ABSTRACT

HEWITT, ANDREW SCOTT. Coupling Organic Molecules to Topological Insulators. (Under the direction of Dr. Daniel Dougherty.)

Macroscopic systems displaying quantum behavior can be investigated to gain insights into the fundamental nature of our universe. Topological insulators (TIs) are a recent example of such systems exhibiting exotic physical phenomenon in condensed matter. These topologically nontrivial materials are bulk insulating and have spin-momentum locked surface states as a result of its interface with a normal insulator. The topological surface states (TSS) are guaranteed by the materials topological invariant, and for materials studied in this thesis, protected by time-reversal symmetry (TRS). The TSS exist in ambient conditions with no need for external applied fields allowing investigations of its nature relatively easy and obvious interest for spintronic devices. Organic molecules represent an electronic and magnetic knob by which one can tune the properties of the substrate of interest and are also of interest for spintronic applications. The organic-TI interface is a new unexplored playground to observe and probe novel physics.

The surface is a unique environment for each solid and must be characterized by surface sensitive techniques. Prototypical TIs of study have been the van der Waals (vdW) layered binary chalcogenides. Characterization of the surface of cleaved Bi$_2$Se$_3$ samples by X-ray photoemission spectroscopy (XPS) and angle-resolved photoemission spectroscopy (ARPES) show that coexisting surface terminations are probable if performed in air, while in-situ cleaves are terminated as expected along a vDW layer. The electronic structure depends on the surface termination illustrating the important question of surface effects on the TSS.

Breaking TRS in these systems is predicted to result in the quantum anomalous hall effect and topological magnetoelectric effects. Ferromagnetic TIs are expected to have a gapped TSS that can be measured by ARPES. We investigated bulk Cr-doping of the TI Bi$_{1.5}$Sb$_{0.5}$Te$_{1.7}$Se$_{1.3}$ (BSTS) studied by XPS and ARPES. Low-doped samples have detectable concentrations of Cr near the surface, however higher-doped samples show no evidence for Cr-dopants. Powder x-ray diffraction shows Cr$_x$Se$_y$ impurities in higher Cr-doped samples. This suggests that phase segregation is likely occurring and represents the general limitation of bulk-doping.

An alternative approach to breaking TRS can be attempted by adsorbing the magnetic molecules onto the surface. The paramagnetic organic molecule manganese phthalocyanine (MnPc) on the TI Bi$_2$Te$_3$ was characterized by a combination of ARPES and scanning tunneling spectroscopy (STS). We observe the emergence of a new hybrid-interface state resulting from the mixing of the MnPc orbitals with the
substrate electronic orbitals. Other studies of phthalocyanine molecules on TIs in addition to ours highlight the possibility of emerging electronic states at the organic-TI interface.
DEDICATION

To my Family
BIOGRAPHY

Andy Hewitt received his Bachelors of Science in physics at North Carolina State University. During his undergraduate career his work on the growth and characterization of organic thin films earned 3 undergraduate research awards and 2 summer internships at the National Institute of Science and Technology in Gaithersburg, MD. He completed his Masters of Science in physics in 2014 at N.C. State University and started a multi-disciplinary collaboration to grow and characterize Topological Insulators. The main instruments he’s used to study these systems are photoelectron spectroscopy and scanning tunneling microscopy/spectroscopy.
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I’d like to thank my family for their love and support throughout my life and this journey. My mom has always encouraged me to push myself to be a better person and student. My dad inspired me to pursue a career in science from a young age. My brother and sister have always provided love and support through the roller-coaster of emotions that is the graduate school experience. Without your support I would not have been able to succeed.

My friends in physics and in the Dougherty group have also provided much support and guidance. Jingying helped to train me on the STM and spent long hours acquiring data by my side in the lab. She has a solid understanding of surface science physics and great insight. I’d also like to thank Terry for inspiring me to be the best possible scientist I can be. From helping me fixing my car numerous times, displaying his brilliance for the scientific process, and convincing me to continue for my Ph.D., I couldn’t have done this without your friendship. Ben, Matt, and Jon have also provided support during this process as well as many good jam sessions.

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CHAPTER 1 TOPOLOGICAL INSULATORS

1.1 Introduction to Topological Insulators

Technology in our everyday life mainly consists of electronic devices in which electrical current is used to operate a device, however, it was only recently discovered that spin-dependent phenomena can be realized in functional devices.[3] Memory devices (i.e. hard disk drives) rely on a change in the resistance of sandwiched ferromagnetic thin films to store information. This represents a paradigm shift to exploit the quantum mechanical nature of spin. Of course, to operate and build logic circuits to make use of this phenomenon electrical current is needed. It was unveiled in the past decade that there exists a class of materials which harbor spin-textured gapless surface states on a bulk insulating material existing in ambient conditions with no external magnetic field required as guaranteed by the materials topological invariant.[4, 5] These topological insulators (TIs) are a promising candidate for low power consumption devices (e.g. transistors).[6, 7] Experiments on their spin to charge current conversion efficiency and spin polarization have shown their promise for spintronic devices[8, 9], in addition to theoretical and experimental work showing controlled functionality of topological states with an electric field.[10, 11] Furthermore, exotic phenomena such as the magnetic monopole and majorana fermions have been predicted to be observable in TI systems.[12, 13]

TIs are a condensed matter phenomenon that was first discovered in the 1980s in the two-dimensional (2D) integer and fractional quantum hall states.[14] These materials are manifestations of topological invariants which protect their edge states such that the quantization of the Hall conductivity has been measured to 1 part in 10^9 and are physically understood in terms of its Berry phase.[5, 15] It is interesting and worth noting that the Berry phase was first discovered for quantum adiabatic transport of particles in a slowly varying applied field before later being applied to Bloch wave functions.

While the integer quantum hall effect (IQHE) requires an external magnetic field to be applied in order to observe the edge states, the experimental discovery of the spin hall effect, transverse spin current under an electric field, in nonmagnetic systems in 2004 was a turning point in topological condensed matter community.[16] This showed that interesting spin phenomenon can be realized in materials without the need of large magnetic fields. The quantized version of the spin hall effect in an insulator (QSHE), which would provide chiral spin-polarized edge states, was proposed a year later involving a model of graphene with spin-orbit coupling (SOC).[17] however the SOC in graphene is too small to allow experimental observation of the predicted behavior of this material. An independent proposal for the QSHE by Bernevig, Hughes, and Zhang in 2006 in thin layers of HgTe/CdTe[18] and was experimentally realized the following year by König et al.[19]

Theoretical and experimental studies beginning in 2007 have generalized this emergent quantum state to three-dimensions (3D) and demonstrated the topological nature of the surface states.[20] Since
then, TIs have become an active research area in condensed matter from both theory and experiments. As this is a relatively new field, there is a rush to publish the ‘more exciting’ results leaving basic surface science questions largely unaddressed. This rapidly expanding field requires careful and diligent sample characterization because although its quantum phenomena are guaranteed by its invariant, real world conditions can complicate the study of the interesting TI physics. The new results of this thesis are largely focused upon identifying surface phenomena that interfere with access to TI physics. These include unusual surface termination (Chapter 3), bulk dopant segregation (Chapter 4), and topologically trivial adsorbate-induced interface states (Chapter 5).

In the present Chapter, a brief background in solid states physics is provided focusing on the concepts of a crystalline solid and its electronic structure that are most relevant to TI studies. This is followed by an introduction to the topological band theory of solids where the $\mathbb{Z}_2$ topological invariant, time-reversal symmetry, and TI properties are discussed. Next, a historical perspective of experimental evidence for 3D TIs is given for context on the approaches used for controlling and modifying the properties of TIs. This leads into a section highlighting the current materials science challenges for synthesis and characterization of these materials. A section on molecular orbital (MO) theory is provided illustrating the advantages of using organic molecules as an alternative approach to controlling and modifying TIs. Finally, an overview of the literature of the experimental results of organic-TI interfaces is discussed.

1.2 Crystallography Background

Crystallography was celebrated worldwide in 2014 as the International Year of Crystallography being recognized by the United Nations for, “its importance in our understanding of the material nature of the world”. The atomic building blocks of our universe are of course too small to be imaged optically but can be detected by diffracting high energy photons from a periodic array of atoms revealing their physical structure. This thesis consists of primarily of experimental studies of single crystals and a background of physics of solid states will be of use.

We begin by considering a general periodic array of atoms in 3D which consists of all points with positions vectors of the form

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3$$

where $\mathbf{a}_i$ are any three vectors not in the same plane and $n_i$ range through all integer values. This defines the Bravais lattice structure of a single crystal where the lattice constants, $a_i$, are typically on the order of Ångstroms. The primitive unit cell, called the Wigner-Seitz cell, has the same symmetry of the Bravais lattice but is encloses a closer region of space about a lattice point than to any other point in the lattice,
and is often chosen to describe the crystal structure. The diffraction of light in these crystallographic materials rely on photons interfering constructively directly probing its periodicity.

The reciprocal lattice is a fundamental concept in condensed matter and is defined to be a dual vector space to the real space lattice using the basis vectors:

\[
\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}
\]

\[
\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}
\]

\[
\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}
\]

The reciprocal lattice can then be described by the set of all wave vectors, where \(k_i\) are integers

\[
\mathbf{K} = k_1 \mathbf{b}_1 + k_2 \mathbf{b}_2 + k_3 \mathbf{b}_3
\]

The first Brillouin zone (BZ) is the Wigner-Seitz primitive cell of the reciprocal lattice and while they refer to identical geometries the former is typically used in the condensed matter community. Since real materials are made up of some Avogadro’s number of atoms the consideration of this system as infinite is justified, although it is important to examine the effects of the boundaries (i.e. surfaces). The plane of the BZ that defines the surface is indicated by its miller indices \((hkl)\) corresponding to a plane normal to the reciprocal lattice vector \(h \mathbf{b}_1 + k \mathbf{b}_2 + l \mathbf{b}_3\). It is important to note that complete knowledge of all observables of the electrons (e.g. dispersion) is contained within this unit cell.

The electronic structure of these crystalline solids can be approximated with an independent electron model considering a one-electron potential \(U(r)\). The electrons that are solutions to the Schrodinger equation with a periodic potential are referred to as Bloch electrons. These allowed electronic states form energy bands which is Bloch band theory. The next section shows how this approximation can be used to obtain the electronic band structure of solids.

1.3 Tight-Binding Model
The Schrodinger equation for the one-electron Hamiltonian, $\mathcal{H}$, with a periodic potential $U(r + R) = U(r)$ is:

$$ \mathcal{H}\psi = \left( -\frac{\hbar^2}{2m} \nabla^2 + U(r) \right) \psi = E\psi $$ \hspace{1cm} (1.6)

The Bloch wavefunction satisfies the Schrodinger equation for a periodic potential which gives a good approximation for the states of an electron in single crystals.[21]

$$ \psi(r + R) = e^{ikr}\psi(r) $$ \hspace{1cm} (1.7)

Bands of allowed states are formed in solid crystalline materials where their energetic position in reciprocal space (henceforth $k$-space) depend on the crystals symmetry and chemical properties. Conductors have overlapping conduction and valence bands whereas insulators, which include semiconductors, have a gap in these bands.

The tight-binding model begins by considering a localized wave function at each atomic site in a lattice. In the single-particle view, first suppose we have a 1D lattice of $N$ atoms separated by a distance, $a$. We can write the Bloch wave function as:

$$ |\Psi\rangle = \frac{1}{\sqrt{N}} \sum_R e^{ikR} |\Phi_s(r - R)\rangle $$ \hspace{1cm} (1.8)

where the atomic positions are labelled by $R$ and only an $s$-orbital basis $\Phi_s$ is being considered. The goal is to solve the time-independent Schrodinger equation ($\mathcal{H}|\Psi\rangle = E|\Psi\rangle$) considering only summing over nearest-neighbors and ignoring direct overlap ($<\Phi_s|\Phi_s(r - R)\rangle = 0$). To do this, we project the $s$-orbital as follows:

$$ <\Phi_s|\mathcal{H}|\Psi\rangle = E <\Phi_s|\Psi\rangle $$ \hspace{1cm} (1.9)

where the wave function is

$$ |\Psi\rangle = \frac{1}{\sqrt{N}} (|\Phi_s\rangle + e^{ika}|\Phi_s(r - a)\rangle + e^{-ika}|\Phi_s(r + a)\rangle) $$ \hspace{1cm} (1.10)

which includes the nearest neighbors at $r + a$ and $r - a$. The left hand side can then be written as:
\[
< \Phi_s(\mathbf{r})|\mathcal{H}|\Psi > = \frac{1}{\sqrt{N}} ( < \Phi_s|\mathcal{H}|\Phi_s > + e^{ika} < \Phi_s|\mathcal{H}|\Phi_s(r-a) > + e^{-ika} < \Phi_s|\mathcal{H}|\Phi_s(r+a) > )
\]

This reduces to

\[
< \Phi_s(\mathbf{r})|\mathcal{H}|\Psi > = \frac{1}{\sqrt{N}} (E_s + te^{ika} + te^{-ika})
\]

where \(E_s\) is the energy of the \(s\)-orbital and \(t\) is the hopping term which characterizes the tunneling of an electron from one site to its nearest-neighbor. The right hand side of Equation 1.9 is:

\[
E < \Phi_s|\Psi > = \frac{1}{\sqrt{N}} (E < \Phi_s|\Phi_s > + E e^{ika} < \Phi_s|\Phi_s(r-a) > + E e^{-ika} < \Phi_s|\Phi_s(r+a) >)
\]

The last two terms are equal to zero and then is reduced to

\[
E < \Phi_s|\Psi > \geq \frac{1}{\sqrt{N}} E
\]

And putting the left and right hand side back together

\[
\frac{1}{\sqrt{N}} (E_s + te^{ika} + te^{-ika}) = \frac{1}{\sqrt{N}} E
\]

And finally solving for \(E\) we get

\[
E = E_s - 2tcos(ka)
\]

This is showing the dispersion relation, \(E(k)\), and the allowed energy states that make up the band structure in a crystal. While this is only a 1D model with a single band, it qualitatively shows how a tight-binding approach can be used to elucidate the band structure of a material.

**1.4 Topological Band Theory**
The insulating state of crystalline solids has a chemical potential which falls in the electronic energy gap of the bulk Bloch bands. We know that a semiconductor also has a band gap, and therefore can be regarded as an insulator and so the question arises: Are all insulators fundamentally the same? The answer is surprisingly no, and the fundamental property that distinguishes these states of matter is the topology of the band structure.

The IQHE is an insulator with a nontrivial topology, in which electrons with quantized Landau levels drift with cyclotron orbit frequency under an applied field. It was realized by Thouless, Kohmoto, Nightingale, and den Nijs (TKNN) that the IQHE is topologically nontrivial and they showed that in this system the \( k \)-space can be mapped to a nontrivial Hilbert space and its topology can be specified by an integer topological invariant. The connection of this 2D TI and the 3D TI is through the Chern invariant and can be physically understood in terms of the Berry phase.[4, 5, 22] It is imperative to emphasis that the topological \( Z_2 \) invariant from 2D to 3D is a nontrivial generalization. Physically this can be understood by noting that by stacking 2D TIs vertically does not guarantee chiral edge states on the top and bottom surfaces. Therefore, these are unique phases of matter but have important parallels and the pedagogical account provides context for the recent rapid development in the TI field.

The Berry phase is a modification to the wave-function distinct from its dynamical phase. To see this, consider the Bloch Hamiltonian:

\[
\mathcal{H}\psi_{nk} = E_{nk}\psi_{nk}
\]

for the \( n \)th eigenstate \( \psi \) at position \( k \). The Bloch theorem allows this to be written as a plane wave times a function with the same periodicity of Bravais lattice:

\[
\psi_{nk}(r) = e^{ikr}u_{nk}(r)
\]

where \( u_{nk}(r + R) = u_{nk}(r) \) for all \( R \) in the Bravais lattice. The Berry connection, \( A_n \), is given by:

\[
A_n = i < \psi_{nk}\nabla_k|\psi_{nk}>
\]

When \( k \) is transported around a closed loop, such as an electron in a cyclotron motion, \( |\psi_{nk}> \) acquires a Berry phase which is calculated by the line integral of the Berry connection. That is, the quantum-
mechanical system accumulates a phase factor after completing a closed path in $k$-space. The curl of the Berry connection defined as the Berry curvature, $\mathbf{F}_m$:

$$\mathbf{F}_m = \nabla_m \times \mathbf{A}_m$$  \hspace{1cm} 1.20

and the TKNN invariant, also called the Chern number, is the integral of the Berry curvature over the Brillouin zone:

$$n_m = \frac{1}{2\pi} \int d^2k \mathbf{F}_m$$  \hspace{1cm} 1.21

That is, it is equal to the Berry phase of the Bloch wavefunction calculated around the Brillouin zone boundary divided by $2\pi$. The total Chern number summed over all the contribution from the $n$th band, $n_m$ is equal to $n$:

$$n = \sum_{m=1}^{N} n_m$$  \hspace{1cm} 1.22

is connected to the Hall conductivity such that $\sigma_{xy} = Ne^2/h$, where $n = N$. This tells us that the quantum Hall state is a TRS-breaking system an is often referred to as a Chern insulator. The quantum spin Hall state is the spin version of the IQHE and can be thought of as two copies of the quantum Hall system with spin-polarized chiral edge states, recovering the TRS of the system.[4] Kane and Mele showed that the topological invariant for TRS systems can be characterized by a $Z_2$ index[23] which is formulated below.

A TRS system is can be described by first introducing the time-reversal operator which is antiunitary and its form is given below:

$$\Theta = e^{i\pi S_i}K,$$  \hspace{1cm} 1.23

where $S_i$ are the Pauli spin matrices and $K$ is the complex conjugate operator. When $\mathcal{H}$ preserves TRS then $\mathcal{H}(k)$ satisfies the following relation:
\[
\Theta \mathcal{H}(\mathbf{k}) \Theta^{-1} = \mathcal{H}(-\mathbf{k})
\]

where \( \mathbf{k} \) represent Bloch wave vectors. The Bloch energy bands are then degenerate at the time-reversal invariant momentum (TRIM) in the BZ and are referred to as Kramers pairs.\[^4\] In a 2D BZ there are 4 TRIMs and for the 3D BZ there are 8 TRIMs.\[^24\] To formulate the \( Z_2 \) topological invariant and its connection to the Berry phase, a unitary matrix is defined:

\[
w_{mn}(\mathbf{k}) = \langle u_{m,-\mathbf{k}} | \Theta | u_{n,\mathbf{k}} \rangle
\]

where \( m, n \) indicate the quantum numbers and \( \mathbf{k} \) is the momentum quantum number for the respective eigenstates. The Bloch states are then related by:

\[
|u_{m,\mathbf{k}}\rangle = \sum_n w_{mn}^*(\mathbf{k}) \Theta |u_{n,\mathbf{k}}\rangle
\]

The unitary matrix has the following relation:

\[
w_{nm}(-\mathbf{k}) = -w_{mn}(\mathbf{k})
\]

which means that it becomes antisymmetric at a TRIM \( \Lambda \). For a skew-symmetric matrix, the square of a polynomial can be written for its matrix entries. The value of the polynomial applied to the coefficients of the matrix is called the pfaffian. In general, the determinant of an antisymmetric matrix is equal to the square of its Pfaffian (\( \text{Pf}(A)^2 = \det(A) \))[\(^4\), \(^5\)]

\[
\delta_\alpha = \frac{\text{Pf}[w(\Lambda_\alpha)]}{\sqrt{\text{Det}[w(\Lambda_\alpha)]}} = \pm 1
\]

The \( Z_2 \) invariant, \( \nu \), for a 2D system is then:

\[
(-1)^\nu = \prod_{\alpha=1}^{4} \delta_\alpha
\]

The number of Kramers pairs of edge modes, \( N_K \), is related to the change in the \( Z_2 \) index across the interface by:
\[ N_K = \Delta \nu \mod 2 \]  

The topological invariant $Z_2$ index can be thought of as the number of times an edge states crosses the Fermi level between 0 and $\pi/a$ as even or odd, where $a$ is the crystal’s lattice constant.[4] The $Z_2$ invariant in a 3D crystal with inversion symmetry has parity eigenstates with eigenvalues $\xi_m(\Lambda_a) = \pm 1$ and is then:

\[ \delta_a = \prod_m \xi_m(\Lambda_a) \]  

The ingredients for a TI are now given by a bulk insulating material that has an odd number of inversions at the TRIM. The topological invariant must change at the boundary of a trivial and nontrivial insulator resulting in the closing of the energy gap.

Surface states can arise when the potential barrier formed at the crystal termination is such that an allowed state exists which decays exponentially away from the surface as shown by Shockley.[25] These states are confined only to the surface and they are often referred to as a 2D electron-gas (2DEG). The atomic layer at the termination of the crystal has some electron density above the surface and the near surface charges will arrange such that an electric dipole is formed at the surface. When a strong SOC is present at the surface,

\[ \mathcal{H}_{\text{SOC}} \propto (\mathbf{E} \times \mathbf{p}) \cdot \sigma \]  

the potential gradient can create a Rashba splitting of the spin degenerate surface state such as on the Au(111) surface.
Until 2015, the Rashba split surface states of Au(111) were thought to be topologically distinct from the TSS, often being described as a clear example of a topologically trivial surface state. This is now being disputed as theoretical and experimental investigations have claimed these states to be topologically derived surface states again demonstrating the very fast pace of this field.[26] The often quoted distinction relied on the TSS being linearly dispersing, at least near the Dirac point, and these new results indicate that the warping term is strong enough to distort the dispersion. This occurs in Bi$_2$Te$_3$ away from the Dirac point where the Fermi surface evolves from a cone-like to snowflake-like due to the strength of the $\lambda$ SOC term. The surface BZ of TIs studied in this thesis is shown in Figure 1.2 with the symmetry points labelled and a circle with arrows indicating the spin texture of the TSS which also illustrate the forbidden backscattering in absence of a spin-flip mechanism.

**Figure 1.1** Cartoon picture of an electronic state confined to the surface of a material (left) which decays exponentially into the bulk and vacuum. The topological invariant must change at the surface of a TI which closes the energy gap resulting in the spin-textured TSS.
1.5 Model Hamiltonian for Binary TIs

The theoretical development for TR invariant systems characterized by a $Z_2$ topological index used the tight-binding model for graphene with strong spin-orbit coupling. This model includes the $\pi$-orbitals of the honeycomb carbon atoms near K and K’ in the hexagonal BZ, considers the symmetry of the lattice, and includes spin with TRS spin-orbit interactions. Kane and Mele predicted that for a finite SOC the material would become a quantum spin hall insulator, however the intrinsic SOC is very weak and difficult to observe experimentally. An independent proposal by Berneving, Hughes, and Zhang (BHZ model) considered the $s$- and $p$-orbitals of HgTe with a cubic zinc-blende crystal structure lead to the first experimental discovery of the first 2D TI.

The band structure of the binary chalcogenide 3D TIs, $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_2\text{Se}_3$, was examined in detail by Liu et al. and derived the model Hamiltonian for these systems in a few ways.[1] The important symmetry for these 3D TIs, in addition to TRS, is inversion symmetry. The unit cell has two equivalent Bi atoms and two equivalent Se or Te atoms and one inequivalent Se or Te atom where the inversion occurs. Only the p-orbitals are considered for in their band structure calculation as these are the outermost electron shells. The bonding within the unit cell is of covalent nature and is stronger than the van der Waals force that holds the layers together. I will outline the inversion of the Bi and Te/Se bands following the symmetry arguments in Section II from Lui et al.

The Bi atomic $p$-orbitals are higher in energy than the Se/Te atomic $p$-orbitals and then considering the bonds formed within a QL, the hybridized Bi states are pushed up while the Se states are
pushed down. Since the inversion center Se/Te atom forms a bond with both Bi atoms, it is more stable and therefore lower in energy and no longer being considered. The new states consist of bonding and antibonding orbitals and it is convenient to write these orbitals in terms of a definitive parity. The parity operation flips the sign of one spatial coordinate and the parity operator is \( P \). This can be seen by considering a \( \pi \)-bond formed by two \( p_z \) orbitals making bonding states, \( |\pi> \) (see Figure 1.6 (c)) have a parity of -1 and antibonding states, \( |\pi^*> \), have parity +1. That is

\[
P|\pi> = -|\pi>
\]
\[
P|\pi^*> = +|\pi^*> \quad 1.33
\]

The bonding and antibonding states are written as a linear combination of the equivalent atomic orbitals so that 4 new states are formed. The bonding states of Bi are pushed down while the antibonding states of Se/Te are pushed up towards the Fermi level. As the crystal structure is layered, the \( p_z \) orbitals have a different interaction than the \( p_x \) and \( p_y \) orbitals, and they are pushed toward the Fermi level. That is, before taking SOC into account, the conduction band mainly consists of Bi \( p_z \) orbitals while the valence band mainly consists of Se \( p_z \) orbitals. The SOC couples the \( p_z \) orbitals to a linear combination of \( p_x \) and \( p_y \) orbitals, and when strong enough will induce a level crossing of states of opposite parity. So, the inversion of these states of mixed atomic-orbitals and opposite parity at a time-reversal invariant momenta distinguishes these materials as topologically nontrivial insulators.

Note that the inversion occurs only at a single point in the BZ and so, considering only a single band, will have positive parity and negative parity at various points in the BZ. Because the parity eigenvalues are discrete, there cannot be a smooth transformation from one eigenvalue to the other. In this sense the bulk bands are of mixed character and are a hybridization of conduction and valence bands. Additionally, it is important to note here that insulating is defined as an energy gap between conduction and valence bands at every point in the BZ and does not necessarily mean the material will be electrically insulating. In fact, a major materials science challenge is to be able to synthesize crystals with very low bulk free carriers.

The low-energy effective Hamiltonian for the binary TIs in the bulk was derived by Liu et al.[1] by symmetry principles and \( k \cdot p \) perturbation theory. It is a four band model that effectively describes the behavior of the conduction and valence bands near the Gamma-point.

\[
\mathcal{H}(k) = \epsilon_{0\perp}(k)I_{4\times4} + \begin{pmatrix}
M(k) & A_1 k_z & 0 & A_2 k_-\\
A_1 k_z & -M(k) & A_2 k_- & 0 \\
0 & A_2 k_+ & M(k) & -A_1 k_z \\
A_2 k_+ & 0 & -A_1 k_z & -M(k)
\end{pmatrix} + o(k^2) \quad 1.35
\]
where \( k_\pm = k_x \pm ik_y, \varepsilon_0(k) = C + D_1 k_x^2 + D_2 k_y^2, \) and \( M(k) = M - B_1 k_x^2 - B_2 k_y^2. \) The coefficients used for the band structure plots are given in table IV of Liu et al.[1]

The model Hamiltonian is written in the basis of \(|P_1^\pm, \pm \frac{1}{2}\rangle\) and \(|P_2^\pm, \pm \frac{1}{2}\rangle\), where \(|P_1^\pm, \pm \frac{1}{2}\rangle = \frac{1}{\sqrt{2}} (|B_{\pm \frac{1}{2}}\rangle \mp |B_{\pm \frac{1}{2}}^\prime\rangle)\) is the combination of bonding and antibonding orbitals for bismuth p-orbitals and \(|P_2^\pm, \pm \frac{1}{2}\rangle = \frac{1}{\sqrt{2}} (|S_{\pm \frac{1}{2}}\rangle \mp |S_{\pm \frac{1}{2}}^\prime\rangle)\) is a combination of bonding and antibonding orbitals for selenium giving a definitive parity for each state. Diagonalizing the matrix gives the eigenvalues and eigenvectors for these states and is shown in Figure 1.3. The order of the spin-degenerate bands is inverted near \( k=0 \) while maintaining an energy gap which characterizes the nontrivial topology of these materials.

![Energy dispersion of Bi₂Te₃](image)

**Figure 1.3** Plot of the four band model Hamiltonian for Bi₂Te₃ from Liu et al.[1] The blue and red circles represent the orbital character of the lower (valence) and upper (conduction) bands. An inversion of the orbital character of the bands occurs near the Gamma-point (\( k||=0 \)) illustrating the nontrivial topology of this material’s band structure.

The topological surface states are obtained by diagonalizing the Hamiltonian in Equation 1.35 with an open boundary condition resulting in the following surface Hamiltonian[1, 20]
\[ \mathcal{H}(\mathbf{k}) = E_0(k) + v_k(k_x\sigma_y - k_y\sigma_x) + \frac{\lambda}{2}(k_x^2 + k_y^2)\sigma_z \]  \hspace{1cm} (1.36)

where \( E_0(k) \) is the energetic position of the Dirac point, \( k_{\pm} = k_x \pm ik_y \), \( v_k \) is the Fermi velocity, and \( \lambda \) is a SOC warping parameter. The solution then gives the surface band dispersion relation:

\[ E_{\pm}(\mathbf{k}) = E_0(k) \pm \sqrt{v_k^2k^2 + \lambda^2k^6\cos^6(3\theta)} \]  \hspace{1cm} (1.37)

where \( \pm \) represent the unoccupied and occupied bands which touch at the Dirac point. The topological surface states are spin-chiral and gapless as a result of applying these boundary conditions (illustrated in Figure 1.2). Notice that the energy of the Dirac fermions is proportional to their velocity, i.e. linear dispersion, in contrast to the 2DEG which disperses quadratically (\( E(k) \propto v^2 \)).

The dispersion of the surface states can be directly measured by photoelectron spectroscopy and scanning tunneling microscopy as described in the next Chapter and the next section overviews the use of these experimental techniques in the discovery of 3D TIs.

### 1.6 Experimental Evidence for 3D Topological Insulators

What experimental evidence is necessary in order to determine that a material is indeed a TI? This requires a surface sensitive technique to determine the existence of a TSS and that the material is bulk-insulating. The instrumental workhorse for probing TIs has been angle-resolved photoemission spectroscopy (ARPES) which maps photoemitted electrons energy to their position in \( k \)-space (see Chp. 2). Spin-resolved data is necessary to determine that the TSS electron’s spin is locked perpendicularly to their momenta. As will be discussed below, synthesis of TIs has a materials science challenge of reducing charge carriers, and only it is only when the sample is sufficiently insulating with high surface carrier mobility that a material can be confirmed as a TI through transport. To do so it must be shown that the sample has transport occurring through the surface and that the carriers are indeed Dirac fermions. These are completed through sample-size dependence on conductance and determining the \( \pi \) Berry phase from quantum oscillations.\[^{[19, 27]}\]

Experimental proof of a strong 3D TI was first achieved using photoelectron spectroscopy to map the 2D topological surface state in the alloy Bi\(_{1-x}\)Sb\(_x\).[28] Bismuth is a semimetal which is where the BCB and BVB touch, with topologically trivial surface states. When Antimony is substituted in at concentrations of \( x > 4\% \), these bands separate and the material becomes a trivial insulator. Increasing the Sb concentration to \( x > 8\% \) pulls the conduction band minima below the valence band maxima.
resulting in a quantum phase transition to a nontrivial insulator and consequently, a nontrivial surface state appears in addition to the trivial surface states of Bi. To prove it’s a strong 3D TI, resistivity as function of temperature for Sb concentrations of x=0 and x =0.1 is presented showing the semimetallic and insulating character, respectively. The topological nature of the surface state was determined by ARPES mapping the near Ef photoemitted electrons at the TRIM which showed a Kramers degenerate point. The TSS was further supported by varying the incident photon energy which allows probing in the direction perpendicular to the surface and found that this feature does not disperse (i.e. it’s a surface state). These measurements are consistent with a strong 3D TI and was quickly confirmed when spin-resolved ARPES provided the first direct evidence of a π Berry phase by showing the spin polarization indeed rotates by 360° around the Fermi surface.[29]

The complex surface state structure of Bi$_{1-x}$Sb$_x$ make this material an unsuitable candidate for detailed studies of the interesting physics associated with the TSS as it coexists with trivial surface states. TIs with a single TSS were predicted by Zhang et al. in the binary class of binary materials Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$, the same year proposing a low-energy effective Hamiltonian model to describe the bulk band structure.[1] Experimental photoelectron spectroscopy studies of these materials quickly confirmed them to be strong 3D TIs. These quickly became the prototypical TIs as the synthesis of binary phases of materials is simpler in principal and can produce higher purity samples. The $Z_2$ topological invariant is (1;000) which supports a single TSS centered at the Γ point of the surface BZ which ideally provides a simple topological Dirac cone to experimentally probe. However, in practice there are inherent challenges in accessing the TSS in each of these systems which will be addressed below.

1.7 Breaking Time-Reversal Symmetry

The $Z_2$ topological invariant in strong 3D TIs guarantees a gapless surface state unless TRS is broken. Ferromagnetic ordering mediated by the surface Dirac electrons has been proposed theoretically to break TRS where the exchange coupling of the Dirac electron spin, $\sigma$, and the localized spin of the magnetic impurity, $S$, are modeled by the Hamiltonian:

$$\mathcal{H} = \hbar v (k \times \hat{z}) \cdot \sigma - J n_0 S_z \sigma_z$$  \hspace{1cm} (1.38)

where $v$ is the fermi velocity, $\sigma_i$ are the Pauli matricies, $J$ is the exchange interaction, $n_0$ is the average dopant density. The first term is the massless Dirac Hamiltonian describing the TSS and the second term is a perturbation due to an exchanged coupled magnetic impurity which opwns a gap at the original Dirac point. This is for the simple case of a homogenous ferromagnetic state with magnetization parallel to the surface normal $\hat{z}$.
When TRS is broken, a gap opens in the TSS resulting in the quantum anomalous hall effect (QAHE), that is a quantized Hall effect without an external magnetic field.[30] The surface state dispersion can then be written:

\[ E_{\pm}(k) = E_D \pm \sqrt{(\hbar v)^2 k^2 + \Delta^2} \]

where \( E_D \) is the energy of the Dirac point and \( \Delta = Jn_0 S_z \sigma_z / 2 \) is the size of the magnetically induced Dirac-mass gap.[31]

The approaches to breaking TRS have been to bulk-dope the TI during the synthesis process and more recently organic molecules have been used.[32-37] Bulk-doping with magnetic impurities may be a suitable route for this magnetic dopant approach as ferromagnetic ordering with perpendicular magnetic anisotropies has been achieved.[38, 39] However, because the TSS exists at the surface it may be more advantageous to use magnetic organic molecules deposited on the surface to elucidate the interaction of the TSS with a magnetic impurity.[40]

The nature of topology in condensed matter can then be investigated as it is TRS that guarantees the existence of a TSS. Understanding how magnetic dopants interact with the TSS is important. An indication of breaking TRS is a gap opening in the TSS as the spin degeneracy at the Dirac point is lifted. The opening of a gap in the TSS has been also been studied by ARPES and has been found in TIs that lack the out of plane ferromagnetism required to break TRS, possible caused by impurity-induced resonance states.[41] Transport measurements have possibly observed the quantum anomalous Hall effect in magnetically doped TIs although at the very low temperature of \( \sim 30 \) mK.[42] Thus, there are a lot of opportunities to investigate this symmetry breaking in these systems, particularly in the choice of magnetic impurity, as well as understanding the impact of nonmagnetic impurities in the formation of a gapped surface state.

1.8 Surface Science Challenges for TI Research

Beginning with Bi$_2$Se$_3$, materials science challenges in the growth and surface complexities (e.g. aging effects[43]) have provided opportunities for surface scientists to address. In particular, the as-grown Bi$_2$Se$_3$ single crystals are degenerately \( n \)-doped due to Se-vacancies with bulk carrier densities on the order of \( 10^{19} \) cm\(^{-3} \) resulting in the chemical potential falling in the conduction band.[44] Distinguishing the surface and bulk carriers is simpler experimentally when the \( E_F \) is in the bulk band gap for transport measurements. It’s been shown that the chemical potential can be tuned through bulk-doping with Ca reducing the number of \( n \)-type carriers.[29] This introduces other issues in probing the Dirac cone physics, such as strong scattering, suggesting alternative methods of doping.[45] Additional complexities
are present as strong band bending at the surface of Bi$_2$Se$_3$ has been shown to create a coexisting 2-DEG with the TSS.[43] Furthermore, it is expected that cleaving this material would result in a Se-terminated surface, as these are the layers that are bound by the weaker vdW forces. However, as will be shown in Chapter 3, cleaving Bi$_2$Se$_3$ can result in coexisting Bi- and Se-terminated which strongly modifies the valence band structure.[46]

Bi$_2$Te$_3$ alleviates some of the synthesis issues, as it can be grown in both n- and p-type by varying the composition concentration of the initial growth, however the carrier density is still difficult to reduce. Additionally, the Dirac point is below the top of the M-shaped valence band. This presents an experimental challenge in accessing the interesting physics of the TSS as, for example, scattering vectors between the TSS and BVB are available making quasiparticle interference analysis challenging. Additionally, due to strong SOC from the Te, the TSS becomes warped from conical to a snowflake-like shape away from the Dirac point. Contrarily, the TSS of Bi$_2$Se$_3$ is conical far away from the Dirac point and above the BVB maximum which is ideal to probe the TSS. However, as mentioned earlier this material is difficult to synthesize as an insulator.

It is interesting from a pedagogical viewpoint that the ternary tetradymite TI Bi$_2$Te$_2$Se was subsequently found to be naturally grown with large bulk resistivity and then expanded to the quaternary tetradymite solid solution of Bi$_{2-x}$Sb$_x$Te$_{2-y}$Se$_y$ (BSTS), all of which have a hexagonal BZ with a single Dirac cone at the Γ-point. Altering the composition of BSTS addresses many of the issues inherent in binary TIs, specifically by having the chemical potential fall in the band gap and to Dirac point pulled above the top of the BVB. These chalcogenide compounds crystallize in a tetradymite structure which consists of van-Der Waals (vdW) bonded quintuple layer (QL) (e.g. Se-Bi-Se-Bi-Se) stacked in an A-B-C-A-B-C manner so that the unit cell encompasses three QLs.
Bulk-doping has been the typical approach used to modify the properties of TIs where dopants may be substituted at a lattice point or intercalate between the QLs. As is shown in Chapter 4, issues of phase-segregation can complicate the synthesis process. This is illustrative of some of the basic materials science challenges that have yet to be addressed in this new and exciting field. The next section outlines an alternative approach which is to use organic molecules.

1.9 Molecular Orbital Theory

Organic molecules are another avenue for controlling and modifying the properties of TIs and is a term which generally applies to hydrocarbon based molecules. One advantage to this approach is the chemical tunability offered by modifying some molecule constituent changing its physical properties. The phthalocyanine molecule is a dye used in commercial applications and one of the most studied molecules for its optical, electronic, and magnetic properties.\[47, 48\] It is a planar molecule consisting of aromatic macrocycles and substitution of a central transition-metal atom allows for tuning of its electronic and magnetic properties. In this section molecular orbital theory will be used to understand the properties of MPcs.

**Figure 1.4** Crystal structure of layered binary TIs showing the unit cell and QL stacking (a). The hexagonal (111) atomic surface representative of the crystal termination for a perfect cleave (b).
Bonding of atoms in molecules consists of an overlap of electron densities and it is useful to recall the symmetry of the atomic orbitals. For instance, consider a p-orbital which has a lobe pointed towards an s-orbital. This has a symmetry that allows for the orbitals to overlap which results in a σ bond, however if the p- and s-orbital are arranged as in Figure 1.5 (b), then they will have no overlap and not result in a bond forming. A π-bond is formed by two p-orbitals (Figure 1.5 (c)), for example, that have both of their lobes overlapping. The valence electrons in Carbon occupy the p-orbitals and allow for a hybridization of C p-orbitals resulting in delocalized electrons referred to as a π-electron cloud. This is one of the many reasons organics have received a lot of attention for electronic devices.

**Figure 1.5** Schematic drawing of atomic orbitals s, p, and d and their symmetry.

Ligand-field theory is a useful tool for describing how the symmetry of a transition metal compound splits these energetically degenerate atomic orbitals and arrange into molecular orbitals.[49] Essentially the theory uses the molecules symmetry to classify it to a point group specifying the possible linear combination of atomic orbitals (LCAO). So by knowing the symmetry of the molecule, the ordering of its bonding and antibonding MOs can be elucidated. It is noted that this is a qualitative description and the ordering needs to be verified by experiments.
The MPc molecule has a central transition-metal with valence electrons in its d-orbitals that split according to its D₄h point group. In ligand-field theory the principal axis is determined by the axis with the highest symmetry, which is four-fold in this case. The D denotes the dihedral group which contain two n-fold axes perpendicular to the principal axis. The h denotes a horizontal mirror plane that exists perpendicular to the principle plane. The rotations and mirror planes for this point group are shown in Figure 1.7 overlaid on the MPc molecule. Character tables for each point group can be easily looked up and show the allowed symmetries and ordering of molecular orbitals.

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Figure 1.6 (a) sigma bond formed by overlap of an s and p orbital. (b) Zero overlap between s and p orbitals resulting in no bond. (c) pi-bond formed by the overlap of two p orbitals.
The d-shell for the D_{4h} point group are arranged as shown in Figure 1.8 and the occupation is shown for the MnPc molecule. Filling of the d-shell occurs as the 3d transition-metal increases in atomic number changing the properties of MPc molecule. Magnetism in thin films of the half-filled d-shell MPcs has been reported and single molecules can be thought of as molecular magnets.\[48\] Single molecules are of course paramagnetic as no preferential ordering occurs whereas in thin films ferromagnetic ordering can occur. The rich physics of the MPc molecules can be appreciated from an applied side, for example in the case of CuPc and organic photovoltaics, as well as from a fundamental perspective in the case of studying the Kondo effect. Systematic study of the 3d-transition-metal Pc molecules have identified the role of d-shell filling as well as the isoindole ligands in its adsorption, electronic, and magnetic properties. These molecules offer a playground to investigate the relatively new field of organic-TI interfaces. In particular, the random distribution of magnetic atoms in bulk-doping can be eliminated as complete monolayers of an MPc can be grown.

1.10 Survey of Organic-TI interface
The first experimental study of the organic-TI system was performed on the electron acceptor molecule F4-TCNQ on the degenerately n-doped Bi2Se3. Kim et al. showed the fundamental signature of the TSS in ambipolar electron transport on the surface of a bulk insulating film for the first time.[50] This established small organic molecules in the TI field as a tunable knob for controlling bulk doping. Our group further investigated this system by characterizing the charge transfer, work function shift, and growth morphology of F4-TCNQ on Bi2Se3 TI samples grown by binary melt and hybrid physical-chemical vapor deposition.[51] This molecule and the unflorinated TCNQ have also recently been shown to tune the carrier density of BSTS and convert it to a p- or n-type semiconductor. It is therefore clear that electronic-doping TIs via organic molecules is a nondestructive approach for controlling carrier types.[52]

Molecules can also be used as an approach to breaking TRS in TI systems. The first studies of MPcs on TIs were performed by STM groups on the system MnPc/ Bi2Te3[53] and FePc/Bi2Te3[37] in 2014. Since then, there have been a handful of experimental studies of the MPC-TI interface with general agreements that the TSS remains unperturbed by the organic molecules.[54-56] Differences in monolayer growth and charge-transfer effects have been observed that depend on the d-shell filling where the spatially extended dz2 orbital lies close to the Fermi level for the lower atomic numbers.[57]

The organic-TI studies thus far have led to interesting observations such as protection of the TSS and hybrid-interface states forming (HIS), and even theoretical predictions for a 2D organic TI in a metal-
organic framework.[56, 58, 59] Careful analysis of quasiparticle interference data is needed to understand the scattering potential associated with an adsorbed magnetic molecule. In particular, spin-resolved measurements are likely needed to elucidate the interactions of a magnetic potential on the TSS.[60]

The next chapter will review the analytical instruments and experimental methods that were used followed by presentation of three selected studies:

In Chapter 3 a photoemission spectroscopy study on the surface termination of the TI Bi$_2$Se$_3$ is presented. It is shown that the environment in which the crystal is cleaved has a mechanical effect resulting in different terminated surface which strongly modifies the valence band electronic structure. This work has been published in the Journal of Vacuum Science and Technology B.

Chapter 4 presents a photoemission study of Cr-doping the topological insulator BSTS as a route to breaking TRS. It is shown that for high concentrations of Cr, impurity phases are formed during the synthesis suggesting an alternative route to break TRS in TIs.

Chapter 5 presents a systematic study of the organic molecule MnPc adsorbed on Bi$_2$Te$_3$ showing a previously unobserved hybrid-interface state (HIS). Photoelectron spectroscopy shows charge transfer occurring and the HIS forming.

References


31. Lee, I., et al., Imaging Dirac-mass disorder from magnetic dopant atoms in the ferromagnetic topological insulator Cr$_x$(Bi$_{0.1}$Sb$_{0.9}$)$_2$-xTe$_3$. Proceedings of the National Academy of Sciences, 2015. **112**(5): p. 1316-1321.


CHAPTER 2 EXPERIMENTAL METHODS

2.1 Surface Science

The surface of a crystal can host novel states of matter and experimentally we want to be sure that the surface is what we’re measuring. At the atomic level there are processes such as physiadsorption and phase transition and it is therefore necessary to diminish the number of these particles so that an isolated system can be used to perform experiments. A surface scientist only considers something to be clean once it’s been annealed in a vacuum.

![Figure 2.1](image)

Figure 2.1 Annealing a Cr-crystal in the UHV STM chamber.

This mantra does not excuse a messy room but is a key component to experiments. Our ambient environment is filled with particles that interfere with samples we’re interested in studying and therefore must be removed. The surface sensitive techniques used can generally be divided into spatially-averaged and local probe instruments. Each analytical tool fundamentally relies on Fermi’s golden rule[61]

\[
\mathcal{W} = \frac{2\pi}{\hbar} |\langle f | \mathcal{H}' | i \rangle|^2 \rho
\]

where \( \mathcal{H}' \) is the perturbation matrix between final and initial states and \( \rho \) is the density of final states. This gives the effectively constant transition rate between eigenstates of a system for a given perturbation. The application of this golden rule for photoemission and scanning tunneling experiments are presented after an introduction to the experimental requirements for these measurements.
Surface science experiments are typically performed in high vacuum (HV) systems where pressure is on the order of $10^{-6}$ Torr or less and for measurements ultrahigh vacuum systems are used where pressure is less than $10^{-8}$ Torr. This can be directly seen by considering the kinetic theory of gases for the adsorption of molecules on a surface. The time constant to form a monolayer on a surface is given by:

$$
\tau = \frac{n_0 \sqrt{2\pi mk_B T}}{P} \tag{2.2}
$$

where $n_0$ is the number of molecules in a monolayer, $m$ is the mass of the molecule, $T$ is the temperature and $P$ is the pressure. Thus, it takes approximately 1 second for a monolayer to form at room temperature in a system at $10^{-6}$ Torr. This time-constant also depends on the sticking coefficient, between 0 and 1, of the molecule and surface and is unique to each system.

Another reason for UHV requirements for experimental measurement techniques can be seen by the mean free path of particles described by the kinetic theory of gases.

$$
\lambda = \frac{k_B T}{P \sigma^2} \tag{2.3}
$$

Photoemission spectroscopy, for instance, requires analyzing an electron’s energy emitted from a surface and so it needs to reach the detector before interacting with other particles. Additionally for cryogenic measurements, a vacuum is necessary as water condensation can be problematic.
The analysis systems in this chapter contain two vacuum chambers separated by a valve lock. One chamber is used to load samples and can reach HV/UHV conditions, then transferred to a chamber with analysis instruments in requiring \( \sim 10^{10} \) Torr or better. HV conditions can be reached with simple mechanical pumps. The roughing pump can reach pressure in the \( 10^{-3} \) Torr range and operates by an iterative process of moving gas from the chamber into an expanded piston cavity which is then sealed, recompressed, and expelled from the pump. A turbomolecular (“turbo”) pump can then reach HV conditions by evacuating gas particles with a series of turbine blades spinning at frequencies of \( \sim 1500 \) Hz. Lower pressures can then be reached by wrapping the chamber system with heating tape and covered with aluminum foil (“baking out”) evaporating the water, and other molecules, from the chamber walls. This is a mandatory procedure in order to reach UHV conditions and all analysis chambers are baked out after being exposed to air. The introductory sample loading (“intro”) chamber is often exposed to air and is typically not necessary to bake out. Every experiment and sample have different needs so it is important to take care when using these systems.

Pressure in these systems is measured by either a ‘hot’ ion gauge or ‘cold’ cathode gauge both of which operate based on ionizing the gas molecules of a system. The hot-filament ion gauge uses thermionic emission of electrons which are accelerated to a grid and collected by a wire whose current is then converted to a pressure. The cold-cathode gauge utilizes electric and magnetic fields to trap electrons in a plasma which can then ionize gas molecules on impact and collected at the cathode giving an indirect
measurement of the pressure. Accurate measurements of the gas density become difficult at pressures below 10-11 Torr which is beyond our experimental capabilities in this lab. The hot ion gauge is sufficient for HV/UHV conditions and the cold gauge is sufficient for HV conditions.

The samples studied in this thesis are vdW layered materials allowing them to be cleaved along a natural crystal plane (perpendicular to the c-axis) ideally creating an atomically flat sample. Visual inspection of the TI sample should indicate the quality of the cleave by the shininess. While this process can produce macroscopic atomically flat regions, there are always unit cell steps which can be verified by scanning probe microscopy.

Partial cleaves of the unit cell can also happen as well and the environment in which a TI is cleaved has been shown to result in coexisting surface terminations. It is therefore best to perform cleaves in vacuum to maximize the probability of a good cleave. In the case of other samples, such as Cr(001), cycles of annealing (Figure 2.1) and ion radiation are used with various recipes in order to produce clean surfaces.

Molecules are thermally sublimed onto a substrate surface through a process called Organic Molecule Beam Deposition (OMBD). Powder of the molecule is placed in a quartz crucible which is wrapped in Tantalum wire and sealed in a vacuum chamber. Current is then passed through the wire with an external power supply connected via feedthroughs heating the wire and crucible. Water and other impurities are expelled from the powder (outgassed) prior to the powder subliming and this process can vary in time length depending on the molecule. A quartz crystal microbalance is often used to establish

![Figure 2.3](image-url) Synthesized Bi$_2$Te$_3$ crystals by Jonathon Boltersdorf in the Maggard chemistry group at N. C. State University (left). A flat and shiny surface can be seen for these bulk samples and are on the order of a few mm. Atomic resolution of a step-edge for a vacuum cleaved crystal where triangular subsurface defects can be seen.
the molecular flux. It consists of an oscillating (~8 MHz) Au crystal where the change in frequency of oscillation is used to compute the amount of deposited molecules. This generates a nominal value for the thickness of the molecular film which then needs to be verified experimentally.

![Box chamber diagram of OMBD. A sample is mounted near the QCM flux monitor and sublimed molecules spray from a quartz crucible heated by a Ta-wire.](image)

**Figure 2.4** Box chamber diagram of OMBD. A sample is mounted near the QCM flux monitor and sublimed molecules spray from a quartz crucible heated by a Ta-wire.

### 2.2 Photoelectron Spectroscopy Theory

The techniques discussed in this section are X-ray photoelectron spectroscopy, which can determine near-surface chemical compositions, and angle-resolved photoelectron spectroscopy (ARPES), which maps the emitted photoelectrons as a function of their energy and momentum. Photoelectron spectroscopy (PES) is the general term for the technique that utilizes Einstein’s fundamental photoelectric equation relating a photon of energy, $hν$, and the maximum kinetic energy of the emitted electrons, $E_{kin}^{max}$, to the minimum energy required to remove the electron from a solid (work function) $\phi$:

$$E_{kin}^{max} = hν - \phi$$
Conservation of momentum and energy give the following equations where $E_B$ is the binding energy of an electron in its respective orbital and referenced as a positive number with respect to the Fermi level:

$$E_{kin} = \hbar \nu - \phi - |E_B| \quad 2.5$$

$$p_\parallel = \hbar k_\parallel = \sqrt{2mE_{kin}} \sin \theta \quad 2.6$$

For ARPES measurements low photon energy, where $\hbar \nu < 100 \text{ eV}$, allows for greater energy and momentum resolution as can be seen by the following equation:

$$\Delta k_\parallel \approx \sqrt{2mE_{kin}/\hbar^2 \cos \theta \Delta \theta} \quad 2.7$$

where $\Delta \theta$ is the finite acceptance angle of the electron analyzer.[62]

As discussed earlier, the photoemitted electrons must reach the analyzer requiring vacuum conditions and their inelastic mean free path (IMFP) to escape the sample surface is on the order of 5-10 Å, depending on the material and the kinetic energy of the electron. The IMFP is the average distance between inelastic collisions and follows a, “universal curve”, meaning that the errors are so much larger for measuring the IMFP values than their actual values that it’s difficult to distinguishing between materials values.[63] This process is therefore a highly surface sensitive technique and other measurement techniques are needed for studying bulk properties of a material.

The PES process can be described by the three-step model which, although is purely phenomenological, is successful in describing the data. The three independent and sequential steps of the photoemission process are:

1) Optical excitation of an electron in the bulk of the solid
2) Travel of the excited electron to the surface of the solid
3) Escape of the photoelectron from the solid into vacuum

Fermi’s golden rule can be used to approximate the transition probability, $w_{fi}$, for the optical excitation of the $N$-electron from its ground state, , and one of the possible final states, , by:

$$w_{fi} = \frac{2\pi}{\hbar} <\Psi_i^N|\mathcal{H}_{int}|\Psi_f^N>^2 \delta(E_f^N - E_i^N - \hbar \nu) \quad 2.8$$
where the energies equal stuff. The perturbation Hamiltonian is given by:

$$\mathcal{H}_{\text{int}} = -\frac{e}{2mc} (A \cdot p + p \cdot A) = -\frac{e}{mc} A \cdot p$$  \hspace{1cm} (2.9)

where $A$ is the electromagnetic vector potential and $p$ is the momentum operator. Here the gauge choice is chosen to be zero and quadratic terms dropped as they are negligible in the linear optical regime, and takes $A$ to be constant, i.e. $\nabla \cdot A = 0$. The photoemission steps can then be taken with the sudden approximation which assumes the process is instantaneous simplifying the calculation. The total photoemission intensity measured is then[62]:

$$\sum_{f, i} |M_{f, i}^{k}|^2 \sum_{m} |c_{m, i}|^2 \delta(E_{\text{kin}}^i + E_{m}^{N-1} - E_{i}^{N} - \hbar\nu)$$  \hspace{1cm} (2.10)

XPS uses higher photon energies which creates core holes and the most common approximation to analyze spectra is the equivalent-core approximation. This assumes that the spatial extent of the core electrons is small compared to that of the valence electrons for a given atom. The photo-ionized core-hole system can then be approximated by hypothetically adding a proton to the nucleus (Z+1). The binding energy (BE) measured of the emitted electrons are dependent on the local environment. For instance, a sample that has been oxidized will show some weight on the high-BE side of the spectra as oxygen has removed some charge, changing the screening of the core-hole, and results in a more tightly-bound state. The shape of a spectral feature is a convolution of three components:

$$\Delta E = \sqrt{\Delta E_{n}^2 + \Delta E_{p}^2 + \Delta E_{a}^2}$$  \hspace{1cm} (2.11)

where $\Delta E_{n}$ is the intrinsic core-level line width, $\Delta E_{n}$ is the width of the photon source, and $\Delta E_{a}$ is the width of the electron analyzer resolution. The line widths of the photon sources for standard Mg Kα and Al Kα are 0.70 eV and 0.85 eV, respectively. The analyzer line shape is a Gaussian and is ~0.1 eV for the electron analyzers used in this thesis. The intrinsic core-level width can be determined from the uncertainty principle:

$$\Delta E_{n} = \frac{\hbar}{\tau} = \frac{4.1 \times 10^{-15}}{\tau} \text{eV} \cdot \text{s}$$  \hspace{1cm} (2.12)
where \( \tau \) is the lifetime of the core-hole, which is on the order of \( 10^{15} \) to \( 10^{13} \) s giving line widths between 0.04 eV and 4 eV and is a Lorentzian line shape.[62]

Analysis of XPS spectra for relative chemical compositions is then accomplished by comparing intensities of the measured core levels. A survey spectrum is first performed to scan over the entire BE range indicating the elements present near the surface of a sample. Detailed scans over the regions of interest are measured to give accurate intensities of the core-levels. The photoelectron counts per second (intensity) is then given by:

\[
n = \frac{I}{f \cdot \sigma \cdot \theta \cdot y \cdot \lambda \cdot T}
\]  

where \( n \) = number of atoms per cm\(^3\), \( f \) is the X-ray flux, \( \sigma \) is the photoelectric cross section of the atomic orbital, \( \theta \) is the angular efficiency factor for the instrument, \( y \) is the probability of a photon causing the ejection of a photoelectron, \( \lambda \) is the IMFP, \( A \) is the area of the sample, and \( T \) is the detection frequency. This assumes a homogenous sample and the denominator is defined as the atomic sensitivity factor which is unique for each analyzer and elemental photoelectron transition. To compare the near surface chemical composition, one then takes the area of the convoluted Gauss-Lorentzian peak divided by its atomic sensitivity factor summed over all detected elements giving the total intensity by which one divides the constituent element of interest.

\[
C_x = \frac{n_x}{\sum n_i} = \sum \frac{I_x}{\sum(I_i)}
\]  

It is not always necessary to determine the total intensity as, for instance, determining the amount of deposited molecules can be inferred through calculating the relative compositions of a peak unique to the molecule and substrate. An example of this is in our work of F\(_4\)TCNQ on Bi\(_2\)Se\(_3\) where the relative F 1s and Bi 4f intensities indicate the amount of molecules adsorbed to the surface.[51] Analysis like this is not straightforward, as the morphology of the adsorbed molecules can form by layers and/or islands which by definition changes the surface affecting which photoelectrons can be ejected from the sample.

### 2.3 Photoelectron Spectroscopy Experiment and Equipment
In our PES systems, photons are created by bombarding high energy electrons (10-15 kV) into an Al or Mg foil. The emission spectra of these targets are dominated by the Ka1,2 transition at 1486.6 eV and 1253.6 eV and also used because of their small line widths. These x-rays are energetic enough to excite core electron transitions from a sample and the energy of the emitted photoelectron depends on its bonding environment. In the ARPES/UPS system, photons are created by a He gas discharge lamp. A HV chamber is filled with He gas that is ignited into a plasma with an emission energy of 21.2 eV (He-I) used to excite BVB transitions. The photoemitted electrons are collected by an analyzer measuring their kinetic energy and samples are grounded so that as electrons leave the sample it does not become charged. One type of electron analyzer used was the hemispherical type and the other was a cylindrical mirror analyzer.

Figure 2.5 (a) Cylindrical mirror analyzer illustration showing the two stages and electron trajectory. The beams of photoelectrons are focused on an electron multiplier recording the number of counts per second. The higher resolution hemispherical analyzer (b) containing an electrostatic lens used to discriminate the entrance of photoelectrons according to their kinetic energy.
The cylindrical mirror analyzer consists of two cylinders held at a potential difference with entrance and exit slits on the inner cylinder. The CMA shown in Figure 2.5 (a) is a double-pass analyzer which allows for higher resolution. The kinetic energies of the photoelectrons are measured by varying the potential of the inner and outer cylinders. Higher energy resolution can be achieved by having a preretardation stage (electrostatic lens, Figure 2.5 (b)) which determines the energy of the electrons entering the analyzer, referred to as the pass-energy. This has a minimum effect on the energy spread of the photoelectrons, although for low energy measurements, such as the work function, application of a bias to the sample can typically give the photoelectrons enough energy to overcome the electrostatic lens effects.

2.4 Scanning Tunneling Microscopy/Spectroscopy

The real-space imaging technique offered by STM is a powerful analytical tool which Binnig and Rohrer earned a Nobel prize in physics for its invention at IBM.[64] It is an ultra-high resolution instrument capable of atomic-resolution, and even atomic-scale control, of surfaces. Commercial microscopes are available now which can operate in ambient air and a range of temperatures cementing its role in the surface sciences.

The physical process by which this instrument operates is through quantum mechanical tunneling of electrons between a metal tip and a sample surface. The metal tip is very sharp and ideally is a cone with a single atom at the end, and once approached to within Angstroms of the surface a tunneling current between the probe and surface occurs. The tip is then rostered across the surface providing real-space images of atoms and molecules. This can be modeled with a simple model of tunneling through a 1D rectangular barrier such that the tunneling current depends exponentially on the barrier width

\[ I \propto \left( \frac{V}{d} \right) e^{-A/\Phi d} \tag{2.15} \]

where \( V \) is the bias across the tunneling barrier, \( d \) is the barrier width, and \( \Phi \) is the average barrier height. Thus, it can be seen that STM is extremely sensitive to atomic-scale features as for every Angstrom change in barrier width there is about an order of magnitude change in the tunneling current making it valuable for atomic-scale studies of surfaces.
A more accurate and useful approach to understanding the operation of the STM was modeled by Tersoff and Hamann using a spherically symmetric wave function for a tip and first order time-dependent perturbation theory to compute the tunneling current across a 3D barrier.[65, 66] Essentially this calculates tunneling current using Fermi’s golden rule for the overlap of the wave functions of a tip and sample separated by an insulator. This relies on the matrix element proposed by Bardeen for the transition between two states given by the integral over a surface in the vacuum gap region.[67] The tunneling current is then given by:

\[
I = \int_0^{eV} \rho_s(E - eV)\rho_t(E)T(z, V, E)dE
\]

The tunneling current is therefore some combination of both tip and sample wave function and while we want to learn about the sample wave function, the tip wave function is unknown and uncontrollable. Therefore straightforward analysis of ‘heights’ in STM images can be limited. Adjusting the bias voltage of the tunneling junction controls whether the states are occupied or unoccupied.

Scanning tunneling spectroscopy involves positioning the tip over a feature of interest to measure the local density of states at a point. It is a powerful tool that can, for instance, measure the superconducting gap[68], image potential states[69], as well as differentiate metal and ligand orbitals.[53] Electron tunneling through an insulating layer of a few nanometers between metal electrodes was
established as a way to measure the density of states of the insulating material prior to the invention of the STM.[70, 71] Applying a bias to this junction produces a measureable tunneling current and the normalized differential conductance is proportional to the density of states.

\[
\frac{V}{\frac{dI}{dV}} \propto \rho_s(eV)
\]

STS can be operated in constant height mode which is previously described, as well as constant current mode. The latter has been developed more recent theoretically and offers the advantage of a more stable tunneling junction in the case of molecules.[72]

The STM experiments performed in this thesis were done with an Omicron Variable-Temperature 100 XA STM. The head of the STM unit contains piezoelectric ceramic tubes which are operated by applying a voltage that expands or contracts the tube in a given direction. These fine precision devices allows positioning of the tip to within tunneling distances. Vibrational noise isolation is therefore crucial in order to reliably scan across atomic and molecular features and several steps are taken to achieve this. The whole chamber, including intro chamber, are on N\textsubscript{2} floating legs. The entire head unit of the STM is then lowered by disengaging from a locked position and supported by low resonant frequency springs. Additional damping is provided by strong rare-earth magnets attached near the copper block supporting the STM tip and sample. These induce eddy currents in the copper block should it move further reducing the vibrational noise.

The metal tip used for these experiments was a chemically etched W-tip. Processing of the tip is typically done by applying pulsed biases between tip and sample during experiments. When first loading a tip from air it is necessary to anneal and even electron bombard the tip to remove contaminations. These methods can also be used to condition the tip when the pulsed biases are not achieving the desired results, as well as to clean it from molecules after an experiment.

References


CHAPTER 3 COEXISTING BI AND SE TERMINATED SURFACE OF CLEAVED BI$_2$SE$_3$ CRYSTALS

3.1 Preface

The 3D TI field is a rapidly developing field providing many opportunities for surface scientists to address materials characterization of these novel quantum states of matter. As the atomic layer of the crystal structure is changed, the bulk-boundary correspondence questions whether the TSS will survive. Modification of the electronic valence band structure must occur as the surface is now of a different chemical composition. Below is our publication of our study of co-existing surface terminations of the TI Bi2Se3 resolving the controversy and highlighting the importance of surface characterization.
Evidence for the coexistence of both Bi and Se terminations of the topological insulator Bi$_2$Se$_3$ is presented that is connected with details of sample storage and cleaving procedures. X-ray photoelectron spectroscopy of the Bi 4f core levels show a lower binding energy component indicative of metallic Bi near the sample surface. Single crystals stored and cleaved in high vacuum predominantly show the usual Se surface termination while those stored in air for long periods of time have a high probability for Bi termination. The different terminations have very different electronic structures as measured by angle resolved photoelectron spectroscopy. Our photoemission studies show the Se-terminated electronic structure can be recovered after annealing at 400 °C.
3.2 Introduction

Strong three-dimensional topological insulators (3D TI) are bulk insulators with a metallic surface state in which carrier spin is "locked" perpendicular to crystal momentum. The spin-textured topological surface state (TSS) is robust to crystal defects that preserve time-reversal symmetry due to a bulk-derived topological $Z_2$ invariant. This robustness makes the TSS promising for applications in spintronic devices.\[73-76\] The strong 3D TI Bi$_2$Se$_3$ is widely recognized as the simplest prototype for this system because of its single Dirac cone and relatively large band gap (~0.3 eV).\[73, 75-80\] Angle-resolved photoelectron spectroscopy (ARPES) measurements have confirmed the spin texture in the TSS Dirac cone.\[76\] Recent transport measurements on a molecule-doped Bi$_2$Se$_3$ crystal have probed for the first time the TSS and show evidence for the expected ambipolar transport in a Dirac-like surface state band.\[81\]

Despite the early success in establishing Bi$_2$Se$_3$ as a prototype 3D TI, there are numerous challenges of surface characterization that must be met. For example, typical single crystals of Bi$_2$Se$_3$ are degenerately $n$-doped due to the presence of Se vacancies.\[75, 79, 81, 82\] This results in strong band bending at the solid-vacuum interface that varies slowly over time after a fresh cleave of the single crystal\[80, 83\] as bulk charge rearranges in response to the creation of a new surface. Moreover, the band bending can lead to the confinement of a 2D electron gas at the surface that coexists with the more interesting TSS\[74, 77, 80, 84\] which provides an added complication to isolating the charge transport characteristics unique to TI materials.

The bulk crystal of Bi$_2$Se$_3$ has a rhombohedral crystal structure (space group D3d (R3m) composed of stacked atomic planes in a quintuple layer (QL) of Se(1)-Bi-Se(2)-Bi-Se(1). The quintuple layers are held together by weak van der Waals interactions between adjacent Se(1) planes similar to the binding between S-terminated layers in MoS$_2$.\[85\] This suggests that a Se-terminated surface is preferentially exposed after mechanical cleavage of bulk Bi$_2$Se$_3$ crystals.\[86\] Further complexity in this material can be understood based on the fact that Bi$_2$Se$_3$ can be regarded as one example of an infinite series of compounds expressed\[87, 88\] as $(\text{Bi}_2)_n(\text{Bi}_2\text{Se}_3)_m$ (i.e. with $n=0$, $m=1$). This series of possible compositions represents an alloy between stable Bi-bilayers and stable Bi$_2$Se$_3$ quintuple layers. A surface reconstruction may favor the formation of these Bi-bilayers at the surface. The strongly layered structure of Bi$_2$Se$_3$ makes the possibility of alloys and intercalation compounds significant. In fact, this is another opportunity for structure-property control in the material class.

Recently, the details of the surface termination of cleaved Bi$_2$Se$_3$ single crystals have been debated. In contradiction to the good rationale for expecting a Se-terminated surface, low energy ion scattering spectroscopy experiments reported clear evidence for a Bi-terminated surface after cleavage.\[89\] However, separate low energy electron diffraction and grazing incidence X-ray diffraction
measurements found only evidence for the expected Se-termination.[90] These contrasting observations have obvious implications for understanding and controlling the details of surface electronic structure. In particular, Hoffmann and co-workers point out that surface electronic structure cannot be expected to be identical for different surface atomic structures.[90] In addition, strong electronic structure modifications have been reported for Bi-bilayer terminated samples in the alloy series (Bi$_2$)$_n$(Bi$_2$Se$_3$)$_m$.[91, 92]

In this paper we present evidence for the coexistence of two different surface terminations for cleaved Bi$_2$Se$_3$ single crystals that may help to reconcile conflicting reports. We use X-ray photoelectron spectroscopy of the Bi 4f core levels to show a low binding energy (BE) component indicative of metallic Bi at the surface in addition to the expected core level for a Se-terminated surface. We find that sample storage and cleaving under conditions where intercalation of ambient gases can occur leads to a high probability for a Bi-rich surface termination. Angle resolved photoelectron spectroscopy shows that this unusual surface termination has a very different occupied electronic structure than the well-known Se termination, but is in agreement with ARPES studies of surfaces intentionally prepared with Bi-bilayer terminations.[91] In-vacuum annealing is observed to eliminate the Bi-bilayer surface termination and recover Se-terminated electronic band structure.

3.3 Experimental Methods

Single crystals of Bi$_2$Se$_3$ were synthesized in a binary melt of elemental Bi beads (Aldrich, 99.999%; 1-5mm particle size) and Se pellets (Aldrich, 99.999%; <5mm particle size) following a procedure from the literature.[93] The crystals synthesized in-house were characterized by high-resolution powder X-ray diffraction (PXRD) on an INEL diffractometer using Cu Kα (λ = 1.54 Å) radiation from a sealed-tube X-ray generator (35 kV, 30 mA) using a curved position sensitive detector (CPS120), as well as on a Rigaku R-Axis Spider (40 kV, 36 mA) equipped with a curved image-plate detector. Lattice parameters of the molten flux prepared samples were refined using the Materials Studio JADE 9 least squares based refinement program. The orientation of large cleavages planes in crystals was verified by X-ray diffraction (Bragg-Brentano XRD – Rigaku SmartLab using Cu Kα (λ=1.54 nm)). The crystals cleave easily perpendicular to the c-axis. In addition to these crystals grown in-house, two separate commercial samples of nominally stoichiometric Bi$_2$Se$_3$ (Cradley Crystals) were characterized by low energy electron diffraction and X-ray diffraction in θ-2θ mode and then studied extensively by XPS. No systematic differences between surface termination effects between commercial and in-house crystals were observed.

The electronic structure of commercial crystals was characterization by photoemission spectroscopy using a 150 mm mean radius hemispherical analyzer (Specs Phoibos 150) at room temperature in ultra-high vacuum (UHV) (base pressure~ 2x10^{-10} Torr). Angle resolved photoelectron
spectroscopy (ARPES) was performed using a He I light source (Specs UVS 100, $h\nu=21.2$ eV). The sample was rotated with respect to the electron analyzer to measure the dispersion of the occupied electronic states. Both Mg Kα ($h\nu=1253.6$ eV) and monochromatic Al Kα ($h\nu=1486.7$ eV) light sources were used for X-ray photoelectron spectroscopy (XPS). Samples were annealed in UHV by electron bombardment.

A statistical survey of surface termination was conducted to assess the impact of different cleaving procedures and storage conditions. Air-cleaves were performed manually in ambient environment with Scotch tape. Samples were cleaved, then loaded into a sample elevator in a load-lock chamber and immediately pumped to high vacuum conditions ($P \approx 10^{-7}$ Torr, less than 5 min air exposure). In addition to air cleaves by hand, a magnetic sample transfer arm was used for ambient air-cleaves with carbon tape (Ted Pella) in the vented load-lock chamber. *In-situ* cleaves were performed with the same magnetic transfer arm procedure in the load-lock chamber under high vacuum conditions. Crystals were stored prior to cleaving either in ambient atmospheric conditions or in a rough vacuum desiccator. For the statistical studies, the surface termination was determined by XPS in UHV (base pressure $\approx 2 \times 10^{-10}$ Torr) with a Riber MAC-2 analyzer using Mg Kα light source ($h\nu=1253.6$ eV). All cleaves in this study were performed at room temperature.

The quality of the synthesized crystals was determined by a variety of probing instruments. Diffraction patterns of the in-house crystals are shown in the high resolution PXRD shown in Figure 3.1. The peaks are in good agreement with the calculated peaks for Bi$_2$Se$_3$. The consistency in the PXRD spectra across samples indicates an identical crystal structure from the various initial compositions. The unit cell parameters of the in-house crystals (Table 3.1) are also consistent and agree with the literature[87] which confirm the quality of the crystals studied.

![Figure 3.1 PXRD of in-house crystals of various starting compositions compared to calculated values for Bi$_2$Se$_3$](image)

**Table 3.1** Calculated lattice parameters from PXRD of the different starting compositions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>Volume (Å$^3$)</th>
<th>Spacegroup</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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3.3 Results and Discussion

3.3.a XPS Observation of Bi-rich Surface Termination

The chemical composition near the surface of cleaved samples was determined by XPS. Figure 3.2 shows Bi 4f core level spectra that show two significantly different bonding environments for the Bi atom. The singly-peaked doublet (blue) is the Bi 4f spin-orbit (SO) doublet for Bi-Se bonds in Bi$_2$Se$_3$ consistent with the literature [86, 94, 95]. The broader doublet (red) shows the Bi 4f doublet where each member is a convolution of two peaks due to different coexisting Bi bonding environments. The high and low binding energy (BE) components are assigned to Bi-Se and metallic Bi-Bi bonds respectively as indicated in the plot. We refer to surfaces with the broadened Bi 4f spectra seen in Figure 2 as "Bi-rich" and the more narrow 4f's as “bulk-terminated”. The peak positions were determined by subtracting a Shirley background and fitting the components with a GL30 peak with CASA XPS software (see also supplemental information for more details of XPS quantification). We observe an upward shift of ~0.8 eV in BE for the Bi-Se component of the Bi 4f core level. This is consistent with the core level shift for Bi$_2$Se$_3$ crystals compared with metallic Bi[96], though significantly smaller compared to the shifts in Bi 5d core level spectra for coexisting Bi-bilayers and a QL, where the Bi-Se component is shifted to higher BE by 1.8 eV than the Bi-Bi component.[91] In our experiments, the relative amount of low binding energy Bi-Bi component was somewhat variable for different cleaves. In bulk-terminated samples, the atomic percentage of Bi in the XPS probing depth was always close to the stoichiometric value of 40%, while in Bi-rich samples it varied from 60% to 51%.

![Figure 3.2 Bi4f core level spectra for the Se rich (blue) and Bi rich (red) surfaces. The low BE component is metallic Bi bonds near the surface in addition to the Bi-Se bonds from a coexisting QL.](image)
To determine the origin of the Bi-rich termination, a statistical survey (Table 3.2) was performed to clarify the impact of the cleaving conditions. Both commercial and home grown crystals were used with no clear systematic differences. Manually performed air-cleaves with Scotch tape have a 69 ± 11% probability to show the Bi-rich termination. This is only marginally reduced to 48 ± 14% for air-cleaves using the cleaving procedure with the magnetic transfer arm in an effort to establish mechanical reproducibility. Air-cleaves with Scotch tape for single crystals of Bi$_2$Se$_3$ are known to be particularly susceptible to defects[97]. To avoid these defects, multiple air-cleaves are typically performed to obtain a large flat reflective surface[86], on which the experiments are performed. The type of tape used for cleaving can be ruled out as carbon tape was used for both in-situ and ex-situ cleaves. Sample storage had a significant impact on the type of termination, with a further reduction to 25 ± 18% of samples stored in rough vacuum showing a Bi-rich termination.

Table 3.2 Statistical survey of the surface termination resulting from different cleaving procedures

<table>
<thead>
<tr>
<th>Cleaving Procedure</th>
<th>Bi-rich</th>
<th>Bulk-terminated</th>
<th>Total # of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-cleave with Scotch tape</td>
<td>37</td>
<td>17</td>
<td>54</td>
</tr>
<tr>
<td>Air-cleave with C-tape on transfer arm</td>
<td>11</td>
<td>12</td>
<td>23</td>
</tr>
<tr>
<td>In-situ cleave w/ C-tape on Transfer arm</td>
<td>0</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>Air-cleave for samples stored in Vacuum desiccator</td>
<td>2</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>

In contrast to the prevalence of Bi-rich terminations for air-cleaved samples, 100% of in-situ cleaved samples show the typical bulk termination. Exposure to ambient environment during the cleave diminishes this surface homogeneity, leading to the observed Bi-rich terminations. In regards to the controversy over surface termination, the different results are most likely due to the differing details of sample storage, handling, and/or cleavage that result in different elemental terminations at the surface for the two experiments.

Based on our observations presented above, the origin of the Bi rich termination can be attributed to air intercalants in the layered crystal that alter the weak-link between Se(1) planes in the crystal leading
to a high probability for exposing a different surface termination. We stress that after cleavage, we have not observed any systematic differences in trace oxygen or carbon contamination between bulk-terminated and Bi-rich surfaces. This shows that the production of a Bi-rich surface results from a predominantly mechanical effect induced by air intercalants. Evidently, intercalants change the energetics of the cleaving process but do not remain in significant quantities after cleaving. This interpretation is consistent with our observation of a significant reduction in probability of obtaining a Bi-rich surface for air-cleaved samples that had been stored in a vacuum dessicator prior to the experiment. The *in-situ* cleaved samples are under high vacuum for several hours prior to cleaving during which time ambient intercalants may be removed and cleavage is overwhelmingly likely along the Se(1)-Se(1) weak link. An alternative explanation, that Bi-rich regions already exist within our crystals, is strongly disfavored because our crystal structures are in agreement with the literature for all compositions. Most importantly, *in-situ* cleaves are consistently bulk-terminated and this would not be the case if samples contained random Bi-rich inclusions. In addition, samples that showed Bi-rich terminations after an air-cleave only showed bulk terminations when cleaved in vacuum.

We also stress that commercially obtained crystals behave identically to in-house crystals, including a range of in-house compositions. We regard this as evidence that variable surface terminations are a common possibility in this material. Note that for all of our samples with Bi-termination, the low binding energy Bi-Bi component of the Bi 4f core peaks was never more intense than the Bi-Se component. This can be directly compared to the Bi 5d spectra in Ref. 18 for their majority Se-terminated surface.

### 3.3.b Electronic Structure and Surface Morphology of Bi-terminated Surfaces

In this section we describe the low energy electronic structure of Bi rich surfaces showing both metallic Bi and Bi-Se components in their 4f core level spectra. These two components are clearly resolved in the Bi 4f SO doublet measured with monochromatic Al Kα radiation for a sample cleaved in air with Scotch tape (Figure 3.3). Annealing this sample in vacuum at 200 °C reduces the relative intensity

![Figure 3.3](image)

**Figure 3.3** Core level spectra for Bi-rich surface. The as loaded sample (red) shows a broad SO doublet. The low BE component attributed to the Bi-bilayer is reduced after annealing to 250 °C (green) and completely removed after 400 °C (blue).
of the low BE metallic Bi component. This low BE component is completely removed after further annealing to 400 °C.

Figure 3.4a shows ARPES measurements for the 200 °C annealed sample. Evidence for Bi-bilayer termination is present in core level XPS confirming the metallic Bi-rich composition near the surface. A weakly dispersing valence band structure is observed which can be directly compared to recent ARPES work, where a coexisting Bi-bilayer and QL were found to result in an upward dispersing energy band with a minimum near 0.5 eV at the surface Brillouin zone center.[88, 91] The calculated band structure for the Bi-bilayer and QL shows a band from the Bi-bilayer around ~0.5 eV, in agreement with these results.[89, 91] Based on this agreement, we interpret the Bi-rich terminations obtained by cleaving air-intercalated crystals as composed of coexisting Bi-bilayers with ordinary QL (Se) terminated surfaces. Interestingly, the electronic structure that we observe is different than a recent ARPES study of a Bi-bilayer grown by molecular beam epitaxy on top of Bi$_2$Se$_3$ single crystals which show a band dispersing downward around the zone center at lower binding energy.[98]

This comparison highlights the sensitivity of surface electronic structure to the details of surface termination. It is clear that the band structure we observe most resembles that of crystals purposefully-grown with Bi-bilayers between QL's for which cleaving can result in an inhomogeneous surface.[88, 91] This is a crucial comparison since it impacts the topologically-nontrivial properties of the surface electronic structure. The electronic states observed by Valla et al.[88] are very similar to those in Figure 4a and were identified as the result of a shift further below the Fermi level of the bulk terminated band structure. This idea is also consistent with our observations, though higher resolution ARPES including spin polarization are needed for conclusive understanding of the topological character of the bands in Figure 4a. Taken together, these observations can be understood based on the theoretical prediction[99] that arbitrary changes in surface potential that preserve time reversal symmetry preserve the topological properties of the surface states on Bi$_2$Se$_3$ and can only change the energy of the Dirac point and curvature of the TSS band. These changes are not topological but are crucial to understand in considering device applications for the purposes of doping control and interfacial band alignment.

ARPES measurements after annealing at 400 °C are shown in Figure 3.4b. An intense energy band dispersing up toward the Fermi level is observed along with a weaker downward dispersing band at higher BE. A clear contrast can be made with the 200 °C sample, where the intensities and the dispersion
of the bands are very different. The electronic band structure of the 400 °C annealed sample displays dispersing bands with intensities similar to the typical band structure of bulk-terminated $n$-doped Bi$_2$Se$_3$ single crystals$^{1,3-7,10}$. The upward dispersing band with a maximum intensity at ~0.1 eV BE (at 0°) is assigned as the bulk conduction band. The TSS is not clearly resolved in this data taken with a sample temperature slightly above room temperature but the downward-dispersing band can be confidently assigned at the bulk valence band of Bi$_2$Se$_3$. Since the melting point of metallic Bi is only 200 °C, we infer that annealing to 400 °C desorbs the Bi-rich surface regions preferentially, leaving behind a fully bulk-terminated surface with the usual Bi$_2$Se$_3$ band structure.

### 3.4 Summary and Conclusions

We have observed the prevalent coexistence of Bi and Se terminations of air cleaved surfaces of Bi$_2$Se$_3$. Our photoemission study of the surface composition for cleaved single crystals shows that cleaving in air tends to lead to metallic Bi-rich regions. We identify ambient intercalants to be a major cause of this unexpected inhomogeneous surface since samples stored in a vacuum desiccator have a reduced probability of Bi-rich terminations. In addition, 100% of in-situ cleaves in high vacuum result in the expected Se-termination. The Bi-rich surfaces have a strongly modified occupied band structure as shown by ARPES that is in agreements with other electronic structure measurements for related crystals intentionally prepared with Bi-rich terminations.$^{[88, 91]}$ The well-known band structure of Se-terminated Bi$_2$Se$_3$ is recovered upon annealing to 400 °C due to thermal desorption of Bi-rich regions.

The recent conflicting results$^{[89, 90]}$ about surface termination of cleaved Bi$_2$Se$_3$ most likely originate from differing sample storage and cleavage procedures between different experiments. In our experiments, single crystals cleaved in vacuum were observed to have the expected Se-termination. However, it is clear that the surface is air-sensitive and different approaches for storage and mechanical cleavage could result in different surface terminations$^{[97]}$. Most notably, our observations suggest that
Bi$_2$Se$_3$ cleaved in air has a high probability (>50%) to exhibit an inhomogeneous surface with electronic structure very different than the “prototype” TI often expected based on pioneering ARPES studies[73, 75-78, 81, 100]. This is a cautionary example in the ongoing effort to characterize transport in TSSs where the method of Scotch tape cleavage is routine. A micro-LEED and XPS study of this structure would be a valuable experiment to examine the 2D crystallography of the differently-terminated surface domains.

As increasingly complex multi-component layered materials[89, 91, 101-103] are considered in the field of topological insulators and superconductors, it is important to maintain a keen awareness of the complexities possible at their surfaces. Inhomogeneous surfaces are a major challenge for transport experiments that may not be easily combined with surface characterization. However, the surface complexity described here and evident in other works[75, 77, 78] [80, 84, 89, 91, 97] present a great opportunity for diverse electronic property control in topological materials.
References

CHAPTER 4 CR-DOPING OF THE TOPOLOGICAL INSULATOR Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3}

4.1 Preface

The quaternary 3D TI Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3} (BSTS) was the first TI to show spin-polarized conductance in a highly resistive bulk crystal.\[104\] As mentioned in Chapter 1, this solid solution solves some of the defect chemistry in the binary TIs and is thus an excellent candidate to study bulk magnetic-doping.\[4\] A consequence of this breaking of TRS is that a gap in the TSS opens, analogous to adding mass acquisition of the Dirac fermions, and results in the quantum anomalous hall effect (QAHE).\[5\] This has been observed at very low temperatures, below 1 K, by transport measurements.\[42, 105, 106\] Increasing the transition temperature, T_c, of the ferromagnetic phase is important to realize these novel phases as well as for applications to real world devices.\[107\] In the following work, we study Cr-doping BSTS showing that at 4% Cr the sample is a bulk insulator with an antiferromagnetic transition around 50 K. We also show evidence for phase segregation for high concentrations, which questions the origin of the magnetic response and illustrates some of the complexities in this approach to breaking TRS in TIs.
Cr-doping of the topological insulator Bi\textsubscript{1.5}Sb\textsubscript{0.5}Te\textsubscript{1.7}Se\textsubscript{1.3}

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Abstract

The topological insulator (TI) Bi\textsubscript{1.5-x}Sb\textsubscript{x}Cr\textsubscript{x}Te\textsubscript{1.7}Se\textsubscript{1.3} (Cr-BSTS) was doped with Cr (0% ≤ x ≥ 20%) in a solid solution growth to investigate the impact of magnetic dopants on the electrical and magnetic properties of this material. Powder x-ray diffraction (PXRD) of the Cr-BSTS samples match calculated patterns for BSTS for samples taken from the middle ampoule suggesting Cr site-substitution. However, PXRD taken from the top and bottom of the growths reveal Cr\textsubscript{x}Se\textsubscript{y} impurity phases at high doping concentrations (x=20%). X-ray photoemission spectroscopy show the presence of Cr 2p peaks up to 4% Cr. These measurements suggest that phase-segregation likely occurs at Cr-doping higher than x=4%. Ultraviolet photoelectron spectroscopy reveals a p-doping effect with an upward shift of ~0.5 eV for the 4% Cr-BSTS. Resistivity versus temperature measurements show an insulating trend with an upturn in resistivity at ~75 K for this and superconducting quantum interference device measurements show an antiferromagnetic ordering below 50 K. This temperature is consistent with the Cr\textsubscript{x}Se\textsubscript{y} phase calling into question the origin of the observed magnetic ordering. These results highlight the challenges in synthesizing magnetically-doped TIs and the importance of complimentary tools for chemical and structural characterization.

4.2 Materials Science Challenge in TI Synthesis

Magnetic doping of topological insulators (TIs) is expected to break the time-reversal symmetry (TRS) of the system resulting in the quantum anomalous hall effect\cite{30, 108-110} and has been observed in magnetically-doped bismuth chalcogenides at very low temperatures.\cite{42, 111} Experimental observations of magnetically induced gap-opening\cite{32} and the opening of backscattering channels\cite{112} in 3d transition-metal doped TIs further suggest bulk-doping to be a viable route to synthesize a ferromagnetic TI. However, complexities can occur for measuring the massive-Dirac surface states as has been seen, for example, in the work of Liu et al. where they observed the size of the gapped topological surface state varies at the nm scale.\cite{31} and in the work of Sanchez-Barriga et al. where they measure a
nonmagnetic gap-opening of the TSS.[41] These results highlight the essential need for basic structural, chemical, electronic, and magnetic characterization of magnetic doping in TIs.

A major material science challenge in the TI field has been to eliminate bulk charge carriers such that the interesting physics of the spin-textured topological surface state (TSS) can cleanly be accessed.[113] The materials Bi$_2$Se$_3$ and Bi$_2$Te$_3$ have been considered prototypical strong 3D TIs as they are a binary compound with a single Dirac cone.[4, 5] Unfortunately, Bi$_2$Se$_3$ is typically grown as an n-type material owing to Se-vacancies making the TSS difficult to probe.[45] Bi$_2$Te$_3$ has the its own complexity in that its Dirac point is buried in the bulk valence band (BVB) which can allow scattering between bulk and surface states.[114] The ternary TI material Bi$_2$Te$_2$Se (BTS) has a similar quintuple layer (QL) crystal structure, Te-Bi-Se-Bi-Te, and has been previously investigated because of its electronic, chemical and structural properties that result in ordered.[113, 115, 116] The ordered QLs in the crystal structure reduces defect formations and has been shown to yield a large bulk resistivity.[113, 117-119] Advantages of the BTS phase include the suppression of Se vacancies and Te-Bi antisite defects as a result of the preferable Se-Bi bonding between Bi layers. The ordered nature of the BTS phase controls point defects in the layered structures in order to maintain the properties necessary for an ideal topological insulator. In comparison to the commonly investigated Bi$_2$Se$_3$ (BS) and Bi$_2$Te$_3$ (BT) TIs, the BTS phase maintains the simple surface-state structure of BS without a significant amount of Se vacancies and can be grown without being highly metallic like BT as a result of Bi-Te antisite defects.[33, 115-119] The robust chemical and structural characteristics of the BTS phase make it an ideal candidate for further investigations using a solid-solution systems and doping to tune the material properties.

Recently, the Bi$_{1.5}$Sb$_{0.5}$Te$_{1.7}$Se$_{1.3}$ (BSTS) solid solution, with the same crystal structure as Bi$_2$Te$_2$Se ($R3m$), has been investigated for its high insulating bulk and tunable Dirac carriers.[113] The BSTS crystal structure is comprised of Te/Se-Bi/Sb-Se-Bi/Sb-Te/Se quintuple layers, making it a solid-solution with 30% of the Te sites occupied by Se and 25% of the Bi sites occupied by Sb. The advantages of BSTS is a bulk insulating crystal as grown with a Dirac point above the top of the BVB and with a recent report of charge-current-induced spin polarization[104] this material is an ideal TI to study. The properties of the layered BSTS solid solution can further be tuned by doping with a magnetic transition metal, as has been shown for Cr-doped BST.[120, 121]

In this work we investigate Cr-doping the quaternary TI BSTS for nominal concentrations of Cr up to 20%. It is suggested that Cr can be successfully substituted in the BSTS single crystals for concentrations up to 4% and at higher concentrations phase segregation of Cr$_x$Se$_{1-x}$ impurities likely occurs by powder x-ray diffraction and x-ray photoelectron spectroscopy results. The 4% Cr sample shows insulating transport characteristics at all temperatures and an antiferromagnetic phase transition at ~ 50 K by magnetometry measurements. Ultra-violet photoelectron spectroscopy suggests a $p$-doping effect that
is expected for Cr-doping. While it is expected for BS and BT to remain an insulator at 4% Cr-doping,[122] the similar observed Neel temperature to Cr$_3$Se$_4$ [123] and appearance of these impurities at higher concentrations cannot rule out that possibility these phases exist in our 4% Cr crystals. These results suggest that at 4% Cr-doping, BSTS may be a broken-TRS TI material, however further characterization is needed to identify the source of magnetism in this system.

4.3 Experimental methods

High-quality single crystals of the Bi$_{1.5}$Sb$_{0.5}$Te$_{1.7}$Se$_{1.3}$ (BSTS) solid solution were grown by flame-sealing stoichiometric amounts of reagent grade Bi beads (Sigma Aldrich, 99.999%; 1-5 mm particle size), Sb pellets (Alfa Aesar, 99.9999%; 1 mm), Te crystal flakes (Sigma Aldrich, 99.999%; 2-8 mm), and Se beads (Sigma Aldrich, 99.99%; < 5 mm) in evacuated quartz tubes according to previously reported methods.[113] The reactant mixture was heated to 850 °C over a period of 4 h in order to achieve a melt, held at 850 °C for 48 h, followed by cooling over 24 h to 550 °C and annealing at that temperature for 96 h, and then cooled to room temperature over a period of 24 h. Intermittent agitation of the reaction vessel at 850 °C was used in order to ensure the homogeneity of the melt. This synthesis procedure was also used to prepare Cr-doped BSTS samples by replacing Bi with 0.25%, 1%, 4%, 7%, 10%, and 20% Cr, which can be represented by the general formula Bi$_{1.5-x}$Sb$_{0.5}$Cr$_x$Te$_{1.7}$Se$_{1.3}$.

The Cr-doped BSTS crystals were characterized by high-resolution powder X-ray diffraction (PXRD) on an INEL diffractometer using Cu K$_{α1}$ (λ = 1.54056 Å) radiation from a sealed-tube X-ray generator (35 kV, 30 mA) using a curved position sensitive detector (CPS120) in order to confirm that all the samples maintained the same crystal structure ($R3m$) in high-purity. The lattice parameters of the Cr-BSTS solid-solution crystals were refined using the JADE 9 least squares based refinement program. The crystal structures of Cr-BSTS were generated using the VESTA (ver. 3.0), a structural model software.[124]

X-ray photoelectron spectroscopy (XPS) was performed using an Al K-α source (hν = 1486.7 eV) and ultra-violet photoelectron spectroscopy (UPS) with a Specs UVS 300 He I (hν = 21.2 ev) light source using a hemispherical electron analyzer (Specs Phoibos 150 mm) where the base pressure of the system was ~1x10$^{-10}$ mbar. The single crystals of Cr-BSTS were cleaved in situ in high vacuum (P ~ 1x10$^{-7}$ mbar) and at room temperature prior to XPS analysis. The spectra have been energy-calibrated to the C 1s line at 284.5 eV.

Transport characterization was performed using a quantum design ever cool physical property measurements system with a base temperature of 2 K. Magnetization measurements were performed with a quantum design ever cool magnetic property measurements system with a base temperature of 2 K and magnetic field range up to 7 T.
4.4 Structural Details

The doping of BSTS with Cr is expected to substitute at the Bi/Sb sites[125-128] and yield a site-disordered structure with Te/Se-Bi/Sb/Cr-Se-Bi/Sb/Cr-Te/Se QLs, as shown in Figure 4.1(a). This mixing ideally remedies the defect-chemistry inherent in BS and BT and at this composition is expected to place the Dirac-cone at the Fermi level. The (111) surface of the Cr-BSTS samples is shown in Figure 4.1(b) showing its hexagonal symmetry.

Figure 4.1 (a) Crystal structure of the Bi_{1.5-x}Cr_{x}Sb_{0.5}Te_{1.7}Se_{1.3} solid solution comprised of quintuple layers. (b) A view along the c-axis of the hexagonal layers is outlined in black, and the magenta, yellow, and green spheres represent the Bi/Sb/Cr, Te, and Se atoms, respectively.

The phase purity of the Cr-doped BSTS samples was determined by PXRD in comparison to the calculated powder pattern of BSTS, as shown in Figure 4.2. The detection limit of the diffractometer is ~5% and because only a small fraction of the crystallites in a sample contribute to the diffraction signal, minute impurity phases cannot be detected. The matching of the measured and calculated peaks suggest that the primary phase present in the PXRD samples are BSTS. Lattice constant refinements were performed starting from the previously reported ordered Bi_{2}Te_{2}Se (R̅3m) crystal structure, as listed in Table 4.1, and were found to be relatively unchanged with increased doping of Cr into the Bi-site.[115]

This suggests the possibility of Cr substituting into the Bi-sites, but does not rule out other scenarios, such as intercalation between QLs and phase segregation. PXRD at the top and bottom of the growth boule reveal Cr_{x}Se_{y} impurity phases for the highest nominal Cr loading into the growth ampoule as shown in Figure 4.3. The resolution limitation of the instrument prevents us from distinguishing the impurity phase between Cr_{0.68}Se and Cr_{2}Se_{3}, however a clear impurity phase is present in these samples. The data shown
in Figure 4.2 was taken on samples from the middle of the boule, from which all subsequent characterization measurements were taken.

![Figure 4.2. Powder X-ray diffraction pattern calculated from the crystal structure of Bi$_{1.5}$Sb$_{0.5}$Te$_{1.7}$Se$_{1.3}$ (BSTS) and experimental patterns of pure 0-20% Cr-doped BSTS crystals. The most intense peaks are labeled with their Miller indices (hkl) on the calculated patterns.](image)

Table 4.1. Refined lattice constants of the experimental powder diffraction data for Bi$_{1.5}$Sb$_{0.5}$Te$_{1.7}$Se$_{1.3}$ (BSTS) performed using the Jade 9 software starting from the reported crystal structure of the ordered Bi$_2$Te$_2$Se ($R\bar{3}m$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSTS</td>
<td>4.253(5)</td>
<td>29.82(5)</td>
<td>467.27</td>
</tr>
<tr>
<td>0.25% Cr-BSTS</td>
<td>4.257(3)</td>
<td>29.91(3)</td>
<td>469.54</td>
</tr>
<tr>
<td>1% Cr-BSTS</td>
<td>4.245(2)</td>
<td>29.81(3)</td>
<td>465.35</td>
</tr>
<tr>
<td>4% Cr-BSTS</td>
<td>4.244(5)</td>
<td>30.02(5)</td>
<td>468.55</td>
</tr>
<tr>
<td>7% Cr-BSTS</td>
<td>4.251(7)</td>
<td>29.83(7)</td>
<td>467.00</td>
</tr>
<tr>
<td>10% Cr-BSTS</td>
<td>4.256(2)</td>
<td>29.92(2)</td>
<td>469.57</td>
</tr>
<tr>
<td>20% Cr-BSTS</td>
<td>4.257(2)</td>
<td>30.01(1)</td>
<td>471.31</td>
</tr>
</tbody>
</table>
4.5 Chemical Composition

The near-surface chemical composition of the series of Cr-BSTS crystals was investigated by XPS. Figure 4.4 shows the Cr $2p$ and Te $3d$ core level spectra for 0-4 % (a) and 7-20 % (b). The Te $3d$ doublet appears at 572 eV and 582.5 eV for all samples as expected. The Cr $2p$ doublet can be seen in the lowest doped sample 0.25% Cr as a small peak at 576 eV and 586.5 eV and grows in intensity with increasing nominal Cr-content to 4%. Note that for the 1% sample, a hiccup in the x-ray source is responsible for the noise around 588 eV. It is interesting that for the higher doped samples (7-20%) there is absolutely no evidence for Cr in these samples. All samples for these experiments showed flat and shiny surfaces with no indication for a poorly cleaved sample. The PXRD and refined lattice constants shows similar crystal structure for the Cr-BSTS series which when combined with XPS results suggests a phase segregation is occurring at the nominal doping level of 4%.

Figure 4.3 PXRD of the 20% Cr-BSTS sample showing the top (green), middle (blue), and bottom (pink) of the single crystal. Calculated PXRD patterns are shown for BSTS (black) and Cr$_{0.68}$Se (red). The Cr$_{0.68}$Se impurity is observed to segregate to the top of the crystal, and no residual impurity is observed in the middle or bottom of the crystal.
XPS for the Sb 3d levels are shown in Figure 4.5 for 0%-4% Cr. The 1% Cr-BSTS sample shows additional peaks in the O 1s region indicating possible contamination. It is also an anomaly in that it shows metallic character with an insulating ground state as evidenced by transport data (Figure 4.6c). The Cr-content is comparable to the 4% sample as evidenced by XPS data (Figure 4.4 (a)). Although no impurity peaks are seen in PXRD (Figure 4.2), there is an observable oxygen contamination. Considering the metallic transport properties of the 1% Cr sample, we suggest that these samples were likely contaminated in the growth process or during the cleave adding trace impurities resulting in a higher carrier concentration.
The valence band structure of the 0% Cr-BSTS and 4% Cr-BSTS samples was probed by UPS. Figure 4.4 shows the normal photoemission spectra (i.e. Γ-point) for the 0% Cr-BSTS (black) and 4% Cr-BSTS (red). The bulk valence band (BVB) is located at ~0.35 eV and the TSS can be seen as the peak near the Fermi level in agreement with the literature.[113] It can be ruled out that this feature is a bulk conduction band (BCB) because of the transport measurements (next section) results show a clear semiconducting trend. The 4% Cr-BSTS BVB is shifted up in binding energy (BE) by ~0.05 eV indicating a \( p \)-doping effect. The TSS of the Cr-doped sample is difficult to resolve with a low intensity and suggests that the Dirac point may be at or near the Fermi level as would be expected from a rigid shift of the undoped spectrum.

Figure 4.5 XPS spectra of Sb 3d and O 1s core levels for 0%, 0.25%, 1%, and 4% Cr-BSTS. A strong doublet peak is observed for all samples for the spin-split Sb 3d state. A noticeable amount of oxygen contamination is observed for the 1% Cr-BSTS (orange spectrum).

4.6 Electronic Structure

The valence band structure of the 0% Cr-BSTS and 4% Cr-BSTS samples was probed by UPS.

Figure 4.4 shows the normal photoemission spectra (i.e. Γ-point) for the 0% Cr-BSTS (black) and 4% Cr-BSTS (red). The bulk valence band (BVB) is located at ~0.35 eV and the TSS can be seen as the peak near the Fermi level in agreement with the literature.[113] It can be ruled out that this feature is a bulk conduction band (BCB) because of the transport measurements (next section) results show a clear semiconducting trend. The 4% Cr-BSTS BVB is shifted up in binding energy (BE) by ~0.05 eV indicating a \( p \)-doping effect. The TSS of the Cr-doped sample is difficult to resolve with a low intensity and suggests that the Dirac point may be at or near the Fermi level as would be expected from a rigid shift of the undoped spectrum.
4.7 Magnetic and Charge Transport Properties

Transport and magnetization measurements were performed on the series of Cr-doped BSTS crystals to reveal the electronic and magnetic structure changes. Resistivity as a function of temperature results for the 0%, 0.25 %, 1%, and 4% Cr-BSTS samples are shown in Figure 4.7 (a-d). A metallic-like trend is observed down to ~50 K then transitions to an insulating ground state for the 0% and 0.25% Cr samples (Figure 4.7 (a) and (b)). This behavior is common for small band-gap semiconductors with high carrier-concentrations.[45] The 4% Cr-BSTS sample, however, shows an increase in resistivity throughout with a sharp increase at ~ 50K. This indicates this sample is a bulk insulator with low carrier-concentrations. Hall-effect measurements could be performed as a future experiment to determine the carrier-concentrations and type.

Figure 4.6 UPS at the Γ-point for 0% (black) and 4% (blue). A clear shift towards higher binding energy is observed for the BVB for the 4% Cr sample.
Figure 4.8 (a-d) shows the magnetic moment versus temperature for the 0-4% Cr-BSTS samples. For the low doped samples, 0-1% Cr, a decreasing moment as a function of temperature is seen (a-c) indicating a diamagnetic response for these crystals. The 4% Cr-BSTS sample shows magnetic behavior with an antiferromagnetic transition at \( \sim 50 \) K. Magnetic and transport properties of \( \text{Cr}_x\text{Se}_y\text{Te}_z \) systems have been previously studied and \( \text{Cr}_3\text{Se}_4 \) compounds have been shown to Neel temperatures around 40 K.[123, 129, 130] We have shown that phase segregation of \( \text{Cr}_3\text{Se}_4 \) impurities occur at higher doping-concentrations and because of the sensitivity of the PXRD measurements, we cannot rule out the possibility of these impurities as the source of the magnetic response. Further experiments, such as x-ray absorption and circular dichroism spectroscopy analysis could be performed to elucidate origin of the magnetic response and determine if Cr are substituting at the Bi/Sb sites.[128]

Figure 4.7 Resistivity (m\( \Omega \) cm) as a function of temperature (K) for 0%, 0.25%, 1%, and 4% Cr-BSTS (a, b, c, and d respectively). An upward turn in resistivity is observed for all samples below \( \sim 75 \) K indicative of an insulating ground state. The 1% Cr-BSTS is an anomaly showing metallic behavior before transitioning to the insulating state. This is possibly due to the oxidation contamination (See Figure 4.8).
Conclusions

To summarize, we have investigated the crystal, magnetic, and electronic structure and near surface chemical composition of the Cr-doped Ti BSTS. Higher doped samples (x>4%) show no evidence of Cr-dopants by XPS and PXRD of the 20% Cr shows Cr$_{x}$Se$_{y}$ impurity phases which suggests phase segregation is likely occurring for high nominal concentrations of Cr and has been seen in other magnetically doped TIs.[131] The 4% Cr-doped BSTS crystals are bulk insulating with antiferromagnetic ordering as shown by magnetotransport measurements. UPS reveals a p-doping effect with an upward shift of ~0.5 eV and suggests the 4%-Cr sample is a possible candidate for investigating breaking TRS in strong 3D TIs, however, because of the similar transition temperature to Cr$_{2}$Se$_{3}$ and limitations of PXRD, unambiguous determination of the origin of this magnetic response requires further experiments on the synthesis and phase purity of these bulk-doped samples.

Figure 4.8 Magnetization (emu/gm) as a function of temperature (K) for the 0%, 0.25%, 1%, and 4% Cr-BSTS (a, b, c, and d). The gentle upslope in the 0%, 0.25%, and 1% indicates a diamagnetic response. The 4% Cr-BSTS sample has a peak indicating an antiferromagnetic phase transition around 50 K.
These findings provide insight in the materials science challenges of magnetically doping TIs through bulk methods. The materials science challenge of a having a bulk insulating and cleanly accessible Dirac point in TIs has been demonstrated for BSTS confirming previous reports of this material.[104, 113] The transport and UPS results of the Cr-doped BSTS crystals suggest that this TI is a promising candidate for future experiments investigating the nature of breaking TRS. [42, 107, 120] Another route would be to consider other magnetic dopants such as V or Mn as these have been shown to successfully create ferromagnetic TIs[35, 111], or the use of magnetic molecules such as transitional metal phthalocyanines.[37, 53, 54, 132]

Acknowledgments
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References


15. Lee, I., et al., Imaging Dirac-mass disorder from magnetic dopant atoms in the ferromagnetic topological insulator \(\text{Cr}_x\text{Bi}_0.1\text{Sb}_0.9\text{Te}_3\). Proceedings of the National Academy of Sciences, 2015. 112(5): p. 1316-1321.


CHAPTER 5 LOCAL MOLECULAR ADSORBATE HYBRIDIZATION AT A TOPOLOGICAL INSULATOR SURFACE

The coupling of the organic molecule Manganese Phthalocyanine to the topological insulator Bi$_2$Te$_3$ was investigated by a combination of spectroscopic and microscopic techniques. An earlier study by STM/STS presents a mystery in that a strong coupling occurs, with no apparent interaction with the TSS.\textsuperscript{[53]} In this prepared manuscript, we report a new hybrid-interface state (HIS) form by UPS and ARPES at \(~0.4 \text{ eV. The HIS is shown to be localized at the molecular adsorption site by STS. The morphology was characterized by STM and AFM show the molecules to form an ordered close-packed layer that transitions to layer + island growth. These results confirm that MnPc can be effectively coupled to the TI Bi$_2$Te$_3$.}
Local Molecular Adsorbate Hybridization at a Topological Insulator Surface
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2 Department of Chemistry, North Carolina State University

Abstract
The coupling of the organic molecule Manganese Phthalocyanine (MnPc) to the topological insulator Bi₂Te₃ was investigated by a combination of spatially-averaged and local spectroscopy techniques. The modification of the bulk bands was tracked by angle-resolved photoemission spectroscopy with increasing MnPc coverage showing the appearance of a hybrid-interface state. We show the state to be localized at the molecular adsorption site by scanning tunneling spectroscopy. A mechanism is suggested for the formation of the HIS of MnPc on Bi₂Te₃ involving the MnPc d₂ and Te p-orbitals.

5.1 Introduction
Topological insulators (TIs) are a prime candidate for studying interface effects due to their spin-textured surface states on a bulk insulating material.[4, 133] These topological surface states (TSS) are protected by time-reversal symmetry making them robust against defects and perturbations that preserve this symmetry.[134] Studies of the organic-metal interface have produced exciting and unexpected results, such as beating the Stoner criterion[135] and the Kondo effect[136]. Modification of the magnetic and electronic properties of TIs has mainly focused on the technique of bulk or surface doping leaving room for organic molecules to control TIs.[42, 111, 137] The organic-TI interface is a unique opportunity to probe the coupling of organic molecules to a bulk insulating material with a spin-momentum locked surface state. Transition-metal phthalocyanine molecules (MPcs) are promising molecular candidates considering their success in creating interesting spin-interfaces with metals.[138-143] The ability to tune the central metal atom offers the potential to selectively couple MPcs to the orbitals of the substrate.[54, 144, 145]

While earlier studies of organic-TI interfaces focused on chemical tuning of the bulk band structure in order to access the TSS[50, 51], there have been three recent reports of HIS forming at the organic-TI interface with a phthalocyanine derivative molecule. A recent scanning-tunneling microscopy/spectroscopy (STM/STS) experiment that the organic molecules Manganese Phthalocyanine (MnPc) can be coupled to the TI Bi₂Te₃ such that HIS forms in the unoccupied states.[53] The TSS was reported to be unaffected by the MnPc molecules as a lack of surface state scattering was observed by differential conductance mapping of the interface. Additionally, it was shown through a density-functional theory (DFT) and angle-resolved photoemission spectroscopy (ARPES) experiment that the
metal-free phthalocyanine (H$_2$Pc) can form a HIS in the occupied states of the TI Bi$_2$Se$_3$, while leaving the TSS intact.[132] Interestingly, the organic molecules C60 and sulfur phthalocyanine did not form a HIS with Bi$_2$Se$_3$ suggesting that the molecule-substrate adsorption strength determines the HIS formation. Finally, an ARPES study of CoPc on Bi$_2$Se$_3$ shows not only the formation of a HIS, but also the suppression of the TSS wave function at the organic-TI interface.[55]

Here we show the emergence of a new HIS between the organic molecule MnPc and TI Bi$_2$Te$_3$ through a combination of ARPES and STS experiments. We observe an $n$-doping consistent with previous reports at moderate coverage with the emergence of a new HIS around 0.4 eV below the Fermi level by ARPES. This HIS is further confirmed by STS and shown to be localized at the molecular adsorption site. Contrary to previous reports we show close-packing of MnPc molecules suggesting a temperature-dependent adsorption scenario. Additionally, we suggest a mechanism involving the MnPc and Bi$_2$Te$_3$ orbitals and comment on the burial of the TSS below the first quintuple layer.

5.2 Experimental Methods

Manganese Phthalocyanines (MnPc) was purchased from Sigma Aldrich and was outgassed in a quartz ampule in high vacuum (P ~1 x 10$^{-7}$ Torr) to remove impurities prior to use. A stable flux was verified with a quartz crystal microbalance at approximately 0.1 Å/s for organic molecular beam deposition of MnPc molecules. Single crystals of Bi$_2$Te$_3$ were synthesized in a binary melt according to the literature (ref). The crystals were cleaved in high vacuum (P ~1 x 10$^{-7}$ Torr) to ensure a clean surface for measurements. The angle-resolved photoemission experiments were performed with a Specs 150 mm hemispherical analyzer using the Specs UVS 300 He I ($h\nu = 21.2$ ev) light source in ultra-high vacuum (P ~3 x 10$^{-11}$ Torr). Although our system lacks a 2D detector, we are able to probe $k$-space by physically rotating the sample as we have previously demonstrated.[46] Local probing of electronic structure was performed by differential conductance (dI/dV) scanning-tunneling spectroscopy (STS) (Omicron VT-XA 100/500 scanning tunneling microscope (STM)) mounted with W-tips at ~130 K in UHV. Morphology for initial coverage is shown by STM at ~ 130 K while higher coverage morphology was determined by atomic-force microscopy (AFM) (Asylum Research MFP-3D, Budget Sensors Tap300Al-G tips) in AC mode in air.

5.3 Results and Discussion

Figure 5.1 (a) shows the background subtracted ARPES for the freshly in-situ cleaved Bi$_2$Te$_3$. The Fermi level ($E_f$) is indicated by a dashed white line. The well-known M-shape dispersion of the bulk valence band (BVB) is clearly observed.[4, 133, 134] The top of the BVB is at ~0.1 eV below $E_f$ and the
TSS can be seen dispersing up through $E_f$ indicating our samples are indeed bulk insulators. Note that the energy resolution of our experiment at room temperature is $\sim 0.1$ eV and angular resolution of $\sim 0.1 \text{ Å}^{-1}$.

The modification of the electronic structure of $\text{Bi}_2\text{Te}_3$ after adsorption of $\sim 0.13$ molecules/nm$^2$ of MnPc is shown in Figure 5.1 (b). The appearance of the bulk conduction band (BCB) is observed around $E_f$ consistent with earlier reports of $n$-doping.[53] The broadened BVBs are dispersing despite the scattering that is known to occur for photoelectrons on a molecular covered substrate.[146] At this coverage the electronic structure closely resembles that of the clean $\text{Bi}_2\text{Te}_3$ shifted down in energy by $\sim 0.1$ eV with broadened features at this energy range.

The situation at higher-coverage is quite different (Figure 5.1 (c)). The M-shape of the BVB is no longer present and instead a broad and weakly-dispersing state emerges at $\sim 0.4$ eV. We identify this as a previously unreported HIS formed by the mixing of MnPc and $\text{Bi}_2\text{Te}_3$ electronic states. This HIS can be directly compared to the work of Jakobs et al. who showed a similar state forming between H$_2$Pc and Bi$_2$Se$_3$ which has a similar dispersion and spans several eV in energy-space.[132] Our energy and angular resolution limit our analysis of the presence of the TSS at this coverage, however it has been suggested that the TSS wave function is pushed below the first QL.

For completeness, the full range ARPES which tracks the change in the deeply bound electronic states is shown in Figure 5.2 (a). The M-shape of the top of the BVB (Figure 5.1 (a)) can be observed around 0.1 eV for the freshly cleaved $\text{Bi}_2\text{Te}_3$. The maximum spectral intensity feature for the BVB occurs at $\sim 0.8$ eV for the $\Gamma$-point at 0.0 Å$^{-1}$ and disperses toward higher binding energy. All of these features are consistent with the literature indicating our starting sample is of pristine condition.[147] Moreover, the
clean ARPES shows very dispersive bulk bands which allow us to easily identify the changes due to adsorption of MnPc.

The broadening of the BVB for the initial MnPc coverage of ~0.13 molecules/nm² (Figure 5.2b) is visible as well as the appearance of the BCB at the Fermi level in the full range ARPES. The molecular orbitals (MOs) of the MnPc molecule are clearly observed as a weakly-dispersing peak centered around 1.0 eV. A more detailed analysis of the contribution to this peak is presented below for normal emission data.

Increasing the coverage to ~0.28 molecules/nm² results in a weakly dispersing ARPES map (Figure 5.2c). The M-shape of the BVB maximum and BCB are no longer visible and instead a feature near 0.4 eV can be seen, however the overall intensity of the MnPc MOs dominates the signal making identification of the new HIS difficult.

![Figure 5.2](image)

**Figure 5.2** ARPES maps of clean (a), ~0.13 Mol/nm² (b), and ~0.28 Mol/nm² (c) with Fermi level indicated by dashed white line. The bulk bands can clearly be seen dispersing with a maximum intensity at 0.8 eV for the Γ-point at 0.0 Å⁻¹ and an M-shape at the top of the BVB. The appearance of the MnPc molecular orbitals (MOs) can be seen after depositing ~0.13 Mol/nm² (b). The BCB can also be seen as the MnPc molecules n-dope Bi₂Te₃. Increasing the molecular coverage to ~0.28 Mol/nm² (c) reveals a new hybrid-interface state emerging at 0.4 eV below E_f along with an increase in intensity and decrease in dispersion of the MnPc MOs.

The normal emission UPS spectra in Figure 5.3 allows us to easily identify the occupied electronic states with consideration of their dispersion. The background subtracted spectra in Figure 5.3 (a) shows the downward shift of the BVB upon going from clean to ~ 0.13 molecules/nm² of MnPc which also brings the BCB below the Fermi level. The MOs can be distinguished from the deeper lying BVBs in the clean spectra at ~0.7 eV due to their positions, which are consistent with the literature, and their dispersion. The spectrum for the ~ 0.28 molecules/nm² are again dominated by the MnPc MOs and a broad energy state can be seen near 0.4 eV that is assigned as the new HIS. The difference spectra in Fig. 3b allows these states to be more readily assigned. The MOs of the adsorbed MnPc molecules consists of ligand derived π-state at ~ 1.5 eV and a d-π* state ~ 0.9 eV.[148] The MO π-state of a_1u symmetry is composed of the C and N 2p orbitals of the ligands which have a higher cross-section (i.e. higher
probability of emission by a factor of ~3) than the state of eg symmetry at 0.9 eV resulting from a mixture of the MnPc d orbitals with e_g symmetry (dxz and dyz) with the ligands π* state of e_g symmetry.[57, 149] This is further supported by the increased intensity of the a_{1u} state at higher coverages (Fig 3b).

Focusing on the normal emission UPS difference spectra near the Fermi (Figure 5.3 (b)) level allows a clear picture of the coupling process of MnPc to Bi_2Te_3. The BVB is identified by the feature around 0.3 eV that has been shifted down for a coverage of ~ 0.13 molecules/nm^2. We note that due to the M-shape of the valence band, this feature is not the top of the BVB, but where the sides of the M-shape meet at Γ-point at 0.0 Å^(-1) as seen in the ARPES maps of Fig. 1. The dispersion of this feature allows the unambiguous identification as the BVB. The bottom of the BCB can also be seen near the Fermi level confirming the electron transfer from MnPc to Bi_2Te_3. The emergence of the HIS is identified as the broad spectral feature in Fig 3d near 0.4 eV for a coverage of ~ 0.28 molecules/nm^2. The difference spectrum confirms the presence of a new state at this molecular coverage.

![Figure 5.3](image)

**Figure 5.3** Normal emission (k||=0 (Å^(-1))) for the molecule-covered surfaces (a) showing the downward shift of the BVB and appearance of BCB at a coverage of ~0.13Mol/nm^2 (red) and the broad HIS at ~0.28 Mol/nm^2 (blue). The difference spectrum allows us to cleanly identify the new spectral feature at 0.4 eV to be a new HIS. These spectra were background subtracted and normalized from the maximum spectral feature to the BVB of the clean surface.

The initial growth morphology of MnPc on Bi_2Te_3 is shown in Fig 5.4 (a). Flat-lying molecules are observed with a weak tendency to cluster and form chains. Second layer growth can also be seen consistent with previous work[54], however we observe clear formations of close packed molecules upon increasing coverage (Figure 5.4 (b)) which is contrary to the claim of an independent temperature adsorption scenario.[53] AFM was performed on the sample whose ARPES is shown in Figure 5.1 (c) which shows clustering of islands 4-6 nm in height and several 100 nm in length. These studies suggest an initial flat-lying growth mechanism which transitions into standing islands of MnPc molecules.
STS measurements of the MnPc molecule adsorbed surface were performed to investigate the local electronic structure. The HIS is further confirmed in Fig. 5 which shows dI/dV STS on and off the molecule taken at a coverage shown in Fig. 4b. This shows a broad peak near -0.4 V for spectra on the molecule (red) indicating the HIS is localized at the molecular adsorption site. Although this coverage is less than that of the HIS ARPES, we can rule out this feature as the BVB as it appears only on the molecule. It is plausible that this state was seen in the work by Sessi et al. in Fig. 3 where a broad shoulder in the STS spectra on the ligand near -0.5 V at the onset of the HOMO which can be seen near -1.0 V. This feature is not commented on as the focus is on the feature near +0.5 V identified as a HIS.

Figure 5.4 STM of MnPc on Bi₂Te₃ for different coverages. The initial growth (a) consists of disperse molecules with some tendency to form chains indicated by white dashed lines. Increasing the coverage reveals previously unobserved close-packed structures (b). AFM shows islands forming at higher coverages.
Observation of the localization of the HIS to the molecular adsorption site in addition to the ARPES results suggests a mixing of the MnPc d-orbitals with the Te p-orbitals resulting in a new bonding and anti-bonding state. The isolated MnPc molecules has D_{4h} symmetry, however the orbital configuration and occupation of the MnPc d-orbitals has been disputed.\[148\] It has recently been shown that the gas phase and thin film exhibit different configurations by UPS suggesting competing electronic ordering.\[2\] Earlier work by Kraus et al. demonstrate that these photoemission measurements can neglect to measure the excited states near the Fermi level as the peaks associated with these MOs are extremely sensitive to photon energy.\[149, 150\] Additionally, the filling of the D_{4h} configuration for Mn with five d-electrons would lead to a splitting of the degenerate e_g states in a Jahn-Teller fashion.\[151\] This tells us that the naïve assumption of this single electron consideration cannot fully explain the orbital configuration, especially at the interface.

Comparison with the literature does allow us to shed light on the possible MOs involved at this interface. To begin with, the often quoted HOMO of a_{1u} symmetry has been established to reside at \sim 1.5 eV for thick films.\[150, 152\] For thin films its location is closer to the Fermi level, \sim 1.2 eV similar to our observations, and moves to higher binding energy with increasing film thickness suggesting this MO is involved in the charge transfer.\[57, 148, 149\] The peak in UPS at \sim 0.9 eV is attributed to the doubly degenerate e_g orbital (d_{xz}/d_{yz} + \pi^*), as observed for other UPS measurements for MnPc on metals.\[150\] The a_{1g} (d_{x^2}) orbital of MnPc has the most overlap with the substrate p_z orbitals and is the likely candidate

![Figure 5.5 STS dl/dV spectra of MnPc/Bi2Te3 system on (red) and off (black) the molecule. The HIS is observed to be at the molecular site as the feature at -0.4 V is only observed on the molecule. Spectra off the molecule show a mostly featureless spectra dominated by the tunneling background signal.](image-url)
for the HIS. This claim is supported by comparison with MnPc on Ag(111) where a HIS is observed around -0.5 eV in addition to the $a_{1u}$ and $e_g$ MOs.[153] Further understanding of the mechanisms behind the MOs involved in the HIS could be elucidated by x-ray magnetic dichroism and absorption spectroscopy.

Recent photoemission spectroscopy studies of the organic-TI interface have shown that indeed a HIS can form near the Fermi level.[55, 132] Furthermore, the use of different photon energies showed that the surface sensitive UPS spectra (where $h\nu \geq 21.2$ eV) is mainly dominated by the HIS feature suppressing the intensity from the TSS. Lower photon energy ($h\nu \sim 6$ eV) probes deeper into a material showing the reemergence of the TSS spectral intensity and Caputo et al. suggest explicitly that the TSS is buried below the first quintuple layer.[55, 132] Our observations are consistent with these reports, pointing towards a complex organic-TI electronic interaction including the formation of a HIS and possible burying of the TSS wave function below the first QL. It interesting that MnPc do not act as scattering potentials once adsorbed to Bi$_2$Te$_3$ [53] however, a bias dependent analysis of the wavelength modulation is needed in order to prove the topological origin of the surface state[154]. It is possible that the suppression of the TSS would result in a diminished scattering pattern at the adsorption site of MnPc. Furthermore, spin-polarized measurements may be necessary to study the effects of magnetic adsorbates on TIs.[60]

5.4 Conclusions

In summary, we have detected a previously unreported HIS at the organic-TI interface of MnPc on Bi$_2$Te$_3$ through a combination of space-averaged (ARPES) and local probing (STS) of electronic states. The emergence of the HIS is shown by ARPES for an increasing coverage of MnPc molecules and shown to be localized at the molecular adsorption site by STS. Contrary to previous reports[53], we observe networks of close-packed molecules by STM indicating a clear temperature-dependent adsorption scenario. The detection of multiple HIS in the MnPc Bi$_2$Te$_3$ system illustrates the need for further characterization. Further experiments involving spin-resolved STM/STS could reveal the origin of this feature as well as elucidate the interaction of a magnetic molecule on the TSS. The demonstration of HIS at the organic-TI interface in this work and others illustrate the need for additional studies on the effects of molecular adsorbates on the TSS.

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References


31. Lee, I., et al., Imaging Dirac-mass disorder from magnetic dopant atoms in the ferromagnetic topological insulator Crx(Bi0.1Sb0.9)2-xTe3. Proceedings of the National Academy of Sciences, 2015. 112(5): p. 1316-1321.


