Structural and Electronic Properties of Topological Insulators and Nodal line Semimetals

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SAMBHAB DAN

DEPARTMENT OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY

(BANARAS HINDU UNIVERSITY)

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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

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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

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भा०प्रौ०सं०/(का०हि०वि०)/IIT (BHU)
वाराणसी/Varanasi-221005

भारतीय प्रौद्योगिकी संस्थान
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I would like to dedicate this thesis to my beloved family . . .

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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}, λ = 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 $Cu_{0.1}Bi_{1.9}Te_3$ 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 kz 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 kz 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.

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