

Structural and Electronic Properties of Topological Insulators and Nodal line Semimetals



THESIS SUBMITTED IN PARTIAL FULFILLMENT FOR THE AWARD OF

THE DEGREE OF

Doctor of Philosophy

by

SAMBHAB DAN

DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY

(BANARAS HINDU UNIVERSITY)

VARANASI – 221 005

ROLL NUMBER
17171501

YEAR OF SUBMISSION
2023



भारतीय
प्रौद्योगिकी
संस्थान
काशी हिन्दू विश्वविद्यालय



INDIAN
INSTITUTE OF
TECHNOLOGY
BANARAS HINDU UNIVERSITY

CERTIFICATE

It is certified that the work contained in the thesis titled **The Structural and Electronic Properties of Topological Insulators and Nodal line Semimetals** by **Sambhab Dan** has been carried out under my supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of **Doctor of Philosophy**.

Supervisor
Dr. Swapnil Patil
Department of Physics
Indian Institute Of Technology
(Banaras Hindu University)
Varanasi – 221 005
Assistant Professor
Department of Physics
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005



भारतीय
प्रौद्योगिकी
संस्थान
काशी हिन्दू विश्वविद्यालय



INDIAN
INSTITUTE OF
TECHNOLOGY
BANARAS HINDU UNIVERSITY

DECLARATION BY THE CANDIDATE

I, **Sambhab Dan**, certify that the work embodied in this thesis is my own bona fide work and carried out by me under the supervision of **Dr. Swapnil Patil** from **December 2017** to **June 2023**, at the **Department of Physics**, Indian Institute of Technology (Banaras Hindu University), Varanasi. The matter embodied in this thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

Date: May 26, 2023
Place: Varanasi, India

Sambhab Dan
Signature of the Student

CERTIFICATE BY THE SUPERVISOR

It is certified that the above statement made by the student is correct to the best of my knowledge.


Supervisor
Dr. Swapnil Patil
Department of Physics
Indian Institute Of Technology
(Banaras Hindu University)
Varanasi – 221 005

Assistant Professor
Department of Physics
Indian Institute of Technology
(Banaras Hindu University)
Varanasi-221005


Signature of Head of Department
HEAD/विभागाध्यक्ष
भौतिकी विभाग/Deptt. of Physics
वा०प्रौ०सं०/(का०हि०वि०)/IIT (BHU)
वाराणसी/Varanasi-221005



भारतीय
प्रौद्योगिकी
संस्थान
वाराणसी हिन्दू विश्वविद्यालय



INDIAN
INSTITUTE OF
TECHNOLOGY
BANARAS HINDU UNIVERSITY

COPYRIGHT TRANSFER CERTIFICATE

Title of the Thesis: The Structural and Electronic Properties of Topological Insulators and Nodal line Semimetals

Name of the Student: Sambhab Dan

COPYRIGHT TRANSFER

The undersigned hereby assigns to the Indian Institute of Technology (Banaras Hindu University), Varanasi all rights under copyright that may exist in and for the above thesis submitted for the award of the Doctor of Philosophy in Physics.

Date: May 26, 2023
Place: Varanasi, India

Sambhab Dan
Signature of the Student

Note: However, the author may reproduce or authorize others to reproduce material extracted verbatim from the thesis or derivative of the thesis for author's personal use provided that the source and the Institute's copyright notice are indicated.

I would like to dedicate this thesis to my beloved family . . .

ACKNOWLEDGEMENT

If I were the only one to make an effort, this pile of printed papers would never see the light of day. I would want to take this opportunity to thank those individuals who, without them, it would not have been feasible for me to finish the thesis. There may only be one name on the title page of this thesis, yet many hands went into its compilation. I would like to thank my supervisor Dr. Swapnil Patil, for giving me the incredible opportunity to study the fascinating field of quantum matter, one of the most ground-breaking discoveries in the field of condensed matter physics in the past several years. Throughout my research work, he remains my friend, philosopher, and guide; and has been an invaluable source of trust, support, direction, and scientific conversation, for which I am eternally grateful. Without his helpful guidance, precious time, thoughtful cooperation, and tremendous work freedom, I would not have been able to finish my doctoral thesis. I would like to express my gratitude to my advisor, HOD, Professor Sandip Chatterjee, for the insightful conversation and unwavering support. Without his encouragement, my Ph.D. work would not even have had a chance to begin. The advice and experience that he shared will remain immortal throughout my future endeavour.

I am grateful to Dr. Shiv Kumar (Hiroshima Synchrotron Radiation Center, Japan) for the ARPES measurement, which required a great deal of expertise, a significant amount of time, and a high level of technical expertise. He carried out some really impressive measurements using the “Laser ARPES” as well as “High-resolution synchrotron ARPES,” both of which are now unavailable in India. A significant portion of our research work is going through the ‘ARPES data analysis’, and without his consistent help and willingness to share his expertise, it would be next to impossible for us to continue working in this field. He is not only an experienced collaborator but also a friend of mine and a well-wisher

who will continue to work with me in the years to come. I appreciate Dr. Swarup Panda (Bennett Univesity, India) for sharing hands-on experience in the DFT study. During the COVID-19 pandemic, when the entire country was in a lockdown situation, I gained some fundamental but incredibly useful knowledge that assisted me in successfully calculating some DFT problems. He welcomed me into his workplace and has remained supportive of me even up to this day in relation to any DFT-related concerns I may have had. I would like to extend my gratitude to my senior colleague Dr. Vinod Kumar Gangwar (my senior colleague) for his advice on the growth of single crystals and other information relating to the topological material. I would also thank my friend Kuldeep Kargeti (Bennett Univesity, India) for his tremendous help and hours of discussion in solving DFT-related issues. I would like to thank Dr. Ramchandra Sahoo (Tokyo Institute of Technology, Japan) for extending his helping hand in transport measurement during the very crucial time of my Ph.D. tenure. I would like to thank my friend Ms. Anumita Bose (IISc Bangalore, India) for delivering some excellent theoretical results in a short time span.

I would like to express my gratitude to Dr. Sujay Chakraborty (PPMS Incharge, UGC-DAE Kalpakkam, India) for allowing 15 T PPMS for the quantum oscillation study. I also want to express my gratefulness to Prof. Chandan Mazumdar (Saha Institute of Nuclear Physics, Kolkata, India) for allowing resistivity and temperature-dependent XRD study, Dr. Satyen Saha (Dept. of Chemistry, BHU, India) for allowing the temperature-dependent Raman study, prof. Kenya Shimada (Hiroshima Synchrotron Radiation Center, Japan) for collaborating on Laser and Synchrotron ARPES measurement, Prof. Anup K. Ghose (Dept. of Physics. BHU, India) for allowing the instrumental facility of sample growth, Dr. Awadhesh Narayan (IISc Bangalore) for collaborating theoretical work, Dr. Neeraj Mehta (Dept. of Physics, BHU, India) for helping single-crystal growth. I express my gratitude to my RPEC member Dr. B.N. Pal (School of material science, IIT BHU) for his significant scientific discussion. I express my gratefulness to Prof. Prabhakar Singh and Prof. Debaprasad Giri for their inspiration and support. I also wish to thank all the faculty members and non-teaching staff of the Department of Physic, IIT (BHU) Varanasi for their motivation, selfless support, and suggestions. I would like to express my grati-

tude to new faculty members who are nearly my friends, such as Dr. Somnath Nag, Dr. Vidya Binoi Karak, Dr. Prasun Dutta, etc.

I would like to thank my friend Deenanath Gangwar (research scholar, UGC, DAE Kalpakkam, India) and Abhineet Verma (research scholar, BHU, India) for successfully executing the transport measurement and T-dependent Raman measurement respectively. I want to express my gratitude to Kamata Ji for sharing his technical know-how and unique skill for vacuum (quartz) sealing. I want to share my gratefulness to my lab mate Sunil Verma, Dr. Rajesh Tripathi, and Deepak Gond. We spent a lot of time together in the lab, and they quickly became some of my closest friends. I would like to extend my gratitude to my former lab partner Debarati Pal, who just completed her PhD, for her excellent cooperation from the very beginning of the journey. I want to thank Arkadeb Pal, one of my senior and close friends, for his great companion and scientific discussion in the early stage of my Ph.D. tenure. I also want to thank Somnath Roy, my senior friend for his joyful companion. My appreciation also goes to my colleagues working in our group for their great help during my PhD journey- Dr. Abhishek Singh, Dr. Rahul. Singh, Dr. Prince Gupta, Dr. Surajit Ghosh, Dr. Vinod Kumar Gangwar, Dr. Prajyoti Singh, Dr. Mahima Singh, Ms. Khyati Anand, Ms. Seema Kumari, Mrs. Labanya Ghosh, Mr. Satya Vijay Kumar, Ms. Srishti Dixit, Mr. Dheeraj Kumar, Ms. Neha Patel, Ms. Swayangsiddha Ghosh, Ms. Asmitha Mekala, and Ms. Sneha Yadav, Mr. Vishnu Sharma, Mr. Nandkishor Pal, Mr. Atul Kumar, Mr. Madhusmita Jena, and Mr. Shivsakti Tiwari. I would like to thank all my hostel and campus friends- Swapan (One of my close companions), Ashish, Ravi, Ajeet, Abhishek, Pankaj, and Jaydeep for being such pleasant and joyful companions in my whole Ph.D. journey.

Finally, my deepest gratitude to my family, without whom this thesis could not be possible. To begin, I would like to offer my sincere appreciation to my elder brother, Dr. Shovan Dan, for the tremendous support he has provided me with. Given that he works in the same field as me, the assistance I have received is a product of my good fortune, and the support I have received is beyond my ability to adequately describe it. In addition, I would

like to thank my sister-in-law Dr. Binita Mondal, one of my well-wishers, for giving me love and happiness whenever I required it, my special thank also go to my little nephew Kalpo (Krishna) whose innocence never fails to brighten my day. I will always be grateful to the late Mr. Kalipada Dan, my paternal grandfather, and Mr. Anath Bandhu Som, my maternal grandfather, for their encouragement and blessing as I pursued my Ph.D.

My heartfelt gratitude goes out to my parent Mr. Shyamal Kumar Dan and Mrs. Tandra Som Dan, the two most important persons in my life, for always being there to cheer me on, inspire me, and back me up. I learned perseverance, diligence, and morality from my parents. Their sacrifices have taught me the value of honesty and kindness above everything else. This thesis, I believe, is more properly theirs than mine.

In the end, my sincere gratitude to the MHRD for providing the fellowship, training, a wonderful learning experience, and a chance to collaborate with people with significant expertise in the field outside my institute. My warm thanks to the CIFC, IIT (BHU) for the instrumental facility, Param Shivay supercomputing facility, Institute server facility, and the DST-SERB, India grant.

Preface

In this thesis, we have discussed the structural and electronic properties of topological insulators and topological nodal line semimetals. Our discussion centered on the experimental band structure, Fermi surface topology, electrical transport properties, and some theoretical simulation with the help of density functional theory. In the case of topological insulators, the surface states are conducting, and bulk remains insulators, giving rise to a distinguishable surface and bulk band structure. The surface state of the topological insulators contains time-reversal symmetry-protected Dirac cones, and conduction occurs through the Dirac point (touching point of conduction and valence band). On the contrary, in the case of a topological nodal line semimetal, the nodal line is protected by crystalline symmetry in the bulk band of the compound. In other words, the locus of the Dirac point extends as a line or a loop in the Brillouin Zone (BZ). Both types of compounds show unique physical properties which we have verified experimentally. We start our experiment with single crystal growth along with structural analysis of the compound using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The electrical transport properties are performed by a physical properties measurement system (PPMS). The band structure studies of the novel compounds are carried out by angle-resolved photoelectron spectroscopy (ARPES). The Fermi surface topology of the compounds is studied by Shubnikov–de Haas oscillation. Our whole study is categorized into eight chapters.

In **Chapter-1**, we discuss the preliminary understanding of the topological insulator, Dirac and Weyl semimetal, and nodal line semimetal. We have discussed the topological band structure of the compound starting from the quantum Hall effect. We have explained how the mathematics of topology (which deals only with any object's shape) is closely related

to the topological band structure. We elaborately discuss the band-inversion phenomena in the electronic structure upon the application of spin-orbit coupling. These phenomena take the prime role in generating non-trivial insulating phases of the compound. Here, we have also explained the role of symmetries that protects the band crossing. The different types of symmetries are discussed, for example, the Dirac cone in the surface state of the topological insulator is protected by time-reversal symmetry, whereas in the case of Dirac semimetal or nodal line semimetal, the ‘crystalline symmetry’ takes a prime role. We also explained how the locus of the Dirac point could be extended as a line or a loop in the BZ of the compound. The phenomenon be visualized as ranging from a zero-dimensional nodal point to a higher-dimensional nodal structure. In this section’s last portion, we briefly discussed the ‘role of single crystallinity’ for ARPES and quantum oscillation measurement.

In **Chapter-2**, we have elaborated on the single crystal synthesis and characterization technique. We have explained the fundamental science and technical skill behind the crystal growing phenomena. For structural analysis, we have performed XRD (CuK_α , $\lambda = 1.54$) for powder and single crystal. We have also performed XPS for the chemical analysis of the compound. From the electrical transport properties, we use a physical properties measurement system from 2–400 K in the magnetic field range 0–9 T. The sample was mounted in the four-probe puck using Cu wires and silver paste to perform transport studies. The vibrational modes of the compound have been checked using a Raman spectrometer attached to a CCD camera and illuminated by 633 nm laser excitation. The Laser-ARPES measurements were performed using a photon energy of 6.3 eV and synchrotron ARPES were performed with variable photon energy 25–95 eV in the ultra-high vacuum (10^{-11} torr). For Shunikov–de Haas oscillation study, we have measured magnetoresistance up to 15 T at low temperatures.

In **Chapter-3**, we have explained metal–semiconductor phase transition in $\text{Cu}_{0.1}\text{Bi}_{1.9}\text{Te}_3$ topological insulator. To discuss the underlying phenomena, we first performed temperature-dependent XRD and observed that metal–semiconductor phase transition is not accompanied by structural phase transition. Furthermore, we performed a temperature-dependent Raman study which gives a Raman mode anomaly close to transition temperature. Such

kind of observation hints at an electronic transition at the transition temperature. Finally, we have performed the temperature-dependent ARPES study. The ARPES results indicate that the surface state of the compound remains intact throughout the whole temperature range, but the bulk band of the compound modulates significantly with the temperature variation. Our detailed observation suggests that the metal–semiconductor phase transition of the novel topological insulator originates from the bulk band of the compound. We give a quantitative analysis of the resistivity data with the help of two carrier Drude’s models using the parameters derived from the temperature-dependent ARPES data. The analysis satisfactorily simulates the experimental resistivity data and delivers an excellent justification for the novel phenomena.

In **Chapter-4**, we have discussed the magnetic field-induced up-turn resistivity and the origin of extremely high magnetoresistance (XMR) in the topological nodal line semimetal InBi. The up-turn in resistivity is observed when we apply a magnetic field in the temperature-dependent resistivity data. Our detailed investigation suggests that this kind of phenomenon originates from the excitonic gap opening on the application of the magnetic field. The excitonic gap opened at the Fermi level on the linearly dispersing band on the application of the magnetic field. So, the higher the magnetic field, the higher the excitonic gap and consequently higher the up-turn-like behavior. We performed analysis to extract a few extremely useful parameters to explain the results. We also bring in some additional algebraic analysis and formulate new expressions for the magnetoresistance regarding the underlined phenomena. To understand the role of carrier concentration, we have measured ρ_{xx} and ρ_{xy} and hence calculate σ_{xx} and σ_{xy} . We have derived the carrier concentration and mobility of electrons and holes from the two-carrier fitting. We observed that electrons and holes contribute equally to the particular temperature regime where XMR is observed. The phenomena indicate that carrier compensation is one of the primary reasons for the XMR of the compound.

In **Chapter-5**, we studied the Fermi surface topology of the nodal line semimetal InBi. We have performed the Shubnikov—de Haas oscillation study at a high magnetic field (7–15 T) and successfully identified three Fermi pockets of the compound. During the quantum

oscillation study, the magnetic field is applied on the ab-plane of the compound, and hence the extremum orbit of the Fermi pocket in the aforementioned direction is obtained. We successfully mapped the compound's full 3D Fermi surface topology. As our compound is slightly electron-doped, the size of the electron and hole pockets modulate accordingly. The shape and size of all the Fermi pockets are very close to the density functional theory (DFT)-generated results. The full 3D Fermi surface topology along with the electron and hole doping of each Fermi pocket are simulated from the DFT result. Furthermore, we have given a detailed discussion of temperature and magnetic field-dependent amplitude damping of the oscillatory data. From the oscillatory signal, we have calculated the effective mass of the carrier, the Dingle temperature, and the quantum mobility of the compound for the first time.

In **Chapter-6**, we have shown the experimental realization of the type-II Dirac cone in the InBi compound. We have performed a photon energy-dependent synchrotron ARPES study in the 25–95 eV energy range. The compound is easily cleavable along ab-plane, and we performed a photon energy-dependent ARPES study to probe the Dirac cone lying along the k_z direction of the 3D BZ. As the Dirac cone is tilted (type II), it is extremely difficult to probe the Dirac cone from the direct E vs. k_z plot. So, we take an alternative approach to probe it. First, we run the DFT along k_z -direction and identify the particular bands which form the Dirac cone. Next, we observed the energy dispersion of the same bands in the k_x – k_y plane at several values of k_z from the DFT. We tally the DFT results with the ARPES data for each k_z value. Our study indicates that the DFT-generated result is very close to the experimental band structure for all k_z . Hence, verifies the novel non-trivial Dirac cone protected by crystalline symmetry.

In **Chapter-7**, we deal with the Cu-substituted Bi_2Te_3 topological insulator's electronic band structure and defect-induced behavior. The pristine Bi_2Te_3 compound has a unique band structure: the bulk band is semiconducting, and the surface band is metallic. However, here, we report the modulation of the bulk-band structure with the injection of Cu atoms in the pristine Bi_2Te_3 compound. Our *ab initio* simulation reveals that 5 at. % of Cu substitution in Bi site transforms the electronic ground state of Bi_2Te_3 to a *p*-type one.

In contrast, the intercalation of Cu atoms by a similar amount turns the electronic ground state of Bi_2Te_3 into an n -type one. We have also discussed the band structure of the carrier-compensated configuration of the Cu-substituted Bi_2Te_3 compound with the creation of Te vacancy. Our simulation gives an excellent agreement with the experimentally verified result.

In **Chapter-8**, we have discussed the future scope and application of the novel compound. We mainly focus on the Majorana fermion-driven topological superconductor, magnetic topological insulator, and the future application of topological insulators in spintronics devices, ultrafast photodetection, and quantum computations.

Contents

1	Introduction: A bibliographic review	1
1.1	Introduction to topology	2
1.2	Topological nature of Hall conductivity	3
1.3	Effect of magnetic field on Bloch electrons	4
1.4	Nobel prize (2016)	5
1.5	The foundation of Chern Insulator (2D TI)	8
1.6	From 2D TI to 3D TI	12
1.7	The Dirac semimetal, Weyl semimetal and nodal line semimetal	13
1.8	Importance of single crystal growth	16
1.8.1	Role of single crystallinity in (a) physical properties and (b) crystal anisotropy	16
1.8.2	Role of single crystallinity in (a) ARPES (b) Quantum oscillation study	17
2	Single crystal growth and characterization tools	19
2.1	Single crystal growth technique	19
2.1.1	CVT method	21
2.1.2	Flux method	22
2.1.3	Bridgman technique	23
2.2	Experimental characterization tools	24
2.2.1	Diffraction of X-rays (XRD)	24
2.2.2	Laue diffraction pattern	28

2.2.3	Electric resistivity (ρ_{xx})	30
2.2.4	Hall resistivity (ρ_{xy})	31
2.2.5	Shubnikov–de Haas (SdH) oscillation	31
2.2.6	Photoemission Spectroscopy	34
2.2.7	Angle-resolved photoemission spectroscopy (ARPES)	35
2.2.8	Raman effect	38
3	Unravelling the obscure electronic transition and tuning of Fermi level in Cu substituted Bi_2Te_3 compound	41
3.1	Introduction	41
3.2	Results and discussion	42
3.2.1	Crystal growth and structural analysis	42
3.2.2	Resistivity	44
3.2.3	Temperature dependent Raman study	45
3.2.4	Effect on magnetic field in $\rho(T)$ pattern	48
3.2.5	ARPES study	49
3.2.6	Drude’s model and anomalous resistivity	51
3.2.7	Temperature independent scattering	53
3.3	Conclusion	55
4	Magnetic field induced up-turn resistivity and low temperature carrier compensation in nodal line semimetal InBi	57
4.1	Introduction	57
4.2	Experimental details and theoretical methods	59
4.3	Results and discussion	60
4.3.1	Structural characterization	60
4.3.2	Magnetic field dependent $\rho(T)$	62
4.3.3	Magnetic field dependent excitonic gap	66
4.3.4	Origin of turn-on behavior	66
4.3.5	Step by step algebraic analysis of the resistivity up-turn	70

4.3.6	Temperature dependent $\rho(B)$	72
4.3.7	Hall resistivity study	73
4.3.8	The Hall resistivity at 50 K	77
4.4	Conclusion	78
5	Shubnikov–de Haas oscillation and 3D Fermi surface topology of nodal line semimetal InBi	79
5.1	Introduction	79
5.2	Experimental verification	80
5.2.1	Frequency from β -sheets (F_β)	83
5.2.2	Frequency from δ -sheets (F_δ)	84
5.2.3	Frequency from α -sheets (F_α)	85
5.2.4	Frequency from γ -sheets (F_γ)	87
5.2.5	Temperature dependent raw oscillatory data at 3 K	87
5.3	The study of effective mass and Dingle Temperature	89
5.4	Conclusion	91
6	Experimental realization of non-trivial <i>Type-II</i> Dirac cone in InBi	93
6.1	Introduction	93
6.2	Experimental details and theoretical methods	94
6.3	Result and discussion	96
6.4	Conclusion	101
7	First principle study of defect induced band structure in Cu substituted Bi₂Te₃ topological insulator	103
7.1	Introduction	103
7.2	Methods	104
7.2.1	Step by step procedure of unit cell preparation	105
7.2.2	Simulation methodology and software used	105
7.3	Result and Discussion	105
7.3.1	The pristine one	105

CONTENTS

7.3.2	The Cu substitution in Bi site	106
7.3.3	The Carrier neutral configuration	107
7.3.4	The Cu intercalation in the Van der Walls gap	107
7.4	Conclusion	108
8	Summery and future scope	109
8.1	Summery	109
8.2	Future scope	110
9	Publication	113

List of Figures

1.1	Transformation of a coffee mug to a donut through continuous deformation. During the transformation genus number (g) remain fixed. ($g = 1$). (Image is taken from Ref. [3])	2
1.2	The topological classification of different geometries. The genus number is defined as how many numbers of holes the particular object contains. (Figure is recreated from Ref. [5])	4
1.3	Illustration showing the evolution of geometrical and topological parameters. Geometrical characteristics, such the surface-to-volume ratio, change constantly as a sphere becomes a torus by elongation and end-to-end connection, but a topological parameter known as a topological invariant changes abruptly and discontinuously. A discontinuous deformation is a deformation that modifies the topological invariant as opposed to a continuous deformation, which does not affect the topological invariant. A topological phase transition occurs when two topologically inequivalent states change concomitant to the change of the topological invariant. (Figure is taken from the Ref. [11])	6
1.4	The topological phase transition from ‘trivial insulator’ to ‘non-trivial insulator’ is equivalent to the change in genus number. (Image is taken from Ref. [12])	8

1.5	The phenomena of band inversion due to the presence of SOC. (Dashed lines) The hybridization of inverted band generates the metallic surface state. (Solid line in the right hand) The non-trivial bulk band. (Figure is taken from Ref. [13])	8
1.6	The edge states of different classes of compound. (a and d) Quantum Hall state where only one edge state is observed. (b and e) The edge state of 2D TI. The edge state is completely spin-polarized. Two distinct channels are created for up and down spin. (c-f) The surface state of 3D TI. The surface state is completely spin-polarized and hence it shows the spin-momentum locking. (Figure is taken from Ref [14])	9
1.7	The surface band structure of TI. (Left panel) The experimental surface band of Bi_2Se_3 from ARPES study. (Middle panel) The schematic diagram 3D surface Dirac cone which excellently matches with the experimental one. (Right panel) The direction of spin with respect to momentum for Dirac Fermion. (Image is taken from Ref. [26])	12
1.8	(a) The surface Dirac cone while bulk remain in insulating phase in TI. (b) Example of a <i>type-I</i> Weyl node where conduction and valence band create a point in the constant energy plane. (c) Example of a <i>type-II</i> Weyl node where conduction and valence band create a pocket in the constant energy plane. ((Figure is recreated from the Ref. [11]))	13
1.9	The several classes of topological materials. (1) The Dirac semimetal. (b) The Weyl semimetal. (c) The nodal loop semimetal (bottom left), and nodal line semimetal (bootm right). (Figure is taken from Ref. [27]) . . .	14
1.10	The catalog of various classes of topological material that can sustain different classes of symmetries. (I = Invesion symmetry, TR = Time reversal symmetry), (Figure is taken from Ref. [27])	14
2.1	The naturally grown large quartz crystal (The photo is taken from the of-ficial website of the natural history museum of Bern[33])	20

2.2	Instruments used for single crystal synthesis. (a) Muffle furnace, (b) Two zone furnace for CVT growth and (c) Centrifuge machine which is used for separating the single crystal from the molten flux during the flux growth. (Photograph is taken from our laboratory)	23
2.3	The schematic and working principle of the Bridgman technique of single crystal growth. (Photo is taken from the Ref. [34])	24
2.4	The Bridgman single crystal growth furnace. (Photograph taken from our laboratory)	25
2.5	The photograph of lab grown single crystal.	26
2.6	Schematic diagram of the X-ray diffraction and the formulation of Bragg's law.	27
2.7	Schematic diagram of the Laue diffraction set up. (Upper panel) The transmission method. (Lower panel) The back-reflection method	29
2.8	The resistivity measurement set up. (Upper panel) The normal resistivity ρ_{xx} . (Lower panel) The Hall resistivity ρ_{xy}	30
2.9	15 T ppms machine for magnetotransport studies	32
2.10	Formation of Landau tube on the application of the magnetic field. (Left panel) with the increase of magnetic field, the width of the Landau tubes increase. (Middle panel) The extremum areas of the Landau tube are indicated by the red circle. The frequency of the quantum oscillation is proportional to this area. (c) The mathematical relation between the frequency of oscillation and extremum area of Fermi pockets. (This figure is recreated from the Ref [36])	32
2.11	Schematic diagram of angled-resolved photo-emission spectroscopy (The photo of analyzer is taken from Ref. [39])	35
2.12	The beamline ARPES machine. (Photograph taken from the 'Hiroshima Synchrotron Radiation Center')	37

- 2.13 The schematic diagram of the Raman effect, (Yellow) Incident ray and Rayleigh scattering, (Red) Stokes Raman scattering, (Indigo) Anti-Stokes Raman scattering. 38
- 3.1 Room temperature XRD pattern of the compound $\text{Bi}_{1.9}\text{Cu}_{0.1}\text{Te}_3$; in powdered form (Left panel) and in Single crystalline form (Middle panel). Cu core level XPS spectra of $\text{Bi}_{1.9}\text{Cu}_{0.1}\text{Te}_3$ (Right panel). Binding energies of $\text{Cu-}2p_{3/2}$ and $\text{Cu-}2p_{1/2}$ are similar to the pure Cu. (932.6 and 952.5 eV) 43
- 3.2 (a) Simulated $\rho(T)$ pattern with the variation of bandgap, (b) T -dependent position of the bulk valence band top, (c) T -dependent position of the bulk valence band top with respect to Dirac point energy, (d) T -dependent position of the Dirac point energy, (e) variation of electron and hole density and (f) variation of relaxation time are shown in the figure. 44
- 3.3 (a) Five mono atomic planes of a quintuple layer, (b) possible vibrational modes, (c) Raman spectra at 100 K and 350 K, (d) T -dependent Raman spectra as three dimensional contour plot, (e) T -dependent FWHM, (f) T -dependent mode frequency (g) The 3D contour-plot of T -dependent powder XRD pattern (enlarged view of highest-intense peak (015) are shown separately) and (h) T -dependent lattice parameters and volume are shown in the picture. 46
- 3.4 $\rho(T)$ pattern of $\text{Cu}_{0.1}\text{Bi}_{1.9}\text{Te}_3$ with (Orange) and without (Green) magnetic field 48
- 3.5 T -dependent ARPES data at (a) 150 K, (b) 250 K and (c) 300 K. The bulk valence band and the DC are shown as black and white dashed line. The solid white lines are drawn parallel to the Dirac point energy. At 300 K ARPES data, bottom edge of the bulk conduction band is shown by solid blue line to show the bulk band-gap of the compound. 49

3.6	The MDC second derivative plot of the ARPES data taken at (a) 150 K; (b) 250 K, and (c) 300 K. Solid red lines are drawn parallel to the top edge of the bulk valence band. At 150 K top edge of the bulk valence band lies at Fermi level indicating the bulk metallic phase. The position of bulk valence band top with respect to Dirac point energy are indicated by white arrow.	49
3.7	Scattering coming from the volume (red dot), volume+surface (blue dot) and corresponding fittings (black solid line) to calculate band-gap. . . .	54
4.1	(a) The unit cell of InBi compound. (b) The BZ structure and the high symmetry points along which DFT calculation is performed. (c) The band-structure along high symmetry points. The band-1 (red) and band-2 (blue) are only two bands that provide carriers' density at E_F . (d) The ab -planes of InBi. (e) The XRD peaks which originated from the ab plane. (Inset) The photograph of conical shape InBi single crystal. (f) The XPS spectrum of InBi	61
4.2	(a) $\rho(T)$ measured at 3–100 K with the application of 0–9 T magnetic field. (b)After performing $\frac{\partial \rho(T)}{\partial T}$ (to calculate turn-on temperature). The T_m and T_i are indicated in the inset figure. (c) The variation of T_m and T_i with the magnetic field. Triangle formed by T_m and T_i are shown by a pink shaded area.	62

- 4.3 (a) Calculated $MR\%$ with the application of 3 T, 6 T and 9 T magnetic field. (b) Experimental $\rho(T)$ without any magnetic field and different type of fitted functions. Data upto 20 K is shown in the inset figure. (c) Experimental and simulated $\rho(T)$ with the application of the 6 T magnetic field. The colour code for the different n remain same as previous. (d) Simulated $\rho(T)$ under the application of 0–9 T magnetic field. Experimental $\rho(T)$ (shown as black dashed lines) are plotted over the theoretically generated one. The $\rho_{turn-on}$ as a function of T_m is indicated by a solid magenta line. The $\frac{\partial \rho(T)}{\partial T}$ of the theoretically generated patterns are shown in the inset figure. (e) Variation of turn-on temperature as a function of B and the fitted pattern. (f) Simulated $\rho(6, T)$ with the variation of α 63
- 4.4 3D contour plot of simulated data. (a) $\rho(B, T)$ (b) $\frac{\partial [\rho(B, T)]}{\partial T}$ 64
- 4.5 The calculation of excitonic gap. (a) The $\log(\rho)$ vs T^{-1} fitting, the slope of the particular regions ($T_i < T < T_m$) are shown by the dashed magenta line. (b) The variation of excitonic gap with the magnetic field. 66
- 4.6 (a) The $\rho(B)$ measured at 3–100 K with the application of 0–9 T magnetic field. (b) The $MR\%$ as a function of B that is calculated from the experimental $\rho(B)$. (c) The $\log - \log$ plot of $MR\%$ as a function of $B/\rho(0, T)$. The fitted line based on the Kohler's law is shown in a solid magenta line. The fitted line for 3 K is separately shown in the inset figure. 73
- 4.7 The $\rho_{xy}(B)$ from +9 T to -9 T at (a) 3 K, (b) 10 K, (c) 25 K and (d) 50 K. (e) The $\rho_{xy}(B)$ from 0–9 T with the temperature range 3–50 K 74
- 4.8 (a) $\sigma_{xx}(B)$ and its corresponding fittings, (inset) logarithmic plot of $\sigma_{xx}(B)$ as a function of magnetic field and temperature in a 3D contour plot. (b) $\sigma_{xy}(B)$ and its corresponding fittings, (inset) logarithmic plot of $\sigma_{xy}(B)$ as a function of magnetic field and temperature in a 3D contour plot. (c) The temperature-dependent electron and hole density which are estimated from the two carrier model. (d) The temperature-dependent electron and hole mobility which are estimated from the two carrier model. 75

- 4.9 The Hall resistivity at 50 K. The experimental Hall data from +9 T $\rightarrow$ -9 T is indicated by the red line. The experimental Hall data from 0 T $\rightarrow$ +9 T and -9 T $\rightarrow$ 0 T are indicated by the black line. The result (for the complete cycle of the magnetic field) after smoothing by adjacent averaging is shown by the green line. 77
- 5.1 The bandstructure of the band-1 is shown in red. The allowed states marked by red shaded area denoted the electron-like pocket. The γ and α pockets are generated from the band-1. The bandstructure of the band-2 is shown in blue. The allowed states marked by blue shaded area denoted the hole-like pockets. The β and δ pockets are generated from the band-2. 80
- 5.2 (a) The electron pockets come from band-1. The γ and α sheets are lying at high symmetric Z and R points respectively. (b) The hole pockets come from band-2. The β and δ sheets are lying at high symmetric Γ and M points respectively. 81
- 5.3 Fermi sheets in k_x - k_y plane at several k_z cut. (a) Several k_x - k_y plane in 3D BZ where the 2D contours are plotted. (b)-(d) The contours in blue coming from band-2. the areas of β and δ sheets are continuously decreasing from CUT-1 to CUT-4. The arrow mark in CUT-1 indicates the extremum area of the corresponding pockets. (f)-(i) The contours in red coming from band-1. the areas of α and γ sheets are continuously increasing from CUT-5 to CUT-8. The arrow mark in CUT-8 indicates the extremum area of the corresponding pockets. 81
- 5.4 The FFT spectrum and SdH oscillation. (a) The FFT spectrum calculated at 7-15 T field from the second derivative of the MR data. The red arrow indicates the extremum orbits of the corresponding pockets from where frequency peaks are coming. (b) The actual MR data from where FFT is performed. (c)-(e) The deconvoluted spectrum coming from corresponding pocket at 3 K. 83

5.5	Data taken from Meyer <i>et al.</i> [121]. Angle dependent variation of three major frequencies F_β , F_γ and F_δ	84
5.6	The variation of FS from hole doping to electron doping. (a)-(e) The evolution of 3D BZ from hole doping to electron doping. (f) The shape of the γ pocket at $E = E_F$. (g)-(i) The evolution of α pocket from hole doped to electron doped. The extremum orbit parallel to k_x - k_y plane is shown by the red arrow. The substantial hole doping split the α pocket by two parts. (j) The shape of the β pocket at $E = E_F$. (k)-(m) The evolution of β pocket from hole doped to electron doped. The extremum orbit parallel to k_x - k_y plane is shown by red dotted line.	86
5.7	(a) Oscillatory components of the resistivity data (calculated from the 2 nd derivative) measured at several temperatures. (Inset) The enlarged view of data that lies within the orange colored rectangle. (b) The time scale spectra of F_γ derived at several temperatures.	88
5.8	Raw oscillations originate from the corresponding Fermi sheet at 3 K. (Left panel) Actual resistance data and the oscillations originate from the particular Fermi sheet as a function of inverse magnetic field. (Right panel) Actual resistance data and the oscillations originate from the particular Fermi sheet as a function of magnetic field.	89
5.9	(a) Calculation of m^* from T -dependent amplitude of SdH oscillation. (b) The amplitude-simulation using L-K formula to derive T_D	90
6.1	(Upper left) The BZ of InBi indicating the high symmetry points. (Upper right) The symmetry protected <i>type-II</i> Dirac cone along Γ - Z line. (Lower right) The evolution of bands parallel to the Γ - M direction with the variation of k_z	95
6.2	Photon energy dependent ARPES spectra parallel to the high symmetry line M - Γ - M	97

6.3	Extracted band structure for the particular k -path. The DFT generated band structure are shown by the dashed line. (Centre) The DFT generated 2D Dirac cone (lies parallel to <i>cut 5</i>)	98
6.4	(Left panel) Schematic of BZ indicating high symmetry points. (Middle panel) 2D dispersion of the Dirac cone in k_x - k_y plane (along <i>cut 5</i>). The symmetric energy-dispersion near Dirac point is indicated by the orange circle, (Right panel) the energy dispersion along Γ -Z- Γ -M plane. The asymmetric energy-dispersion near Dirac point is indicated by the orange circle	99
6.5	The surface state of InBi along M - Γ - M direction. The green circle indicates the position of bulk Dirac cone	100
6.6	Band dispersions obtained from low energy $k.p$ model. Electronic spectra obtained from the low energy $k.p$ model for InBi along (left) Γ -Z and (right) M' - Γ' - M' (parallel to M - Γ - M and A -Z- A) direction.	101
7.1	Unit cell of rhombohedral (space group: R-3m, 166) Bi_2Te_3 crystal. . . .	104
7.2	Simulated band-structure of the configurations: (a) pure Bi_2Te_3 compound, (b) Cu-substituted compound, (c) Cu-substituted with carrier neutral configuration and (d) Cu intercalated in the Van der Waal gap.	106

List of Tables

3.1	Frequency of the Raman modes at 100 K and 300 K of the compound $\text{Cu}_{0.1}\text{Bi}_{1.9}\text{Te}_3$	46
3.2	Resistivity data for Bi_2Te_3 thin film	54
5.1	Fermi sheets properties	83
5.2	Parameters derived from the F_γ oscillation. m^* , effective mass; T_D , Dingle temperature; τ , relaxation time and μ_q , quantum mobility.	90
