systems With Inversion Symmetry

The approach to compute Z_2 invariant for inversion symmetric system is relatively straightforward. The product of the parity eigen values of the time reversal partner of the bands over the occupied bands at TRIM points provide the Z_2 index. In 2D, there are four $((0,0,0), (\pi,0,0) \text{ and } (\pi,\pi,0) \text{ for a square lattice})$ TRIM points and it is eight $((0,0,0), (\pi,0,0), (\pi,\pi,0)$ and (π,π,π) for a cubic lattice) in 3D. In 2D, there is one unique ν that define the Z_2 invariant which separate non-trivial phase from trivial phase. However, in 3D, the picture is complicated. Four distinct Z_2 ($\nu_0; \nu_1, \nu_2, \nu_3$) can be constructed that define the topological state of the material. If $\nu_0=1$, it is considered to be a "strong topological insulator" in a sense that the gapless SSs are inevitable to appear on the surfaces under the weak TRS invariant perturbations. In contrast, if $\nu_0=0$ and any of the other three is nonzero, the phase is called "weak topological insulator". The "weak topological insulator" can be considered as a stacking of 2D QSH insulator in certain direction and it is supposed to be less robust.

Fu and Kane came up with a new quantity [81], $\delta_i = \Pr[w(\Lambda_i)]/\sqrt{Det[w(\Lambda_i)]} = \pm 1$. Here, Pf stands for Pfaffian of a unitary matrix $[w(\Lambda_i)]$ where the matrix elements of $[w(\Lambda_i)]$ is $w_{mn}(\mathbf{k}) = \langle u_m(\mathbf{k}) | T | u_n(-\mathbf{k}) \rangle$. $|u_n(\mathbf{k}) \rangle$ are the nth band Bloch states. T is the time-reversal operator and Λ_i denotes the TRIM points. The Z_2 is given by (ν for 2D and ν_0 for 3D)

$$(-1)^{\nu} = \prod_{i=1}^{n} \delta_i, \qquad (1.18)$$

with n is 4 for 2D and it is 8 for 3D. The other three invariants can be computed considering a particular set of four TRIM points in a certain plane using a relation similar to the equation Eq. 1.18. These three invariants (ν_1, ν_2, ν_3) represents the topological nature (spin quantum Hall phase) of the corresponding planes.

Systems Without Inversion Symmetry

The above parity analysis does not work for non-centrosymmetric system as it is not possible to decompose the parity eigen value at the TRIM points in the absence of inversion symmetry (IS) in the crystal. However, Z_2 can be computed for such system using the equation as proposed by Fu and Kane as [82],

$$Z_2 = \frac{1}{2\pi} \left[\oint_{\partial \tau} A(\mathbf{k}) dl - \int_{\tau} F(\mathbf{k}) d\tau \right] \mod 2$$
 (1.19)

where $A(\mathbf{k}) = i \sum_{n=1}^{N} \langle u_n(k) | \nabla_k | u_n(k) \rangle$ is the Berry connection over the occupied filled bands, and $F(\mathbf{k}) = \nabla_k \times A(\mathbf{k})$ is the Berry curvature.

To get the 3D version of Z_2 , we have to consider six different planes composed by the six set of TRIM points. Then computing



Figure 1.4: The known nontrivial HgTe is adiabatically transformed into Heusler compound YPtSb. Adapted from Ref. [56].

the Z_2 invariant for each plane using the Eq. 1.19 and involving them altogether one can get the Z_2 for the whole 3D BZ.

1.3.2 Adiabatic Continuation Approach

Adiabatic continuation approach is another simple yet powerful method to identify the topological state of a material (sample material) considering a known TI as the reference compound. If the sample and the reference materials are adiabatically connected, the state of reference material is a TI. In contrast, it is a trivial insulator if they are not adiabatically connected. Here the adiabatic connection means simply the transformation of electronic band order from sample material to reference TI without closing and reopening the energy gap with the perturbations. The perturbations can be external pressure, strain, doping or changing the atomic number very smoothly.

Figure 1.4 shows how HgTe and half Heusler compound YPtSb are structurally equivalent. Without closing and reopening the energy gap, HgTe can be transformed to YPtSb through a hypothetical crystal structure transformation. Let us consider the HgTe crystal, in which we insert Kr atoms at the similar Wyckoff positing of zinc blend structure such that the hypothetical KrHgTe looks like a half Heusler compound. Here, the Kr does not effect the electronic structure much apart from changing the lattice constants. Then the nuclear charges of Kr, Hg, and Te are need to soothly adjusted



Figure 1.5: Band gap closes and reopen in a topological phase transition through a Dirac metal phase.

by changing the ingredient atoms of the crystal. For KrHgTe, the nuclear charge can set using the equations, $Z_{Kr} = 36 + 2x + y$, $Z_{Hg} = 80 - 2x$ and $Z_{Te} = 52 - y$. Now, in the phase space, during the transformation from x=0, y=0 (i.e HgTe) to x=1, y=1 (i.e YPtSb), the low energy Hamiltonian does not close and reopen the energy gap, proving that HgTe and YPtSb are adiabatically connected and topologically equivalent.

Figure 1.5 shows the evolution of energy gap under some external tuning parameters such as pressure, strain or doping etc. Let the M < 0 represents a non-trivial band gap whereas it is trivial if M > 0. Fig. 1.5(a) and (b) are topologically equivalent as they can be adiabatically tuned to each other without changing the sign of M. However, to go to Fig. 1.5 (d) from Fig. 1.5 (a) or (b), the gap has to be closed through the critical point and reopen it again. Therefore, the topological state of (a) or (b) and (d) are distinct. The critical phase Fig. 1.5 (c) i.e, M = 0 is called Dirac semimetal (DSM) phase. A DSM phase is unavoidable when a trivial insulator transforms to a TI under the under the external tuning. The technique seems to be simple yet so difficult in a sense that the method requires larger number of calculations by continuously changing the external parameters.

1.3.3 Surface State Computation

Because of the non-trivial band ordering in the bulk, the unique SSs are guaranteed to appear on the boundary of the crystal when it is exposed to vacuum or another trivial material. This is called bulk-boundary correspondence. Thus the appearance of such SSs can be considered as one of the primary signature of a topological phase transition. For a 3D bulk, to get the SSs, a slab geometry is required and for 2d material, the boundary is an edge. Topological SSs connect the valence and conduction bands and supposed to be appeared inside the bulk inverted gap. Two surface bands form Dirac like linear dispersion and the degeneracy is protected at TRIM point by TRS. The SSs are robust under the weak time-reversal invariant perturbations such as dangling bonds on the surface.

For the computation of SSs of TI, first principles calculation is particularly demanding. A large slab geometry is to be constructed and then projecting the surface atomic contribution over the slab band structure, the topological Dirac cone dispersion can be visualized. Note that, the thickness of the slab should be large to avoid the interaction between top and bottom surfaces. Such interaction can open up the Dirac cone and make it massive [83]. For instance, to get the gapless surface states of Bi_2Se_3 surfaces, the slab thickness has to be at least six quintuple layers (QLs) thick along the *c*-axis as shown in Fig. 1.6 [83].

Another kind of SSs which appear on the surface of material owing to the absence of IS at the terminated surface. This SSs are originated from the interplay of broken IS and strong SOC. Although the Hamiltonian of Rashba SSs and topological SSs look similar, they appear on the surfaces for different physics. Topological SSs are robust as it is a consequence of topology of bulk electronic structure. However, the Rashba SSs can be easily tuned by external perturbations, such as surface doping, electric field and



Figure 1.6: Measured ARPES spectra of Bi_2Se_3 films of 1, 2, 3, 5 and 6 QL at room temperature. Adapted from Reference [83].

so on [84, 85]. The topological SSs Hamiltonian (which is also similar to Rashba Hamiltonian) is $H_R = \frac{k^2}{2m} \pm \alpha_r(\mathbf{q} \times \sigma)$. First term is the kinetic energy term and second term is Rashba term. For a Rashba SSs, the kinetic energy dominates at large \mathbf{q} and decoupled spin bands bend towards high energy. However, for topological SSs, α_r dominates the kinetic energy (i.e, $\alpha_r > \frac{k^2}{2m}$) even at higher momentum **q** and they are then bound to connect the CB and VB because of bulk-boundary correspondence. Note that, both the SSs look similar near the nodal points which are protected by TRS. It is to be noted that Rashba SSs do not enjoy the protection like topological SSs, hence they are not robust. More importantly, both the SSs can appear on the same surface together [84, 85]. In such situation, the Rashba SSs can be tuned very easily to disappear by surface purterbations, such as surface doping. However, the topological SSs will remain their if the doping strength is not too high. However, the external purterbations have to be such that it respect the TRS of the system for both cases.

1.4 Topological Semimetal

The concept of topology firmly established in CMP through the discovery of TIs as an introduction of a new phase of matter whose ground state electronic structure is insulating. The classification of topology in gaped systems further been extended to gapless semimetal phase of material, called topological semimetal (TSM) where the topology of the wave function mainly depends on the collective low energy excitation at the vicinity of the multi-fold degenerate nodal points. Such multi-fold degenerate nodal points may carry some topological numbers which ensure the bulk-boundary correspondence in the crystal. Stability of the nodal points often strongly associated with the crystalline symmetries of the system.

The classification of TSM has done on the co-dimension and the dispersion of bands near the nodal points. If the degeneracy is a line-degeneracy, it is a nodal line semimetal (NLS) [37-45].The point degenerate TSMs are further classified into Dirac semimetal (DSM) [8–14], Weyl semimetal (WSM) [30–36], triple point semimetal (TPSM) [18–29] and so on depending on the degree of degeneracy of the nodal points, i.e., whether it is a twofold (WSM), three-fold (TSM) or four-fold (DSM) degenerate nodal point. The low-energy Dirac and Weyl crossings in condensed matter system are analogous to the relativistic Dirac and Weyl particles in high energy physics. However, the TPSM does not have any high energy analogue in the quantum field theory. The TPSM is considered to be the intermediate state of the other two phases. All these three semimetals have been theoretically predicted and experimentally verified in various condensed matter systems holding appropriate crystalline symmetries. Precise Breaking of the crystalline symmetries and TRS can tune the band degeneracies which further drives the system from one semimetal phase to other semimetal or gaped states. For an example, crystals having inversion symmetry with C_{3v} little group along some high-symmetry line (HSL) in Brillouin zone (BZ) could provide four fold Dirac node if there is an accidental band crossing on that HSL. Two triply degenerate nodes (TDN) can be formed by simply breaking the inversion symmetry (keeping C_{3v} intact). These pairs of TDN can further be splitted into four Weyl points (WP) when lowering C_{3v} to C_3 (breaking

vertical mirror plane). Finally, TI phase could be realized by further breaking the C_3 symmetry. Due to the presence of non-trivial band topology and unique arc states, TSMs show various intriguing quantum phenomenon in transport experiments, such as planer Hall effect [86], chiral anomaly [87] so on.

Over the last few years, the research on TSMs extensively involved with the advanced theoretical ideas, first principles simulation driven material predictions and experimental realization through photoemmision and transport measurements. In particular, first principles predictions of TSMs have played an important role to develop the field, providing the guiding principle of material search. The knowledge of symmetry also play an important role in the field of of TSM to determine the nature of the band degeneracy at the nodal points. Symmetry provides the insight of the intercorelation between the distinct TSM phases and the transparent guidance for the phase transition among them. Thus, the symmetry relates the crystal structure and corresponding electronic structure in a natural way. In the subsequent paragraphs and chapters, the application of symmetry in condensed matter systems will be exemplified through several examples of TSMs, such as Weyl semimetal, Dirac semimetal, triple point semimetal, Nodal line semimetal so on.

1.4.1 Weyl Semimetal

We start with a 2×2 Hamiltonian $H = f_1 \sigma_x + f_2 \sigma_y + f_3 \sigma_3$ and then ask the question of what brings the two energy levels of this Hamiltonian together to make a degeneracy. This can not be achieved by tuning any one or two of the parameters of the Hamiltonian. All the three parameters f_1 , f_2 and f_3 need to be tuned simultaneously to zero. Such a degenerate points is stable by itself in three dimension as it does not required any symmetry of the system, named as Weyl node. Such degenerate nodal point have been discussed in the context of Berry phase physics and thus, naturally extended to the topological structure of the ground state wavefunction of the system.

In the presence of SOC, energy bands are doubly degenerate if the TRS and IS of the system are respected simultaneously. In a TRS invariant system, $T^2 = -1$ if SOC is considered which ensure the double degeneracy at the TRIM points. Adding IS to the system, we have $(TI)^2 = -1$ which readily ensures the double degeneracy over the whole BZ. As such, all the crystal possess Weyl fermion at its TRIM points (if TRS is respected) as the two-fold Kramer's degeneracy can be considered as a Weyl nodes. However, the quadratic kinetic energy term dominates and bands do not disperse linearly even very close to the nodal points. So, an accidental degeneracy that are captured in Hamiltonian $H(\mathbf{k}) = f_0 \mathbb{I} + f_1(\mathbf{k})\sigma_x + f_2(\mathbf{k})\sigma_y + f_3(\mathbf{k})\sigma_3$ provide the Weyl excitation near the nodal point. For this Hamiltonian, to get the point degeneracy, all the three parameters f_1 , f_2 and f_3 have to be adjusted to zero simultaneously. The Weyl nodes are stable in momentum space in a sense that, adding a symmetry allowed term in the Hamiltonian will only shifts the position of the node. The annihilation of two Weyl nodes having opposite charges is possible only when they are tuned to be together in a single point in momentum space.

As the Weyl nodes do not essentially require any symmetry to be appeared, it can be found in various compounds in a quite natural way. Let's now concentrate on the physics near the Weyl nodes and on its topological aspects. The dispersion near the band touching point can discussed by expanding the Hamiltonian around $\mathbf{k} = \delta \mathbf{k} + \mathbf{k}_0$ as

$$H(\mathbf{k}) \sim f_0 \mathbb{I} + \mathbf{v}_0 \cdot \delta \mathbf{k} \mathbb{I} + \sum_{a=x,y,z} \mathbf{v}_a \cdot \delta \mathbf{k} \sigma_a$$
(1.20)

where \mathbf{v}_{μ} denotes the effective velocities as give by $\mathbf{v}_{\mu} = \nabla_k f_{\mu}(\mathbf{k})|_{\mathbf{k}=\mathbf{k}_0}$. If we consider the spacial case with $\mathbf{v}_0 = 0$ and $\mathbf{v}_a = v_0 \hat{a}$ (a = 1,2,3), we get the Weyl equations

$$i\partial_t \psi_{\pm} = H_{\pm} \psi_{\pm}$$
$$H_{\pm} = \mp \mathbf{p} \cdot \sigma. \tag{1.21}$$

To make the connection with the topology, we compute the Berry flux over a small spherical surface enclosing the Weyl node which is exactly $2\pi C$. Here, C denotes the Chern number and given by $C = \operatorname{sign}(\mathbf{v}_x \cdot \mathbf{v}_y \times \mathbf{v}_z)$. $C = \pm 1$ depending on the Weyl node whether it is source of sink of monopole of Berry flux. The integration of Berry curvature over the full BZ must be zero to make the total Chern number of the crystal to vanish. This is the Nielsen-Ninomiya theorem [88] that says, the Weyl nodes comes in pair with opposite chirality. It is always possible to decouple a 4×4 massless Dirac Hamiltonian into two 2×2 Weyl Hamiltonians with opposite chiralitis. This will be discussed in detail later. Another important fact that the Berry curvature is odd under TRS i.e, $F_n^{ab}(\mathbf{k}) = -F_n^{ab}(-\mathbf{k})$ and even under IS i.e, $F_n^{ab}(\mathbf{k}) = F_n^{ab}(-\mathbf{k})$. Under both the TRS and IS, Berry curvature vanishes. So, the symmetries of Berry curvature provide the more formal picture of Nielsen-Ninomiya theorem for Weyl fermions and demonstrate that the Weyls are allowed if and only if at least one of them (TRS and IS) are broken.

Broken TRS allows the crystal to possess WSM phase even if the IS is preserved. Minimal number of Weyl nodes (at least two) are possible to achieve as \mathbf{k} and $-\mathbf{k}$ are not connected by TRS in this case. Some of the WSMs in this class that have been theoretically predicted or experimentally verified are magnetic pyrochlores $A_2Ir_2O_7$ (A = Y, Eu, Nd, Sm, or Pr) [36], ferromagnetic half-metal $HgCr_2Se_4$ [89], layered half metal $Co_3Sn_2S_2$ [90], Co-based Heusler alloys [91] and so on. IS broken WSM is more complicated than TRS broken WSM because the number of Weyl nodes come in larger number in it as the electronic structure is exactly same in one half of the BZ to the other half because of the presence of TRS. Thus, the minimal number of Weyl nodes in a IS broken crystal are four. Although it is complicated to analyze the nodal points in BZ, the IS broken WSM is superior from the experimental perspective. For instance, it is always simpler to perform ARPES experiments in a nonmagnetic crystal. Also, the effect of external magnetic field can be well understood in a TRS invariant system than a magnetically ordered system. Number of WSM of this class are relatively large. Some of them are TaAs [34], TaP [92], NbAs [93], MoTe₂ [94], WP_2 [95] so on.

WSM compounds with point like Fermi surface (FS)(Fig. 1.7(a)) at the nodal points have been studied extensively and referred as type-I semimetals. There are classes where these Dirac or Weyl nodes get sufficiently tilted in the momentum space shifting the point like FS to a contour like FS (Fig. 1.7(b)). Such contour like FS yields strikingly different physics as compared to type-I semimetal, and are called type-II WSM. In three dimension (3D), the most generalized Weyl Hamiltonian can be written as; $H(\mathbf{k}) =$ $\sum k_i v_{ij} \sigma_j$, where i = (x, y, z) and $j = (\theta, x, y, z)$, σ_j 's are the identity and Pauli matrices. The Weyl point is robust as it uses all the Pauli matrices, provided det $[v_{ij}] \neq 0$. v_{ij} 's (j = x, y, z) are the coefficients that determine the velocity of the bands in each direction. v_{i0} defines the energy offset of nodal point with respect to the Fermi level. For an ideal WSM, Fermi level should pass through the Weyl node such



Figure 1.7: (a) Type-I Dirac node and corresponding point like Fermi surface (FS) at the nodal point. (b) Type-II Dirac node and corresponding contour like FS.

that $v_{i0} = 0$. The eigen values of this Hamiltonian can be written as; $\epsilon_{\pm}(\mathbf{k}) = k_i v_{i0} \pm \sqrt{\sum_{j \neq 0} (k_i v_{i,j})^2} = T(\mathbf{k}) \pm U(\mathbf{k})$. $T(\mathbf{k})$ and $U(\mathbf{k})$ can be considered as the kinetic and potential energy of the Hamiltonian. $T(\mathbf{k})$ is the linear function of momentum which introduce a tilting term into the energy spectrums if $|T(\mathbf{k})| > |U(\mathbf{k})|$ along some \mathbf{k} direction. This condition breaks the Lorentz invariance in quantum field theory but not important in condensed matter system as the nodal points are protected by either non-trivial topology or space group symmetry. The above discussion of generalized model Hamiltonian is similarly applicable in DSM compounds. However, the Dirac Hamiltonian is not robust against symmetry breaking perturbations and needs extra crystalline symmetries to protect the Dirac nodes from opening up a gap. Some of the potential type-II WSM are MoTe₂ [94], WP₂ [95] so on.

1.4.2 Dirac Semimetal

Simultaneous presence of TRS and IS enforce all the bands to be doubly degenerate when SOC is considered. The crossing of such two such bands create a four-fold degenerate Dirac node [8–14]. In the presence of both TRS and IS, two Weyl nodes with opposite charges become energetically degenerate with the annihilation of their Chern numbers. The four-fold degenerate Dirac node becomes topologically unprotected as it has zero Chern number and the residual momentum-conserving terms of the Hamiltonian corresponding to the two degenerate bands can mix up together near the Dirac node and open up a gap at the nodal point. However, such mixing of bands can be forbidden in the presence of suitable space group symmetries in the system and in such case, Dirac nodes become the symmetry protected degeneracies. Also, as discussed previously, the quantum critical point at the phase boundary between trivial insulator and Z_2 insulator is a Dirac phase which occur when the parameters of the Hamiltonian are tuned smoothly to close and reopen the energy gap of the system. This is sometimes named as "three dimensional graphenes". But for DSM, the gap is supposed to be symmetry protected even in the presence of strong SOC unlike the graphene where SOC open up a quantum spin insulating gap.

Band inversion plays an important role to decide the topological order of an insulator. If the manifold is gaped and bands are inverted, it is possible to define the Z_2 topological invariant for that system. If the Z_2 index is zero, the insulator is a trivial insulator, otherwise the system is a TI, as discussed in previous sections. However, if the crystal holds certain rotational symmetry, the band inversion between CBM and VBM leads to a semimetalic state instead of the insulating phase. The band hybridization is prohibited along the rotation axis because of the symmetry. As such, they form a nodal degeneracy at the crossing points. Perhaps, it is the simplest root to achieve a DSM state. Now, consider a crystal which have both TRS and IS simultaneously. The energy eigen value transforms under TRS and IS as $E_{n,\uparrow}(\mathbf{k}) = E_{n,\downarrow}(-\mathbf{k})$ and $E_{n,\sigma}(\mathbf{k}) = E_{n,\sigma}(-\mathbf{k})$ respectively. Simultaneous operation of both TRS and IS requires $E_{n,\uparrow}(\mathbf{k}) = E_{n,\downarrow}(\mathbf{k})$ which ensure the doubly degenerate manifolds at every **k**. When such two doubly degenerate bands get inverted and the bands possess distinct rotation eigen values along the rotation axis, they form four-fold degenerate gapless state. The band dispersion is linear near the nodal point, named as Dirac cone. Unlike the Dirac cone of TI on the surface which is protected by a topological invariant, the bulk Dirac cone in a DSM is protected by crystalline symmetry of the system.

 A_3Bi (A = Na, K, Rb) [96] class are the first predicted DSM compounds in this category. Later, Na₃Bi [11] has been experimentally verified. Cd₃As₂ [14] comes as the first verified DSM compounds. Figure 1.8(a,b) shows the band structures of Na₃Bi and Cd₃As₂ respectively. For Na₃Bi, six-fold rotation symmetry and the other mirror planes ensure the Dirac crossings on the C₆ axis where as it is four-fold rotation which plays the role in Dirac compound Cd₃As₂.

To get a better understanding, we can can write a low energy k.p Hamiltonian for both Na₃Bi and Cd₃As₂ around the Γ point as

$$H(\mathbf{k}) = \epsilon_{\mathbf{0}}(\mathbf{k})\mathbb{I} + \begin{pmatrix} M(\mathbf{k}) & Ak_{+} & Dk_{-} & -B^{*}(\mathbf{k}) \\ Ak_{-} & -M(\mathbf{k}) & B^{*}(\mathbf{k}) & 0 \\ Dk_{+} & B(\mathbf{k}) & M(\mathbf{k}) & Ak_{-} \\ -B(\mathbf{k}) & 0 & Ak_{+} & -M(\mathbf{k}) \end{pmatrix}$$
(1.22)

where $\epsilon_0(\mathbf{k}) = C_0 + C_1 k_z^2 + C_2 (k_x^2 + k_y^2), \quad k_{\pm} = k_x \pm i k_y, \quad M(\mathbf{k}) = -M_0 + M_1 k_z^2 + M_2 (k_x^2 + k_y^2)$ with $M_0, M_1, M_2 > 0$ to confirm the band inversion, i.e, the value of M(k) (positive or negative) particularly decide whether the compound is an insulator or DSM. The Finite value of parameter D introduces broken inversion symmetry. Therefore, D = 0 for centro-symmetric DSM. The eigenvalues of the above Hamiltonian are,

$$E(\mathbf{k}) = \epsilon_0(\mathbf{k}) \pm \sqrt{M(\mathbf{k})^2 + A^2 k_+ k_- + |B(\mathbf{k})|^2}$$
(1.23)

and the position of nodal points occur at $k_z = \pm \sqrt{M_0/M_1}$.



Figure 1.8: (a,b) Band structures of Na₃Bi and Cd₃As₃, calculated using *first-principles* computations. For both compounds the Dirac nodes lie on the rotation axis (C₆ and C₄) due to the band inversion between CBM and VBM at the Γ point. (a) and (b) are adapted from Ref. [96] and [105].

Some nonsymmorphic space groups enforce bands to be degenerate at certain high symmetry points. Such degeneracies can be four-fold and the dispersion of bands near the degenerate point is linear in nature. These symmetry enforced electronic excitation can be captured within the form of Dirac Hamiltonian [97]. Therefor, we call it symmetry enforced DSM. This symmetry enforced nodal points at the high-symmetry momenta must have to associate with a four-dimensional IRs of the little group. Due to the nonsymmorphic symmetry, these type of nodal points locate at the zone boundary. β -BiO₂ is the first proposed material to be host symmetry enforced DSM whose nodal points are located near to the Fermi level and the Dirac degeneracies do not associate with extra trivial Fermi pockets [97]. The crystal structure and corresponding electronic structures are shown in Fig. 1.9. The nodal points are located at X points. Although, β -BiO₂ is a potentially good compound in terms of position of nodal points and trivial Fermi pockets, it is unfortunately chemically unstable. Later, few potential compounds have been identified as symmetry enforced DSM in the distorted spinels such as $BiZnSiO_4$, $BiCaSiO_4$, $BiAlInO_4$ so on [98]. Some other compounds such as HfI_3 , AMo_3X_3 (A = (Na, K, Rb, In, Tl) and X = (Se, Te)) have also been theoretically predicted to host symmetry enforced DSM phase, yet to be experimentally verified [99].



Figure 1.9: (a,b) Crystal structure of β -BiO₂ and corresponding BZ. (c) Band structure of β -BiO₂ along the high symmetry lines and (d) 3D view of the Dirac nodes at X points. Adapted from Ref. [97].

1.4.3 Triple Point Semimetals

Triple Point Semimetal is an intermediate state of four-fold DSM and two-fold WSM. Unlike DSM and WSM, TPSMs in condensed matter system does not have any high energy analog. It occurs in crystal completely because of the space group symmetry of the system. For instance, having threefold rotational symmetry with a vertical mirror plane in a TRS preserving crystal can lead to a pair of triply degenerate nodal points on the C₃ axis in the absence of IS. A Dirac node can be achieved by keeping the inversion intact in such a symmetry environment. However, if the vertical mirror symmetry is broken, it produces four Weyl nodes from two triple points reducing the band degeneracies into two-fold. For the realization of triply degenerate nodal point at certain \mathbf{k} in BZ, the little group of that \mathbf{k} need to contain both contain 1D an 2D representations. A symmorphic C_{3v} point group satisfies these criteria and allows triply degenerate nodes on the rotation axis.



Figure 1.10: (a) Triple point fermion states in ZrTe along the Γ -A direction. (b,c) Zoomed view of the band structures near the nodal points G₁ and G₂. (d) Schematic representation of inverted band structure of HgTe and LuPtBi type Half-Heusler class. The characters of the bands are denoted by the irreducible representations of C_{3v} group along the rotation axis. (a-c) are adapted from Ref. [231] and (d) is adapted from Ref. [259].

Similar to the DSM, triply degenerate nodal points can occur due to band inversion between VBM and CBM having different symmetry characters and the band crossings on the rotation axis are stabilized by the space group symmetries. Lets consider two bands $j_z = \pm 1/2$ and $j_z = \pm 3/2$ which get inverted at the Γ point. On the C₃ rotation axis, $j_z = \pm 1/2$ bands form doubly degenerate state (actually, the symmetry character of this band is dictated by the 2D representation Λ_6). $j_z = \pm 3/2$ bands (consist of 1D representation Λ_4 or Λ_5) are doubly degenerate (Kramer's degenerate) at Γ point but split along the rotation axis. A pair of triply degenerate nodes form if the $j_z = \pm 1/2$ bands crosses the $j_z = \pm 3/2$ on the C₃ axis as shown in Fig 1.10.

The first material class which have been proposed to have this new TPSM state is WC-type binary AB class [231], where A = (Zr, Nb, Mo, Ta, W) and B = (C, N, P, S, Te). Fig 1.10 (a,b) shows the triple point nodes of ZrTe on the rotation axis. LuPtBi type Half-Heusler and LiMgPdSb type quaternary-Heusler alloy class are another material class which become potential avenue for TPSM investigations [259]. The schematic representation of LuPtBi type Half-Heusler class is shown in Fig 1.10 (d). On the other hand, the first experimental confirmations of TPSM states have achieved through the ARPES measurements on MoP [232] and MoC [233] by probing both the bulk band structures as well as the surface Fermi arcs.

1.4.4 Nodal Line Semimetals

Till now, we have discussed only point degeneracies of TSMs. Topological nodal line semimetal (NLS) is another class of TSM which features gapless states between VBM and CBM along the one dimensional (1D) line. The gapless excitations in NLS require more complex symmetry environment than the point degenerate TSM such as DSM, WSM, TPSM etc. In general, the line degeneracies between CBM and VBM occur when the eigen values of the CBM and VBM are symmetrically distinct along certain rotation axis or on a mirror invariant plane of BZ. The NLS state can also occur due to nontrivial band topology which can be associated with some kind of topological invariant, such as quantized Berry phase, quantized monopole charge and so on. There are various class of NLS depending on the topological states of wavefunction, Fermi surface topology, co-dimension of degeneracy of the band crossing, underlying space group symmetry of the crystal and multiple nodal line linking structure etc. Depending on the topology of the ground state wavefunction of a NLS, we can primarily divide NLS in three classes as, (i) Z_2 Berry phase NLS whose topological character can be defined as the Z_2 quantized Berry Phase, (ii) Z_2 monopole NLS for which a quantized Z_2 monopole charge can be defined to represent the topological character of the line node, and (iii) mirror and glide mirror symmetry protected NLS. ZrSiS [40], TiB₂ [166], Mg₃Bi₂ [102] are some of the representative compounds Z_2 Berry phase NLS. The electronic structure of ABC-stacked graphdyne shows the Z_2 monopole NLS properties [103]. CaAgP [43] and PbTaSe₂ [104] family are two material classes which belong to mirror and glide mirror

symmetry protected NLS category.

Computational Formalism

2.1 Denisty Functional Theory

Density Functional Theory(DFT) has been emerged as a versatile tool to study the structural, electronic, optical properties of molecular and material based systems with a crux idea of replacing high dimensional wavefunction with electron density drastically reducing the complexity of many-body Schrödinger equation. The framework of DFT is based on two important theorems formulated by Hohenberg and Kohn [106].

2.1.1 Many-Body Problem

A many body Schrödinger equation for a system comprising of n electrons at coordinates $r_1, r_2, ..., r_n$ and N nuclei at coordinates R_1 , $R_2, ..., R_N$ in atomic units can be written as;

$$\left[\frac{1}{2}\sum_{n}\nabla_{n}^{2} - \frac{1}{2}\sum_{N}\nabla_{N}^{2} - \sum_{N,n}\frac{1}{|R_{N} - r_{n}|}\right]\psi + \left[\frac{1}{2}\sum_{N\neq M}\frac{1}{|R_{N} - R_{M}|} + \frac{1}{2}\sum_{n\neq m}\frac{1}{|r_{n} - r_{m}|}\right]\psi = E\psi \quad (2.1)$$

where the first and second terms in the Hamiltonian correspond to kinetic energy of electrons and nuclei and the remaining three terms represent potential energy due to nuclei-electron, nucleinuclei and electron-electron coulomb interactions, respectively. Applying the Born-Oppenheimer approximation [107] considering the high relative mass ratio of nuclei and electrons, decouple the the Hamiltonian and hence can be applied to solve electronic wavefunction with an explicit consideration of nuclear terms. Now Eqn. 2.1 can be simplified as,

$$\left[-\frac{1}{2}\sum_{n}\nabla_{n}^{2}-\sum_{N,n}\frac{1}{|R_{N}-r_{n}|}+\frac{1}{2}\sum_{n\neq m}\frac{1}{|r_{n}-r_{m}|}\right]\psi=E\psi\quad(2.2)$$

However, the complexity of Eqn. 2.2 exponentially increases with the system size and obtaining an analytical solution is extremely difficult. Hence approximations are required to solve the many-body Schrödinger equation and derive properties of the system.

2.1.2 Mean-Field Approximation

In the mean field approximation, the electron-electron interaction term in the many-body Hamiltonian is simplified by considering each electron to experience an average coulomb interaction from other all remaining electrons. The potential acting on a single electron known as Hartree potential can be written as,

$$V_H(r) = \int \frac{n(\acute{r})}{|r-\acute{r}|} d\acute{r}$$
(2.3)

Now, the N-dimensional many body Schrödinger equation can be split into N one-dimensional single-particle equations as,

$$\left[-\frac{\nabla^2}{2} - \sum_{N,n} \frac{1}{|R_N - r_n|} + \int \frac{n(\acute{r})}{|r - \acute{r}|} d\acute{r}\right] \phi_i(r) = \epsilon_i \phi_i(r) \qquad (2.4)$$

where $\phi_i(r)$ is the single electron wavefunction corresponding to an eigenvalue ϵ_i However, this approximation does not inculcate the quantum nature of electron correlation accurately.

2.1.3 Hartree-Fock Method

Hartree and Fock devised a method for determining the wavefunctions in Eqn. 2.4 where the minimization of energy with respect to these wavefunctions leads to a set of single-particle equations known as Hartree-Fock equations [109] which can be represented as ,

$$\left[-\frac{\nabla^2}{2} - \sum_{N,n} \frac{1}{|R_N - r_n|} + \int \frac{n(\acute{r})}{|r - \acute{r}|} d\acute{r}\right] + \int V_x(r, \acute{r})\phi(\acute{r})dr = \epsilon_i\phi_i(r)$$
(2.5)

where the extra potential which spans over all occupied single particle states can be represented as,

$$V_x(r, \acute{r}) = -\sum_i \frac{\phi_i(r)\phi_i(\acute{r})}{|r - \acute{r}|}$$
(2.6)

which is a more accurate approximation for the electron correlation compared to the classical mean-field approximation. These single particle equations are solved self-consistently to obtain the energy and other properties of the system.

2.1.4 Hohenberg-Kohn Theorems

Theorem 1

The Hohenberg-Kohn first theorem states that the external potential $V_{\text{ext}}(\mathbf{r})$ of any system of interacting particles is uniquely determined by the ground state electron density $\rho_0(r)$. Any ground state property of the system can be expressed as a functional of ground state electron density.

$$\langle \psi | \Omega | \psi \rangle = \Omega[\rho_0(r)] \tag{2.7}$$

Theorem 2

This theorem states that the exact ground state energy E_0 can be defined as the least value of the functional of energy and the density minimizing this functional is the exact ground state density of the system. Therefore any trial density $\rho(\hat{r})$ and corresponding energy $E[\rho(\hat{r})]$ would be an equal or greater approximation to the true density and energy of the system, respectively.

$$E_0 \le E[\hat{\rho(r)}] = T[\hat{\rho(r)}] + E_{Nn}[\hat{\rho(r)}] + E_{nn}[\hat{\rho(r)}]$$
(2.8)

where the terms in the right hand side represent kinetic energy of electrons, potential energy due to nuclei-electron interaction and electron-electron interaction, respectively as functionals of density. This theorem allows to adapt a variational approach by starting from a reasonable density and minimize it towards the true density via a self consistent method which is implemented in many of DFT based softwares.

2.1.5 Kohn-Sham Equations

Kohn and Sham proposed a method to construct the energy functional of electron density by mapping a many-body system to a fictious noninteracting system with the same density [110]. The total energy functional according to Kohn-Sham method can be written as,

$$E[\rho(r)] = T[\rho(r)] + V_{ext}[\rho(r)] + V_H[\rho(r)] + E_{xc}[\rho(r)]$$
(2.9)

where the first three terms in Eqn. 2.5 can be expanded as

$$T[\rho(r)] = \sum_{i} \int \phi_i^* \frac{\nabla^2}{2} \phi_i(r) dr \qquad (2.10)$$

$$V_{ext}[\rho(r)] = \int V_{ext}(r)d^3r \qquad (2.11)$$

$$V_{H}[\rho(r)] = \int \int \frac{\rho(r)\rho(\dot{r})}{|r-\dot{r}|} dr^{3} d\dot{r}^{3}$$
(2.12)

The first term is the kinetic energy functional, second is the potential energy functional of nuclear-electron interaction, third is functional of electron-electron coulomb interaction (Hartree energy). All these terms are similar to the Eqn. 2.4 in the mean-field approximation whereas the final term $E_{xc}[\rho(r)]$ is the exchange-correlation energy which includes the non-classical contributions in the functional. Because all the terms except this unknown part can be determined from the electron density and the electron density can be obtained by a variational approach minimizing the energy with respect to density, this leads to a set of equations similar to Hartree-Fock equations which are known as Kohn-Sham equations and can be written as,

$$\left[-\frac{\nabla^2}{2} - \sum_{N,n} \frac{1}{|R_N - r_n|} + \int \frac{n(\acute{r})}{|r - \acute{r}|} d\acute{r} + V_{xc}(r)\right] \phi_i(r) = \epsilon_i \phi_i(r)$$
(2.13)

where $\phi_i(r)$ are Kohn-Sham orbitals and the external potential, $V_{xc}(r)$ is related to the exchange-correlation energy as

$$V_{xc}(r) = \frac{\delta E_{xc}[\rho(r)]}{\delta\rho(r)}$$
(2.14)

Therefore, if the exchange-correlation energy is known, the Kohn-Sham equations can be self-consistently solved to obtain a ground state density and other related quantities. The most important part of any DFT calculations is the choice of a reasonable exchange-correlation functional and several approximations have been developed with this objective.

2.1.6 Exchange-Correlation Functional Approximations in DFT

Local Density Approximation (LDA)

The local density approximation treats the system to have an energy density at every point equivalent to that of a homogeneous electron density gas system which has the same electron density at that points [111]. The exchange correlation functional under this approximation can be written as

$$E_{xc}^{LDA} = \int \varepsilon_{xc}(\rho_0) d^3r |_{\rho_0 \to \rho_r}$$
(2.15)

where $\varepsilon_{xc}(\rho_0)$ is the exchange correlation energy of a homogeneous system when its electron density ρ_0 is equal to that of a real inhomogeneous system ρ_r . Though LDA can be successfully applied for certain systems with smooth density variation, it fails to explain properties of majority of systems of physical or chemical interest.

Generalized Gradient Approximation (GGA)

In the generalized gradient approximation proposed as an advancement of LDA, along with the electron density, its gradient is also evaluated replacing the local nature of density functional under LDA to nonlocal [112, 113]. The exchange-correlation functional under GGA can be given as,

$$E_{xc}^{GGA} = E_{xc}[\rho_r, \nabla \rho_r] \tag{2.16}$$

The examples of GGA functionals include Perdew-Burke-Ernzerhof(PBE) [114], revised Perdew-Burke-Ernzerhof (RPBE)
[115, 116] and so on. These functionals have been successfully used to predict the structural, energetic properties of both molecular and solid-state systems.

Hybrid Functionals

In contrast to LDA and GGA based functionals, the hybrid functionals incorporate a Hartree-Fock level exchange correlation obtained by solving noninteracting Kohn-Sham orbitals as a correction to the coulomb interaction term. [117] Different hybrid functionals have been developed by varying the percentage of Hartree-Fock level inclusion in the functional. One of the important hybrid functionals widely used for solid state systems is Heyd-Scuseria-Ernzerhof Screened-Exchange Hybrid functional(HSE) which is based on the GGA-PBE approximation along with short range Hartree-Fock exchange [118, 119]. The HSE functional form can be represented as,

$$E_{xc}^{HSE} = aE_{xc}^{SR,HF}(w) + (1-a)E_x^{SR,PBE} + E_x^{LR,PBE}(w) + E_c^{PBE}$$
(2.17)

Where SR and LR denotes short range and long range exchanges, a is the mixing coefficient and w is the Hartree-Fock screening parameter. The HSE functional includes 25% short-range HF exchange without any long-range HF exchange by retaining a PBE correlation. The latest version of HSE (HSE06) incorporates an w value of 0.11 Bohr⁻¹ and has been identified to be accurately predicting the electronic and optical properties of materials.

2.1.7 Bloch Method and Plane-Wave Basis Set

Bloch formulated a method to determine the wavefunction of electrons under a periodic potential in a solid system by making them quasi-periodic with incorporating a function $u_k(r)$ having the periodicity of the potential [120] such that the wavefunctions take the form,

$$\psi_k(r) = u_k(r) \exp(ik.r) \tag{2.18}$$

where k is the wave vector. This allows a platform for determining the real space quantities like energy, charge density in the periodic form. The periodic function $u_k(r)$ can be expanded in three dimension as

$$u_k(r) = \sum_G c_n(G) \exp(iG.r)$$
(2.19)

and hence Eqn. 2.18 can be now modified as

$$\psi_k(r) = \sum_G c_n(G) \exp(i(K+G).r)$$
 (2.20)

Now, by using a plane wave basis set consisting of basis functions of the form $\phi_i(r) = A \exp(ik.r)$ the Kohn-Sham equations for the periodic wavefuction can be derived as

$$\left[-\frac{1}{2}\nabla^2 + U_{eff}\right]\sum_G c_n(G)\exp(i(K+G).r) = \varepsilon_{nk}\sum_G c_n(G)\exp(i(K+G).r)$$
(2.21)

where U_{eff} is the effective potential acting on the electrons. By diagonalizing a matrix formulated from these equations followed by self-consistent minimization process, the wave functions $\phi_i(r)$ and corresponding eigenvalues ε_{nk} can be calculated [121, 122]. The plot of these eigenvalues with wave vector \mathbf{k} yields the band structure which can be employed to study the electronic as well optical properties of the system.

2.2 Maximally Localized Wannier Functions

The electronic ground state of a system is calculate by considering a set of single-particle orbitals and their occupations within independent-particle approximation. For crystalline solid, this single-particle orbitals are generally the Bloch states, $\psi_{n\mathbf{k}}$ where n represents the band index and \mathbf{k} is the crystal momentum. Although this has been widely used to compute the electronic states, alternative representations are also possible. One of such alternative representation is Wannier representation [123, 124] where one performs a gauge dependent unitary transformation of the Bloch states $\psi_{n\mathbf{k}}$ to a set of "Wannier functions" (WFs). These WFs are not unique in choice and they are not the eigenstates of the Hamiltonian like Bloch eigenstates. Localization of these WFs in real space is a procedure to choose the unitary transformation uniquely.

Bloch's theorem says,

$$\psi_{n\mathbf{k}} = u_{n\mathbf{k}}(\mathbf{r}) \exp^{i\mathbf{k}\cdot\mathbf{r}},\tag{2.22}$$

where $u_{n\mathbf{k}}(\mathbf{r})$ are the Bloch periodic part which satisfy the relation, $u_{n\mathbf{k}}(\mathbf{r}) = u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R})$. **R** is the real space lattice vector. For a set of isolated bands, the periodic Bloch states can equivalently be transformed into same number of WFs via one discrete and one continuous unitary transformations. The transformation equation is

$$|w_{n\mathbf{R}}\rangle = V \int_{BZ} \frac{d\mathbf{k}}{(2\pi)^3} \exp^{-i\mathbf{k}\cdot\mathbf{R}} \sum_{m=1}^{J} |\psi_{m\mathbf{k}}\rangle U_{mn\mathbf{k}}.$$
 (2.23)

The WF, $w_{n\mathbf{R}}(\mathbf{r}) = w_{n\mathbf{R}}(\mathbf{r} - \mathbf{R})$) are periodic in real space. J represents the number of isolated bands. Please note that the unitary matrix $U_{mn\mathbf{k}}$ is not unique. This can uniquely be determined by the minimization of the sum of quadratic spreads of WFs. That quadratic spread of WFs are given by

$$\Omega = \sum_{n=1}^{J} [\langle w_{n\mathbf{p}} | \mathbf{r} \cdot \mathbf{r} | w_{n\mathbf{p}} \rangle - \langle w_{n\mathbf{p}} | \mathbf{r} | w_{n\mathbf{p}} \rangle |^2].$$
(2.24)

Here, **o** is the reference point about which the WFs have to be minimized. The Ω can be decomposed into two parts. One is gauge invariant which will remain same under the action of $U_{mn\mathbf{k}}$ on the Bloch states. Therefor, this part of spread sum do not need to minimize. However, the other part is gauge dependent and need to apply the minimization process to determine the transformation matrix uniquely.

2.3 Computational Parameters

The first-principle calculations were carried out using projector augmented wave (PAW) [125] formalism based on Density Functional Theory (DFT) as implemented in the Vienna Ab Initio Simulation Package (VASP). [126, 127] The generalized-gradient approximation by Perdew-Burke- Ernzerhof (PBE) [127] was employed to describe the exchange and correlation. Force (energy) criterion was set up to 0.01 eV/Å(10⁻⁶ eV) in all calculations. An energy cut off of 500 eV is used to truncate the plane-wave basis sets. The Brillouin zones (BZs) are integrated using densed Γ -centered kmesh for all compounds. HSE06 [128] level of hybrid functional calculations were carried out to check the accuracy of the PBE calculations. Spin orbit coupling is included in all the calculations. Tight-binding (TB) Hamiltonians were constructed using maximally localized Wannier functions (MLWFs) [129–131] obtained from wannier90 package [132]. The topological properties including surface spectrum and Fermi surface were analyzed based on the iterative Green's function [133–135] method implemented in Wannier-Tools package [136].

Chapter 3

Topological Insulator and Nodal Line Semimetal

Symmetry protected nontrivial band topology has become an area of paramount research interest for unraveling novel dimensions in condensed matter physics [137, 138]. The time reversal invariant topological insulator (TI) has stimulated intense interests due to their intriguing properties, such as gapless boundary states, unconventional spin texture and so on [139-141]. The recent years have witnessed a series of theoretical developments which have enabled us to classify the Z_2 type non-magnetic band insulators. For example, the Z_2 even (ordinary) and Z_2 odd (topological) states are separated by a topological phase transition, where the bulk gap diminishes during the adiabatic deformation between these two states [142]. In two-dimensional (2D) systems, Z_2 odd class can be distinguished by the odd number of Kramer's pairs of counter propagating helical edge states, whereas in three-dimensional (3D) systems, it can be characterized by the odd number of Fermi loops of the surface band that encloses certain high symmetry points in the Brillouin zones (BZ) [139]. Soon after the experimental realization of quantum spin hall effect in 2D HgTe quantum wall [140], a number of 2D and 3D TI systems have been theoretically predicted and experimentally verified [143–146]. In fact, the search for new TI has been extended to zintl compounds [147, 148, 151], antiperovskites [149], and heavy fermion f-electron Kondo type of systems [150].

With the conceptual development in the topological field, research on topological material has been extended from insulators to semimetals and metals [152–154]. In topological semimetals, symmetry protected band crossing or accidental band touching leads to a nontrivial band topology in 3D momentum space. The topological properties of such semimetals mainly depend on the degeneracy of the bands at the crossing/touching point. A zero dimensional band crossing with two and four fold band degeneracy defines the Dirac [152] and Weyl semimetal [153], respectively, which are quasiparticle counterparts of Dirac and Weyl fermions in high energy physics. Low energy Dirac fermions in condensed matter are essentially protected by time reversal symmetry (TRS), inversion symmetry (IS) and certain crystal symmetry. Quasi-particle Weyl fermion state can be realized by breaking either space inversion or time reversal of crystal [153]. On the contrary, in quantum field theory, Dirac and Weyl fermions are strictly restricted by Lorentz invariance. However, in case of nodal line semimetal (NLS), the conduction and valence band touches along a line to form a one dimensional close loop [154]. The characteristic feature of Dirac semimetal (DS) is a point like Fermi surface (FS) at the crossing point [152], whereas it is 1D circle for NLS [154]. But for Weyl semimetal (WS), FS forms an open arc like surface states, instead of closed FS [153]. Due to the nontrivial FSs, all the topological semimetals show some exotic phenomena, such as quantum magneto-resistance [155], chiral anomaly [156] etc.

NLS are the precursor states for other topological phases. In general, spinful nodal lines are not robust in the presence of a mass term in Hamiltonian [157], which can be explained by simple co-dimensional analysis. Thus, inclusion of spin orbit coupling (SOC) can convert the NLS state to DS, WS or TI by opening up a gap around the nodal loop. However, in the presence of an extra crystalline symmetry, nodal line can be robust [157]. Owing to the unique properties such as torus-shaped Fermi surface, relatively higher density of states and interaction induced instability of the FS, NLS can provide a unique playground for the quasi-particle correlations and unusual transport studies [154].

In this chapter, we explore the possibility of controlling topological order in a series of ternary compounds XX'Bi (X = Na, K, Rb, Cs and X' = Ca, Sr). The XX'Bi compounds have a noncentrosymmetric hexagonal structure with $P\overline{6}2m$ (# 189) space group as shown in Fig. 3.1(a). These compounds show interesting topological properties (including NLS state) which can be tuned under various external factors. Recently, NaBaBi has been theoretically studied and predicted to be a topological insulator under hydrostatic pressure [158].

3.1 Tuning of Topological Insulating Phase

Topological insulating state can be predicted in a material if it shows band inversion driven by spin-orbit coupling [141]. As the strength of spin-orbit coupling increases with heavy elements, we have systematically studied X-X' elements from group I(A)-II(A) of the periodic table. The electronic structures of all these compounds have been performed using the GGA level of theory. Here, we have mainly discussed NaSrBi and NaCaBi compounds. Our findings related to all other compounds are discussed briefly. Fig. 3.1(c-f) presents the electronic structures of NaSrBi and NaCaBi compounds. In the absence of SOC, the conduction band minima (CBM) and valence band maxima (VBM) at Γ point are dominated by Sr/Ca *s* and Bi p_z orbital as shown in Fig. 3.1(c,e). However, inclusion of SOC results in an inverted band order between Sr/Ca *s* and Bi p_z orbitals at Γ point with a direct band gap of ~80(100) meV at Γ point for



Figure 3.1: (a) Hexagonal crystal structure of XX'Bi, (b) Corresponding Brillouin zone (BZ) and two-dimensional BZ projected onto (001) surface. Electronic structures of NaSrBi (c-d) and NaCaBi (e-f) with (W/) and without (W/O) SOC. Red and blue symbols in (c-f) indicate the orbital contributions of Sr/Ca s orbital and Bi p_z orbital. The sizes of the symbols are proportional to the weightage of the orbitals.

NaSrBi(NaCaBi) as shown in Fig. 3.1(d,f) which clearly indicate the non-trivial band topology in these systems.

As the GGA method underestimates the band gap and overestimates the band inversion, we have used the hybrid functional HSE06 to confirm the predicted non-trivial topology. It turns out that the band inversion between Sr/Ca s orbital and Bi p_z orbital disappears at HSE06 level and both of these materials show trivial band order. In order to check the evolution of non-trivial band order, we have applied external effects such as pressure, strain and



Figure 3.2: Band gap vs. hydrostatic/bi-axial strain(%) for (a) NaSrBi and (b) NaCaBi using HSE06 calculations. Trivial and non-trivial regions for both type of strains are marked by arrowheads.

doping. We find that NaSrBi (NaCaBi) system shows a topological insulating behavior under strain (both hydrostatic as well as biaxial strain induced by epitaxial mismatch). Topological non-trivial properties also emerge in these materials if we partially/fully substitute Na by K, Rb, and Cs in these compounds.

3.1.1 Hydrostatic Pressure

We have performed electronic structure calculations on NaSrBi and NaCaBi systems under hydrostatic expansion. A trivial to nontrivial phase transition occurs at about -2 GPa ($\sim 1\%$ expansion in lattice parameter) and both the materials sustain non-trivial band order at higher expansion, as shown in Fig. 3.2. The calculated bulk modulus for NaSrBi and NaCaBi are 21 GPa and 22 GPa respectively. It ensures that such non-trivial band ordering could be realized under low strain.

Interestingly, hydrostatic compression also gives non-trivial band ordering of band inversion between Bi-p and Ca/Sr d bands in these systems. Our calculation show that a large amount of compression (25 GPa) gives non-trivial band ordering. Fig. 3.3 shows band structure of NaSrBi at 14.5, 19.7 and 25.6 GPa compressive pressure. At around 25.6 Gpa (12% of lattice compression), a p-d band inversion occurs between Sr dz₂ and Bi p_z orbitals. The lattice



Figure 3.3: PBE bulk electronic structure of NaSrBi with SOC at (a) 14.5 GPa (b) 19.7 GPa and (c) 25.6 GPa compressive pressure.

compression shift the Sr s orbital towards higher energy where as Sr d orbital pushed down to realize band inversion between Sr dz₂ and Bi p_z as shown in the Fig. 3.3(c). The local environment of Sr and Na atom in NaSrBi is octahedral and tetrahedral which is distorted by Bi atoms. Application of compressive pressure increase the distortion of Sr octahedral which interns stabilize the Sr dz₂ more. In the same time due to increase of coulomb repulsion between Sr⁺₂ state and Bi⁻₃ in the tetrahedral site, Sr s orbital destabilize and shift towards higher energy. Therefore, comparative to p-d band inversion, it is much easier to get s-p band inversion by lattice expansion (around 1% of lattice expansion). Hence, we consider only the hydrostatic expansion and investigated the non-trivial properties of both materials under 3% lattice expansion.

Using HSE06 exchange correlation functional, we found trivial band ordering for both NaSrBi and NaCaBi at their respective ambient conditions (Fig. 3.5(a & d)). Therefore, we have applied hydrostatic pressure (HP) in terms of lattice expansion and checked the evolution of bands topology around the Fermi level at Γ point. A trivial to non-trivial phase transition occurs at -2 GPa (around 1% expansion in lattice parameter) and both the materials hold their non-trivial band ordering at higher pressures as well. Here, we studied the topological properties of both the systems at 3% HP. Fig. 3.4 shows the bulk electronic structure of both the systems at 3% HP using PBE and HSE06 exchange correlation functional. The



Figure 3.4: Band structures using PBE and HSE06 functionals at 3% HP with SOC (a & b) for NaSrBi and (c & d) for NaCaBi.

calculated electronic structures using PBE and HSE06 show similar band ordering for both the systems.

3.1.2 Bi-axial Strain

we have investigated the electronic properties of these materials under biaxial strain (BAS). Experimentally, biaxial strain can be realized by substrate induced lattice mismatch. Accordingly, we have applied biaxial strain along [110] direction to observe the band evolution around the Fermi level. Figure 3.2 shows the change in the band gap and trivial to non-trivial transform under biaxial strain for NaSrBi and NaCaBi. The trivial and non-trivial regions are mentioned in the plots using arrowheads. Above 1.6% (1.4%) biaxial strain, band inversion occurs in NaSrBi (NaCaBi), which sustains its non-



Figure 3.5: Band structures (using HSE06) of (a) pure and (b) 3% biaxial strained NaSrBi. (c) evolution of Wannier charge center along k_2 for NaSrBi. (d-f) Respective plots for NaCaBi

trivial band ordering even at higher strain. Furthermore, we have simulated the bulk band structure for NaSrBi and NaCaBi at +3%biaxial strain as shown in Fig. 3.5. Figure 3.5(b,e) clearly shows band inversion between Sr/Ca s and Bi p_z orbitals at Γ point. To further confirm the topological non-trivialness, we have calculated the topological Z_2 invariant. Owing to the inversion asymmetry in the crystal structure, the parity is not a good quantum number of the Bloch eigenstates. Therefore, parity counting method proposed by Fu and Kane is not applicable here. [159] As such we have adopted the method of Wannier charge center (WCC) evolution in half BZ to calculate the Z_2 invariant along the k_2 direction, as shown in Fig. 3.5(c,f). It is clear from the figure that the WCC evolution lines cut the reference line one (odd) and zero (even) times in the $k_3 = 0$ and π planes respectively, for both the systems. Thus the pressure-induced band inversion exhibits a topological phase transition from a trivial insulator to topological insulator.



Figure 3.6: Band structures using HSE06 functional in the presence of SOC. Left and right panel for NaSrBi and NaCaBi respectively with 33% and 66% doping concentrations.

3.1.3 Doping

Doping or alloying is a promising strategy for hydrostatic expansion/compression of lattice parameters. Therefore, we have doped K, Rb, and Cs at the Na site. Doping with bigger atoms leads to an expansion of lattice parameters, which in turn naturally causes a band inversion instead of a physical hydrostatic expansion imposed on the material. We have calculated the HSE06 band structures replacing one Na atom by one Rb or Cs atom in the unit cell, giving Na_{0.66}X_{0.33}CaBi and Na_{0.66}X_{0.33}SrBi compounds. Fig. 3.6 shows the bulk band structures of Na_{0.66}Rb_{0.33}CaBi and Na_{0.66}Cs_{0.33}CaBi alloys. Due to the doping by large sized atoms, the lattice expands and gives a band inversion naturally instead of an external pressure. It is clear from the Fig. 3.6 that the non-trivial band gap increases for higher doping concentrations.



Figure 3.7: (a)Surface dispersion and (b,c) surface density of states for top and bottom surface layers for NaSrBi. (d-f) shows the similar plots for NaCaBi

3.2 Surface States and Spin texture of Topological Insulator

The non-trivial band topology suggests an interesting surface state [138]. Henceforth, we have studied surface electronic structure of NaSrBi and NaCaBi compounds. Initially, we constructed the slab Hamiltonian from maximally localized wannier functions (MLWF) for Na s, Ca/Sr s and Bi p orbitals. Then we have projected the band structure onto the (001) surface by using the iterative Green's function method as implemented in Wannier-Tool. The surface states of NaSrB and NaCaBi in ambient pressure using PBE exchange correlation functional are shown in Fig. 3.7.

We have also calculated surface spectra for NaSrBi and NaCaBi at +3% BAS along [110]. The calculated bulk electronic structures using GGA and HSE06 show similar band ordering for both the systems. Hence it is reasonable to expect similar surface dispersion at GGA and HSE06 level of calculations. Therefore, we



Figure 3.8: (a) Surface dispersion, and surface density of states (SS) for (b) top, and (c) bottom surface layers of NaSrBi under +3% BAS along [110]. (d-f) Respective plots for NaCaBi. The corresponding spin textures around the Fermi energy are shown in their respective insets.

took the GGA functional to construct the MLWFs and then simulated the surface dispersions for TI phases of two compounds at +3% BAS along [110]. The surface dispersion is shown in Fig. 3.8. Since the slab calculation involves two surfaces, the corresponding surface bands and spectral intensity maps for both surface (top and bottom) are given.

In the slab model, the top surface is terminated by a X-Bi layer, while the bottom surface is truncated at X'-Bi layer. The asymmetric surface truncation leads to different surface potentials which in turn results into two non-identical Dirac cones lying at different energy as shown in Fig. 3.8. Another characteristic feature of topological surface state is the helical spin texture. To address this, we have projected the spin directions on the FS of the slab, which is located just above the DP and we find a spin momentum locking feature as shown in Fig. 3.8. This again confirms the topological non-trivial behavior in both the systems. Similar to most other TI



Figure 3.9: HSE06 bulk electronic structures of CsSrBi, CsCaBi and RbSrBi. Top panel without SOC and bottom panel with SOC.

materials, the surface Dirac Cone of both the systems exhibits left handed spin texture for top surface states (TSS). The bottom surface states, however, exhibit right handed spin texture for the Dirac Cone in both the materials.

3.3 Nodal Line Semimetal

3.3.1 Bulk Topology

In a topological nodal line semi-metal, the bands cross each other due to band inversion and they form a closed loop instead of discrete points around the Fermi level. In contrast to WSs, which have an open arc like FS, [153] NLSs are characterized by the 1D closed ring (a line shape FS) and 2D topological drumhead surface state [154]. The distinguishing characteristic of these drumhead surface state is that they are nearly dispersionless and therefore, have a large density of states near E_F . Such flat bands and large density of states could provide a potential play ground for the high temperature superconductivity, magnetism, and other related phenomenons.

Here we demonstrate that the materials NaSrBi (NaCaBi) can be transformed into a nodal line semi-metal by complete replacement of Na atom by Rb or Cs. Our detailed calculations predict that the class of systems XX'Bi (X = Rb, Cs and X' = Ca, Sr) are NLS and show drumhead-like surface flat band. Bulk band structures for all these systems are shown in Figure 3.9. Of these, we have chosen RbCaBi for detailed analysis here. Figure 3.10(a,c)shows the band structure of RbCaBi with an inverted band order and 1-D torus like bulk Fermi surface (where conduction and valence band crosses each other along a line) respectively in the absence of SOC. At the Γ point, CBM and VBM have $A_2^{\prime\prime}$ and A_1^\prime representations of the second tation of D_{3h} . Along Γ -M, it becomes A'' and A' representation of C_s where as it takes B_2 and A_1 representation of C_{2v} along Γ -K, as indicated in Fig. 3.10(a). The D_{3h} little group at Γ point ensures the presence of σ_h mirror plane perpendicular to the C_3 principle axis. For spinless case, if two bands belonging from two different irreducible representations (IRs) (here IRs are differed by the eigen value of σ_h symmetry) cross each other in the σ_h plane (σ_h plane contains M, Γ and K high symmetry points in the BZ), then the band hybridization will be prohibited due to the point group symmetry protection. All the crossing points on σ_h plane will have now band degeneracy along a one dimensional loop. Hence the two intercrossing bands form the nodal loop structure in the BZ. Therefore, in RbCaBi compound the lowest conduction band and highest valence band cross each other along the nodal line and protected from opening up a gap along the nodal loop.

3.3.2 Surface Sprectrum

From the perspective of bulk boundary correspondence, topologically non-trivial drumhead-like surface states are expected to appear either inside or outside the projected nodal loop on the surface of NLS RbCaBi. In order to calculate the surface states, we have constructed tight-binding Hamiltonian using the method of ML-WFs and the surface states are projected onto (001) surface using the iterative scheme of Green's function technique. Interestingly, we found a nearly flat surface band which is nestled between two bulk Dirac cones on the (001) surface, as shown in Fig. 3.10(d,e). Further, we take SOC effect into consideration and found that a little gap is opened along the nodal line in the bulk band structure (see Fig. 3.10(b)). Our first-principle calculations show that two set of bands with same IRs Λ_5 , which hybridize along Γ -K and open up ~ 10 meV gap at nodal point. However, along Γ -M direction the hybridized gap between the pair of IRs Δ_4 , is almost zero. Similar gap opening along the nodal line is also observed in several other NLS systems e.g. $Cu_3PdN(\sim 60 \text{ meV})$ [161, 162], $ZrSiS(\sim 20)$ meV) [163, 164], TiB₂(~ 25 meV) [165, 166], CaAgBi(~ 80 meV) [167], CaPd($\sim 27 \text{ meV}$) [168] and so on. We have also carried out the surface density of states calculation for our material RbCaBi under SOC effect. Indeed we have found drumhead like surface states in (001) surface as shown in Fig. 3.10(f,g). This, however, is a common feature in almost all the existing NLS compounds [163–166, 168, 169], whenever SOC effect is taken into account in any first principles calculation. Even the experimentally reported other NLS systems, such as TiB₂, ZrSiS, show somewhat concave surface bands as obtained in our case for RbCaBi [Fig. 3.10(f,g)]. As such, we believe that RbCaBi can be a promising candidate for NLS and worthy of careful experimental investigation.

3.4 Conclusion

Using the first-principles calculations, we have predicted topologically non-trivial phases, including nodal line semi-metal states in a series of compounds belonging to the class of XX'Bi (X=Na, K, Rb,



Figure 3.10: (a,b) Bulk electronic structures (using HSE06) of Rb-CaBi without and with SOC. (c) shows Fermi surface plot for NLS phase of RbCaBi. (d,e) are surface density of states (top and bottom) for (001) surface without SOC. (f,g) are same as (b,c) but with SOC effect.

Cs; X'=Ca, Sr). We closely engineer the topology of the bands by applying hydrostatic compression/expansion, bi-axial strain and external doping, which in turn helps to achieve non-trivial band order. Non-triviality is further confirmed by investigating Wannier charge center, surface dispersion and spin texture. NaSrBi and NaCaBi are found to be strong TI under hydrostatic and bi-axial strain. Doping or alloying is another efficient way to control the non-trivial order. Partial or complete replacement of Na by Rb, Cs or K in the compound NaX'Bi (X'=Sr, Ca) helps to intrigue the TI or the NLS phase. We have also studied 1-D bulk Fermi surface and the topological flat surface band properties of systems showing NLS behavior. Possibility of experimental synthesis is confirmed by presenting the chemical stability of all the compounds. We endorse a much higher predictability power of the present report due to the use of HSE06 functionals compared to most of the similar previous reports based on GGA functional. Such accurate ab-initio predictions serve as a guiding path for the discovery of new novel materials.

Chapter 4

Type-II Dirac State and Fragile Fermi Arcs

Collective excitation of elementary electrons warrants several distinct Fermionic behavior in condense matter systems. These Fermions can be classified as Dirac, Majorana, Weyl, triple-point, nodal-line semimetal etc. Although the Dirac Fermions have been realized in high energy experiments, the Weyl and Majorana had not so far been observed until the discovery of topological semimetals and superconductors in low-energy condense matter systems. Dirac semimetals (DSM) [170, 171] and Weyl semimetals (WSM) [172, 173] are the well known topological materials with surface states (SSs) driven Fermi arcs (FAs). In DSM (WSM), four (two) bands cross each other near the Fermi level (E_F) . Such band crossing introduce massless Fermion nature in the low energy excitation which brings several spectacular physical properties, such as, close and open FAs [174], spin Hall effect (SHE) [175], chiral anomaly [176, 177] etc. If two bands of a given crystalline material having inversion symmetries (IS) and time-reversal symmetries (TRS) cross each other in the momentum space, it can host a Dirac like quasi particle excitation near the nodal point. Such quasi particle excitation can be well captured by the relativistic Dirac equation, hence the name DSM. Whether the DSM phase is stable or fragile, it depends on crystal symmetry. For instance, under the TRS preserving condition, the Dirac nodes are stable in systems

with a particular space group symmetry. The four-fold Dirac node splits into two two-fold Weyl nodes with opposite chiralities if either of the IS or TRS is broken.

Till date, several type-I DSM compounds have been theoretically predicted and experimentally verified through the photoemission and transport measurements. In contrast, only a handful number of type-II DSM [180, 182–184, 206] compounds are investigated. The major problem of the existing compounds are the position of nodal points which are far from the E_F and the presence of additional trivial Fermi pockets. For example, extensively studied compounds $PtSe_2$ [183] and $PtTe_2$ [185, 206] have type-II Dirac node around 1 eV below E_F with several trivial band crossings. VAl_3 [186] is another type-II DSM class where nodal points lie above E_F and restrict the photo-emission experiments to probe them. In this paper, using *first principle calculations*, we predict three full Heusler alloys XInPd₂ (X=Ti, Zr, Hf) to showcase the type II DSM properties. This study can guide not only the future photoemission experiments to probe the SSs, but also shed light on the currently debated topic of fragile nature of Fermi arcs and their associated topological origin. Although there exists another compound in this class YPd₂Sn [187], but a detailed study of topological Fermi arcs, SSs and bulk FS driven Lifshitz transition (LT) is lacking. One of the important features of $ZrInPd_2$ and $HfInPd_2$ is that they show superconducting phase transition at temperature 2.19 K and 2.86 K respectively [203, 204]. Previously, topological superconductivity (TSC) have been studied in a general framework of Fermi loop (FL) topology and C_n rotational symmetry lowering in DSM [188, 189]. For example, Dirac compound Cd₃As₂ shows superconductivity under pressure [192]. With the unique orbit-momentum locking near the nodes and the C_4 to C_2 rotational symmetry lowering creates a gap at the nodal points which is speculated to stabilize the TSC phase by increasing the condensation energy [188]. In contrast to

the type-I DSM, bulk FS of type-II DSM is composed of non-trivial electron and hole pockets which may contribute to the formation of the Cooper pairs and allow the compound to become superconducting [195]. Although, very recently, $PdTe_2$ [185] and YIn_3 [193] type-II DSM class have been put forward to ignite the TSC study but these two classes face certain limitations similar to those of $PtTe_2$ and $PtSe_2$, as discussed above. Our full Heusler compound $ZrInPd_2$ is much more superior in the above contexts as it's type-II Dirac node lie almost at E_F with relatively less number of Fermi pockets.

The full Heusler compounds $XInPd_2$ belong to the space group $Fm\overline{3}m$ [194] where X and In have the equivalent Wyckoff positions (0,0,0) and (1/2,1/2,1/2) to form a rock-salt structure and Pd takes sits at (1/4,1/4,1/4) and (3/4,3/4,3/4). The primitive unit cell is shown in Fig. 4.1(a). The bulk Brillouin zone (BZ) and projected (001) and (111) surface BZ are shown in Fig. 4.1(b).

4.1 Symmetry and Bulk topology

4.1.1 Three-Fold Band Degeneracy Without SOC

We establish the physical picture to form DSM phase considering the point group symmetry of the crystal structure and the group commutation relations. Along with the time reversal symmetry (TRS), XInPd₂ have O_h point group symmetry at the center of the BZ which contain global inversion symmetry IS and C_{4v} site symmetry group along Γ -X directions. C_{4v} have the four fold rotation element C_{4z} (for convenience, z-axis (Γ -X direction) is chosen as principle rotation axis) and the M_x mirror plane which contain the C_{4z} axis. Now, without spin-orbit coupling (SOC), the rotation eigen values of \tilde{C}_{4z} are $e^{i2\pi}$, $e^{\pm i\frac{\pi}{2}}$ and $e^{i\pi}$. And we denote the corresponding eigen-



Figure 4.1: (a) Crystal structure of XInPd₂. (b) Bulk and surface Brillouin zones. For ZrInPd₂, (c) orbital projected bulk band structure without SOC. (d) Bulk band structure with SOC. (e) Zoomed view of (d) near the three nodal points DP1, DP2, and DP3 at energy E1, E2 & E3 respectively. (f) HSE06+SOC band structure along Γ -X direction.

states as $\psi_{i2\pi}$, $\psi_{\pm i\frac{\pi}{2}}$ and $\psi_{i\pi}$. With this, we can write the following relations; $\tilde{M}_x \psi_{i2\pi} = \psi_{i2\pi}$, $\tilde{M}_x \psi_{\pm i\frac{\pi}{2}} = \psi_{\mp i\frac{\pi}{2}}$ and $\tilde{M}_x \psi_{i\pi} = \psi_{i\pi}$. The action of mirror transform the rotation eigen states $\psi_{i\frac{\pi}{2}}$ and $\psi_{-i\frac{\pi}{2}}$ to each other. So, $[\tilde{M}_x, \tilde{C}_{4z}] \neq 0$ for $\psi_{i\frac{\pi}{2}}$ and $\psi_{-i\frac{\pi}{2}}$ rotation eigen subspace. Now in conjunction with the above conditions, a generic Hamiltonian for the system commutes with the mirror \tilde{M}_x which enforces the double degeneracy of two eigen states along the C_{4z} axis. Corresponding to this degenerate eigen states, the irreducible representation (IR) is denoted by E and simultaneously $\psi_{i2\pi}$ and $\psi_{i\pi}$ form the non-degenerate eigen space with IRs A₁ and B₂ of C_{4v} group. The crossing point of A₁ and B₂ bands form the two-fold nodal point where as, E and A₁(B₂) crossing point forms the threefold degenerate nodal point. These bands and corresponding nodal points are shown in the bulk band structure of $ZrInPd_2$ without SOC as shown in Fig. 4.1.

4.1.2 Four-Fold Band Degeneracy With SOC

Inclusion of SOC doubles the eigen space according to double group representation of C_{4v} . Therefore, e_g transform as: $e_g \to \Gamma_8^+$ and $e_u \to \Gamma_8^-$. t_{2g} however, splits into Γ_8^+ and Γ_7^+ (i.e, $t_{2g} \to \Gamma_8^+ \oplus \Gamma_7^+$,) at Γ point of BZ. In contrast, along Γ -X direction, A₁ and B₂ transform into Γ_6 and Γ_7 respectively. On the other hand, E transform as: $E \to \Gamma_6 \oplus \Gamma_7$ as shown in Fig. 4.1(c,d). Note that the two fold Γ_7^+ IR in Fig. 4.1(d) propagate as Γ_7 and simultaneously four fold Γ_8^+ goes into Γ_6 and Γ_7 along Γ -X directions. The dimensional degeneracy of Γ_6 and Γ_7 IRs are two. Hence, any accidental band crossing of these Γ_6 and Γ_7 bands form four fold Dirac node on the C_4 rotation axis. Considering the point group symmetry of XInPd₂. We took ZrInPd₂ as a test case and discussed the detail calculated results. Figure 4.1(c) shows the band structure of $ZrInPd_2$ without spin orbit coupling (SOC). At the Γ point near E_F , the major contribution comes from the Zr_{2g} orbitals and band above this has dominant $\operatorname{Zr-e}_q$ contribution. $\operatorname{Zr-t}_{2q}$ split into E and B₂ bands along Γ -X direction whereas e_g transform into two singly degenerate A_1 and B_1 bands, denoted according to the IRs of C_{4v} little group. A_1 and B_2 bands cross each other to form a 2-fold nodal point (DP) and A_1 intersect with E to form a 3-fold nodal point (TP) as shown in Fig. 4.1(c). Inclusion of SOC doubles the eigen space according to double group representation of C_{4v} . Therefore, e_g transform as: $e_g \to \Gamma_8^+$ and $e_u \to \Gamma_8^-$. However, t_{2g} splits into Γ_8^+ and Γ_7^+ (i.e, $t_{2g} \to \Gamma_8^+ \oplus \Gamma_7^+$,) at Γ point. In contrast, along Γ -X direction, A₁ and B_2 transform into Γ_6 and Γ_7 respectively, whereas E transform as: $E \to \Gamma_6 \oplus \Gamma_7$ as shown in Fig. 4.1(c,d). Note that the 2-fold Γ_7^+ IR

in Fig. 4.1(f) propagate as Γ_7 and simultaneously 4-fold Γ_8^+ goes into Γ_6 and Γ_7 along Γ -X direction. The dimensional degeneracy of Γ_6 and Γ_7 IRs are two. Hence, accidental band degeneracy of these Γ_6 and Γ_7 bands form three Dirac nodes along Γ -X as denoted by DP1, DP2 and DP3 in Fig. 4.1(d). Figure 4.1(e) shows the zoomed view of DP1, DP2 and DP3. For DP1 and DP3, the electron (green) and hole (red) bands, which have similar slope, cross each other to form type-II Dirac nodes. However, DP2 is the type-I like Dirac node owing to the opposite electron and hole band slope. The type-II Dirac node (DP1) lies almost at E_F with small Fermi pockets away from the nodal point. The Chern number (topological index) for a Dirac node is zero as the nodal point can be considered as superposition of two Weyl nodes with opposite topological charges ± 1 . Vanishing of Chern number for a Dirac node and its consequences on the Dirac Fermi arcs will be discussed extensively in the subsequent sections. Unlike Na₃Bi [265] or Cd₃As₂ [266], where non-trivial band inversion $(Z_2=1)$ harbors Dirac crossings, our predicted XInPd₂ do not show band inversion and hence the Dirac nodes are manifested by accidental trivial band crossings. Further, to make sure about the topology and location of these Dirac nodes, a more accurate HSE06 level calculations are also carried out. This calculations give similar results as that of PBE calculation with Dirac nodes more closer to Fermi level, as shown in Fig. 4.1(f).

4.2 k.p Hamiltonian

We use k.p Hamiltonian for ZrInPd₂ to understand the nature of the degeneracies at the center of the Brillouin zone and along the Γ -X axis. The Γ point has O_h cubic symmetry. The generators of O_h group can be chosen as $C_{4z}, M_{[110]}, C_{3,[111]}$, and I. ZrInPd₂ is non-magnetic. So, time reversal symmetry (TRS) is preserved. In the four dimensional Γ_8^+ representation the basis can be chosen as $j_z = \pm 1/2$ and $\pm 3/2$ in spin-orbit space. In this basis the effective k.p Hamiltonian at the Γ point can be written as;

$$H(\mathbf{k}) = \alpha \mathbf{k}^{2} + \begin{pmatrix} \beta/2(2k_{z}^{2} - k_{\parallel}^{2}) & \gamma k_{z}k_{-} & \sqrt{3}/2\beta k_{\parallel}^{2} - i\gamma k_{x}k_{y} & 0\\ \gamma k_{z}k_{+} & -\beta/2(2k_{z}^{2} - k_{\parallel}^{2}) & 0 & \sqrt{3}/2\beta k_{\parallel}^{2} - i\gamma k_{x}k_{y}\\ \sqrt{3}/2\beta k_{\parallel}^{2} + i\gamma k_{x}k_{y} & 0 & -\beta/2(2k_{z}^{2} - k_{\parallel}^{2}) & -\gamma k_{z}k_{-}\\ 0 & \sqrt{3}/2\beta k_{\parallel}^{2} + i\gamma k_{x}k_{y} & -\gamma k_{z}k_{+} & \beta/2(2k_{z}^{2} - k_{\parallel}^{2}) \end{pmatrix}$$
(4.1)

where, $k_{\parallel}^2 = k_x^2 + k_y^2$, $k_{\pm} = k_x \pm i k_y$, and α, β, γ are the parameters of the Hamiltonian. The first term of the above Hamiltonian is just a shifting term which does not effect the physics of the system. The second term can be expand in terms of the linear combination of five 4×4 Dirac matrices, i.e the eigen values will be pairwise degenerate which is consistent with TRS and I symmetry of the system. Moreover, the diagonal elements are zero at the zone center, irrespective of the parameters of the system which ensure the four fold essential degeneracy (Γ_8^+) at the Γ point. This type of essential degeneracy is called quadratic contact point degeneracy and show unusual transport signatures [201].

Now, along Γ -X direction, the Γ_8^+ transform to Γ_6 and Γ_7 representations. We can choose these as basis and C_{4z} , TRS, IS symmetry of the system along Γ -X direction. Under the above conditions, an effective k.p Hamiltonian can be constructed as [202];

$$H(\mathbf{k}) = \epsilon_{0}(\mathbf{k}) + \begin{pmatrix} M(\mathbf{k}) & 0 & iAk_{x}k_{y} & Ak_{z}k_{+} \\ 0 & M(\mathbf{k}) & -Ak_{z}k_{-} & -iAk_{x}k_{y} \\ -iAk_{x}k_{y} & -Ak_{z}k_{+} & -M(\mathbf{k}) & 0 \\ Ak_{z}k_{-} & iAk_{x}k_{y} & 0 & -M(\mathbf{k}) \end{pmatrix}$$
(4.2)

where $\epsilon_0(\mathbf{k}) = D - Ek^2$, $M(\mathbf{k}) = B - Ck^2$, $k^2 = k_x^2 + k_y^2 + k_z^2$ and $k_{\pm} = k_x \pm ik_y$. The eigenvalues of this Hamiltonian are,



Figure 4.2: (a) Zr-In Octahedra (b) Two inter-penetrating tetrahedral configuration in ZrInPd₂. (c) Effect of orbital hybridization, crystal field splitting and formation of Dirac nodes. Region (I) is the atomic energy levels according to Aufbau principle, region (II) represents the energy level formation of octahedra and tetrahedra. Region (III) & (IV) describe the effect of crystal field splitting at Γ point without and with SOC respectively. The bands are designated with their irreducible representations (IRs). Region (V) shows the band representations and formation of nodal points along Γ -X direction or C_{4v} axes. 'd' and 'm' represent Major and minor contributions respectively from a particular atom.

$$E(\mathbf{k}) = \epsilon_0(\mathbf{k}) \pm \sqrt{M(\mathbf{k})^2 + A^2(k_x^2k_y^2 + k_y^2k_z^2 + k_x^2k_z^2))}$$

A, B, C, D, and E are the parameters of the Hamiltonian which we have calculated from the fitting with the first-principles band structure of ZrInPd₂. We have obtained the fitting parameters as; B = 0.621 eV, C = 2.659 eV Å², D = 0.716 eV, E = -3.109 eV Å². The momentum terms corresponding to A is quadratic. Hence, the value of A near the Dirac nodes expected to be very small. Indeed, we got A = 0.001 eV Å². The gapless Dirac node occurs at $k_d = \pm \sqrt{B/C}$. So, the nature of this degeneracy can be attributed as an accidental band degeneracy. For our compounds, the type-II Dirac nodes lie very near to Fermi and makes the compounds ideal candidates for experimental investigations.

4.3 Crystal Field Splitting

To reconfirm the formation of DSM phase in $ZrInPd_2$, we shall now illustrate the above discussion based on the structural and chemical environmental dependent crystal field theory. In full-Heusler alloy, e.g., ZrInPd₂, In atom sits at the center of an octahedra formed by Zr atoms (which sit at the six faces of FCC lattice) as shown in Fig. 4.2(a). Furthermore, Zr and In atoms form two interpenetrating tetrahedra (mutually rotated by 90°) keeping Pd atom at the center of tetrahedra as shown in Fig. 4.2(b). The atomic energy level distributions and the effect of crystal field splitting are shown in Fig. 4.2(c). The shaded box in region II is the pictorial representation of energy levels of octahedra and tetrahedra in the lattice. Region III represents the effect of orbital hybridization and crystal field splitting in the absence of SOC at the Γ point. In region III, the red block (above E_F) corresponds to the energy levels, mainly contributed by octahedral symmetry and the blue block (below E_F) contain the energy levels corresponding to tetrahedral symmetry. The crystal field splitting of d-orbital, due to the O_h environment (in the red block), is further emphasized. The t_{2g} orbitals which are mainly contributed by Zr, lie just below E_F whereas the e_g orbital lie above E_F . Here, in region III, d_1 , d_2 , d_3 , d_4 and d_5 represent the d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$, and d_{z^2} orbitals respectively. Above the e_g level, a_{1g} and t_{1u} are mainly contributed by In s and p like orbital respectively. This is consistent with the point group formalism because the basis function for a_{1g} is spherically symmetric whereas it is linear for t_{1u} . On the other hand, the lower blue block shows the d orbital splitting in tetrahedral environment. Due to the tetrahedral splitting, the e_q orbital falls below the t_{2q} orbital. Note that, though the tetrahedra does not posses IS but the presence of global IS of the crystal structure enforces the definite parity sates to the energy levels of tetrahedra. Region IV shows band splitting



Figure 4.3: (a) Zoomed band structure of $ZrInPd_2$ along Γ -X direction. E1-E5 are different energy cuts around the type-II Dirac node DP1. (b-f) Bulk Fermi surface at different energy cuts E1-E5.

due to SOC. Inclusion of SOC, transform the t_{2g} octahedra level as: $t_{2g} \to \Gamma_8^+ \oplus \Gamma_7^+$. On the other hand e_g goes to Γ_8^+ . Furthermore, the e_u level transform as Γ_8^- . Region V represents the transformation of bands along Γ -X direction starting from Γ point. The detail mechanisms on formation of three Dirac nodes (DP1, DP2 and DP3) have been discussed in previous paragraph.

4.4 Bulk Fermi Surface, Lorentz symmetry breaking and Lifshitz Transition

We will now proceed to understand the bulk FS topology, Lifshitz transition and Lorentz symmetry breaking, for which bulk FS near nodal point DP1 is simulated. The simplest Hamiltonian describing a type-II Weyl node is, $H = c\vec{\sigma} \cdot \vec{p} + vp_z$ [195, 196]. The second term in H tilt the cone along z-direction in the momentum space depending on the relative magnitude of v. For v = 0, the cone is not tilted, it become a type-I semimetal which have point like FS at the nodal point (Fig. 1.7(a)). For 0 < v < c, the cone is tilted. If v > c, the cone is over tilted which results the Fermi level to cross the electron and hole bands, forming contour like Fermi surface connected by the Weyl point, called type-II semimetal (Fig. 1.7(b)). The Lifshitz transition occurs for v=c between these two types of cone. The above scenario is similarly applicable for Dirac nodes but need extra crystalline symmetry to stabilize the Dirac point. Figure 4.3(a)shows a zoomed view of bulk band structure along Γ -X with five energy cuts E1-E5. Figure 4.3(b-f) shows the bulk Fermi surface for respective energy cuts. The red(green) bands indicate the electron(hole) type. For E1 energy cut, the electron type FSs are completely absent where as for E2, a tiny electron FS appear as shown by the arrowhead. E3 corresponds to the nodal point energy and the type-II Dirac nodes are indicated by arrowhead in Fig. 4.3(d). The electron band contribution in the FSs for E4 and E5 energy cut increases progressively. The FSs evolution justify the tilting of Dirac nodes in the momentum space and breaking of Lorentz symmetry. Here, the crystalline symmetry allows such tilting of cones in low energy system without respecting the Lorentz invariance. Although, DP1 in Fig. 4.1(d,f) indicates a type-II Dirac cone, the band effective mass of Γ_6 and Γ_7 clearly hints that the cone is in near critical region (i.e., v=c) between type-I and type-II Dirac states. Similar observations of Fermi surface topology have previously been seen in type-II Dirac and Weyl semimetals and commonly referred as Lifshitz transition in Ref. [187, 212]. Such transition is unique by itself (responsible for exotic phenomenon), and is attributed to the occurrence of superconductivity in ZrInPd₂.

To get more clear picture about the evolution of Fermi surface (FS), we calculated the FSs on a plane spanned by the basis vectors k_1 and k_2 , as shown in Fig. 4.4(a). Figure 4.4(b) shows the FS above 0.075 eV from the Dirac point (DP). Clearly, it shows that the electron pockets (ep) are blunt and hole pockets (hp) do not exist along the C₄ axis (Γ -X direction). In another lower energy cut, as shown in Fig. 4.4(c), ep starts taking a narrow shape, but still do not touch the hp. Moreover, two separated small hole pockets away



Figure 4.4: Bulk Fermi surface of ZrInPd₂ in a 2D plane spanned by basis vectors k_1 and k_2 as shown in (a). (b-f) 2D Fermi surface plots for different chemical potentials. Dirac nodes are shown by the arrowhead in (d). ep and hp represent the electron and hole pockets respectively, which forms the type-II Dirac nodes in (d).

from the Γ -X line in Fig. 4.4(b) starts coming closer and touch each others in Fig. 4.4(c). However, 2D Fermi surface map in Fig. 4.4(d)at an energy cut corresponding to Dirac node, shows that the hp and ep touch and hence form a Dirac node. Further in Fig. 4.4(e), ep become smaller and almost vanishes in Fig. 4.4(f). The 2D FS maps in Fig. 4.4(e,f) clearly shows the ep and hp are moving away from the DP. However, for a wide energy window with respect to type-II Dirac node position, the FS maps are contributed by both electron and hole pockets as observed from Fig. 4.4(b-f). This behavior of FSs justify the strong tilting nature of our type-II Dirac cone and hence it makes type-II Dirac/Weyl semimetals distinct from the type-I counter part. Note that in a type-I semimetal (Dirac or Weyl), for a particular energy cut near the nodal point, the FS is contributed either by electron or hole pocket. Such a phenomena on evolution of Fermi surface maps under the effect of tunable chemical potential is commonly referred as the Lifshitz transition for type-II Dirac/Weyl semimetals.

4.5 Bulk to Boundary Correspondance

Similar to the WSM, DSMs also hold the signature of bulk band degeneracies onto its surfaces. Since one Dirac node can be viewed as superposition of two Weyl nodes, double Fermi arcs (FAs) are expected on the bulk projected surfaces. The topological character of such DSM phase can further be understood from the fragility nature of the surface FAs. Hence surface dispersion and FAs of DSM are worthy of careful investigation both from theoretical and experimental front. To reveal the topological nature of FAs, we investigated the (001) and (111) surfaces. There are six Dirac nodes situated along the six Γ -X direction in the first BZ, as shown in the Fig. 4.1(d). Of these six, four are projected on the (001) surface (indicated by pink dot along $\overline{\Gamma} - \overline{X}$ direction on (001) surface) and the other two on the $\overline{\Gamma}$ point. If we consider that these projected nodes are the source and sink of the surface arcs (though it is not absolutely true for DSM nodes, that will be discussed in detail in the next paragraph), it is expected to get a square like close Fermi loop on (001) surface. However, the (111) surface contains six projected Dirac points as indicated by pink dot along $\overline{\Gamma} - \overline{K}$ direction on (111) surface BZ. Hence, a hexagonal shaped FA expected on this surface. Figure 4.5(a) shows the (001) SS of $ZrInPd_2$ for Zr-In terminated surface. FAs of (001) surface for different energy cuts are shown in Fig. 4.5(b-d). Fig. 4.5(e) shows the (111) SS for Zr terminated surface and Fig. 4.5(f-h) the corresponding FAs at different energy cuts. In Fig. 4.5(b-d & f-h), arcs are simulated using green's function method at E_F , energy of DP1 (E_{dp}) and 0.2 eV below E_F (E_F -(0.2) to show their evolution on both (001) and (111) surfaces. The evolution clearly shows the fragile nature of Dirac arcs and further hints about their topological features. We have also calculated the SSs of both (001) and (111) surface using slab method within the *ab-initio* framework that will be discussed subsequently.



Figure 4.5: Surface states (SSs) and Fermi arcs (FAs) of $ZrInPd_2$ using Green's function method. (a) SSs of (001) surface and (b-d) corresponding FAs for different energy cuts. (e) SSs of (111) surface and (f-h) corresponding FAs for different energy cuts.

4.6 Fragile Dirac Fermi Arcs and Absence of Topological Invariant

M. Kargarian *et al.* [198] and Yun Wu *et al.* [199] have proposed the fragile nature of Dirac arcs, which deform into a Fermi contour, strikingly different from the concept of Chern number protected Weyl arcs and similar to the surface states of a topological insulator. Such Fermi contour may convert to a loop and can also merge into the bulk projected surface Dirac nodes upon the variation of chemical potentials on the surface [199]. The fragile nature of Dirac FAs supports the zero Chern number of Dirac nodes and the absence of topological index mediated protections (although it can be stabilized by certain crystalline symmetry). Figure 4.5(b) is the Fermi arc exactly at the E_F on (001) surface. It is clear from the figure that the arcs are completely disconnected from the bulk projected surface Dirac nodes and they do not even form a close loop. This is different from the nature of Weyl arcs and indeed justify the absence of topological robustness in the bulk system. Interestingly, upon varying the chemical potentials, arcs deformed into the Fermi loop, which is again not connected with the projected Dirac nodes, as observed in Fig. 4.5(c). The Fermi loop, however, sink into sur-


Figure 4.6: Surface states (SSs) of $ZrInPd_2$ using slab model with 50Å slab thickness. (a) SSs of (001) surface (b) SSs of (111) surface. The outermost surface atom's contributions are indicated by red and green symbols.

face DPs with further lowering of chemical potential, as shown in Fig. 4.5(d). For (111) surface, the topological nature of arcs, as shown in Fig. 4.5(f-h), are similar to that of (001) surface. The arc form a loop shape in Fig. 4.5(f). However, they are connected with bulk states in Fig. 4.5(g,h) at other energy windows. Such detailed analysis not only guide the experimentalists to correctly probe the SSs but also establish a strong base to the largely debated topic of the topological nature of Dirac arcs. The take home message of the entire discussion is that a little perturbation in the bulk crystal that do not disturb the responsible crystalline symmetry for the Dirac state can deform the surface FAs to a disconnected Fermi contour. However, these arcs may not be completely destroyed because of the presence of crystal mirror invariant planes which can further provide mirror Chern number protection.

4.7 Surface States Using Slab Model

Further, we have calculated the surface states (SSs) of (001) and (111) surface of $ZrInPd_2$ using slab model. We consider 50Å thick slab with 20Å vacuum to avoid the interaction between periodic mirror image of top and bottom surfaces. For (001) slab, top and bottom surfaces contain the Pd and Zr-In atoms respectively as

shown in Fig. 4.6(a). Fig. 4.6(b) shows the (111) surface with Zr and In termination on the top and bottom surfaces respectively. The topological nature of the SSs from both the methods (Fig. 4.5 and Fig. 4.6) are qualitatively similar. Although, the position of Fermi energy is little bit shifted due to the surface termination potential which we did not consider in Green's function method. In addition few extra band crossings across the Fermi level also appeared in Fig. 4.6 due to the surface dangling bonds.

4.8 Other Similar Compounds

In addition to $ZrInPd_2$, we have simulated the band structure of TiInPd₂ and HfInPd₂ as well and found quite interesting type-II Dirac semi-metal features. The type-II Dirac nodes lie very close to E_F for both the compounds, as shown in Fig. 4.7(a,b). The SSs and Fermi arcs are expected to be similar to $ZrInPd_2$, as they possess very similar bulk band topology. We have discussed the energy location of the DPs for XInPd₂ and compared with previously studied type-II DSMs. We tabulated the position of Dirac nodes with respect to the Fermi level for the existing few well studied type-II Dirac semimetals and compared them with our predicted class. It is clearly evident from the Table. 4.1 that XInPd₂ (X=Zr,Hf,Ti) class of compounds host the Dirac point closest to the Fermi level with respect to other type-II Dirac semimetals. Additionally, XInPd₂ (X=Zr,Hf,Ti) class clearly indicates absence of trivial Fermi pockets (see Fig. 4.7) as compared to other existing Dirac semimetals (DSMs) [206–211]. Close vicinity of the Dirac nodes near E_F and substantial absence of trivial Fermi pockets make the XInPd₂ (X=Zr,Hf,Ti) class superior over other DSMs (including YPd₂Sn and PtSe₂ class) in terms of experimental possibilities. Furthermore, Dirac nodes in YPd₂Sn are above the Fermi level in contrast to XInPd₂ (X=Zr,Hf,Ti) class, which restricts the possibility of probing them in YPd₂Sn using



Figure 4.7: Bulk band structure of (a) TiInPd₂ and (b) HfInPd₂. Green and red lines are the electron and hole like bands respectively.

ARPES experiments. We have also calculated the band structures of $ZrInPd_2$ and $HfInPd_2$ using HSE06 functional which shows that the Dirac nodes moves closer to Fermi level as compared to PBE functional. Within HSE06+SOC level of calculation the DP1 lies at an energy -140 meV and -80 meV below the Fermi level for $ZrInPd_2$ and $HfInPd_2$ respectively.

Table 4.1: The different materials and their energy location of Dirac points (E_{DP}) with respect to Fermi energy (E_F) calculated using generalized gradient approximation. (^a Ref.[Our Work]; ^b Ref. [187]; ^c Ref. [206])

Material	ev	Material	eV
$ZrInPd_2$	-0.21 a	$\mathrm{ZrNi}_{2}\mathrm{Al}$	-0.29 °
$HfInPd_2$	-0.15 ^a	HfNi ₂ Al	-0.26 ^c
$TiInPd_2$	-0.13 a	$\mathrm{ZrPd}_{2}\mathrm{Al}$	-0.27 ^c
PtTe ₂	-0.86 ^b	$ScPd_2Al$	$0.14 \ ^{c}$
$PtSe_2$	-1.19 ^b	$\mathrm{YPd}_2\mathrm{Sn}$	$0.13^{\ c}$
PdTe ₂	-0.54 ^b	$\mathrm{HfPd}_{2}\mathrm{Al}$	-0.23 ^c

4.9 Conclusion

We have predicted three full Heusler compounds $XInPd_2$ (X = Ti, Zr and Hf) as potential candidates for type-II DSM. Among them, ZrInPd₂ and HfInPd₂ has been experimentally synthesized and measured to undergo superconducting transition at 2.19K and 2.86K. The position of the nodal points lie at/near E_F which should facilitate for strong response in the transport measurements. Unlike extensively studied $PtTe_2$ class of compounds, our predicted compounds are more superior for experimental investigation because of the location of nodal point in close vicinity of E_F and relatively less number of trivial Fermi pockets. In the present systems, another type-I and type-II Dirac nodes coexist at a little lower energy along Γ -X. We have carefully studied the bulk FSs at different energy cuts near type-II node (DP1) to investigate the breaking of Lorentz symmetry, tilting of cone and possible Lifshitz transition (LT) of FS. The bulk FSs indicate that ZrInPd₂ lie near the boundary of type-I and type-II semimetal (i.e., at the LT region) which could be an underlying reason for the superconducting transition in these systems. SSs and Fermi arcs are simulated on (001) and (111) surfaces of ZrInPd₂ to investigate the bulk boundary correspondence and their topological nature. Our detail analysis of Fermi arcs not only guide the experimentalists to reliably probe the SSs but also shed light on the largely debated topic of the topological nature of Dirac arcs. We conclude that a little perturbation in the bulk crystal, that do not disturb the responsible crystalline symmetry for the Dirac state, can deform the surface Fermi arcs to a disconnected Fermi contour. As such, the Dirac Fermi arcs are fragile in nature and does not have topological protection like Weyl arcs. SSs are also simulated using slab model. Thus, we believe that XInPd₂ possibly stands as the most ideal material, yet proposed, to host type-II DSM state. We strongly encourage experimental investigations to reconfirm our findings.

Chapter 5

Dirac and Triple Point Fermiology

Symmetry protected multifold band crossings in momentum space often exhibit strong topological response in the transport measurement. A four-fold Dirac node [213] splits into a pair of two-fold Weyl nodes [214] under magnetic field, which in turn shows several anomalous transport signatures; such as anomalous Hall effect (AHE) [215–218], anomalous Nernst effect (ANE) [219–221], non-saturating large magneto-resistance (LMR) [222–224], chiral anomaly [225–228] etc. A pair of opposite monopole charges are created upon the separation of Weyl nodes under either inversion or time reversal symmetry (TRS) breaking conditions. Each of the Weyl nodes are associated with the source or sink of Berry curvature in momentum space [229, 230]. While this fictitious magnetic field like Berry curvature couples to the external magnetic field, it gives rise to such anomalous response in materials. Several Dirac and Weyl semi-metals (DSM and WSM) have been proposed and their topological signatures have been extensively investigated through photoemission and transport measurements. Another type of quasiparticle excitation, different from DSM and WSM is triple point semi-metal (TPSM) states [231–235]. TPSM is believed to be an intermediate phase of relatively higher symmetric DSM and lower symmetric WSM. The topological index for TPSM is still a matter of debate [236, 269], hence it has become a fertile ground for the

topological study in the recent times.

In the present study, we investigated the topological electronic structures of hexagonal noble metals ruthenium (Ru), rhenium (Re) and osmium (Os) based on symmetry analysis and *first-principle* calculations. These systems although look simple on the onset, yet some of their properties are quite puzzling and still requires proper understanding. One of the main motivation to choose these systems is to understand the rich physics behind the various anomalous existing experimental results such as anomalous magneto transport effect [238, 239], anomalous Nernst emf (and their giant quantum oscillation) [240], measured Fermi surface (FS) [261] etc. Close inspection of these experimental results made us speculate the topological origin of the electronic structure of these systems to be responsible for such anomaly. Indeed, our detailed calculations and group theoretical analysis strongly indicate the existence of symmetry protected multiple Dirac Fermionic excitations near the Fermi level (E_F) . We choose Ru as a case study and investigate both the bulk and surface band topology in details. Our calculated Fermi surfaces (FS) for Ru matches fairly well with the previously measured experimental FS [260].

Ru has been extensively studied for its unusual magnetotransport properties under the so called neck-lens magnetic breakdown [238, 239]. For instance, it shows non-saturating LMR in perpendicular magnetic field [239] which is somewhat similar to these in topological semi-metals. Several theories have been proposed to address the origin of such LMR. They are—(i) linear band crossing [245–247] in momentum space as in the case of Cd₃As₂, Na₃Bi and so on, (ii) perfect electron-hole (e-h) compensation [248–251] in WSMs; WTe₂, MoTe₂, PtSn₄ and LaSb (although LaSb has trivial band ordering, multiple Weyl type nodes are present in its band dispersion [252]), and (iii) Lifshitz transition (LT) of Fermi surface (FS) [251] (recently, LT has been found in several topological materials where the phase transition does not break any symmetries but can be described by topological invariants). Apart from aforementioned theories, a topology driven non-trivial origin for the non-saturating LMR has also been predicted by Tafti et al. [253] Another interesting feature of Ru is that it shows finite Nernst emf which shows giant oscillation in(a) for C_{3v} , the representation of rotation eigen states corresponding to their rotation eigen values, and mirror invariant planes. (b) Schematic diagram of formation of three-fold band crossings. Bands are represented by their rotation eigen values. high filed regime [240]. The characteristic curve and the oscillation patterns are quite similar to the non-trivial material Bi_2Se_3 and very different from the Drude like behavior [240, 243]. Keeping these facts in mind, our study reveals the appearance of Dirac surface states (SSs) mediated Fermi arcs on the surface of noble metals (Ru, Re and Os) which is found to be the key origin in understanding the existing problem of transport anomalies. Note that the controversial Shockley type SSs that appear on the surface of noble metals; such as gold (Au), silver (Ag), copper (Cu), platinum (Pt) and palladium (Pd), have recently been interpreted as topologically derived surface states [244].

Symmetry argument has become a very important tool to explore the material physics in recent time. The knowledge of symmetry provides constraint or consent over the tunability of topological phases. We use the crystalline symmetry breaking argument to tune the DSM phase to TPSM phase using alloy mechanism. For example, both Ru and Os show Dirac nature owing to the center of inversion (IS) and C₆ rotation symmetry. However, the binary alloy RuOs breaks the IS and transforms the C₆ into C₃ rotation, which converts the Dirac like excitations to three component Fermionic excitations. The most important advantages of such symmetry adopted tunability is that we can shift the nodal points very close E_F depending on the crystal composition. As such, we have a freedom on the position of the nodal points as well as tunability of the low energy excitations.

5.1 Dirac State Under C_{6v} Symmetry

The presence of D_{6h} point group allow a C_{6v} little group along Γ -A direction in Brillouin zone (BZ). The symmetry elements that C_{6v} contain are identity (E) operation, six (C₆), three (C₃) & twofold (C₂) rotational symmetry about z-axis, three vertical mirror plane (σ_v) and three σ_d mirror plane (σ_d bisect two σ_v mirror). For spin-orbit case, \tilde{C}_6 have six eigenvalues $\exp^{\frac{i2\pi}{6}(n+1/2)}$, where n=0 to 5. The corresponding eigenstates for the \tilde{C}_6 rotation operator, are $\psi_1, \psi_2, \psi_3, \psi_4, \psi_5$, and ψ_6 as shown in Fig. 5.1(a). Now, we have the commutation relations, [$\tilde{\sigma}_v, \tilde{C}_6$] $\neq 0$ and [$\tilde{\sigma}_v, \tilde{C}_3$] $\neq 0$. These two commutation relation gives the following relations,

$$\tilde{\sigma}_v \ \psi_1 = \psi_2 - - - (I)$$

and $\tilde{\sigma}_v \ \psi_3 = \psi_4 - - - (II)$

Further, Hamiltonian commute with $\tilde{\sigma}_v$ i.e, $[H, \tilde{\sigma}_v] = 0$. which gives,

 $\begin{aligned} &H\tilde{\sigma}_v\psi_1 - \tilde{\sigma}_vH\psi_1 = 0\\ &\text{Or, }H\psi_2 - E_1\tilde{\sigma_v}\psi_1 = 0 \text{ [using equation (I)]}\\ &\text{Or, }H\psi_2 - E_1\tilde{\sigma_v}\psi_1 = 0\\ &\text{Or, }E_2\psi_2 - E_1\psi_2 = 0\end{aligned}$

Hence, $E_1 = E_2$. So, the energy eigen value corresponding to \tilde{C}_6 rotation eigen states (ψ_1 and ψ_2) are same. Hence, they form a degenerate eigen space (Γ_7 representation) under the above symmetry. In the similar way, [$\tilde{\sigma}_v$, \tilde{C}_3] $\neq 0$ and [H, $\tilde{\sigma}_v$]= 0 together ensure the degenerate eigen state of ψ_3 and ψ_4 (Γ_8 representation). As all the points along Γ -A direction are invariant under $\tilde{\sigma}_v$, \tilde{C}_6 and



Figure 5.1: (a) For C_{6v} , representation of rotation eigen states corresponding to their rotation eigen values, and and mirror invariant planes (b) schematic diagram of formation of four-fold band crossings. Bands are represented by their rotation eigen values.

 C_3 , these Γ_7 and Γ_8 band representations are applicable along this direction in BZ.

Furthermore, ψ_5 and ψ_6 form a degenerate state (Γ_9 bands) under the action of TRS, C_2 and σ_d symmetry. As $[\tilde{C}_2, \tilde{\sigma}_d] = 0$, we can define a new operator, $\theta = \tilde{C}_2 \ \tilde{\sigma}_d$. In spin rotation space, $\theta^2 = 1$. In the presence of TRS, eventually now we have, $T^2\theta^2 = -1$. This is the local Kramer's theorem, which guaranteed the double degeneracy at every point along Γ -A direction in BZ as this direction is invariant under both \tilde{C}_2 and $\tilde{\sigma}_d$. Now, the two bands having different irreducible representations cross each other along C_6 axis, will form a gap less four fold degenerate Dirac nodes. For Ru, Γ_{7or9} band intersects with another Γ_8 band and form two Dirac nodes on the C_6 rotation axis. The pictorial representation of bands and the formation of Dirac nodes are shown in Fig. 5.1(b).



Figure 5.2: (a) For C_{3v} , the representation of rotation eigen states corresponding to their rotation eigen values, and mirror invariant planes. (b) Schematic diagram of formation of three-fold band crossings. Bands are represented by their rotation eigen values.

5.2 Triple Point Fermion State Under C_{3v} Symmetry

 C_{3v} have identity (E), three-fold (C₃) rotational symmetry about z-axis, and three vertical mirror plane (σ_v) as shown in Fig. 5.2(a). Similar to C_{6v} , in case of $C_{3v}, [\tilde{\sigma}_v, \tilde{C}_3] \neq 0$ and $[H, \tilde{\sigma}_v] = 0$ ensure the degenerate eigen space of ψ_2 and ψ_3 (Γ_4 representation). Absence of σ_d enforce to form non-degenerate representations Γ_5 and Γ_6 . Any accidental band crossing Γ_4 and Γ_{5or6} forms a triply degenerate nodal point as shown in Fig. 5.2(b).

5.3 Dirac Fermion in Metals

Ru, Re and Os, in their elemental phase, crystallize in hexagonalclose-packed structure with P6₃/mmc space group and D_{6h} point group. The crystal structure and Brillouin zones (BZ) are shown in Fig. 5.3(a,b). The two-atom unit cell with particular uniaxial rotational symmetry results more complex electronic Fermi surface topology than the cubic noble metals (Au, Ag, Pt, etc). The pres-



Figure 5.3: (a) Top view of P6₃/mmc crystal structure of metals (b) Brillouin zone (BZ) with high symmetry points and their projections on (001) and (100) surface BZ. (c) Electronic structure of Ruthenium (Ru). Inset in (c) shows small energy window of the shaded region along Γ -A. Γ_i 's are the irreducible representations (IRs) for the bands. The intersection of Γ_{7or8} with Γ_9 results in Dirac nodes. Red(green) dotted line is drawn to show Dirac nodes at energy E1(E2).

ence of D_{6h} point group allow a C_{6v} little group along Γ -A direction in BZ. For Ru, Γ_{7or9} band intersects with Γ_8 band and form two Dirac nodes on the C_6 rotation axis as shown in Fig. 5.3(c). Similar observations and mechanisms have also been observed for Re and Os which will be discussed later in the manuscript. Furthermore, in addition to the above C_{6v} symmetry element, the elements Ru, Re and Os also holds structural inversion. Interplay of inversion symmetry and TRS further ensures Kramer's double degeneracy throughout the BZ. Hence, two doubly degenerate bands belong to different IRs while crossing each other along C_6 direction form a Dirac node and hence the hybridization at the nodal point is prohibited by group orthogonality relations. As such, presence of inversion center provides extra crystalline symmetry protection to the Dirac nodes in addition to C_{6v} . Therefore, the Dirac nodes are stable against inversion breaking perturbation in the presence of C_{6v} symmetry.

5.3.1 Dirac Surface States

The origin of the surface states (SSs) in noble metals (Au, Ag and Cu etc.) can be traced back to Shockley's prediction [254] of SSs which



Figure 5.4: For Ruthenium, (a) Surface dispersion for (001) Miller plane. (b-d) Fermi surface maps on (001) surface at different energy cuts. (e-g) Fermi arcs at different energy cuts on the (010) side surface.

appear inside an inverted energy gap due to band crossing [255, 256]. Very recently, some of these Shockley's SSs have been understood from the topological consideration, with the knowledge of global properties of electronic structure [244]. Another type of SSs, called Rashba SSs, appear due to the absence of translational symmetry on the surface which is quiet a common phenomenon on noble metal surfaces. Although, these Shockley or Rashba SSs can be explained from the free electron theory, but a rigorous topological understanding is required to capture various other anomalous surface behaviors. For example, recently, Zak phase driven large surface polarization charge and flat SSs have been understood from the non-trivial Berry phase in topological Dirac nodal line fcc alkaline earth metals; calcium (Ca), strontium (Sr) and ytterbium (Yb) [257]. Topological nature of Beryllium (Be) have also been explored which indeed shed light on the long standing controversial issues of Be, such as strong deviations from the description of the nearly free-electron theory, anomalously large electron-phonon coupling effect, and large Friedel oscillations etc. [258]

In the above context, Ru, Re and Os are unique as their Dirac like bulk band crossing suggests the appearance of non-trivial sur-

face dispersion and Fermi arc topology onto the surface. Since in DSMs, the main focus is the surface states and the associated Fermi arcs that link the Dirac points, we have investigated the FS map for both (001) and (010) surfaces for Ru as shown in Fig. 5.4. Bulk projected SSs on (001) surface is shown in Fig. 5.4(a). Bulk electronic structure of Ru suggest the appearance of a pair of Dirac nodes (crossing point of Γ_{7or9} , and Γ_8 bands as shown in Fig. 5.3(c)) along Γ -A direction). The projection of these two Dirac nodes on (001) surface fall on $\overline{\Gamma}$ point in the surface BZ (as shown in Fig. 5.3(b)). Moreover, in the energy scale, the positions of two Dirac nodes are separated by a small value. Projection of one Dirac node in energy scale is depicted by blue dot in Fig. 5.4(a). The Dirac like surface states (DSSs), emerging from the Dirac nodes in (001) surface is shown in Fig. 5.4(a). However, the other Dirac node is buried by the bulk Fermi pockets near the $\overline{\Gamma}$ point. Nonetheless, the Fermi arcs for two Dirac nodes can be clearly encapsulated little far from the $\overline{\Gamma}$ point along $\overline{M}(\overline{K})$ direction (see Fig. 5.4(a)) as indicated by DSS1 and DSS2.

The FS maps on (001) surface have been investigated and the evolution of FS topology is observed for three different energy cuts (E1, E2 and E3) as shown in Fig. 5.4(b-d). At energy cut E1, the Dirac SSs, DSS1 and DSS2 are little immersed by bulk bands near $\overline{\Gamma}$, hence we do not observe the clear signature of Dirac SSs mediated FS map at this constant energy cut. However, the signatures and contour patterns of DSSs mediated FS maps are clearly observed for other two energy cuts at E2 and E3 as described in Fig. 5.4(c,d). The two concentric Fermi arcs in Fig. 5.4(d) are indicated by arc1 and arc2. A similar pattern for FS have earlier been observed by photoemission spectroscopy on the hexagonal surface of MoP [232], MoC [233], LuPtBi [259], etc. Most importantly, the FS for Ru is highly consistent with the previous experiments both by Angle-resolved photoemission spectroscopy (ARPES) and de Haas-van

Alphen (dHV) oscillation. [260, 261] However, the explanation based on topological origin of the FS maps in those experiments is lacking.

Furthermore, the DSSs mediated Fermi arc topology, can also be observed on the side surface (010 plane) of Ru. The Γ and A(L) point of bulk BZ fall onto the $\overline{\Gamma}$ and \overline{Z} point on surface BZ (SBZ) of (010) surface. As such, the projected Dirac nodes fall on the $\overline{\Gamma}$ - \overline{Z} line segment in (010) SBZ. A time reversal pair of Dirac nodes is situated on both sides of the $\overline{\Gamma}$ point along $\overline{\Gamma}$ - \overline{Z} line. In the momentum space, a Fermi arc is nested in between this pair of Dirac nodes as shown in Fig. 5.4(e-g). Figure 5.4(e-g) shows the Fermi arc topology on the side surface of Ru for three different energy cuts. For the energy cut very close to Dirac nodes (as shown in Fig. 5.4(e)), two arcs originated from two pair of Dirac nodes are almost degenerate (since, two nodal points are situated very closely in momentum space). As we move away from the Dirac nodes, the two arcs get resolved (Fig. 5.4(f), 5.4(g)).

We now discuss the origin of these SSs and arcs from the topological perspective. A DSM phase is the parent sate of WSM and topological insulator (TI). TI phase can be achieved by opening up a non-trivial gap at the nodal points. In such a case, presence of SSs is guaranteed by topological Z_2 index. On the other hand, two Weyl nodes with opposite chern number sit together to form a Dirac node in momentum space under the precise symmetry enforcement. Such degeneracies of Weyl nodes form a "doubly-degenerate" Fermi arc in DSM phase. However, such type of Fermi arcs may not be protected by topological index. Nevertheless, a crystalline symmetry protected three dimensional DSM phase is stable as long as the symmetries are intact.



Figure 5.5: For RuOs binary alloy, bulk band structure (a) along high-symmetry lines, (b)along Γ -A indicating band IRs (shown by Γ_i s). Triply degenerate nodal points TDNPs (shown by T's). (c) Fermi arc on (010) side surface.

5.4 Triple Point Fermion in Alloys

The alloy driven crystalline symmetry breaking allows us to realize three component Fermionic excitation near E_F , which is different from the Dirac excitation in pure metals Ru, OS and Re. For the binary alloys, e.g. RuOs, the point group symmetry reduces from D_{6h} to D_{3h} . D_{3h} allows it's C_{3v} subgroup symmetry along Γ -A direction. The alloying transforms the crystalline symmetry from C_{6v} (elemental metal) to C_{3v} (binary alloy with space group P $\bar{6}$ m2) and the corresponding band representation changes as; $\Gamma_{8,7} \rightarrow \Gamma_4$ and $\Gamma_9 \rightarrow \Gamma_5 \oplus \Gamma_6$. Further, the strength of $\Gamma_{5,6}$ band splitting and the slop of Γ_4 band collectively determine the number of TDNP (two or four in our binary alloys) on the C₃ rotation axis. Figure 5.5(a,b) shows a case study on the bulk band structure of RuOs alloy. Four triple points are observed in RuOs alloy and they are denoted by T1, T2, T3 and T4 in Fig. 5.5(b). Note that, TDNPs are protected by group orthogonality relations of different IRs. We have also simulated the Fermi arcs nesting on (010) rectangular surface of RuOs alloy, which host triple point (semi)metallic state (see Fig. 5.5(c)). All the TDNPs are projected along the $\overline{\Gamma} - \overline{Z}$ axis on both sides of $\overline{\Gamma}$ point. The Fermi arcs are originated and nested between the TD-NPs as shown in Fig. 5.5(c). The existence of such TDNP induced Fermi arcs on a particular surface is a hallmark of TPSM state for their experimental detection.

5.5 Related Compounds

To get an ideal candidate (in terms of the position of Dirac points (DPs) and TDNPs with respect to E_F), we have simulated the band structure of other metals (Os and Re) and their alloys (ReRu and ReOs). The band structures along the six(three) fold rotation axis are shown in Fig. 5.6. In Table 5.1, we have also listed the compounds with the number of nodal points and their relative position in terms of energy. The spin-orbit coupling strength of Os is highest among these three pure metals, hence the splitting between Γ_7 and Γ_9 is largest which in turn results in a larger separation of DPs for Os in momentum space as shown in Fig. 5.6(b). For ReOs alloy, the nodal points (TDNPs) lie close to E_F as compared to other two alloys, ReRu and RuOs. Furthermore, ReOs only has a single pair of TDNPs, as shown in Fig. 5.6(d).



Figure 5.6: Electronic structure (along Γ -A) for (a) Re, (b) Os, (c) ReRu, and (d) ReOs. Dirac points and TDNPs are represented by DP's and T's respectively.

Table 5.1: Number (#) of DPs or TDNPs and their positions ($\Delta \epsilon$) with respect to E_F for pure metals and their binary alloy.

Metal	DPs $\#$	$\Delta \epsilon \; (\mathrm{eV})$	Alloy	TPs $\#$	$\Delta \epsilon \ (eV)$
Ru	2	-0.45	RuOs	4	0.60
		-0.51			-0.29
					-0.47
					-0.57
Os	2	-0.50	ReOs	2	0.17
		-0.71			0.09
Re	2	0.41	RuRe	4	0.94
		0.17			0.23
					0.06
					-0.35

5.6 Conclusion

The conclusion of this work is mainly three fold; (i) we predict the existence of symmetry-protected Dirac sates in pure elemental metals Ru, Os and Re. We find the unique Dirac-like Fermi arc topology on the (001) and (010) surfaces of these metals. Our calculated Fermi surfaces are consistent with the previous experiments by ARPES and transport measurements. (ii) The presence of such topologically non-trivial Fermi arcs can re-evaluate the understanding behind several anomaly in such metals. We speculate these topological nature of bands in Ru to be responsible for several puzzling behavior such as magnetic break down, large magneto-resistance similar to DSM compound Cd₃As₂, giant Nernst oscillation (similar to Bi₂Se₃) and deviations from the description of the Drude theory. (iii) By precise symmetry-breaking alloy engineering, the Dirac excitations can be tuned to three component fermion excitations. Depending on the combinations, we get two or four pairs of TDNPs along Γ -A directions. The position of TDNPs are very closer to E_F (for RuRe and ReOs alloy) which definitely enable the strong topological response in transport experiments. Finally, these types of transition-metal alloys are extensively synthesized and investigated in the field of catalysis, hence our findings open up a new direction towards that too.

Chapter 6

Broken Symmetry Driven Topological Phase Tuning

The degrees of band degeneracy near the Fermi level classify the topological gapless phases into three distinct categories; namely Dirac Semimetal (DSM) [11–17], Triple point semimetal (TPSM) [18–29], and Weyl Semimetal (WSM) [30–36]. The DSM and WSM are the low energy excitations of relativistic Dirac and Weyl fermions having four and two fold band degeneracies, respectively. However, the TPSM does not have any high energy analogue in the quantum field theory. The TPSM is considered to be the intermediate state of the other two phases. All these three semi-metals have been theoretically predicted and experimentally verified in various condensed matter systems (crystal) holding appropriate crystalline symmetries. On the other hand, topological gapped states have been studied extensively because of its unique bulk to surface correspondence [8-10]. Gradual reduction of the crystalline symmetries removes the band degeneracies which drives the system from one semimetal phase to other semimetal phase and also to gapped states [21, 22]. For an example, crystals having inversion symmetry with C_{3v} little group along some high symmetry line (HSL) in Brillouin zone (BZ) could provide four fold Dirac node if there is an accidental band crossing on that HSL. Two triply degenerate nodes (TDN) can be formed by simply breaking the inversion symmetry (keeping C_{3v} intact). These pairs of TDN can further be splitted into four Weyl points

(WP) when lowering C_{3v} to C_3 (breaking vertical mirror plane). Finally, topological insulator (TI) phase could be realized by further breaking the C_3 symmetry. Although the theoretical pathway is utterly straightforward but the realization of such phase in a single realistic material is non-trivial. Breaking of crystalline symmetry is usually associated with doping, alloying, strain, pressure or some other external perturbations which often destroy the local chemical environment causing the lifting of degeneracies. As a result, the accidental degeneracies are quite fragile under such perturbations.

Doping or alloying has been proven to be an efficient mechanism to tune the materials electronic properties. The advantage of doping or alloying is that one can break the structural symmetry and remove the band degeneracies easily without much affecting the overall electronic structure with proper choice of dopant and doping site. Also from experimental point of view, these approaches are well established to tailor the properties of the materials. Very recently, alloying mechanism has been applied effectively to tune the topological properties of MgTa₂N₃ [21, 22].

In this chapter, we discuss the emergence of various topological semi-metals and topological insulating phase in Cu-doped SrAgAs. We have doped Cu in place of Ag in a precise way such that the doped compound $\operatorname{SrAg}_{1-x}\operatorname{Cu}_x\operatorname{As}$ holds the required crystalline symmetry to induce different topological phases (DSM, TPSM, TI) for different values of x. Unlike previous study [21] on a similar theme, we have also discussed the effect of time reversal symmetry (TRS) breaking and curbs of doping towards the realization of WSM phase. Another key advantage of the present system over the previously reported one is that, all the Dirac and triple point nodes in the current system lie either close or just below the Fermi level. This can greatly help probes such as photo-emission spectroscopy to locate them easily. We confirm the feasibility of the experimental synthesis of the proposed alloys via phonon calculation. Moreover, we confirm the chemical stability of these alloys by simulating their formation energies.

SrAgAs was first synthesized by Albrecht Mewis in 1978 [262] and it belongs to prototype ZrBeSi-type [271] hexagonal family which crystallizes in $P6_3/mmc$ (# 194) space group. The crystal structure (Fig. 6.1(a,b)) can be viewed as staffed graphene layers – the Sr^{2+} cations are staffed between $[Ag^{1+}As^{3-}]^{2-}$ honeycomb network. Such structural arrangements further hold the space inversion symmetry. The presence of time-reversal symmetry (TRS), center of inversion symmetry and C_{3v} little group along the k_z axis leads to generate four-fold Dirac nodes in SrAgAs. Further, in the present work, we replace 50% Ag atoms by Cu to break the inversion symmetry and hence to realize three component TPSM state. Moreover, 25% Cu doping at the Ag sites breaks the C₃ rotational symmetry transforming to C_{2h} symmetry which, in turn, allows to develop a topological insulating phase in SrAg_{0.75}Cu_{0.25}As alloy. Furthermore, for SrAg_{0.75}Cu_{0.25}As, we simulated all possible configurations of Cu dopant sites. Out of them, the structure with the lowest energy configuration (which shows C_{2h} point group symmetry) is chosen to present further results in the manuscript. Nonetheless, all other possible configurations also lead to open up a topologically non-trivial band gap along Γ -A direction which is ensured by its structural point group symmetry. Subsequently, we induce a Weyl semimetal phase in the parent SrAgAs by breaking TRS with the application of external magnetic field.

It is important to note that both Ag and As holds the equivalent wyckoff positions in the unit cell. So the above symmetry lowering mechanism equivalently holds for the doping at As site as well. We chose to present the detailed results for Cu alloying @ Ag site here. A similar realization of various topological phases by alloying antimony (Sb) at As site is discussed.

6.1 Topology and Symmetry of Bulk

We start with a question: what exactly defines the states of a topological material? Is it DSM, TPSM, TI or WSM? The answer lies in its point group symmetry. The central concept is that two bands which are composed with atomic orbitals will cross each other at any k-points in the BZ and the degeneracy of that crossing points will be protected by the site-symmetry group of that points and the band hybridization will be restricted by the group orthogonality relations [30]. The dimension on the irreducible representation (IR) of the corresponding bands define the particular state of the compound.

Now, coming to our parent compound, SrAgAs has D_{6h} point group which immediately suggests that there is an inversion center along with the C_{6v} little group along Γ -A HSL. The electronic structure of SrAgAs in the absence of spin-orbit coupling (SOC) is shown Fig. 6.1(c). The red and blue symbols in the band structure represent the s- and (p_x, p_y) -like orbital character respectively. The topological non-triviality of SrAgAs is dictated by the presence of an inverted band ordering (between s and p_{xy} orbitals) at Γ point near the Fermi level (E_F) , as observed from Fig. 6.1(c). Further, inclusion of SOC splits the band degeneracy and open up a gap at Γ point as shown in Fig. 6.1(d). Under the double group representations in the presence of SOC, the conduction band minima (CBM) at Γ -point holds Γ_9^- (J_z = $\pm \frac{3}{2}$) irreducible representations (IRs). On the other hand, highest occupied valence band maxima (VBM) and second highest VBM posses $\Gamma_7^ (J_z = \pm \frac{1}{2})$ and Γ_7^+ $(J_z = \pm \frac{1}{2})$ IRs respectively. Note that, the Γ_7^+ bands are composed of As-(s)like orbitals. While Γ_7^- and Γ_9^- bands are majorly are contributed by As- (p_x, p_y) orbitals and a very small contribution of Ag-d states. The position of s-like Γ_7^+ and p-like Γ_7^- bands at Γ indicate the band inversion in the presence of SOC, hence the non-trivial band order of



Figure 6.1: (a) Crystal structure of SrAgAs with (b) Hexagonal Bulk Brillouin zone (BZ) and surface BZ. The high symmetry points are shown in BZ. Bulk band structure of SrAgAs (c) without SOC and (d) with SOC. The red (blue) symbols in (c) represents s (p_x, p_y) -like orbital contribution. Γ_i s in (d) indicate different irreducible representations of bands. (e) band structure in k_x - k_y plane surrounding the Dirac point (K_D (0, 0, 0.194 $\frac{\pi}{c}$)).

SrAgAs. Now, along Γ -A direction $\Gamma_7^{+,-}$ and Γ_9^- bands transformed into Γ_7 and Γ_9 IRs according to the linking rule of bands. The Γ_7 and Γ_9 are the representations of C_{6v} little group.

Furthermore, Γ_9 and Γ_7 bands near the Fermi level, have similar slope up to K_D along Γ -A direction. However, the Γ_7 band (which lies near the E_F) suddenly changes its slope and disperse towards the higher energy due to the band repulsion with another Γ_7 band which is originated from Γ_7^+ . Therefore, Γ_7 and Γ_9 bands cross each other at a large momenta $K_D(0, 0, \pm 0.194\frac{\pi}{c})$ and hence a Dirac node has been formed at K_D as shown in Fig. 6.1(d). Figure 6.1(e) shows the in-plane (k_x - k_y plane) band structure with a $k_z=0.194\frac{\pi}{c}$. Interestingly, the Dirac nodes in SrAgAs enjoy the double protection against external perturbations. As the material SrAgAs holds both inversion and time reversal symmetry, all the bands are doubly degenerate over the BZ. Besides, all bands along Γ -A direction are two dimensional IRs, which is ensured by double group representation of C_{6v} . Therefore, any perturbations which breaks the inversion



Figure 6.2: (a) Bulk band structure of TPSM phase in SrAg_{0.5}Cu_{0.5}As alloy. Inset in (a) shows the triply degenerate nodal point TP1(TP2) formed by crossings of $\Lambda_4(\Lambda_5)$ and Λ_6 IRs at around K_{TP}. (b,d) shows the three fold band degeneracy at K_{TP1} (0, 0, 0.180 $\frac{\pi}{c}$) and K_{TP2} (0, 0, 0.183 $\frac{\pi}{c}$) for TP1 and TP2 respectively. (d) Band structure of topological insulating SrAg_{0.75}Cu_{0.25}As. $\Delta_{3,4}$ are the band representations along Γ -A under C_S point group. Two doubly degenerate bands belong to same IRs ($\Delta_3 + \Delta_4$) hybridize at nodal point (K_{TP}) and open up a non-trivial band gap along Γ -A direction.

symmetry but do not interrupt C_{6v} site-symmetry, will not be able to break the Dirac nodes. The breaking of inversion symmetry only removes the band degeneracies and changes the in-plane velocity of the bands away from the C_{6v} -axis. Such a scenario has been realized in non-centrosymmetric $P6_{3}mc$ (# 186) space group materials [270]. We have discussed these story-line of breaking various symmetries and their consequences more explicitly using DFT calculation as well as model Hamiltonian consideration in the subsequent sections.

Next, we induce a triple point semi-metallic (TPSM) phase in $SrAg_{1-x}Cu_xAs$ via symmetry-allowed Copper (Cu) alloying. The parent compound SrAgAs possess two equivalent positions of Agatoms in the unit cell. We replace one of the Ag with a Cu (i.e 50% alloying) to realize TPSM state in SrAgAs. Such alloying breaks the center of inversion, three dihedral mirror planes (σ_d) and C₆ rotational symmetries which in turn deduces the D_{6h} point group symmetry to D_{3h} . The little group along the Γ -A path is now C_{3v} in $SrAg_{1-0.5}Cu_{0.5}As$ alloy. The C_{3v} point group allows two onedimensional (Λ_4 and Λ_5) and one two-dimensional (Λ_6) representations in the 2π spin rotational sub-space. The electronic structure of $SrAg_{0.5}Cu_{0.5}As$ alloy with SOC effect is shown in Fig. 6.2(a). As we go from parent SrAgAs to SrAg_{0.5}Cu_{0.5}As compound, the alloying transforms the Γ_7 bands to Λ_6 band and Γ_9 splits into Λ_4 and Λ_5 (Γ_9 $\rightarrow \Lambda_4 \oplus \Lambda_5$) under C_{3v} . The intersection of Λ_4 (Λ_5) and Λ_6 leads to form a pair of triply degenerate nodal points on k_z -axis as shown in Fig. 6.2(a) inset. The in-plane $(k_x - k_y \text{ plane})$ band structure around the triple points TP1 and TP2 are shown in Fig. 6.2(b) and 6.2(c)respectively, which further confirm the presence of 3-fold degeneracies as has been predicted via group symmetry analysis (inset of Fig. 6.2(a))

Next, we discuss the possible symmetry-breaking mechanism to decompose the four-fold Dirac nodes into two Weyl nodes. Further breaking of vertical mirror (σ_v) symmetry in SrAg_{0.5}Cu_{0.5}As alloy transforms the C_{3v} into C₃ point group. Since the IRs of C₃ point group are one dimensional, the band crossing of two different IRs is two fold degenerate and hence C₃ is an allowed symmetry environment to form a WSM phase. But unfortunately, it is not possible to get such a symmetry environment (C₃) via controlled doping engineering in our material SrAgAs. Another allowed symmetry group for Weyl phase is C_s which can be easily achieved under precise doping concentrations. For example, replacing one Ag by Cu atom in a 2×2×2 supercell ensures C_s group in SrAgAs. Yet another route to observe WSM state is to break TRS symmetry. In facts, from the experimental point of view, breaking of TRS is quite easy (compared to breaking point group symmetry) as it can be done by

Table 6.1: Parity eigenvalues of occupied bands at TRIM points for non-trivial $SrAg_{0.75}Cu_{0.25}As$.

A $(0,0,\pi)$	Γ (0,0,0)	$3M(\pi,0,0)$	3L $(\pi, 0, \pi)$	product
+	—	+	+	—

using an external magnetic field. We, therefore, introduce a Zeeman field along the z-direction in the low energy Dirac Hamiltonian which directly transforms the DSM state into WSM (explained in Fig. 6.5).

Further, breaking of three-fold rotational symmetry will allow to open up a gap along Γ -A line at the nodal point. 25% (x=0.25) Cu alloying in SrAgAs opens up a band gap throughout the BZ. It is important to mention here that breaking of C_3 rotation can convert the system into either gapped TI phase (for C_{2v} and C_{2h}) or WSM (C₂ & C_s) state. In our case, 25% Cu alloying restores the structural inversion symmetry with C_{2h} point group. In such symmetry environment, the alloy $SrAg_{0.75}Cu_{0.25}As$ ensures it's strong topological insulating phase. To observe the evolution of TI phase, we have taken a $2 \times 2 \times 2$ supercell where four out of 16 Ag atoms replaced by Cu atoms. For further study, we considered the energetically most favorable structure of $SrAg_{0.75}Cu_{0.25}As$ alloy. The electronic structure of $SrAg_{0.75}Cu_{0.25}As$ alloy is shown in Fig. 6.2(d) which indeed indicates an insulating phase. To further confirm the topological insulating behavior of SrAg_{0.75}Cu_{0.25}As, we compute the Z_2 index by counting the parity eigen values over the occupied bands in eight time-reversal invariant momenta (TRIM) points as given in Table 6.1. The negative products of all parity eigenvalues at eight TRIM points confirm the TI state in SrAg_{0.75}Cu_{0.25}As alloy with topological index $Z_2=1$.

6.2 Broken Symmetries of SrAg_{1-x}Cu_xAs Compounds

The parent compound SrAgAs (Fig. 6.3(a)) belongs to $P6_3/mmc$ (# 194). The symmetry elements of this compound are identity (E), two three-fold rotation about the c-axis (C_3) , two-fold rotation about the c-axis (C_2) , two six-fold rotation about the c-axis (C_6) , three two-fold rotation axis which goes through the midpoint of the hexagon edges (C'_2) , three two-fold rotation axis which goes through the midpoint of the hexagon corners (C''_2) , inversion (I), two six-fold improper rotation i.e, rotation about C_6 and then reflection across the perpendicular plane to C_6 -axis (S_6), reflection across hexagonal plane (σ_h) , two three-fold improper rotation (S₃), three vertical mirror across plane parallel to hexagon edges (σ_v) and three σ_d across plane containing two hexagonal corners. Among these symmetry elements E(x,y,z), $C_3(-y,x-y,z)$, I(-x,-y,-z) and $S_3(-x,-y,z+\frac{1}{2})$ are the generator of the group. All these symmetry elements are present in Fig. 6.3(a) and possess D_{6h} point group into it. Real space structural symmetry elements are isomorphic to its momentum space. So, D_6h is the point group at the Γ point of the Brillouin zone. Little group at Γ allows its C₆v sub-group along Γ -A direction. Double group representation of C_{6v} allows only two dimensional irreducible representations (IR) (Γ_7 , Γ_8 and Γ_9). So, any accidental band crossing along Γ -A direction will give a four fold Dirac node, which is exactly happen in SrAgAs case.

For 50% of Cu doping, we replace Ag2 by Cu1 in SrAgAs parent compound as shown in Fig. 6.3(b). Such a replacement of Ag by Cu atom breaks the inversion symmetries (as Ag1 and Ag2 were connected by inversion center in SrAgAs in Fig. 6.3(a)). The breaking of inversion symmetry simultaneously removes the three σ_d and six-fold rotation axis as shown in Fig. 6.3(b). Basically, the D_{6h} point group in the parent SrAgAs converted to relatively lower



Figure 6.3: Crystal structure of (a) parent SrAgAs and (b) 50% Cu doped $SrAg_{0.5}Cu_{0.5}As$ and (c) 25% Cu doped $SrAg_{0.75}Cu_{0.25}As$. At 25% Cu doping concentration, we replace four Ag atoms by four Cu atoms and the alloy $SrAg_{0.75}Cu_{0.25}As$ posses C_{2h} point group.

symmetric D_{3h} group in $SrAg_{0.5}Cu_{0.5}As$. D_{3h} has a C_{3v} sub-group along Γ -A direction. Double group representation of C_{3v} has two one-dimensional IRs (Λ_4 and Λ_5) and one two-dimensional IR (Λ_6). These allowed IRs convert one Dirac node into two triply degenerate nodal points as discussed in the main manuscript.

For 25% doping, we have considered all the possible dopant positions and the energetically most favorable structure (Fig. 6.3(c)) is considered for further studies. $SrAg_{0.75}Cu_{0.25}As$ structure further retains its inversion. However, it breaks its C₃ rotational symmetry, which transforms the material into a topological insulator. The summary of the broken symmetries and the corresponding topolog-

Phase	Dirac	Triple	${ m TI}$
	[broken TRS]		
to another		inversion	restored
structure	and inversion	and broken	inversion
from one	$(3 \sigma_v, 3 \sigma_h),$	$(3 \sigma_h \text{ broken}),$	broken,
symmetries	6 mirrors	$3 \sigma_v$ planes	$(3\sigma_v, 3\sigma_h)$
or broken	rotation (C_6) ,	rotation (C_3) ,	6 mirrors
Symmetries	6-fold	3-fold	C_3 broken,
	$(C_{6v} \text{ along } \Gamma - A)$	$(C_{3v} \text{ along } \Gamma - A)$	(C _s along Γ -A)
Point group	D_{6h} at Γ point	D_{3h} at Γ point	C_{2h} at Γ point
Compounds	SrAgAs	$SrAg_{0.5}Cu_{0.5}As$	$SrAg_{0.75}Cu_{0.25}As$

Table 6.2: Point group and symmetry elements for the parent and alloy compounds and corresponding topological phase

ical phases have been listed in Table 6.2.

6.3 Symmetry Broken Phases by Antimony Doping

As both the Ag and As have equivalent Wyckoff positions in lattice, it is expected to show similar symmetry breaking phases under various doping concentrations. Indeed our calculations support our predictions as shown in Fig. 6.4(a-c). Fig. 6.4(a) shows the band structure along Γ -A direction for 25% Sb doping at the As site. Under this doping concentration the compound SrAgAs_{0.75}Sb_{0.25} possesses topological insulating phase. For 50% doping (Fig. 6.4(b)), it holds triple point semi-metal phase similar to 50% of Cu doping at Ag site. Fig. 6.4(c) shows the Dirac state when all the As atoms are replaced with Sb atoms.



Figure 6.4: Band structure for various doping concentration of Sb atoms at As-sites. (a) 25%, (b) 50% and (c)100% replacement of As atoms.

6.4 k.p Hamiltonian

To get a better understanding of the broken symmetry driven various topological phases, we demonstrated a low energy k.p model Hamiltonian around the Γ point. The low energy k.p Hamiltonian can be derived using method of invariants similar to those used in Na₃Bi [265] and Cd₃As₂ [266]. Since our *ab-initio* calculations show that the low energy states are mostly contributed by Sr-s, Ag-s and As-p orbitals, we choose $|S_{\frac{1}{2}}^+, \frac{1}{2}\rangle$, $|P_{\frac{3}{2}}^-, \frac{3}{2}\rangle$, $|S_{\frac{1}{2}}^+, -\frac{1}{2}\rangle$, $|P_{\frac{3}{2}}^-, -\frac{3}{2}\rangle$ as basis sets considering the above atomic like orbitals under inversion, time reversal and D_{6h} symmetry. The superscript \pm in the basis set represents the parity of the states. The 4×4 minimal Hamiltonian around Γ using these basis for D_{6h} point group is given by,

$$H(\mathbf{k}) = \epsilon_{\mathbf{0}}(\mathbf{k}) + \begin{pmatrix} M(\mathbf{k}) & Ak_{+} & Dk_{-} & -B^{*}(\mathbf{k}) \\ Ak_{-} & -M(\mathbf{k}) & B^{*}(\mathbf{k}) & 0 \\ Dk_{+} & B(\mathbf{k}) & M(\mathbf{k}) & Ak_{-} \\ -B(\mathbf{k}) & 0 & Ak_{+} & -M(\mathbf{k}) \end{pmatrix}$$

where $\epsilon_0(\mathbf{k}) = C_0 + C_1 k_z^2 + C_2 (k_x^2 + k_y^2), \quad k_{\pm} = k_x \pm i k_y, \quad M(\mathbf{k}) = -M_0 + M_1 k_z^2 + M_2 (k_x^2 + k_y^2)$ with $M_0, M_1, M_2 > 0$ to confirm the band inversion. Finite value of parameter D introduces broken inversion symmetry. Therefore, D=0 for centro-symmetric Dirac semimetal SrAgAs. The eigenvalues of the above Hamiltonian are,

$$E(\mathbf{k}) = \epsilon_0(\mathbf{k}) \pm \sqrt{M(\mathbf{k})^2 + A^2 k_+ k_-} + |B(\mathbf{k})|^2$$

This eigen value equation gives two gapless solution at $\mathbf{k}_d =$ $(0, 0, \pm \sqrt{M_0/M_1})$, which are nothing but the two Dirac nodes on k_z axis. Under three fold rotational symmetry, the off diagonal term $B(\mathbf{k})$ takes only the higher order form of $B_3k_zk_+^2$. So, in the vicinity of the Dirac nodes, the higher order terms vanish, i.e., $B(\mathbf{k}) =$ 0. We have fitted the energy spectrum of the above model Hamiltonian with *ab-initio* band structure of SrAgAs in the vicinity of Dirac node (Fig. 6.5(a)). The fitting parameters are $C_0 = -0.047$ eV, C_1 =0.942 eV Å², C_2 =179.209 eV Å², M_0 =0.134 eV, M_1 =3.534 eV Å², M_2 =228.122 eV Å², A=5.790 eV Å. As mentioned earlier, the breaking of inversion symmetry still keeps the Dirac node intact on k_z axis because all the bands along the Γ -A have two dimensional IRs of C_{6v} double group. The breaking of inversion center only removes the band degeneracies and changes the effective mass of bands away from the C_{6v} axis. Figure 6.5(b) shows the Dirac node for the inversion breaking term D = 1.0 eV Å. For the case of 25% alloying $(SrAg_{0.75}Cu_{0.25}As)$, broken C₃ rotational symmetry further introduces an additional linear leading order term of $B(\mathbf{k})$ $= B_1 k_z$ into the above Hamiltonian. Now restoring the inversion symmetry (i.e, D = 0) in the Hamiltonian introduces a topological insulating state by opening up a gap at Dirac nodes as shown in Fig. 6.5(c).

Now, concentrating at the neighborhood of the Dirac nodes, we can neglect the higher oder terms (i.e $B(\mathbf{k}) = 0$) which transform the Hamiltonian into block-diagonal form of the 4×4 Dirac Hamiltonian. The block-diagonal form allows the Dirac Hamiltonian to de-couple it into two 2×2 Weyl Hamiltonian. Further addition of magnetic field breaks the degeneracy of the Weyl nodes and separate them in momentum space. Application of an external magnetic



Figure 6.5: Low-energy band dispersion near the nodal points using *first principles* based fitting parameters from k.p model Hamiltonian. (a) Dirac nodes (b) DSM state via breaking of inversion symmetry keeping C_{6v} intact (c) TI states by breaking C_3 rotation symmetry and (d) WSM state via breaking of TRS.

field along z-direction changes the Dirac Hamiltonian as:

$$H_{mag}(\mathbf{k}) = H(\mathbf{k}) + h\sigma_z\tau_z$$

The external magnetic field (h = 0.008 eV) decouples the Dirac nodes into two Weyl nodes and they appear at $\mathbf{k}_{WSM} =$ $(0,0, \pm \sqrt{M_0 \pm h/M_1})$ points on \mathbf{k}_z -axis as shown in Fig. 6.5(d). Schematic diagram of Weyl nodes with their chirality is shown in Fig. 6.8(c).

To calculate the chirality of the Weyl nodes, we write the Hamiltonian under an external magnetic field along Z-direction can be written as;

$$H(\mathbf{k}) = \epsilon_{\mathbf{0}}(\mathbf{k}) + \begin{pmatrix} M(\mathbf{k}) & Ak_{+} & 0 & -B^{*}(\mathbf{k}) \\ Ak_{-} & -M(\mathbf{k}) & B^{*}(\mathbf{k}) & 0 \\ 0 & B(\mathbf{k}) & M(\mathbf{k}) & Ak_{-} \\ -B(\mathbf{k}) & 0 & Ak_{+} & -M(\mathbf{k}) \end{pmatrix} + \begin{pmatrix} h & 0 & 0 & h \\ 0 & -h & 0 & 0 \\ 0 & 0 & -h & 0 \\ 0 & 0 & 0 & h \end{pmatrix}$$

In the vicinity of the nodal points, the higher order terms of B(k) become zero, i.e, B(k) = 0. Hence, the Hamiltonian takes the block diagonal form as;

$$H(\mathbf{k}) = \epsilon_{\mathbf{0}}(\mathbf{k}) + \begin{pmatrix} M(\mathbf{k}) & Ak_{+} & 0 & 0 \\ Ak_{-} & -M(\mathbf{k}) & 0 & 0 \\ 0 & 0 & M(\mathbf{k}) & Ak_{-} \\ 0 & 0 & Ak_{+} & -M(\mathbf{k}) \end{pmatrix} + \begin{pmatrix} h & 0 & 0 & h \\ 0 & -h & 0 & 0 \\ 0 & 0 & -h & 0 \\ 0 & 0 & 0 & h \end{pmatrix}$$

The upper and lower blocks of above H_{mag} form the Weyl nodes on the k_z axis. Now, we consider the lower block of H_{mag} for the calculation of Chern number of the corresponding Weyl node.

$$H_{mag}^{k_{w1}^+} = \epsilon_0(\mathbf{k}) + \begin{pmatrix} M(\mathbf{k}) & Ak_- \\ Ak_+ & -M(\mathbf{k}) \end{pmatrix} + \begin{pmatrix} -h & 0 \\ 0 & h \end{pmatrix}$$

$$\implies H_{mag}^{k_{w1}^{+}} = \epsilon_0(\mathbf{k}) + \mathbf{A}\sigma_{\mathbf{x}}\mathbf{k}_{\mathbf{x}} + \mathbf{A}\sigma_{\mathbf{y}}\mathbf{k}_{\mathbf{y}} + \mathbf{A}\sigma_{\mathbf{z}}\mathbf{k}_{\mathbf{z}}$$

$$\implies H_{mag}^{k_{w1}} = f_0 + f_1 k_x + f_2 k_y + f_3 k_z$$

Where, $f_0 = \epsilon_0(\mathbf{k})$, $f_1 = Ak_x$, $f_2 = Ak_y$, $f_3 = (M(\mathbf{k})+h)$ Now, we can do a Taylor expansion of the Hamiltonian around the nodal point, *i.e* $\mathbf{k} \rightarrow k_{w1}^+ + \delta \mathbf{k}$.

Neglecting the higher order terms, we can rewrite,

$$\begin{aligned} f_{0}(k_{w1}^{+} + \delta k) &\approx f_{0}(k_{w1}^{+}) + f_{0}' \cdot \delta k|_{k_{w1}^{+}} \\ f_{1}(k_{w1}^{+} + \delta k) &\approx f_{1}(k_{w1}^{+}) + f_{1}' \cdot \delta k|_{k_{w1}^{+}} \\ f_{2}(k_{w1}^{+} + \delta k) &\approx f_{2}(k_{w1}^{+}) + f_{2}' \cdot \delta k|_{k_{w1}^{+}} \\ f_{3}(k_{w1}^{+} + \delta k) &\approx f_{3}(k_{w1}^{+}) + f_{3}' \cdot \delta k|_{k_{w1}^{+}} \\ \\ So, \\ H_{mag}^{k_{w1}^{+}} &= f_{0}(k_{w1}^{+}) + f_{0}'(k_{w1}^{+}) \cdot \delta(k) + \sum f_{0}(k_{w1}^{+}) \cdot \sigma_{i} + \sum \sigma_{i} f_{i}' \cdot \delta k|_{k_{w1}^{+}} \end{aligned}$$

Now, $\sum f_0(k_{w1}^+) \cdot \sigma_i = 0$, as the value of f_1 , f_2 and f_3 turn out to be zero from the *first principle* parameters at k_{w1}^+ point. This is the condition to form a two fold degenerate point in three dimensional space.

Now, we can again rewrite the (2x2) Weyl Hamiltonian as;

 $\mathbf{H}_{Weyl}^{k_{w1}^{+}} = \mathbf{f}_{0}(\mathbf{k}_{w1}^{+}) + v_{0} \cdot \delta \mathbf{k} + \sum v_{i} \cdot \delta k|_{k_{w1}^{+}}$

Where, $v_i = \nabla_k f_i|_{k_{w_1}^+}$ and the Chirality can be defined as; $C = \frac{v_1 \cdot (v_2 \times v_3)}{\det[v_1 \cdot (v_2 \times v_3)]}$

Therefore, from the expressions of f_1 , f_2 and f_3 , we get v_1 , v_2 abd v_3 as follows,

$$v_1 = A\hat{\mathbf{i}} = 5.79\hat{\mathbf{i}} \ v_2 = A\hat{\mathbf{j}} = 5.79\hat{\mathbf{j}}$$

 $v_1 = 2M_1 \sqrt{\frac{M_0 + h}{M_1}} \ \hat{\mathbf{k}} = 1.41\hat{\mathbf{k}}$

So, the Chirality (C) of this Weyl node k_{w1}^+ is +1.

Similarly, for the other Weyl node, we consider the upper block of the Hamiltonian H_{mag} and a similar calculation gives; $f_1=Ak_x$, $f_2=-Ak_y$, and $f_3=M(k)$ -h. Hence the Chirality (C) is -1 at this Weyl node. Similarly, the other two nodes along negative k_z direction have Chirality +1,-1 respectively. So, these nodes behave like a source of sink of Berry curvature in momentum space.

6.5 Protection of The Dirac Nodes Against Inversion Breaking Perturbation

We have discussed in the main manuscript about the double protection of Dirac nodes of SrAgAs compound using point group theory and model Hamiltonian. We have revealed that the Dirac nodes are stable against inversion breaking perturbation. Further to this, we



Figure 6.6: (a) Crystal structure with broken inversion symmetry. (b) Band structure along Γ -A direction. All the bands are still doubly degenerate due to little group of Γ -A direction. (c,d) Inplane and three-dimensional view of Dirac node respectively.

have used first-principle calculations to justify our claim. In SrAgAs having point group D_{6h} , the Dirac nodes along Γ -A direction are protected by both inversion-time reversal symmetry and double group representation of C_{6v} . Now, we break the inversion symmetry keeping $C_6 v$ intact along Γ -A direction through structural deformation. As we have discussed that the SrAgAs crystal structure can be viewed as staffed graphene layers; the Sr^{2+} cations are staffed between $[Ag^{1+}As^{3-}]^{2-}$ honeycomb network. To break the inversion, we distort the $[Ag^{1+}As^{3-}]^{2-}$ planer honeycomb network into buckled network as shown in Fig. 6.6(a). Such a deformation transforms the point group symmetry of the structure from D6h to C_{6v} with space group no. 186. Now, C_{6v} have three IRs in its double group representation and all of them are two-dimensional. The double group of C_{6v} now provides the protection to the Dirac nodes without inversion. Fig. 6.6(b) shows the band structure along Γ -A for the distorted crystal structure. In the absence of inversion, the Dirac nodes are still stable and the band degeneracy lifted away from C_6 axis as shown in Fig. 6.6(c,d).

6.6 Band Structure Using HSE06 Functional

We have also checked the band topology of SrAgAs compound using HSE06 exchange correlation functional. Within HSE06, it shows a band gap of 0.2 eV. However, if we apply a small pressure (+3%) of the ambient lattice constant), SrAgAs transforms to a Dirac semimetal with a similar Dirac node as in the case of PBE+SOC results at ambient condition. The rest of the physics, based on the broken symmetry induced topological phases in this compound follows exactly as proposed. As such, the key message of the paper remains unaltered if we consider SrAgAs under small strain. We have done the calculations under both hydrostatic and biaxial strain for SrAgAs which are shown in Fig. 6.7(a,b). Our primary motivation in this paper is to explain the novel physics and the innovative ideas required to achieve all the topological phases known so-far (Dirac semi-metal, triple point semi-metal, Weyl semi-metal and the topological insulator) in a single material. Inherent existence of such a plethora of rich topological properties in a single material is extremely rare.

Nonetheless, SrAgAs is just a test system in this hexagonal family (P6₃/mmc) where such symmetry breaking is possible which gives rise to different topological phases. There are various other systems such as SrAgBi, BaAgBi, SrCuBi in this class, where Dirac semi-metal phase is achievable even at ambient lattice constants within HSE06+SOC framework. Fig. 6.7(c-e) shows the band structure for these three systems. As such, it is not really the system which is the major focus, but rather the physics associated with the symmetry breaking mechanism giving rise to various topological phases.


Figure 6.7: (a)HSE06 band structure of SrAgAs under hydrostatic pressure (+3% expansion of ambient lattice constant), (b) +3% Biaxial strain in the x-y plane, (c) SrAgBi (d) BaAgBi and (e) SrCuBi

6.7 Surface States

Now, we address the surface properties of the compounds on their bulk projected surfaces. Fig. 6.8(a,b) shows the momentum resolved surface density of states and the Fermi arc of SrAgAs on the (100) surface. Two Fermi arcs originate and terminate into two Dirac nodes on the k_z -axis forming a continuous close arc loop on $\overline{\Gamma} \cdot \overline{X} \cdot \overline{U} \cdot \overline{Z}$ plane. Fermi arcs of SrAgAs are somewhat similar to "double Fermi arcs" (two super-imposed Weyl arcs arising out of two Weyl nodes coming together and forming a Dirac node in the presence of particular rotational symmetry) of Na₃Bi and Cd₃As₂. Under specific symmetry-preserving perturbations, a Dirac node of SrAgAs splits into two triple point nodes in SrAg_{0.5}Cu_{0.5}As. Therefore, the corresponding two surface states shrink into two isolated triple point nodes as shown Fig. 6.8(d). We have also simulated the TI



Figure 6.8: Projected (100) surface density of states and corresponding Fermi arcs at Fermi level for (a,b) DSM SrAgAs, (d,e) TPSM SrAg_{0.5}Cu_{0.5}As. (c) Schematic position of Weyl nodes with their chirality. (f) TI surface state projected on (001) surface. Location of Dirac cone is indicated within a box.

surface states on (001) surface, as shown in Fig. 6.8(f). In this case, a non-trivial band gap is opened up using a strain along crystallographic *a-axis*, mimicking the corresponding symmetry breaking. It is important to note that, in the (001) surface BZ, the Γ -A high symmetry line falls on $\overline{\Gamma}$.

In general, robustness of the Fermi arcs come from either symmetry or topology or both. Dirac Fermi arcs are the "doubly degenerate Fermi arcs" and its formation mechanism can be understood from the super-imposition of two Weyl nodes of opposite chirality in momentum space. In that sense, four fold Dirac nodes give rise to the "doubly degenerate Fermi arcs". However, these Fermi arcs are not topologically protected because the Dirac nodes do not have any topological invariant protection [267–269]. Similar to DSM, TPSM Fermi arcs whose protection comes from the crystalline symmetry, are also not topologically protected. In contrast, Weyl nodes always have a non-trivial chern number associated with them and do not need any crystalline symmetry to appear. As such, WSM arcs are more robust than DSM arcs. Considering Dirac state as the parent state of Weyl and topological insulator, one can deform the close Dirac Fermi arc to a Weyl type open Fermi arcs which have nontrivial chern number. Similarly, it can also be converted to a gapped topological phase which owns a Z_2 invariant surface state. Another example is the nodal line semi-metal state, where the nodal loop is protected by crystalline symmetry (in general, mirror reflection) and they have a non-trivial berry phase associated with them. So, a system having a topological invariance is more robust against the external perturbations where as symmetry protected system requires extra care to get its surface signatures.

Dirac Fermi arcs are the "double degenerate Fermi arcs" as its formation mechanism can be understand as the super-imposition of two Weyl nodes of opposite chirality in momentum space. In that sense, four fold Dirac type band degeneracies are the origin of "double degenerate Fermi arcs". However, these Dirac Fermi arcs are not topologically protected as the Dirac nodes do not have any topological invariant protection. Considering Dirac state as the parent state of Weyl and topological insulator, we can deform the close Dirac Fermi arc to a Weyl type open Fermi arcs which have non-trivial chern number. Similarly it can be converted to gapped topological phase which have a \mathbb{Z}_2 invariant surface state. In triple point fermion state (similar to the Dirac semimetal phase whose protection comes from the crystalline symmetry), the Fermi arcs are not topologically protected. In Fig. 6.9, we show the evolution of Fermi arcs of Dirac and triple point phases at different energy range.

The surface calculation of Topological insulating (TI) phase have been performed using Greens function method. Fig. 6.10(a) shows the (001) surface Brillouin zone. It is important to note that, the Γ -A high symmetry line in bulk BZ falls on point of (001) surface BZ. We mimic the TI phase by a very small strain induced symmetry breaking perturbation in the unit cell (just taking a \neq b



Figure 6.9: Fermi arcs of Dirac phase compound SrAgAs (a) at Dirac node (b) at EF+0.5 eV energy range. (c-e) Fermi arcs for triple point phase compound $SrAg_{0.5}Cu_{0.5}As$ (c) at TP1 (d) at TP2 and (e) at EF+0.5 eV energy range.

along crystallographic axis). The bulk band structure is shown in Fig. 6.10(b). As expected, a non trivial band gap opens up at the Dirac point along the Γ -A direction. The (001) TI surface band is shown in Fig. 6.10(c), where the surface bands are clearly visible which are buried within the small bulk band gap (a little below the Fermi level).

6.8 Direction Towards Experimental Realization

We start with the SrAgAs as parent compound. Then, we doped Cu of various concentrations in the Ag sites. So, the doping mechanism can be viewed as transformation from SrAgAs to SrCuAs through some intermediate compounds, such as $SrAg_{0.75}Cu_{0.25}As$ (25% alloying), $SrAg_{0.5}Cu_{0.5}As$ (50% alloying) and $SrAg_{0.25}Cu_{0.75}As$ (75% alloying). Here, we mention that both SrAgAs and SrCuAshave been experimentally synthesized [272] and the experimental lattice constants match well with our first principle calculated val-



Figure 6.10: Bulk and (001) surface Brillouin zone with high symmetry points. (b) Bulk band structure of SrAgAs along Γ -A for a \neq b. (c) Topological surface states in (001) plane. The position of Dirac cone is marked by dotted box in (c).

ues. Some of the important aspects for doping engineering are isovalent dopant, charge neutralization in the structure and size effect. The first two factors can be taken care by choosing dopant atoms from same group of the periodic table. As such, we choose Cu as a dopant element for Ag. The atomic radius of Cu and Ag are 1.28 Åand 1.44 Årespectively. Although Cu and Ag have a difference in atomic radius of 0.16 Å, the intermediate $Ag_{0.75}Cu_{0.25}As$, $SrAg_{0.5}Cu_{0.5}As$, and $SrAg_{0.25}Cu_{0.75}As$ stoichiometries are expected to be stable as both SrAgAs and SrCuAs have been synthesized. Indeed, our phonon calculations support the formation of such intermediate structure (Fig. 6.11). Further, we have calculated the formation energy of the intermediate compounds $SrAg_{0.75}Cu_{0.25}As$ (25% Cu alloying), $SrAg_{0.5}Cu_{0.5}As$ (50% Cu alloying) to check the chemical stability of the compounds. Formation energies are calculated using the formula:

$$\Delta \mathbf{E}_f = \mathbf{E}_{comp} - \sum_{i=1}^n \mathbf{x}_i \mathbf{E}_i,$$

where E_{comp} is the total energy of the compound and E_i represents the energy of the constituent elements in their equilibrium phase, all at their equilibrium lattice constants. x_i is the proportion of i-th element in the compound. Strontium (Sr), Silver (Ag), and Copper (Cu) are simulated in their elemental equilib-



Figure 6.11: Phonon dispersions for various alloys.

rium phase with space group of Fm3m, whereas Arsenic (As) is simulated in it's equilibrium phase with space group R3m. The formation energy of SrAg_{0.5}Cu_{0.5}As and SrAg_{0.75}Cu_{0.25}As are shown in Table 6.3. Such a negative ΔE , supports the chemical stability and hence the experimental possibilities of the intermediate compounds (SrAg_{0.75}Cu_{0.25}As and SrAg_{0.5}Cu_{0.5}As).

Table 6.3: Formation energies (in meV/Atom) for alloys

Compond	Formation Energy (ΔE)
SrCuAs	-0.755
$SrAg_{0.5}Cu_{0.5}As$	-0.784
SrAg _{0.75} Cu _{0.25} As	-0.799
SrAgAs	-0.810

Please note that, SrAgAs is a ternary compound which shares the same space group with prototype ZrBeSi family. All the members of this family crystallize in graphite type honeycomb structure (space group no. 194). The combination of alternate main group based element and transition metal forms the honeycomb network in between alkaline and alkali cation layers. In case of SrAgAs, the Sr²⁺ cations are staffed in between $[Ag^{1+}As^{3-}]^{2-}$ honeycomb network. In general, the honeycomb network allows sp₂ hybridization which is further distorted due to the presence of alkali/alkaline ions. Due to the mean sp₂ type hybridization in these graphite like materials, most of the compounds are either low gapped semiconductor or semi-metal. Considering that there are a substantial number of metallic compounds in this large family (as large as Heusler family), we simply conclude that this material class can be ideal for the experimentalists for topological semi-metal studies.

Now, we have investigated the possibilities of dopant positions in the topological insulating (TI) phase of $SrAg_{0.75}Cu_{0.25}As$ (25% Cu alloying). For 25% Cu alloying, we replace four Ag atoms by Cu in the 2×2×2 supercell of SrAgAs. Furthermore, for $SrAg_{0.75}Cu_{0.25}As$, we checked all possible configurations (nine independent possible configurations) of Cu dopant sites. Out of nine simulated configurations for 25% Cu-doping, only four are energetically non-degenerate. As such, we have given the details of only these 4 inequivalent configurations in Table 6.4. Out of the four configurations, the structure with the lowest energy configuration (Config.-4) is chosen to present further results in the manuscript. Moreover, all the other configurations also allow topologically non-trivial gapped manifold which is also ensured by it's structural point group symmetry as listed in Table 6.4.

Structural	Ground state	Point group	Topological
configurations	energy (eV)	symmetry	phase
Config1	-186.394	C_1	Gapped (TI)
Config2	-186.471	C_i	Gapped (TI)
Config3	-186.133	C_s	Gapped (TI)
Config4	-186.708	C_{2h}	Gapped (TI)
(most stable)			

Table 6.4: Formation energies (in meV/Atom) for alloys

6.9 Conclusion

We predict a single material SrAgAs which can host topologically distinct phases (DSM, TPSM, WSM and TI). Using the appropriate symmetry analysis and *first-principles* calculations, we show that all these distinct topological phases can be realized in SrAgAs via proper alloy engineering. We systematically explain the multi dimensional band degeneracies and phase transition from one to another, within the concept of group theoretical analysis. Further, the non-trivial bulk band signatures of DSM and TPSM have been projected onto the rectangular (100) surface. Our surface analysis indeed show the existence of topological surface states and Fermi arc, originating from the nodal points of DSM and TPSM. We believe that the stoichiometric SrAgAs can serve as a host for all distinct topological phases and hence pave a path for experimentalists to verify the outcomes with appropriate probe. Such discovery of new promising topological candidates using alloy engineering is extremely useful to guide the further design of topological materials.

Intertwined Rashba and Topological Quantum Phenomena

Simultaneous occurrence of two apparently incompatible quantum phenomena in a single material often provide the platform to understand the fundamental inter correlation between the two seemingly different processes in physics. The materials which have such combined quantum properties are called composite quantum compounds(CQCs) [273]. So far, composite phase between superconductivity and topology have been explored in the field of topological superconductivity [274, 275]. Similarly, topological axion insulator is yet another CQ phase between topology and magnetism, which is currently one of the emerging field of interest [276, 277].

Topological non-trivial band ordering and Rashba spin splitting are two apparently distinct quantum phenomena, that can be intertwined through the common requirement of crystal symmetries and spin-orbit coupling (SOC). So far, topological insulator (TI) and ferroelectricity have been coupled in LiGaGe-type polar compounds for which strong SOC and broken inversion symmetry (\mathcal{IS}) are shown to be the two essential prerequisites [278]. These two requirements also pave the path to realize another CQC between nontrivial topology (in the presence of strong SOC) and giant Rashba spin splitting (which requires both inversion breaking and strong SOC). Though the presence of reasonably large Rashba splitting and TI phase have been found in polar semiconductor BiTeI under external pressure, it needs fine tuning of electronic structure [279–281]. Further, a general criterion for the realization of such rich composite phase is still under active search. Here, we report an robust pathway to achieve such CQ phase between Rashba spin physics and topological non-triviality. In particular, we disclose a material platform that can posses non-trivial Weyl semimetal (WSM) and TI phase with a record high Rashba coefficient (α).

Relativistic electrons in solids provide an effective way to control spin degrees of freedom (DOF). For example, in TI, Dirac helical spin can be tuned through proper topological band ordering. Rashba spin splitting is another interesting phenomenon to control the spin DOF using the intrinsic SOC of a crystal with \mathcal{IS} breaking. As such, simultaneous presence of strong SOC and absence of \mathcal{IS} in a crystal are the two essential prerequisite to control both topological and Rashba spin physics. But, the topological gap of TI and strength of Rashba splitting have to be large enough to realize the combined phenomenon in realistic materials. Such coexistent holy combination is extremely rare in real crystals and often requires high precision tuning.

We report a record high Rashba splitting and giant α value in a polar compound $\text{KSnSb}_{1-x}\text{Bi}_x$ which simultaneously possess WSM or TI phase depending on the x value. Using a combined *ab-initio* calculation and group theoretical analysis, we explained the origin of such giant Rashba splitting. We also provide a general guidelines and necessary precautions to be taken to achieve such a composite phase.



Figure 7.1: (a) Crystal structure of KSnSb and KSnBi. (b) Bulk and surface Brillouin zones. Orbital projected PBE+SOC bulk band structure of (c) KSnSb and (d) KSnBi. HSE06+SOC band structures of (e) KSnSb and (f) KSnBi along M- Γ -K direction. α is the value of Rashba coefficient in eVÅ unit. Γ_i 's indicate the band character.

7.1 Bulk Topology

The polar compound KSnSb (KSnBi) belongs to space group P6₃mc which primarily consist of a sp_3 type buckled honeycomb layer with $[SnSb]^{-2}$ ($[SnBi]^{-2}$) charge configuration. $[K]^{+2}$ serve as stuffing layers and generate the net polarization along z-axis as shown in Fig. 7.1(a). The optimized lattice parameters for KSnSb (KSnBi) are a = 4.45 Å, c = 13.28 Å (a = 4.56 Å, c = 13.34 Å) which are in close agreement with experiments [286]. The dynamical stability of both these compounds are also confirmed via the absence of imaginary phonon frequencies [287]. The oppositely charged alternate layers in the crystal structure create a local potential imbalance. This, in turn, results in momentum dependent large Rashba type spin splitting in M- Γ -K plane of the Brillouin zone (BZ) (see Fig. 7.1(b) in both the compounds. Figure 7.1(c,d) shows the band structure of KSnSb and KSnBi with SOC using the PBE functional. The value of α in valence band (VB) for KSnSb (KSnBi) is 3.65 (1.31) eVÅ. This goes against the natural expectation; as Bi has much larger SOC than Sb and hence expected to have larger α value in KSnBi. We will resume and explain the origin of such outcome in the subsequent sections, and also provide a general guidance to achieve high Rashba splitting using symmetry adopted analysis.

7.2 Topological States



Figure 7.2: Evolution of wannier charge center (WCC) of (a,b) KSnSb and (c,d) KSnBi on $k_z=0$ and $k_z=\pi$ plane respectively.

In Fig. 7.1(c,d), the nature of bands at Γ point are labeled according to the irreducible representations (IRs) of C_{6v} point group symmetry. The conduction band minima (CBM) for both the compounds are dominated by *s* like Γ_8 character. The representations of first and second valence band maxima (VBM) of KSnSb are *s*like Γ_8 and *p*-like Γ_9 respectively. The gap between the two maxima (Γ_8 and Γ_9) is the band inversion strength (BIS), denoted by $\pm \Delta$. For KSnSb, the BIS is +ve and hence it is a trivial insulator, while KSnBi is a TI (with $-\Delta$), see Fig. 7.1(d). To ensure the correctness of band ordering, we have also simulated the band structure of the two compounds using HSE06 functional along M- Γ -K direction, see Fig. 7.1(e,f). Apart from small rearrangements, the band ordering



Figure 7.3: (001) projected surface states (SSs) of (a) KSnSb and (b) KSnBi. Inset in (b) shows the topological Dirac Fermi arc (FA) with helical spin texture for KSnBi.

in the two compounds remain the same as that of PBE+SOC prediction. Hence, here after, we have considered only PBE functional for further calculations. We have computed evolution of Wannier charge center (WCC) in the half BZ to calculate the \mathbb{Z}_2 index for both KSnSb and KSnBi. Figure 7.2 shows the evolution WCC along k_x axis in $k_z=0$ and $k_z=\pi$ plane for both the compounds. It is clear from the Fig. 7.2(a,b) that KSnSb is a trivial insulator as the WCC does not encounter any transition over the BZ. However, KSnBi is a topological insulator and corresponding \mathbb{Z}_2 index is 1, because the WCC cut any reference line odd number of times in the BZ, as shown in Fig. 7.2(c,d). The spectral flow of Wannier charge centers on $k_z = 0$ plane reconfirms the topological band inversion at the Γ point for KSnBi, whereas KSnSb has trivial \mathbb{Z}_2 index. Non-trivial nature of KSnBi is further confirmed by the presence of Dirac SSs with helical spin texture, as shown in Fig. 7.3(b). KSnSb, however, does not show such topological SSs (Fig. 7.3(a)) as it is a trivial insulator.

7.3 Rashba Physics

We shall now discuss the nature of band degeneracy and Rashba spin splitting from the context of structural symmetry and the presence of polar axis along z-direction. The point group symmetry at Γ point and along Γ -A direction is C_{6v} . So, the simultaneous presence of $C_6, C_2, 3 \sigma_v$ and $3 \sigma_d$ enforce all the states to be at least doubly degenerate along Γ -A. States at all other points, except eight time-reversal invariant momentum (TRIM) points in the BZ, are singly degenerate. The polar z-axis ensure maximum band splitting in the plane which is perpendicular to the polar axis. The value of momentum offset (Δk) and energy offset (ΔE) for KSnSb are 0.078 $Å^{-1}$ and 142 meV along Γ -K direction, while those for KSnBi are 74 meV and 0.110 \mathring{A}^{-1} respectively. Now, let us resurrect the discussion about getting an unexpectedly large value of α in KSnSb compared to KSnBi, despite having a larger SOC strength in the later. To elucidate this, we write a general k.p Hamiltonian using perturbation theory as (around Γ point);

$$\begin{split} H(\mathbf{k}) &= H(0) + \frac{\hbar^2 k^2}{2m_0} + \frac{\hbar}{m_0} \mathbf{k} \cdot \mathbf{p} + \frac{\hbar}{4m_0^2 c^2} [\nabla \mathbf{V} \times \mathbf{p}] \cdot \sigma + \\ & \frac{\hbar^2}{4m_0^2 c^2} [\nabla \mathbf{V} \times \mathbf{k}] \cdot \sigma, \end{split}$$

where \mathbf{V} , \mathbf{p} and σ represent the crystal potential, momentum operator and Pauli matrix respectively. The 4th and 5th terms in the Hamiltonian are SOC terms which have been added as a perturbation that operate on the Bloch periodic function. The 4th \mathbf{k} independent term represents the atomic SOC, whereas the last \mathbf{k} -dependent term is analogous to the motion of wave packet. Given the fact that the velocity of wave packet is much smaller than the velocity of electrons in atomic orbital, we can neglect the last term. The coupling between 3rd and 4th terms provide the second-order energy correction [282] as;

$$\Delta E_n^{(2)} \propto \sum_{m \neq n} \frac{\langle u_n | (\frac{\hbar}{4m_0^2 c^2} [\nabla \mathbf{V} \times \mathbf{p}] \cdot \sigma) | u_m \rangle \langle u_m | \mathbf{k} \cdot \mathbf{p} | u_n \rangle + c.c}{E_n - E_m}.$$

This energy correction term clearly indicates that the spin splitting does not only depend on the strength of SOC but also on two other very important factors, (i) energy difference $(E_n - E_m)$ between two bands and (ii) the character of the Bloch states corresponding to two bands i.e. spin splitting is possible only if the term $\langle u_n | \frac{\hbar}{4m_0^2 c^2} [\nabla \mathbf{V} \times \mathbf{p}] \cdot \sigma | u_m \rangle$ is symmetrically allowed. As such, the compounds having large SOC strength will produce giant spin splitting in two closely spaced bands only if they have symmetrically same characters. Now, coming back to the crystal symmetry of KSnSb (KSnBi), we can readily construct the Rashba type Hamiltonian imposing the symmetry invariance on the **k.p** Hamiltonian. Around Γ point, the representation of C_n (n=2, 3 & 6), σ_v and σ_d have $e^{-i\sigma_z\pi/n}$, $i\sigma_x$ and $i\sigma_y$ symmetry respectively, where $\sigma_{x,y,z}$ are the Pauli matrices for spin DOF. Using the time reversal operator $(i\sigma_{\nu}K)$ for spin-1/2 particle, one can find the linear order Rashba Hamiltonian as [282];

$$H_R^{C_{6v}} = \alpha (k_x \sigma_y - k_y \sigma_x) \tag{7.1}$$

Now, if we closely look at the band structure of KSnSb and KSnBi (Fig. 7.1), the CBM and VBM of the former has the same character (Γ_8) whereas the later has Γ_8 character for CBM and Γ_9 for VBM. As such, the term $\langle u_n | \frac{\hbar}{4m_0^2c^2} [\nabla \mathbf{V} \times \mathbf{p}] \cdot \sigma | u_m \rangle$ is symmetrically allowed for KSnSb at Γ point , but not for KSnBi. Therefore, even though KSnBi has larger SOC strength, KSnSb provides larger Rashba spin splitting because of the dominance of symmetry related term, as discussed above.



Figure 7.4: Bulk band structures of (a-c) KSnSb and (d-f) KSnBi under 2% (left panel), 4% (middle panel) & 6% (right panel) compressive hydrostatic pressure (HP). α is the value of Rashba coefficient in eVÅ.

To further demonstrate the influence of energy gap and band symmetry on the Rashba splitting, we calculate the band structures of both KSnSb and KSnBi under external pressure. We apply hydrostatic pressure (HP) (which maintains the original crystal symmetry C_{6v}) by reducing the lattice constants by 2%, 4% and 6%. The corresponding band structures are shown in Fig. 7.4(a-c) for KSnSb and 7.4(d-f) for KSnBi respectively. The bands are denoted by the IRs of C_{6v} at the Γ point. It is to be noted that KSnBi still produce a reasonably large splitting in VBM ($\alpha = 2.0$) because of the presence of another Γ_9 band just below the VBM (Fig. 7.4(d)). With increasing pressure, the band gap of KSnSb increases and simultaneously α -value decrease, as expected (Fig. 7.4(a-c)). However, the band gap (at Γ point) for KSnBi decreases with increasing pressure (Fig. 7.4(d-f)), as opposed to KSnSb. This is due to the -ve band gap (energy gap between CBM and VBM at Γ point after band inversion) of KSnBi and compressive pressure gradually decreases the band gap which leads to a trivial insulating band order. With increasing pressure, the energy separation between two Γ_9 valence



Figure 7.5: Rashba spin texture of KSnSb and KSnBi. (a) Projected in-plane S_x spin components on the band structures of KSnSb along K- Γ -M direction. (b-d) Constant energy contour at 250 meV of the in-plane S_x , S_y and out of plane S_z components for KSnSb. (e) S_z component with hexagonally distorted contour for KSnSB_{0.5}Bi_{0.5}, caused by the reduction of symmetry from C_{6v} to C_{3v} . (f) Topological surface spin texture of KSnBi (shown by black arrows in the inner circle) and schematic representation of Rashba spin by red and blue arrows on the projected bulk states.

bands increases giving rise to a decrease in α value, as evident from Fig. 7.4(d-f).

Next, we extend our discussion to the Rashba spin polarization as the hallmark signature of Rashba bands. Figure 7.5(a) shows the projection of S_x spin components on the band structure of KSnSb (at ambient condition) along K- Γ -M direction. As expected, both the inner and outer branches are completely spin polarized and the spin helicity have same sign for both CB and VB, i.e, the inner (outer) branch of both CB and VB have low (high) spin value. This feature is in complete contrast to the extensively studied Rashba semiconductor BiTeI, where spin textures have opposite chirality in VB and CB [283]. Figure 7.5(b-d) shows projected S_x , S_y and S_z spin components on the constant energy contours (CECs) at 250 meV, clearly indicating the purely in-plane nature of the net spin polarization. The out-of-plane S_z component is zero and both the inner and outer branch of CECs are perfectly circular. This can be explained from Rashba Hamiltonian (Eq. 7.1) that allows only linear order terms in **k** and does not involve σ_z spin matrix. Nevertheless, a finite out-of-plane component can be induced over the CECs by reducing the structural symmetry from C_{6v} to C_{3v} . This is because the Rashba Hamiltonian under C_{3v} allows non-zero cubic terms involving σ_z matrix. The Hamiltonian in this case is given by [280],

$$H_R^{C_{3v}} = \alpha (k_x \sigma_y - k_y \sigma_x) + \lambda (3k_x^2 - k_y^2) k_y \sigma_z.$$
(7.2)

The cubic terms not only allow the finite out-of-plane component but also provide a hexagonal distortion in CEC. To explicitly show this, we have computed the Rashba spin texture of $KSnSb_{0.5}Bi_{0.5}$ which posses C_{3v} point group. Figure 7.5(e) shows the S_z component of $KSnSb_{0.5}Bi_{0.5}$ at 250 meV in which the inner branch indeed shows a hexagonal distortion. This hexagonal distortion arises due to the trigonal wrapping of S_z component associated with the cubic term, as clearly visible in Fig. 7.5(e). To understand this from the structural chemistry point of view, we write the basic Rashba Hamiltonian as;

$$H_R = \frac{\hbar}{4m_0^2 c^2} [\nabla \mathbf{V} \times \mathbf{p}] \cdot \sigma.$$
(7.3)

Now, let us consider the perfectly two dimensional free electron gas layers that form in the crystal structure of KSnSb (KSnBi) by the alternate layers of positive $[K]^{+2}$ and negative $[SnSb]^{-2}$ ($[SnBi]^{-2}$) charge clouds such that, the direction of potential gradient is strictly oriented along the z-axis and there is no in-plane anisotropy of charges. For such a situation, the Rashba Hamiltonian



Figure 7.6: Bulk band structures of $\text{KSnSb}_{1-x}\text{Bi}_x$ for (a) x = 0.125, (b) x = 0.25, (c) x = 0.375 and (d) x = 0.5. NI, WSM and TI stands for topologically trivial, Weyl semimetal and topological insulator phases respectively. Δ represents the IRs of bands at Γ point.

takes the form (in x-y plane);

$$H_R = \alpha [\mathbf{k} \times \mathbf{p}_{\parallel}] \cdot \sigma, \tag{7.4}$$

where \mathbf{k} is the unit vector along potential gradient (z-axis) and \mathbf{p}_{\parallel} is the in-plane wave vector. This simple model nicely reproduces our *ab-intio* result of 100% spin polarization of in-plane S_x and S_y components and zero spin polarization of out-of-plane component. The in-plane components are axially symmetric and the signature of \mathcal{TRS} , (i.e., $\mathbf{S}(\mathbf{p}_{\parallel}) = -\mathbf{S}(-\mathbf{p}_{\parallel})$ and $\mathbf{E}(\mathbf{p}_{\parallel}) = \mathbf{E}(-\mathbf{p}_{\parallel})$) are prominent in the spin textures, see Fig. 7.5(b-c). In contrast, $KSnSb_{0.5}Bi_{0.5}$ (with C_{3v} symmetry) possibly acquires an in-plane potential gradient due to its relatively lower symmetry. This in-plane anisotropy induces an out-of-plane S_z component on CECs, see Fig. 7.5(e). Figure 7.5(f) shows the projected surface and bulk bands on (001) plane of KSnBi. As KSnBi is an TI, the Fermi surface (FS) contains both the topological spin (inner circle with black arrows) and the Rashba spin over the bulk CECs (outer dark bulk states with red and blue arrows). The FS is simulated just below the VBM to get both these features.

7.4 Intertwining of Topological and Rashba States

We now ask an important question: how to engineer the band structure so as to retain its topological non-trivial behavior, but enhance Rashba coefficient α . Obviously, external pressure can tune the band topology, as seen in Fig. 7.4, but because of the symmetry constraint, the band splitting (as well as α) reduces significantly. To bypass the symmetry constraints on Rashba splitting, we adopt the alloying induced symmetry-lowering mechanism. Lower symmetric structures allow less number of IRs for defining band characters and hence the CBM and VBM are more probable to have same band characters, that in turn allows higher Rashba splitting. We simulated mixed compounds $KSnSb_{1-x}Bi_x$ (x=0.125,0.25,0.375 and (0.5) using a $2 \times 2 \times 2$ supercell of a 6-atom unit cell, whose band structures are sown in Fig. 7.6 (a-d). For all these x values, the structural symmetry reduces to C_s from C_{6v} . In contrast to C_{6v} , C_s only has two IRs Γ_1 and Γ_2 (say). These two IRs will form Kramer's degeneracy because of \mathcal{TRS} at all the TRIM points. Hence, all the bands of $KSnSb_{1-x}Bi_x$ have same character at Γ point which removes the symmetry restrictions of the Rashba band splitting and hence maximize the value of α . With increasing x (Bi concentration), SOC strength increases and lattice expands as Bi is bigger than Sb. This, in turn, decreases the band gap. The gap closes at x = 0.375 and reopen again through a topological phase transition, as shown in Fig. 7.6. For x = 0.375, the system becomes gapless and host the novel topological WSM phase. Beyond that, at x = 0.5, a topological gap reopens and system becomes a strong TI. Notably, the value of α increase as the gap decrease with the largest value $(\alpha = 4.87 \text{ eV} \text{\AA})$ at gapless WSM phase (x = 0.375). For TI phase (x = 0.5), the α value is reasonably high (3.74 eVÅ). In Table 7.1 and Table 7.2, we listed all the Rashba parameters in VB and CB for

Table 7.1: Rashba energy(ΔE), momentum offset(ΔK), Rashba coefficient(α) and formation energy(ΔE_F) of different materials. All the Values are listed for VB. NI, WSM and TI indicates topologically trivial, Weyl semimetal, and topological insulator phases respectively. ^{*a*}[Our Work], ^{*b*} Ref. [279]

Compound	ΔE	Δk	α	T-phase	ΔE_F
	(meV)	(\mathring{A})	$(eV \mathring{A})$		(meV/atom)
KSnSb^{a}	142	0.078	3.65	NI	-356.92
$\mathrm{KSnSb}_{0.875}\mathrm{Bi}_{0.125}{}^{a}$	138	0.075	3.68	NI	-347.34
$\mathrm{KSnSb}_{0.75}\mathrm{Bi}_{0.25}{}^a$	149	0.070	4.25	NI	-337.96
$\mathrm{KSnSb}_{0.625}\mathrm{Bi}_{0.375}{}^{a}$	161	0.066	4.87	WSM	-328.90
$\mathrm{KSnSb}_{0.5}\mathrm{Bi}_{0.5}{}^a$	148	0.079	3.74	ΤI	-320.14
KSnBi^{a}	74	0.110	1.34	ΤI	-291.19
BiTeI^{b}	100	0.052	3.8	NI	

different values of x and compared them with the previously studied promising Rashba material BiTeI. Formation energies (ΔE_F) and the nature of topological phases of these compounds are also listed. Chemical stability of these compounds are checked by calculating the formation energies using the formula: $\Delta E_f = E_{Comp} - \sum x_i E_i$, where E_{Comp} is the total energy of the compound and E_i is the energy of the constituent elements in their equilibrium phase, all at their optimized equilibrium lattice constants. x_i is the proportion of i^{th} element in the compound.

Table 7.2: Rashba energy(ΔE), momentum offset(ΔK), Rashba coefficient(α) of different materials for CB. NI, WSM and TI indicates topologically trivial, Weyl semimetal, and topological insulator phases respectively.

Compound	$\Delta E \ (\mathrm{meV})$	$\Delta k (\mathring{A})$	$\alpha \ (eV \mathring{A})$	T-phase
KSnSb a	19	0.028	1.29	NI
$\mathrm{KSnSb}_{0.875}\mathrm{Bi}_{0.125}~^a$	23	0.035	1.34	NI
$\mathrm{KSnSb}_{0.75}\mathrm{Bi}_{0.25}$ ^a	32	0.047	1.37	NI
$\mathrm{KSnSb}_{0.625}\mathrm{Bi}_{0.375}~^a$	41	0.062	1.33	WSM
$\mathrm{KSnSb}_{0.5}\mathrm{Bi}_{0.5}$ ^a	23	0.052	0.87	ΤI
KSnBi a	7	0.120	1.17	ΤI

7.5 Conclusion

We use *first-principles* simulation combined with group theoretical analysis to disclose the true origin of giant Rashba splitting in a crystalline system. Taking $KSnSb_{1-x}Bi_x$ as an example system, we show that the crystalline symmetry and energy gap between the bands play crucial role to maximize Rashba energy and coefficient in a broken \mathcal{IS} and strong spin-orbit coupled system. We show that the crystals with lower symmetry are more favorable to yield larger spin splitting. We provide simple yet viable scheme to simultaneously realize the co-existence of Rashba and topologically non-trivial properties in a single material. We achieved a record high value of Rashba coefficient ($\alpha = 4.87 \ eV \text{\AA}$) in KSnSb_{0.625}Bi_{0.375} which simultaneously posses non-trivial WSM phase. We are able to tune the topological phase to TI without much compromising the high Rashba parameters. Our proposed mechanism is robust in a sense that it does not require fine tuning of the system itself, but expected to be applicable to all class of compounds. We strongly believe that our findings are quite insightful along the line of Rashba and topological physics and will surely attract the experimentalists for future studies.

Outcome and Possibilities

8.1 Outcome

The theoretical development of topology in condensed matter physics is relatively new and experimental realization of novel material are restricted within a handful of numbers. The main obstacles with the existing predicted topological materials are as follows; (i) False predictions of topological materials using computationally less costly inaccurate functionals within the DFT formalism, (ii) Finding an ideal material for experimental verification and technological applications are not easy task because a compound may have the expected nontrivial band ordering or degeneracies anywhere in the energy range but tuning them near the Fermi level without presence of other trivial bands is difficult in real material. Hence, an extensive search and fine tuning are needed for such an ideal material realization. Keeping these above limitations in mind, in our calculations, we have used relatively accurate functionals for the prediction of new topological materials, such as topological insulator (TI), nodal line semimetal (NLS), Dirac semimetal (DSM), triple point semimetal (TSM), and Weyl semimetal (WSM), which provide ideal material platform for the experimental verification. To predict the new topological compounds, we have also provided general symmetry based arguments for the presence of such topological properties. Our symmetry-based arguments do not depend on the chemical environment of a crystal, it is rather general and can be employed to any class of compounds to understand its topological characters.

We have shown a symmetry-adapted scheme to drive a topological state to other topological states. Using the broken symmetry mechanism, we have shown a gapless DSM phase can be tuned to a gaped TI phase through intermediate TSM and WSM phases. For example, a system having C_{6v} point-group symmetry along certain direction may provide a four-fold DSM phase. Now, if we break the crystal symmetry in a certain way such that C_{6v} transforms to C_{3v} and then the Dirac node also transforms to two three-fold triple point nodes. Further, if we break C_3 rotation symmetry, it will go to a Weyl phase (if inversion symmetry (IS) is absent) or to a TI phase (if IS is restored). We can tune the topological phases by breaking reversal symmetry (TRS) similar to breaking of crystalline symmetry. Breaking the TRS, the DSM phase converted to a WSM phase. We found an ideal space group (sg. 194) and a group of compounds (SrAgAs and BaAgBi) in which we can perform the above symmetry-broken scheme. We show that alloy engineering in these systems can break the symmetry in a precise way and can ensure all the topological phases.

We have shown a general symmetry-based mechanism, supported by ab-initio calculations to achieve intertwined giant Rashba splitting and topological nontrivial state simultaneously and that can be further tuned robustly. It is believed that broken IS in a strongly spin-orbit coupled system can give Rashba splitting and the amount of that splitting is proportional to spin-orbit strength of the material. However, using purely symmetry based arguments, we show that there are two other parameters which are as important as SOC that need to be taken care of to get a large Rashba value. We show that the energy gap and all the symmetry elements play a similar important role as SOC and broken IS. We considered two IS broken compounds KSnSb and KSnBi (space group is 186 for both

compounds). KSnSb possess trivial band ordering whereas KSnBi is a TI. The computed value of Rashba coefficient (α) for KSnSb is 3.65 eVÅ whereas it only 1.34 eVÅ for KSnBi. These results are apparently surprising because Bi possesses a larger value of SOC than Sb. We then introduce a new parameter called band symmetry (which is closely associated with symmetry of the crystal) to understand this apparently incompatible result. We conclude that the lower symmetric structures are more favorable to have larger Rashba values. Using our the proposed symmetry arguments, we have achieved giant Rashba coefficient (α) 4.87 eVÅ respectively along with nontrivial Weyl semimetal phase in $KSnSb_{0.625}Bi_{0.375}$ which is a low symmetric (C_s group) structure. Similarly, another low-symmetry structure $KSnSb_{0.5}Bi_{0.5}$ poses TI phase with a giant α value of 3.74 eVÅ. Our study not only provides a few CQCs which possess large Rashba splitting and nontrivial topology simultaneously but also a general symmetry based mechanism which can be applicable for any class of compounds.

8.2 Possibilities

My future plan is associated with one of our very recent work (arXiv:2002.11145) on high spin fermions. Here, we focus on high spin excitations in several binary, ternary and quaternary alloys with CoGe and BiSbPt being the representative examples. We found distinct three-fold, four-fold and six-fold chiral fermions in these compounds, which are protected by two non-symmorphic crystal symmetry. Also the surface spectra simulations show that the size of Fermi arcs resulting from these chiral fermions are large, robust and untouched from the bulk states due to the near absence of bulk trivial Fermi pockets. All these features make CoGe as well as BiSbPt a promising topological semimetal candidate to realize double Weyl fermions in future transport measurements. The transport calculations for spin-1/2 Weyl semimetals within semiclassical Boltzmann kinetic theory of wave packet dynamics and Berry phase formalism are well established and that has provided a very simple but elegant explanation for several topological phenomena such as Chiral anomaly, Planar Hall effect and Chiral magneto-resistance effect. in Weyl semimetals and TI. But such analysis for high-spin fermions (such as Double Weyl and spin-1 fermion) are still untouched and therefore needs to be investigated. As we have already investigated the reason for the occurrence of such high spin fermions in crystalline system, now we would like to understand their topological properties in transport using semiclassical Boltzmann kinetic theory and Berry phase formalism.

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