Magnetotransport in Thin Films and Heterostructures of Topological Matter

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Abstract

As our technological achievements in electronic device research are being pushed daily to newer extremes, we are constantly faced with the challenge of sustaining the current level of growth of development. Silicon is reaching its theoretical limits as the ideal material for processing platforms. Similarly, standard ferromagnetic metals will no longer be able to satisfy the requirement of making smaller and smaller nonvolatile memory bits. Topological materials hold promise for a future where progress may be sustained. Such materials host topological surface states that support spin-momentum locked Dirac-like charge carriers. They have been predicted to exist in several material systems and subsequently confirmed by ARPES. One of the biggest obstacles to making topological materials readily available for technological purposes is the fact that their bulk is not quite insulating. This makes surface states difficult to access and manipulate with conventional electrical transport probes.

In this thesis, we have studied two prototypical topological systems, Bi$_2$Te$_2$Se – belonging to the class of $Z_2$ protected topological insulators, and SnTe – a topological crystalline insulator. We use quantum coherent transport to probe the surface spin-momentum locking properties, as well as the spin-orbit coupling of the bulk electrons. Lastly, we look at how the breaking of crystalline symmetry by proximity to a ferromagnet alters the transport in SnTe.

We grew Bi$_2$Te$_2$Se thin films by MBE on Si(111) and studied the quantum coherent transport at low temperature and low magnetic field, as well as the high-field magnetoresistance (MR), which was found to be linear in field. In particular, we proposed a model to explain the high-field linear MR that allowed us to separate surface and bulk contributions to the transport. We were able to extract information pertaining to the spin-orbit coupling occurring for bulk bands in
the presence of a Rashba spin-orbit interaction. Our result yielded a value for the spin-orbit splitting energy, in decent agreement with what is observed in ARPES.

In addition, we optimized the growth of SnTe thin films by MBE on BaF$_2$ (001) and Si (001) substrates. We mainly focused on films grown on BaF$_2$ as we were able to obtain high-quality single crystalline films that are highly lattice matched with BaF$_2$. We demonstrated that film crystallinity, film morphology and the carrier density all improve with increasing growth temperature. We thus observe weak antilocalization (WAL), and study the effect as a function of Fermi level. It was found that the number of WAL channels extracted using the Hikami-Larkin-Nagaoka model increased as the coherence length decreased – a sign of surface-to-bulk scattering. The number of coherent channels also decreased when the Fermi was located deep in the valence band. We attributed this decrease to changes in the bulk Fermi surface topology that may either influence surface-to-bulk coupling or even completely suppress the surface states.

Lastly, we looked at the effect of magnetism in a SnTe-EuS-SnTe trilayer grown by MBE on Si (001). We observed proximity-induced magnetism at the SnTe-EuS interfaces though the anomalous Hall effect. As EuS is a ferromagnetic insulator, it is not expected to participate in the transport. The anomalous Hall effect must thus be a result of magnetism induced in SnTe at the interface between EuS and SnTe. The observed in-plane MR of the trilayer showed evidence of domain-wall-supported one-dimensional conduction as hypothesized for Bi$_2$Se$_3$-EuS. By investigating changes in the intrinsic transport characteristics in the minor hysteresis loop regime, we were able to confirm that the transport is highly correlated to the magnetic domain texture, indicating a strong proximity-induced magnetism in the otherwise nonmagnetic SnTe surface.
For future work, on magnetic-doped TIs, where the topological surface Dirac cone is expected to be gapped, we proposed an analysis scheme based on models that correlate the quantum coherent transport in the TI to the magnitude of the surface state gap.

As we enter the exciting era of topological condensed matter physics, these results will be of importance to the development of future device ideas relying on the manipulation of topological surface states.
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I. **Introduction**

1. **Charge and spin do matter, and so does mass**

   Going back to fundamentals, the most essential properties that make the electron what it is, are its charge, its spin and its mass. Up until the advent of quantum mechanics, science had provided a good understanding of the concepts of charge and mass. Classically speaking, the concept of electricity and conduction in common metals was properly explained by models that were based on Newtonian mechanics and Maxwellian electrodynamics [1, 2], and their application to conduction. The discrete charge quantum of the electron was hypothesized as early as 1838 and it was later identified as a discrete particle by J.J. Thompson in 1897. Measurements of both the electron mass and charge were made as early as 1896.

   The concept of spin, however, evaded common knowledge. It was not until the mid-twentieth century, that quantum mechanics provided a good understanding of spin. Electron spin can be basically visualized as an intrinsic magnetic moment carried by the particle.

   In a sense, the electron can now be thought of as a charged particle having a well-known mass but also as an infinitesimal magnet, having a north pole and a south pole.

2. **Manipulating charge, spin … and mass**

   With the classical knowledge that was available in the nineteenth century, vacuum tubes were engineered as devices that allowed one to manipulate electrical currents, or charge. With the
discovery of the transistor [3] and the p-n junction, a more reliable way of manipulating charges was found. The term electronics was thus coined as a result.

Later on, by the end of the twentieth century, devices that were capable of manipulating and detecting electron spin were invented. Giant magnetoresistance (GMR) [4,5] and tunneling magnetoresistance (TMR) [6] devices were introduced as tools that allowed one to easily measure changes in the electron spin by measuring changes in the resistance of a material under the action of a magnetic field. The GMR and TMR effects thus marked the beginning of the era of spintronics.

Lastly, the mass of the electron still evaded our control. It is commonly known that in solids, electrons behave as if they have a mass that is different from rest mass. The possibility of manipulating the electron mass, remains, however, a challenge. More interestingly, the ability to have no electron mass at all, would allow electrons to behave as relativistic particles. The prospect of having this capability of “switching” the electron mass ON and OFF would thus allow one to be able to physically choose between one theoretical realm and another – namely classical electrons or relativistic electrons.

3. **Graphene: the first Dirac material**

Dirac materials are materials that host relativistic electrons that behave according to the Dirac equation - a relativistic version of the Schrödinger equation. The best example of a Dirac material is graphene. In graphene, electrons behave relativistically, as if they have a no mass. This makes them robust to disorder and able to move “more freely” under the action of an
electric field. Such electronic properties are extremely useful for applications in transistor devices that require high frequency operations for example. The spin degree of freedom is however difficult to manipulate in graphene. Also, the electron mass is graphene is extremely robust to external perturbations. [7]

4. **Topological materials: the versatile cousins of graphene**

A topological material can be most easily described as a slab of material that is a poor conductor in the bulk but a metallic Dirac material on the surface [8,9]. Just like graphene, the surfaces of a topological material host massless electrons [8, 9, 10, 11]. But, unlike graphene, the surface electron spin, its momentum and its mass can be manipulated. Surface electrons have their spin locked to the current direction. This makes electron spin easy to manipulate, possibly even without the use of any magnetic fields. [12, 13, 14]

In addition, the fact that surface electrons have no mass, makes them ideal for uses in low consumption and high frequency electronics. The mass of those electrons travelling at the surface may be turned “ON” or “OFF” applying certain external perturbations, such as magnetic or electric fields [15, 16]. One’s ability to detect and manipulate charge, spin and mass in topological materials, makes them extremely attractive as computing device materials.

In summary, the properties of topological materials can be listed as follows:

- **Semiconducting** bulk that can be made insulating
- Metallic **high-mobility** surface electron states
- **Spin-momentum locked** conduction at the surface
- **Zero mass** electrons at the surface
- **Electron mass may be induced** by external perturbations

From an applications point of view topological materials can be implemented in computer processing devices as well as in memory and storage devices. Table I summarizes a list of applications that make topological materials of extreme importance to study.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Corresponding Technology</th>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dissipationless transport</strong></td>
<td>High frequency, low consumption processing</td>
<td>Low/no Joule heating</td>
</tr>
<tr>
<td><strong>Spin-momentum locking</strong></td>
<td>Smaller Memory bits</td>
<td>Spin on the surface, No fringing fields</td>
</tr>
<tr>
<td><strong>Tunable electron mass</strong></td>
<td>Fast switching transistors</td>
<td>Fast response time</td>
</tr>
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Table I-1. Summary of three important potential applications of topological materials, and the advantages that they represent over current technologies

5. **Making thin films and heterostructures of topological materials: motivation**

As discussed above, topological materials are useful for implementation in commonly used computer processing and memory storage devices. They have been proposed as silicon alternatives as well as potential substitutes for ferromagnetic materials used in memories.
Other uses in science have also been proposed. Topological surfaces are expected to host Majorana Fermions – particles that are their own antiparticle – when in proximity to a superconductor [17, 18]. The realization of magnetic monopole-like surface signatures has also been proposed in topological materials in proximity to a ferromagnet [19].

All of the above possibilities and proposals require one to be able to grow thin films of topological materials and measure their transport properties, as electronic devices are quasi-two-dimensional. This has thus motivated us to study the fundamental electronic transport properties of topological materials in thin film form as a starting point. Secondly, we will look at how magnetism influences the behavior of electrons in topological matter.

6. **The topological insulators and the topological crystalline Insulators**

At the moment, topological materials can be classified into two main classes depending on the symmetry properties that they conserve. A Topological Insulator (TI) is a topological material whose surface states are protected by time-reversal symmetry. The Topological Crystalline Insulator (TCI) is a topological material whose surface states are protected by crystalline symmetry.

Historically, although unknown at the time, the edge states in the integer quantum Hall effect were topological in nature. The field of TIs came into being when a quantum spin Hall effect that conserves time-reversal symmetry was predicted by Kane and Mele in 2005 [20]. Fu, Kane and Mele subsequently predicted the existence of the 3D TI in 2007 [21]. At the same time, S.C. Zhang and L.W. Molenkamp collaboratively predicted and realized the quantum spin Hall state in HgTe/CdTe quantum wells [22]. An observation of a quantized resistance plateau was
reported when the Fermi level is tuned to the gap of the quantum well, where no conduction should exist. This showed that a metallic edge channel does in fact exist in the gap. Nonlocal spin-Hall effect measurements also established the spin-polarized nature of the channel. \cite{22}

Later on in 2009, a BiSb alloy was identified as the first 3D TI by angle-resolved photoemission spectroscopy (ARPES) measurements \cite{23}.

The experimental boom did not however occur until Bi-based TIs were predicted \cite{24} and seen in ARPES \cite{25}. Bi$_2$Se$_3$ and Bi$_2$Te$_3$, in particular, became the prototypical TI materials that were studied most heavily.

In 2011, a TI state based on crystalline symmetry was imagined - the topological crystalline insulator state (TCI) \cite{26} - and later predicted \cite{27} and observed in Sn-Pb chalcogenides \cite{28, 29, 30}. TCI generally have a four-fold or six-fold symmetric crystal structure that can protect an inverted band structure at crystalline symmetric points. TCIs have many properties that are identical to TIs, but also have some very interesting distinctions. The crystalline symmetry property in TCI can be experimentally manipulated more easily with available techniques, such as strain for example.

7. **Objectives of the dissertation**

We thus investigated two topological material systems as follows:

The growth of thin films of Bi$_2$Te$_2$Se – a TI – was carried out for the purpose of accessing information about the surface states at high magnetic fields. The high-field behavior of the resistance was studied in detail.
In addition, the growth of thin films of SnTe – a TCI – was first optimized. The influence of crystalline and morphological disorder on the transport was investigated. The magnetotransport was studied in detail.

In a final step, magnetism was induced in the TCI system by proximity to the ferromagnetic insulator EuS, and its impact on the surface transport was investigated.

This dissertation thus provides insight on how to grow high-quality films of topological materials, and how magnetism and magnetic fields influence the surface electron states.

8. Outline of the dissertation

In the following chapter (II), we introduce the theoretical foundation that was required for this work, and provide a summary of the literature relevant to this dissertation. Most importantly, a brief exposé on TIs and TCIs is presented. The vital role of angle-resolved photoemission spectroscopy (ARPES) and magnetotransport studies is outlined. Relevant state-of-the-art results from the published literature in topological material research will then be discussed. Important theoretical aspects such as quantum coherent transport are introduced.

In chapter III, the various experimental techniques that are used throughout this dissertation are presented and explained.

Chapter IV presents our results on thin films of the TI material Bi$_2$Te$_2$Se grown by molecular beam epitaxy. The growth and structural characterization of those films are discussed in detail. The behavior of the resistance at high magnetic fields is then discussed and a model is proposed to explain the observed linear dependence of the resistance on magnetic field.
Chapter V presents the bulk of our work on TCI SnTe thin films grown by MBE and sputtering. The structural and morphological properties of the grown films were investigated in detail. The quantum coherent behavior of the topological surface states is explored as a function of the film quality. Important findings that discuss how Dirac surface states couple and decouple as a result of disorder are presented. Prospects of manipulating TCI surface states with strain are discussed at the end of the chapter.

Finally, chapter VI discusses how proximity-induced magnetism influences the surface states of TCI SnTe. The growth and characterization of SnTe-EuS heterostructures are discussed. The observation of high conductivity states propagating along magnetic domain walls is reported. Prospects of magnetic doping of TCIs and TIs are also discussed.

II. Theoretical and Experimental Literature Overview

1. Band inversion and topological protection
   a. 2D and 3D topological insulators and time-reversal symmetry

   In the conventional $Z_2$ TI, the system is generally described by a tight binding Hamiltonian that is invariant under time-reversal symmetry [20]. In real cases, it was shown that band inversions at time-reversal symmetric points in the Brillouin zone, such as the $\Gamma$-point in Bi$_2$Se$_3$, can be described by such a Hamiltonian [24]. These band inversions have been shown to occur as a result of strong spin-orbit coupling that mixes the $p_z$ orbital of Se with that of Bi. A Hamiltonian is then formulated for those energy states close to the band gap and is shown to be invariant under time reversal symmetry [24]. The resulting surface states are shown in Fig. II-1(a) for Bi$_2$Se$_3$ along with the crystal structure showing a 1-quintuple layer (1QL≈1nm) made of stack of Se-Bi-Se-Bi-Se atomic layers as shown in Fig. II-1(b).
Figure II-1. (a) Calculated band structure of Bi$_2$Se$_3$ taken from reference 24. (b) Layer structure of Bi-chalcogenide compounds showing the atomic structure of a single QL.

Based on previous observations and calculations made for BiSb alloys [23], Bi$_2$Se$_3$ and Bi$_2$Te$_3$ and Sb$_2$Te$_3$ were predicted to host topological surface states [24]. Subsequently, an important theoretical realization showed that such compounds are 3D TIs down to thicknesses of 5QL below which they become 2D TIs [31,32]. A 3D TI hosts surface states surrounding a semiconducting bulk (Fig II-2(a)). In contrast, a 2D TI hosts 1D edge states surrounding an insulating 2D slab (Fig II-2(b,c)) when the thickness is less than 5QL. The surface wavefunction is shown to penetrate about 3QL into the bulk (Fig II-2(b). A thickness of less than 6QL, would thus cause the top and bottom surface wavefunctions to hybridize. This signals a topological phase transition occurring at 5QL, leading to this change in dimensional character.
Figure II-2. (a) Sketch of a 3D TI with the corresponding surface dispersion as seen by ARPES in reference 32. (b) Wavefunction profile versus thickness taken from reference 31. (c) Sketch of a 2D TI with corresponding surface dispersion as seen by ARPES in reference 32.

Lastly, breaking time reversal symmetry by proximity to a ferromagnet or by magnetic bulk doping was shown to result in a surface band gap [33]. The linear-in-k surface Dirac fermions become nonlinear and acquire mass as a result. This symmetry-breaking is the main reason behind several exotic phenomena that are predicted to occur in TI materials. To name a few, magnetic monopole-like signatures are thought to occur when a TI is in proximity to a ferromagnet [19]. Additionally, a 1D propagating edge state is demonstrated to exist at the surface of a TI in proximity to two oppositely magnetized ferromagnets [34, 35, 8]. Lastly, the quantum anomalous Hall (QAH) effect was predicted and observed in magnetically-doped TIs [36, 37].

b. The topological crystalline insulator and crystalline symmetry

In many reported cases [38, 39], an even number of band inversions may occur in a material. Time-reversal symmetry is no longer enough to result in topologically protected surface states. Instead, the symmetry of the crystal lattice is then the driving mechanism that has to be considered.

The (Pb,Sn) chalcogenides fall under this class of topological materials. Four band inversions are known to occur at the L-points of the rocksalt Brillouin zone in such systems as the Sn content is increased. Due to the crystalline mirror symmetry of the four (001) surface of the non-centrosymmetric rocksalt structure, more specifically the fact that the L-point project onto points that are mirror symmetric with respect to the \{110\} body diagonals, the band
inversion results in four Dirac cones located along the $\Gamma - \bar{X}$ line cuts on the (001) surface [26,27]. This is shown in Fig II-3. A Lifshitz transition, is expected to occur in SnTe as the Fermi level is tuned into the valence. Each pair of topological surface pockets on the (001) surface merges into a single large pocket that is shared between two neighboring Brillouin zones.

In the TCI state, any interaction that breaks crystalline symmetry may gap the surface states and induce a mass to surface electrons. Strain, electric fields as well as magnetic fields can thus perturb the surface states.

![Image](image.png)

Figure II-3. (a) Band structure of SnTe [27]. (b) Fermi surface of the (001) plane in SnTe showing four surface pockets near the $\bar{X}$ points. (c) Calculated Lifshitz transition occurring in the surface states of SnTe as the Fermi level is tuned into the bulk valence band. [27]

2. **Visualizing the band structure with ARPES**

The experimental verification of the existence of topological materials could not have been made without the use of angle-resolved photoemission spectroscopy (ARPES). This powerful technique generates beautiful energy-momentum data of band dispersion, and its limited depth (< few nm) is ideal for probing surface states. The advancement of the field
probably owes its pace to the success of ARPES in efficiently probing band structures as predicted by theory. The first major achievement was without a doubt the observation of the surface states of BiSb [23] which was a major milestone in the field of topological matter. Secondly, the observation of the surface states of Bi$_2$Se$_3$ [24] in ARPES (Fig. II-4(a,b)) and the marvelous agreement that was observed between experiment and theory (Fig. II-4(c)) set the standard for other topological materials to come.

Later on, the surface band gap induced by magnetic doping [40], as well as the confirmation of the TCI state in the (Pb,Sn) chalcogenides both came from ARPES experiments [28, 29, 30]. Time-resolved surface carrier dynamics were then also probed using time-resolved ARPES [41, 42]. And, most importantly, spin-ARPES allowed the determination of the spin texture of topological surface states [43, 44, 45, 46], and the manipulation of the surface electron spin [47]. Results obtained in reference 47 from spin ARPES are shown in Fig. (II-5).

Figure II-4. (a,b) ARPES spectrum along different line cuts showing a Dirac cone at the $\Gamma$ point. [24] (c) Theoretical calculations [24] showing excellent agreement with the ARPES experiments.
Figure II-5. (a) Illustration of the spin-texture in Bi₂Se₃. (b) ARPES spectrum showing the surface states of Bi₂Se₃. Spin-ARPES map taken with a p-polarized (c) laser excitation and an s-polarized (d) excitation. [47]

Let us conclude this paragraph by reminding the reader, that although ARPES is an extremely useful tool to probe the band structure of topological materials, the main objective that would allow topological matter to be implemented in everyday-life technology, is electronic transport. We shall now move on and discuss the progress made in the field using conventional transport probes.

3. Magnetotransport in topological materials

As magnetotransport is the primary technique used in this dissertation, we discuss previously reported results on magnetotransport in topological materials. As most TI and TCI materials are good conductors in the bulk, the trends observed in magnetotransport reflect this coexistence of bulk and surface channels. Two main observations are reported by several groups in different TI and TCI systems, and are discussed here in detail:
(i) Weak antilocalization [48, 49, 50, 51, 52, 53, 54, 55, 56]

(ii) Shubnikov-de-Haas (SdH) Oscillations [57, 58, 59]

Other equally interesting observations include the non-linear Hall effect that is related to the coexistence of bulk and surface transport channels, high-field linear magnetoresistance (LMR), as well as different types of quantum oscillations including Aharonov-Bohm (AB) surface oscillations [60] in nanowires, Altshuler-Aronov-Spivak (AAS) [61] oscillations, and universal conductance fluctuations (UCF) [62].

\[ \text{a. Weak antilocalization:} \]

\[ \text{Overview} \]

Although weak antilocalization (WAL) in not exclusive to topological materials [63, 64, 65, 66], it is evidence of an important feature of the topological surface states, namely, spin-momentum locking. In general, any system having strong spin-orbit coupling would produce WAL. In order to understand WAL, let us start with an ideal situation of complete spin-momentum locking, which can be thought of as an infinitely strong spin-orbit interaction.

In the diffusive regime, an electron makes a number of elastic collisions and changes its path typically every few nanometers, and, as shown in Fig. II-6, may scatter around a loop. Here we invoke the partial-wave properties of an electron as it scatters around random paths and returns to an initial position. If the electron spin is strongly locked to its momentum, then the spin direction would rotate as the momentum rotates around the loop. As the electron scatters around and closes the loop, the spin will have rotated by \( \pi \) (bottom loop in Fig. II-6). The same electron scattering along an opposite loop would have rotated by \( -\pi \) (top loop in Fig. II-6). If the electron can travel around those loops before losing its phase information, then at the
interference point, the net spin rotation would be $2\pi$, which corresponds to a net phase rotation of $\pi$. Interference is thus destructive, so the backscattering channel is suppressed and the total resistance is lowered by a small amount. In WAL, a magnetic field induces a phase shift away from $\pi$, so that the backscattering is increased and the resistance thus increases toward its normal value. In the absence of spin-momentum locking the total phase difference is $2\pi$ and interference is constructive, which leads to an enhancement of backscattering and is known as weak localization (WL).

Figure II-6. An illustration showing the rotation of the spin of a wave-like electron scattering around two oppositely oriented loops. The net phase different between the two loops is $\pi$ and interference is destructive.

So then how is WAL for the case of topological surface states different from that seen in the case of trivial spin-orbit coupled electronic states? The answer to that question lies in the fact that spin-momentum locking is equivalent to saying there is a one-to-one correspondence
between the spin states and momentum states. This is literally an infinitely large spin-orbit interaction. On the other hand, for a system having a finite spin-orbit interaction, WAL is governed by competing length scales. When an electron scatters elastically, it takes the spin a finite time to readjust to its equilibrium direction. The electron thus travels a certain length before the spin is reoriented to its equilibrium position. This is illustrated in Fig. II-7. The length that is travelled before the spin readjusts is the characteristic spin-orbit length $L_{SO}$. In the case of spin-momentum locking $L_{SO}=0$. These effects are only relevant when the electron can retain its phase information along the scattering path. In other words, these effects only matter if the electron can be thought of as a wave.

![Figure II-7](image.png)

Figure II-7. An illustration of a scattering event where the electron momentum changes direction as a result of an elastic collision. Top: spin progressively reorients to the equilibrium position in the case of a trivial spin-orbit coupled system. Bottom: spin immediately readjusts in the case of a topological surface electron. THIS is spin-momentum locking.

Let $L_{\phi}$ be the coherence length – the length that the electron can travel before losing its wavelike phase properties in a solid. Then as long as $L_{\phi} >> L_{SO}$ WAL will be observed. When $L_{\phi} < L_{SO}$ WL may arise, and backscattering will be enhanced instead of reduced. In Dresselhaus or
Rashba spin-orbit [65, 66] systems such as Bi, PbTe or even GaAs, a crossover from WAL to WL is usually observed, since $L_{SO}$ is finite. For topological surface states, WL does not occur, as $L_{SO}=0$, unless bulk states come into play. It is also possible to think in terms of times, by considering the time it takes to reorient a spin compared to the phase coherence time. For spin-momentum locking, $\tau_{SO}=0$, and you get WAL when $\tau_{\phi} \gg \tau_{SO}$.

When a magnetic field is applied to a weakly antilocalized system, a positive logarithmic MR is observed. A magnetic field introduces an Aharonov-Bohm phase shift into the system. But since different electrons scatter around loops of different surface areas, the Aharonov-Bohm phase shift in the system is random. The magnetic field would thus “blur” the net electron phase. All quantum coherent phenomena are destroyed as a result. WAL thus yields a negative magnetoconductance (positive MR) and WL yields a positive magnetoconductance (negative MR). The two behaviors are compared in Fig. II-8.

![Graph showing conductance change vs applied magnetic field for both weak localization (red) and weak antilocalization (blue)](image)

**Figure II-8.** Change in conductance versus applied magnetic field for both weak localization (red) and weak antilocalization (blue)

WAL is generally described by the Hikami-Larkin-Nagaoka model given by [63]:

\[
\Delta G(B) = -\frac{e^2}{2\pi\hbar}\left[\psi\left(\frac{B_\phi + B_{\psi}}{B} + \frac{1}{2}\right) - \ln\left(\frac{B_\phi}{B}\right)\right]
\]

\[
-\frac{e^2}{\pi\hbar}\left[\psi\left(\frac{B_{SO} + B_{\chi}}{B} + \frac{1}{2}\right) - \ln\left(\frac{B_{SO} + B_{\chi}}{B}\right)\right]
\]

\[
+\frac{3e^2}{2\pi\hbar}\left[\psi\left(\frac{4/3B_{SO} + B_{\phi}}{B} + \frac{1}{2}\right) - \ln\left(\frac{(4/3)B_{SO} + B_{\phi}}{B}\right)\right].
\]

In this equation, \( B_i = \frac{\hbar}{4eL_i} \) is the characteristic magnetic field corresponding to each length, where \( i = \phi, SO \) and \( e \) are phase coherence, spin-orbit coupling and elastic scattering, respectively. For spin-momentum locked surface states, \( B_{SO} \sim 1/L_{SO}^2 \) is infinite, so only one term survives and yields a WAL correction of the form:

\[
\Delta G(B) = -\frac{\alpha e^2}{\pi\hbar}\left[\psi\left(\frac{B_\phi}{B} + \frac{1}{2}\right) - \ln\left(\frac{B_\phi}{B}\right)\right].
\]

\( \alpha \) accounts for WAL contributions from different channels such as a bottom surface, an additional surface state, or a bulk state. (\( \alpha = 0.5 \times \text{number of WAL channels} \)). A thorough understanding of \( \alpha \) is thus highly relevant for the study of topological materials as it may allow one to separate the surface conduction from the bulk conduction.

**The number of coherent channels in topological materials**

Experimentally, WAL is probably the most commonly observed effect in transport experiments on TIs at low temperature. It has been studied as a function of thickness (Fig. II-9 [50]), gating voltage (Fig. II-10 [48]), magnetic doping [40, 53, 54], as well as temperature[48, 59, 55].
Figure II-9. Thickness dependence of WAL in Bi$_2$Se$_3$ from reference 50. (a) Magnetoconductance versus field for different QL thicknesses. (b) $\Lambda=\alpha/\pi$, number coherence channels. (c) Coherence length for different QL thicknesses.

Most notably, in 2011, MBE-grown Bi$_2$Se$_3$ films were shown to exhibit WAL for different QL thicknesses (Fig. II-9(a)) [50]. The number of coherent channels was equal to 1, independently from thickness Fig. II-9(b). Hence, it was implied that the measured WAL channel was the surface. All changes in the observed in the WAL of Fig. II-9(a) were explained by a changing coherence length (Fig. II-9(c)). The outlier at a thickness of 3QL is believed to be due to a crossover to the 2D TI state where the surface-states are no longer gapless.

Additionally, later on in the same year, WAL was studied versus gating voltage and temperature [48]. Results from that work are shown in Fig. II-10. The number of coherent channels was seen to change versus gating voltage and temperature. Only the top surface was gated. When the Fermi level is located in the band gap on the top surface (Fig. II-10(c)), two decoupled channels were observed ($\alpha = 1$) (Fig. II-10(d)). When the Fermi level is in the bulk, a single channel was observed ($\alpha = 0.5$) (Fig. II-10(d)). This was interpreted as competition between two length scales, namely, the coherence length $L_\phi$ and the surface-to-bulk scattering
length $L_{SB}$. When the $L_\phi >> L_{SB}$, the surface and the bulk are coupled and act as a single channel ($\alpha = 0.5$). When the $L_\phi < L_{SB}$, the surface and the bulk decouple and yield two separate WAL channels resulting in $\alpha = 1$. A similar trend was observed versus temperature, where $\alpha$ increased from 0.5 to 1 as the temperature was raised while $L_\phi$ decreased (Fig. II-10(e)). [48]

To sum up this part, we would like to stress the complex nature of quantum coherent phenomena in topological materials.

Figure II-10. WAL in Bi$_2$Se$_3$ versus gating voltage and temperature from reference 48. (a) WAL cusp as seen in resistance. (b) WAL transformed to 2D conductance. (c) Resistance versus gating voltage for a top gate. (d) $\alpha$ and $L_\phi$ versus gating voltage. (e) $\alpha$ and $L_\phi$ versus temperature for three samples having different carrier densities. (blue and red have a low carrier density compared to the green triangles). Values in the figure are multiplied by -1.

b. *Shubnikov de-Haas oscillations (SdH)*

SdH oscillations are an extremely reliable tool to conclusively extract surface characteristics. Such oscillations have been observed in several cases where the mobility is high
enough for one to resolve Landau-levels. In short, SdH oscillations arise when the Fermi level crosses broad Landau levels. A strong enough magnetic field ($\mu B \gg 1$) yields widely-separated quantum Landau levels. As the field is swept, the Fermi level crosses several of these discrete energy levels. At the point where the Landau-level density-of-states is highest, the resistance shows a minimum and then increases again to a maximum where the density-of-states is lowest. At that point the resistance results in a maximum and starts dropping again until another resistance minimum is reached at the following Landau level.

The Landau-level spectrum can then be analyzed. Generally, one can only obtain information of higher-order Landau levels. An analysis then extrapolates the recovered spectrum to zero magnetic field. At zero-field, if the intercept is finite, then, there exists a non-dispersing zero energy Landau level, which is the hallmark of Dirac Fermions.

Another hallmark of quantum oscillations arising from Dirac fermions, is the fact that Landau level disperse proportionally to $B^{1/2}$, unlike massive Schrodinger Fermions that disperse linearly in $B$. Finally, one is also able to extract the Fermi velocity from the decay of the oscillations versus temperature and compare it to theory and ARPES data. This technique is even more powerful if a surface sensitive scanning probe is used. We next move on and briefly discuss topological materials in proximity to ferromagnets.

4. **The Magnetic proximity effect**

Dirac surface states in proximity to a ferromagnet are thought to yield exotic physical phenomena. Experimentally, the magnetic proximity effect has been realized in three cases. The observations reported in each case will be briefly discussed.
In Bi$_2$Se$_3$ films capped with EuS (a ferromagnetic insulator) an anomalous Hall voltage was observed, indicating that TI conduction is indeed coupled to magnetism [67]. Moreover, the observation of a hysteretic in-plane isotropic MR was hypothesized to be a result of domain walls that support the quantum anomalous Hall state [67]. In two other instances, Bi$_2$Se$_3$ was capped *ex-situ* with GdN and in another case was grown on EuS. Magnetic proximity was shown to yield a suppression of WAL and an enhancement of the backscattering channel giving rise to WL [68, 69]. This is evidence of broken time-reversal symmetry at the surface.

5. **Summary**

Topological materials have thus been probed by ARPES, transport, and the magnetic proximity effect. We shall now move on and discuss our work as related to other results in the field.
III. Experimental Methods

1. Molecular beam epitaxy

The invention of Molecular Beam Epitaxy (MBE) is credited to J.R. Arthur and A.Y. Cho of Bell Labs [70, 71, 72]. In MBE, elemental or compound materials are generally evaporated from sources contained in electrically heated furnaces – known as Knudsen cells. The evaporated species traverse an ultra-high vacuum (UHV) and deposit on a substrate that is ~ 1/4 meter away from the sources. The temperatures of the sources and the substrate are the most critical parameters that one has to tune.

Several technical achievements were necessary to overcome the difficulties that one commonly encounters in MBE growth. The ultra-high vacuum (UHV) requirement was only achievable after the invention of proper pump systems that allowed one to reach pressures lower than $10^{-9}$ torr at a reasonable cost. MBE was most commonly used to grow III-V semiconductor compounds such as GaAs but can be used to grow any material that can be evaporated conveniently. MBE was essential in the discovery of several physical phenomena the most important of which are the integer and fractional quantum Hall effects.

In this dissertation, the growth of TI and TCI thin films was carried out in an MBE at the MIT Francis Bitter Magnet Lab. A diagram of the MBE is shown in Fig. III-1. The chamber is kept under UHV ($P_{\text{base}} \approx 5 \times 10^{-10}$ torr) by two cryogenic pumps. A load lock that can be pumped down to as low as $1 \times 10^{-7}$ torr by a turbo pump allows one to load samples without venting the main chamber. The load lock is also equipped with an RF-magnetron sputtering source that can be used as a deposition source for capping layers, tunnel barriers or metal contacts. Argon, nitrogen, and oxygen can be fed into the load lock.
Substrates are mounted on the transfer arm and can be moved in and out of the chamber once the load lock pressure is low enough. Sources can be evaporated from four Knudsen cells and two electron gun (e-gun) setups that can support five sources each. A shutter separates all the sources from the substrate located on the top side of the main chamber. Thickness monitors, located below the shutter, allow one to monitor the thickness of the growing film in real time during the growth. Lastly, a mask apparatus is used to shadow parts of the substrate in order to step-wise vary film thickness and pattern different shapes in-situ during the growth.

The substrate temperature can be controlled by a heater and by circulating liquid-N$_2$ through the sample holder. It can be varied between -196 °C and 340 °C.

Typically, Bi, Se and Te are evaporated from Knudsen cells. Transition metals such as Mn and Cr as well as Sn and EuS are evaporated from electron gun (e-gun) sources as they require
higher temperatures to evaporate. In addition, an Al₂O₃ e-gun source is used to cap the samples before removal to atmosphere.

2. Substrate preparation

In MBE growth, substrate preparation is critical. The initiation of the growth is highly dependent on the substrate surface termination. We will thus discuss in detail how BaF₂, Al₂O₃, and Si substrates are generally prepared.

*Barium Fluoride – BaF₂*

Epi-ready BaF₂ substrates can be acquired from MTI-crystals.

1. Sonicate the substrate in acetone for about 2 min.
2. Dip in isopropanol for a few seconds, then remove and blow away the liquid with N₂.
3. Mount on carrier with frame on top or with silver paste (blow over the substrate with N₂ for a few seconds if using silver paste) and load in the load lock.
4. Warning! Sample may fall when the roughing pump is started if silver is used. Keep your eye on the substrate until the turbo valve opens.
5. Wait for the pressure to reach ~5×10⁻⁶ torr
6. Start warming up the substrate.
7. Anneal in vacuum at 340°C for about two hours
8. Or anneal in vacuum at 500°C if possible for about 15 min (This capability was unavailable when this work was done.)
Sapphire – Al₂O₃

Epiready Al₂O₃ substrates can be acquired from MTI-crystal Corporation®.

1. Sonicate the substrate in acetone for about 2 min.
2. Dip in isopropanol for a few seconds, then remove and blow away the liquid with N₂.
3. Mount on carrier with frame on top or with silver paste (blow over the substrate with N₂ for a few seconds if using silver paste) and load in the load lock.
4. Wait for the pressure to reach ~5×10⁻⁶ torr.
5. Start warming up the substrate.
6. When the temperature reaches 340°C etch the samples in an O₂ plasma as described below:

O₂ flush

1. Close the turbo pump valve (from the PC interface).
2. Open the O₂ cylinder and the green valve next to the cylinder.
3. Open the needle valve on the O₂ line gently and then close it finger tight (DO NOT over tighten it).
4. Open the yellow O₂ valve.
5. When the pressure hits 2 torr, open the turbo valve and pump on the load lock for about a minute to clean the O₂ line.
6. Then adjust the needle valve to reach a pressure of about 60 mtorr.
7. Let O₂ flow for a minute.
8. Close the needle valve GENTLY.
10. Adjust the yellow valve to get a pressure of about 100 mtorr. Close completely when the pressure hits 90 mtorr.

**Plasma Etch**

Notice: The power supply is located on the rack facing the He compressors.

The plasma will etch the substrate that is looking down inside the load lock (i.e. the substrate that is sitting in the position that you can read on the MBE arm).

1. **ON:**
   a. Switch on the power supply.
   b. Then hit the **RED ON** button.
   c. Power up to **100mA** quickly (watch the left gauge).
   d. Etch for **20 seconds**.

2. **OFF:**
   a. Power down quickly to 0mA.
   b. Hit the **BLACK OFF** button.
   c. Switch off the power supply.

7. Evacuate the O₂ from the load lock by closing all O₂ valves. Transfer to the main chamber when the pressure in the load lock is below 0.8×10⁻⁶ torr.

---

*Silicon – Si*
1. Dip in acetone for a few seconds then replace the acetone in the beaker and sonicate the substrate for about 2 min.

2. Dip in isopropanol for a few seconds.

3. Dip in 10% sulfuric acid $\text{H}_2\text{SO}_4$ for 1min. WARNING! $\text{H}_2\text{SO}_4$ is a highly corrosive acid. You MUST be properly trained to use it. You MUST read the Material Safety Data Sheet (MSDS) before use.

4. Transfer the substrate to ethanol and leave until ready to etch in hydrofluoric acid.

**Etching Si in HF**

WARNING! HF is highly corrosive acid.

You MUST be properly trained to use HF. You MUST read the MSDS before use.

You MUST wear appropriate protective equipment listed below (no exceptions!):

- A face mask.
- A lab coat.
- An acid apron.
- Nitrile gloves.
- Rubber gloves.

ALWAYS work under a fume hood.

5. Remove the Si substrate from the ethanol bath.

6. Dip in HF for 60 seconds.

7. Remove from HF and blow all traces of HF left on the substrate under the fume hood.

8. Mount on substrate carrier and load in vacuum in under 10min.
This process results in a hydrogen terminated Si surface.

3. **Sputtering**

Sputtering, also known as cathodic pulverization, is a deposition process by which a target material is bombarded by a noble gas (usually Ar) plasma to create a cloud of material species that can travel through a vacuum and deposit on a substrate. The sputtering system in the Heiman lab is equipped with a turbo pump that allows the system to reach pressures as low as $3 \times 10^{-7}$ torr. Codeposition of at most two materials can be performed. The chamber is equipped with three sputtering heads that can be used separately. Ar and O$_2$ can be fed through the chamber at a regulated flow rate. A composite SnTe target is used to sputter deposit SnTe films in this work. Additional target materials include PbTe and Al$_2$O$_3$.

4. **Patterning: Photolithography and Ion Milling**

Standard photolithography is generally used to pattern Hall bars. Dark masks were generated by AutoSketch and printed by PageWorks in Cambridge on transparencies. Figure III-2 shows the Hall bar mask. The Hall bar masks result in patterns that are 1 mm in length and 300 μm in width. A positive resist, Shipley 1813 (or 1832) is used in the patterning process. The recipe is summarized as follows:

For Shipley 1813:

1. Spin-coat the sample with the photoresist by rotating at 4000 RPM for 60 seconds.
2. Bake the sample at 120 °C for 2 min to harden the resist.
3. Mount the desired mask and irradiate the sample with UV light for 2 minutes.
4. Develop in MF-319 developer for about 4 minutes. Check to see if the pattern is developed properly, preferably under an optical microscope.

5. Bake at 100 °C for 1 min to harden the final pattern.

For expired Shipley 1832 (currently in use):

1. Spin coat at 6000 RPM for 60 seconds.

2. Bake at 100 °C for 30 seconds to harden the resist.

3. Mount the desired mask and irradiate for 5 minutes in UV light.

4. Develop in MF-319 for about 5 minutes. Expired resist tends to harden faster, and might take longer to develop.

5. Bake at 100 °C for 1 min to harden the final pattern.

Milling:

6. Transfer the patterned sample to the ion miller, evacuate the ion miller chamber. It usually takes 20 minutes to pump down to ~10^-7 torr.

7. Use an argon flow equivalent to a pressure of 2×10^-4 torr on the gauge.

8. Set the beam power supply to 10 mA. This will be the current used during the milling.

9. Mill the sample by exposing to the beam for 30 seconds and then covering for 15 seconds repeatedly to avoid heating. Keep in mind the etching rates of the materials in use. For Bi$_2$Te$_2$Se and SnTe, typical etching rates were ~20-24 nm/min.

10. After milling the sample, dissolve the left over resist with acetone. Then dip in isopropanol for a few seconds and then in water for another few seconds, and blow away the liquid with pressurized nitrogen.
The Hall bar should now be ready to use.

![Hall bar mask illustration](image)

**Figure III-2: Illustration of Hall bar mask.**

5. **X-ray Diffraction**

X-ray diffraction (XRD) is performed to characterize all grown thin films. A Philips PANalytical X-ray diffractometer equipped with a Cu-K\(_\alpha\) source is used for standard diffraction characterization. 2θ-ω as well as ω scans can be easily performed with the single-axis geometry that is available.

More elaborate XRD studies were performed at beamline 33ID-D of the Advanced Photon Source at Argonne National Laboratory. A Ge (111) crystal is used to monochromate the X-ray beam. A beam-energy of 13.8 keV was used. The station is equipped with a 6-circle goniometer that allows for extremely versatile diffraction geometries. In-plane and out-of-plane diffraction lines can easily be probed.

6. **Atomic Force Microscopy**

A Bruker Nanoscope V atomic force microscope (AFM) was used to characterize the surface topography of our films. A Si tip is usually used in soft tapping mode. This allows us to probe steps that are as small as 1-2 nm in height. AFM images are shown elsewhere in the thesis.
7. Magnetotransport: the cryo-free magnet and the 7K cryostat

High-field magnetotransport experiments were carried out in a cryo-free 14 T Cryogenics Limited magnet at temperatures down to 7 K. The superconducting magnet coil is kept at 3 K by a Sumitomo closed-cycle compressed He circulator setup. The field can be continuously swept between 0 and ±14 T. A switch controls the field polarity by running current clockwise or counterclockwise through the superconducting coil.

The transport station is equipped with a He-free cryostat that allows one to cool samples down to approximately 7 K.

8. SQUID magnetometry

A Quantum Design MPMS XL-5 SQUID magnetometer was used to characterize the magnetic properties of different films. The SQUID can be operated at temperatures between 1.8 and 400 K. The sample space contains He exchange gas, but the cooling takes place in an isolated coaxial space outside the sample space. He flow to the cooling space is automatically controlled by two valves. A heater coupled to the valves allows an extremely precise temperature control of the sample space. The MPMS is equipped with an EverCool option where a cold head re-condenses He vapors in the bath and allows for very efficient He-usage.

A superconducting magnet is cooled by the same He-bath and can be swept continuously between -5 and +5T. The field can also be approached using a “no overshoot” setting that makes sure the field never exceeds the desired value. The flux in the superconducting magnet can also be accurately set to ±0.2 Oe using an “oscillate” field approach that can eliminate most of the trapped flux lines.
The magnetic moment is measured by a reciprocating sample technique (RSO) that oscillates the sample through a pair of SQUID pick-up coils. Moments as low as $10^{-7}$ emu can be reliably measured. Upon employing proper averaging techniques, the resolution can be extended down to $10^{-8}$ emu.

9. The modified transport probe

A standard Quantum Design transport probe containing electrical wires can be inserted in the sample space and allows one to measure magnetoresistance and Hall effect in the SQUID. This probe was modified by installing a small round 10-pin socket at the end, enabling samples to be mounted on 10-pin headers and easily changed. A detailed description of the modified probe can be found in reference 73.

The top end of the probe is shown in Fig. III-3 (a). A 10-pin electrical cord can be plugged into the electrical connector shown in the figure and connects the probe to a multiterminal box that connects to the external electronics. The bottom end of the probe is shown in Fig. III-3(b). It has a row of 10 screws that are internally factory-wired to the rectangular connector at the top of the probe.

The modified probe offers the user several possible measurement geometries. In normal operation where the field is applied parallel to the film plane, samples are mounted on a flat area behind the screws and wires must be applied to link the sample to the screw connections (Fig III-3(d)). The pictured probe has been modified to accommodate for measurements in perpendicular fields. By attaching a small circular 10-pin header to the end of the probe one can mount samples on its bottom end (Fig III-3(c)). A standard 10-pin “Augat Interconnect 8059-2G10” header is used, but the diameter must be machined down to a diameter of about 7.5 – 8.0 mm in order to
provide sufficient clearance in the 9 mm inside diameter of the sample tube of the magnetometer. After machining, the header is mounted on the probe end by a small diameter (2-56) nylon screw placed through a hole in the center of the header. A small plastic bracket is fashioned to accept the screw holding the header and is mounted on the flat part of the probe end with two small screws. The socket pins are then wired to the row of screws on the probe. Insulated copper wires were soldered to the pins using lead-tin solder, and then attached to the contact screws. Once attached and wired, the socket is ready to accept plug-in headers that are mounted with samples. Many samples can now be interchanged by simply plugging and unplugging the headers into the socket (Fig. III-3(d)).

![Fig III-3. Different components of the modified transport probe](image)

The probe can be inserted into the instrument after adjusting the position of the adjustable flange at the top end of the probe shown in Fig. III-3(a). The sample should be located 121.0 ± 2 cm [73, 74] below the adjustable flange to position it in the center of the magnet. That distance should be checked as it may be different depending on the particular instrument used.

Let us then present a standard operating procedure to mount and setup the transport probe for use.
Sample/Probe Mounting

1. Mount a sample on a 7.5 mm diameter Augat 10-pin header and wire it as desired.

2. Plug the resulting header onto the end of the probe, shown in Fig. III-3(d). Keep in mind that contacts 4 and 5 are shorted. The wiring diagram is straightforward; the numbering goes counter clockwise on the probe head (looking at the probe end or mounted sample) starting with the pin marked by a black line as number 1.

3. Adjust the height so that the top black flange is 121 cm above the sample. This ensures that the sample is close to the center of the SQUID pick up coils where the magnetic field is most homogeneous.

4. Cover your sample with a short piece of straw (split lengthwise) to protect the fragile wiring while loading.

5. Load the sample using the DC head instead of the RSO. Purge the sample space and then open the butterfly valve and start lowering the sample into the chamber.

6. **Warning!** At the valve area, the tube narrows down. The edges might touch your sample and damage the wiring if you are not careful.

7. Once the probe is in place, tighten down the screws on the top flange and plug the external cord that is connected to the plug box into the top 10-pin plug on the probe.

**Electronics**

8. Connect the current sources and voltmeters to the probe.

9. Connect the current sources and voltmeters to the PC via a GPIB interface. All voltmeters and power sources including lock-in amplifiers should be setup to communicate via GPIB addresses 11 or 15. This avoids conflicts with other SQUID functionalities.
10. (For Keithley 2400 and Keithley 2182). In order to check proper communications, go to Tools/Diagnostics/GPIB/Send GPIB commands. Type in the GPIB address usually 11 for K2182 and 15 for K2400, type “READ:??” into the command line and press the “Send and Read” button. You should get a reading of the voltmeter display on the computer screen. The K2400 may return a buzz sound after you press “Send and Read”.

11. All systems are now ready to perform transport measurements.

12. You may set up a sequence as desired. Use the EDCInitialize and EDCExecute sequence commands in Multiview to communicate with your voltmeters.

13. Both commands will prompt you to input a proper .dll file that communicates with the appropriate voltmeter. Use K2400.dll for the Keithley 2400, K2182.dll for the Keithley 2182, SR830_xx.dll and SR830_xy.dll for Stanford Research SR830 lock-in amplifiers. SR830_xx is generally used for the MR pair and communicates via address 11 and SR830_xy is used for the Hall pair and communicates via address 15.

14. You are now ready to perform transport measurements in the SQUID.

15. If new electronics is to be used, a Delphi 7 source code has to be compiled to generate a proper .dll file corresponding to the new device.
IV. Bi-based Topological Insulators thin films: growth and magnetotransport

1. Growth and characterization of Bi$_2$Te$_2$Se (BTS-221) thin films on Si (111)

   a. Overview of materials research on BTS-221

   BTS-221 was independently identified by two groups, [59,75] in transport experiments on bulk single crystals grown using a Bridgeman method, as the most bulk insulating TI. The resistivity was found to be at least two orders of magnitude greater than that of Bi$_2$Se$_3$ and Bi$_2$Te$_3$. This led to the observation of Shubnikov-de-Haas oscillations and a non-linear Hall effect that were both attributed to the surface states [59, 75]. Attempts to grow confined structures of BTS subsequently followed [76].

   The reason behind the high resistivity in bulk materials of BTS-221 was argued to result from a significant reduction in atomic defects, mostly Se vacancies that were thought to occupy lattice sites where the bonding is ionic [75]. As shown in Fig. IV-1, the R-3m structure of BTS-221 is characterized by two different chalcogene sites. Site I binds only to Bi via an ionic bond, while site II makes an ionic bind to Bi from one end and another weaker van der Waals bond to a chalcogen atom from the other end. In BTS-221, Se only occupies site I, and is hence less prone to vacate the lattice. Site II is occupied by Te atoms that do not tend to vacate the lattice as easily, but rather swap position with Bi atoms. This swapping probability is also reduced upon the inclusion of Se atoms in site I. BTS-221 is thus less prone to Se vacancies (donors) and Te$_{Bi}$ antisites (acceptors) and is hence more insulating than both the Te and Se compounds.
The atomic ordering of BTS-221 has in fact been known for quite some time. [77]. It was actually found that as Se is doped into Bi$_2$Te$_3$ the lattice constant depends linearly on the doping concentration as per Vegard’s law, [77] but deviates from that linear dependence around the region where [Te]/[Se]=2. This deviation is evidence that a discontinuous lattice deformation occurs which can be explained by the fact Se doping starts affecting a different lattice site when [Te]/[Se] crosses 2.

We thus found it useful to investigate the growth of BTS-221 thin films for the purpose of possibly achieving this less defective ordered phase. It was however found that at low film thicknesses, Te starts vacating the lattice instead of making antisite swaps with Bi, which resulted in more n-doping from Te vacancies. This behavior was seen in Bi$_2$Te$_3$ when exposed to atmospheric conditions. The main motivation behind BTS-221 is thus diminished in thin films. In what follows we study the crystal structure and transport characteristics of BTS-221 thin films.

**b. Growth on Si (111): an X-ray diffraction analysis**
BTS-221 was grown on Si (111) by MBE at different thicknesses. Si substrates were initially etched in 10%-hydrofluoric acid:H₂O in order to remove the native amorphous oxide layer, then loaded into the load lock chamber in under 5 min. The H-terminated Si surface is protected from oxidation if the film is exposed to atmosphere for such short time periods. The substrates are then heated in the UHV growth chamber to the growth temperature that was generally fixed at 200 °C. The growth was carried out under stochiometric flux of Bi:Te:Se ~ 2:2:1.

Figure IV-2. (a) Standard X-ray diffraction of a BTS-221 film comparing a film grown on HF-etched Si(111) (red) to a film grown on the native oxide (blue). (b) (0003) and (0006) Bragg reflections showing Kiessig fringes for the film grown on HF-etched Si (111).

One attempt to vary the growth recipe was made. The temperature was increased to 300 °C and an excess of Te and Se was used so that Bi:Te:Se ~ 2:11:5. This growth resulted in a phase segregation. Two phases of different [Te]/[Se] content were identified in XRD. Subsequently, the low temperature/stochiometric flux method was used throughout.
Interestingly, it was found that the oriented BTS-221 grows along the c-axis regardless of whether the native oxide was etched or not as shown in the X-ray diffraction pattern in Fig. IV-2. Removal of the native oxide however resulted in smoother films since Kiessig fringes were only observed in films that were grown on etched Si (Fig. IV-2(b)). The lattice constants of the films varied within 0.15 Å of the bulk lattice constant of BTS-221, generally exceeding it by a small amount. This meant that most of our BTS-221 films are actually Te rich.

Figure IV-3. Lattice constant from X-ray diffraction measurements performed on different BTS films versus atomic Te/Se flux ratio. Note that films have different thicknesses; strain is not taken into account in this plot. The pink triangle denotes the value for bulk BTS-221. The light blue square denotes the value for bulk BTS-212.

Figure IV-3 shows a distribution of the resulting c-axis lattice constants obtained in different films, all falling close to the bulk value for BTS-221. Note that strain is not taken into account in Fig. IV-3. The c-lattice constant at nominal stochiometric concentrations was seen to
decrease with increasing thickness, indicating that the lattice constant is elongated out of the film plane as a result of compressive in-plane strain. The in-plane lattice constant of Si (111) is \( a(110) = 7.65 \, \text{Å} \), which gives \( a(110)/2 = 3.83 \, \text{Å} \). It is thus conceivable that since \( a(\text{BTS-221}) = 4.28 \, \text{Å} \), a two-to-one quasi-epitaxial relation is achieved and the resulting film is compressed in the plane.

c. Atomic ordering

Moreover, it is of some importance to study the atomic ordering of our films. It can be investigated by examining the integrated intensity ratios of the (00 12):(00 15) and the (00 3):(00 6) peaks. Structure factor calculations are made for different Te:Se mixing ratios between site I and site II and compared to the data from several stochiometric samples.

![Graph showing intensity ratio variation with Site II Te/(Te+Se) content.](image)

Figure IV-4. Calculated and measured variation of the X-ray diffraction peak intensity ratios as a function of Te content in site II of the BTS unit cell. Calculated results are shown for the (0003) / (0006) Bragg peaks (blue curve) and the (000 12) / (000 15) peaks (red curve). Experimental ratios taken from two films are shown by the solid black points.
Figure IV-4 shows the calculated relative intensity ratio of the (0003) peak to the (0006) peak and the (00012) peak to the (00015) peak, as a function of atomic site disorder. The x-axis in Fig. IV-4 is the relative ratio of Te atoms to the total number of atoms in site II of the crystal structure. This quantity is a relative measure of the atomic disorder strength considered in the calculations. Experimental results obtained from two films that are 30 nm and 40 nm thick are shown by the points in Fig. IV-4, where $I_{3/6} = 0.28$ and $I_{12/15} = 0.13$. This indicates atomic ordering of at least 95% on site II not considering possible but less likely mixing with Bi-sites. The peak intensity measured in thinner films resulted in $I_{3/6} > 0.3$, due to complications from Kiessig fringes in the XRD pattern. Henceforth, results from thinner films are deemed inaccurate and not considered in this analysis.

\[ \text{d. Transport characteristics} \]

The resistivity in all of our BTS-221 films did not satisfy the expected high resistivity seen in bulk single crystals [59, 75], and was always on the order of a few mΩcm, similar to what is measured in Bi$_2$Se$_3$ and Bi$_2$Te$_3$. The resistivity versus temperature consistently shows a metallic behavior, decreasing as the temperature as lowered. This is shown in Fig. IV-5 for a 15 nm thick film. At low temperatures the resistivity upturn is thought to be a result of electron-electron interactions. [78]
The electron density in our films varied between $3 \times 10^{19}$ and $7 \times 10^{19}$ cm$^{-3}$. This is unlikely to be an exclusive result of Se vacancies; Te vacancies must be considered as a possible type of lattice defect in BTS-221. If we consider the fact that Bi$_2$Se$_3$ usually has a carrier density that is of the same order of magnitude as a result of Se vacancies, and assume that most vacancies occur on site II, then by reducing the amount of Se on site II down to 5 %, one should naively expect the carrier density to decrease by a factor of 20, assuming the probability of forming a Se vacancy is not dependent on the amount of Se on site II. This does not seem to be the case in our films. Te atoms must thus be also vacating the lattice. This agrees with results from Bi$_2$Te$_3$ films that also show n-type behavior as opposed to bulk Bi$_2$Te$_3$ single crystals that are usually p-type.

We have reached a point where the quality of our BTS films is similar to standard Bi$_2$Se$_3$ and Bi$_2$Te$_3$ films [48, 49, 50, 51] already considered in the literature. We will proceed and study quantum coherent behavior in the MR at low temperatures and high magnetic fields.

Figure IV-5. Resistivity versus temperature in a 15 nm BTS-221 film.
2. Weak antilocalization in BTS

\[ a. \text{Weak antilocalization and decoherence in TI films} \]

Our BTS-221 films clearly exhibit weak antilocalization (WAL) for fields below 5 T. The MR was measured in films of varying thickness and a robust weak WAL cusp was reproducibly observed between 2 K and 50 K. Figure IV-6 shows the cusp at different temperatures up to 5 T for a 15 nm film.

![Figure IV-6. Weak antilocalization at different temperatures in a 15 nm BTS-221 film.](image)

The MR is analyzed using the Hikami-Larkin-Nagaoka (HLN) [63, 64] model for quantum coherence, where the field-induced change in conduction is given by:

\[
\Delta G(B) = -\frac{\alpha e^2}{\pi \hbar} \left[ \psi\left(\frac{h}{4eL^2B} + \frac{1}{2}\right) - \ln\left(\frac{h}{4eL^2B}\right) \right].
\]
The $\alpha$-parameter counts the number of coherent channels, and the coherence length $L$ can be extracted for different temperatures. The behaviors of $L$ and $\alpha$ versus temperature are shown in Fig. IV-7. $L$ decays following a power law $\sim T^{-0.62\pm0.02}$. It has been shown that electron-electron collisions lead to a power law with an exponent of $-3/4$ for decoherence in 3D, whereas an exponent of $-1/2$ is evidence of decoherence in 2D [79]. Our exponent falls in between the 2D and the 3D limits, suggesting a possible interplay between the two limits. $\alpha$ on the other hand shows a slight increase that is thought to be result of surface-to-bulk scattering [48]. As $L$ decays, the surface-to-bulk scattering length approaches $L$, since electrons are no longer able to traverse the bulk and scatter from one surface to the other coherently. Different coherent channels in the films start to decouple as a result. This results in an increase in the value of $\alpha$ approaching 1. [48, 52] The physical origin of the multiple contributing channels will be discussed later in the next paragraph.

![Figure IV-7. Coherence length (a) and number of coherent channels (b) versus temperature versus temperature extracted using the HLN model from the MR of a 15nm thick BTS-221 film.](image)
The interplay between surface and bulk coherent transport seems to be evident from the previous analysis. In a thinner, 9 nm sample, the two regimes were seen to decouple as a function of temperature. The behavior of $L$ versus temperature for the 9 nm film is shown in Figure IV-8. Two different power laws can be fit to the data, respectively, above and below 7 K. At low temperature, the coherence length decays proportionally to $T^{-0.49\pm 0.04}$ indicative of decoherence in 2D. Above 7 K, the decay is proportional to $T^{-0.75\pm 0.02}$, suggesting a dominant 3D decoherence regime. [79]

![Figure IV-8. Coherence length versus temperature extracted using the HLN model from the MR of a 9 nm thick BTS-221 film.](image)

The crossover from 2D to 3D decoherence occurs when $L \geq 30$ nm. This is still larger than the film thickness, suggesting that the physics is not determined exclusively by the coherence length relative to film thickness. Also, the mean-free-path in the 9 nm film is estimated to be 4 nm, which is still smaller than the film thickness. Changes in resistivity versus temperature are similar to what is seen Fig. IV-6 and do not suggest any dramatic changes. However, we do observe a resistivity minimum close to 10 K, suggesting evidence of electron-
electron interactions as discussed by Liu et al. [78]. In the case of Bi$_2$Se$_3$ it was suggested that in the ultra-thin limit, electron-electron interaction cannot be screened efficiently. This leads to stronger long range electron-electron interactions that deplete the density-of-states close to the Fermi level [78]. This is based on the work of Altshuler and Aharonov in 2D disordered metals. [80] They point out that quantum corrections to the resistivity may come into play and yield an increase in resistivity versus temperature below ~10 K. The impact of such an interaction on MR has not been established and remains an open question.

A big question that arises next, concerns the bulk electrons of such TI materials and their contribution to transport. We attempt to answer this question by looking at the high-field MR of BTS.

3. Linear magnetoresistance

   a. Observation of linear magnetoresistance in BTS films

   Linear magnetoresistance (LMR) is observed in all BTS-221 films grown on Si (111) above fields of ~4 T, in addition to the WAL at low fields discussed earlier. Three films of different thickness (9 nm, 15 nm, 42 nm) were thoroughly studied. The slope of the LMR exhibited only a slight decrease with increasing temperature, as illustrated in the typical MR versus temperature plot shown in Fig. IV-6. A detailed analysis of the LMR was performed; the high-field slope was extracted and compared to the mobility and the carrier density at each temperature and compared to commonly accepted LMR models [81, 82, 83, 84]. None of the models resulted in satisfactory agreement.
We thus developed a model to explain LMR in terms of quantum coherence [55, 63]. The model allows us to separate surface and bulk contributions, and may shed light on the role of spin-orbit coupling in the quantum coherent transport of bulk electrons.

Figure IV-9(a) shows the commonly observed behavior of the high-field MR in BTS-221 thin films at different temperatures between 7 K and 150 K, and up to a field of 14 T. The WAL cusp progressively widens as the coherence length gets smaller. At high fields, a persistent positive MR is observed. The trend is linear in field and does not vary much with temperature. Similar trends were also observed on other TI materials. [56, 85, 86, 87, 88]

![Figure IV-9(a)](image-url)

Figure IV-9. (a) Change in resistance versus magnetic field measured at different temperatures between 7 K and 147K, in a 15 nm thick BTS-221 film. (b) High-field slope (red) compared to the sample mobility (blue). The solid curves are guides for the eye.

In what follows we discuss the LMR in light of two models: (1) the quantum model of A.A. Abrikosov [82, 82]; and (2) the classical model of Parish and Littlewood [83, 84]. Both models do not yield good agreement. We do however succeed in adapting a variant of the HLN model to the observed MR. Our modified HLN model is thoroughly discussed and fit to data taken in samples of different thickness. [55, 63]
b. Unsatisfactory agreement with previous models

Over the last 3 years, LMR was observed in different TI systems, and was generally attributed to the quantum LMR developed by A.A. Abrikosov [81, 82] to explain LMR in Ag$_2$Te [89, 90]. The Abrikosov quantum model predicts a linear MR in materials having a linear band dispersion such as graphene or TIs. An additional crucial assumption is made by Abrikosov; a single Landau level should be occupied by all carriers – this is the extreme magnetic quantum limit [81, 82]. This assumption seems plausible in graphene, where the carrier density is generally low [91], and in some cases in Ag-chalcogenides and InSb [89, 90]. It is however very unlikely to be achieved at small Landau level filling fractions in TIs having carrier densities on the order of $10^{19}$ cm$^{-3}$. This can easily be excluded by looking at experimental Landau level dispersion data from STM experiments, where at least 10 Landau-levels are observed within ~200 meV at 11 T, in lightly electron doped samples [92]. Furthermore, being near the magnetic quantum limit would give rise to Shubnikov-de-Haas MR oscillations that would mask the linear dependence.

Another possible model that could explain the behavior is the Parish-Littlewood model of classical MR [83, 84]. In the classical model, structural inhomogeneities cause the MR to acquire a non-saturating Hall-like Lorentz component that is linear with field. The slope of the MR was shown to be proportional to the mobility [93]. If the disorder is strong enough the slope would instead be proportional to the spread in mobility, which is much more difficult to quantify. Figure IV-9(b) shows a plot of the change in the MR slope and the change in mobility versus temperature for the 15 nm thick sample. No clear correlation between the slope and the mobility can be seen. Experimentally, classical LMR has been correlated with mobility in cases where the mobility changes by several orders of magnitude over similar ranges. For the case of BTS-221,
however, mobility does not vary by more than 20 % between 7 K and 150 K. We are thus unable to provide conclusive evidence for classical LMR.

We thus suggest a model that is more suitable for TIs, which is based on the HLN model [63].

c. The modified HLN model

Since the HLN model is known to reliably satisfy the low-field WAL regime in TIs, we shall describe the full MR trend with a variant of the standard model. We start by going back to the full form of the HLN model. Prior to making any simplifying assumptions, three different terms can contribute to the quantum coherent correction in the HLN model, so in the absence of magnetic scattering we start with [63, 64] the full HLN model:

\[
\Delta G(B) = -\frac{e^2}{2\pi\hbar} \left[ \psi \left( \frac{B_{\phi}}{B} + \frac{1}{2} \right) - \ln \left( \frac{B_{\phi}}{B} \right) \right] \\
- \frac{e^2}{2\pi\hbar} \left[ \psi \left( \frac{B_{SO} + B_{e}}{B} + \frac{1}{2} \right) - \ln \left( \frac{B_{SO} + B_{e}}{B} \right) \right] \\
+ \frac{3e^2}{2\pi\hbar} \left[ \psi \left( \frac{(4/3)B_{SO} + B_{e}}{B} + \frac{1}{2} \right) - \ln \left( \frac{(4/3)B_{SO} + B_{e}}{B} \right) \right].
\]

Here \( B_i = \hbar/4eL_i \). \( L_{SO} \) is the spin orbit scattering length, \( L_e \) is the elastic mean free path, \( L_{\phi} \) is the coherence length. \( e \) and \( h \) have their usual meaning. In Bi-based TIs, the spin-orbit length is short, \( B_{SO} \sim 2 \) T, and since the mean-free-path does exceed a few nanometers, \( B_e \) is generally close to 10 T. Accordingly, in the low-field limit \( B \ll B_e \) and \( B \ll B_{SO} \) the HLN model reduces to its conventional form [52, 63, 64]:

\[
\Delta G(B) = -\frac{ae^2}{\pi\hbar} \left[ \psi \left( \frac{\hbar}{4eL^2B} + \frac{1}{2} \right) - \ln \left( \frac{\hbar}{4eL^2B} \right) \right].
\]
Additionally, for topological surface states having the spin-momentum locking property, $B_{SO}$ can be thought of as infinite [52]. The form stated above, would thus generally hold for surface states. For bulk states at high magnetic fields, the higher order terms might have to be taken into account.

As discussed in the previous section, the above expression yields good agreement below 5 T, but deviates at high fields. It is thus likely that by 14 T we are no longer in the regime where $B < B_e$ and $B < B_{SO}$ for bulk states. High order terms should thus be accounted for, possibly as a result of a 2D bulk channels contributing.

Fortunately, HLN also mention that for $B < B_e$ and $B < B_{SO}$ the higher order terms can be approximated by a parabolic function [63]:

$$\beta_\phi B^2 = -\frac{e^2}{24\pi h} \left[ \frac{B}{B_{SO} + B_e} \right] + \frac{3e^2}{48\pi h} \left[ \frac{B}{(4/3)B_{SO} + B}\right].$$

In addition, a cyclotronic MR term must also be included for the sake of completeness. Such a term would also yield a parabolic term of the form:

$$\beta_\phi B^2 = -\mu_{MR} G_0 B^2.$$

Here, $\mu_{MR}$ is the MR mobility and $G_0$ is the zero-field conductance.

Our modified HLN model hence becomes:

$$\Delta G(B) = -\frac{e^2}{\pi h} \left[ \psi \left( \frac{h}{4eL^2 B} + \frac{1}{2} \right) - \ln \left( \frac{h}{4eL^2 B} \right) \right] + \beta B^2.$$
where we have combined all the parabolic terms together in the last term. This modified HLN model is then fit to our data, and yields good agreement at all temperatures, in all field regimes, which is shown in Fig. IV-10. [55]

d. The Modified HLN model: data analysis versus temperatures

Figure IV-10(a) shows the data and model fitting up to 14 T, and for temperatures between 7 K and 147 K. Additionally, we show the contributions of different terms in the model in Figs. IV-10 (b,c). At 7 K, the digamma and logarithm yield a good fit to the WAL cusp. At higher fields the saturating logarithm is then compensated by the parabolic term which yields a quasi-linear trend up to 14 T. At 147 K, the digamma and logarithmic functions are in their low-field limits, as the coherence length is significantly shorter. These terms can now be approximated by a parabolic term with a sub-parabolic high-field behavior that adds to the modifying parabola ($\beta B^2$) and yields a linear high field trend.
Figure IV-10. (a) Magnetoresistance measured between 7 K and 147 K, showing curve fits from the modified HLN model. (b,c) Magnetoconductance showing fits to the modified HLN model and different components of the model at 7 K (b) and 147 K (c).

Moreover, we are able to extract fit parameters $\alpha$, $\beta$ and $L$, at all the considered temperatures. This is shown in Fig. IV-11 up to 85 K. $L$ is seen to decay following a power law of exponent $-3/4$, indicating bulk decoherence in 3D [64, 79]. $\alpha$ increases as a result of increasing channel decoupling as discussed earlier. Values of $\alpha > 1$ are likely to be a result of coexisting bulk and surface channels as has been discussed in several works [48, 52].

Figure IV-11. Parameters obtained from fitting the MR data to the modified HLN model as a function of temperature. (a) Fit parameters $L$ (black) and $\alpha$ (red). (b) Parabolic $\beta$-parameter.

e. *The spin-orbit length of the bulk channel*

We now discuss the physical relevance of the modifying parabolic term $\beta$. As shown earlier, $\beta$ can be broken down into a quantum $\beta_q$ and a classical $\beta_c$ part:

$$\beta_q B^2 = - \frac{e^2}{24\pi\hbar} \left[ \frac{B}{B_{SO} + B_c} \right]^2 + \frac{3e^2}{48\pi\hbar} \left[ \frac{B}{(4/3)B_{SO} + B_c} \right]^2$$
By extracting $B_e$ ($L_e = 4 \text{ nm}$) from the Hall mobility and assuming $\mu_{\text{MR}} = \mu$, the spin-orbit characteristic field and scattering length can be extracted: $B_{SO} = 4.3 \text{ T}$ ($L_{SO} = 6 \text{ nm}$), which is of the same order of magnitude as that found in Bi$_2$Se$_3$ [48]. This explicitly shows that a finite spin-orbit length exists, likely to arise from a bulk contribution in this system. The spin-splitting in the bulk bands corresponding to the estimated $B_{SO}$ can then be calculated, using the following:

$$\Delta_{SO} = \sqrt{\frac{B_{SO} \hbar^2 e}{m^2 k_f}}$$

$k_f$ is the Fermi wavevector, and the effective mass is estimated to be around 0.15$m_e$ [94]. We estimate $\Delta_{SO} \approx 0.2 \text{eV}$ in slight agreement with what is observed for the bulk bands of Bi$_2$Se$_3$ ($\sim 0.1 \text{eV}$). [95, 96]. This is however expected, since Te atoms enhance the spin-orbit interaction. Also, atmospheric contaminants are likely to enhance Rashba-splitting due to band bending resulting from the uncontrolled adsorption of atomic species in air. This contrasts with what is reported in ARPES [95] where the level of CO contamination was systematically controlled, and measurements were made in ultra-high vacuum.

Going back and considering the broader picture, one can break down the observed quantum coherent WAL into two parts. The first is the surface WAL given by the HLN equation for $\alpha = 1$:

$$\Delta G(B) = -\frac{e^2}{\pi \hbar} \left[ \psi \left( \frac{\hbar}{4eL^2 B} + \frac{1}{2} \right) - \ln \left( \frac{\hbar}{4eL^2 B} \right) \right].$$

The second is an additional bulk 2D conduction band contributing as a WAL channel with finite Rashba spin-orbit coupling, yielding a parabolic correction given by:
\[ \Delta G(B) = -\frac{e^2}{2\pi \hbar} \left[ \psi \left( \frac{\hbar}{4eL^2 B} + \frac{1}{2} \right) - \ln \left( \frac{\hbar}{4eL^2 B} \right) \right] + \beta_q B^2. \]

\[ \beta_q B^2 = -\frac{e^2}{24\pi \hbar} \left( \frac{B}{B_{SO} + B_e} \right)^2 + \frac{3e^2}{48\pi \hbar} \left( \frac{B}{(4/3)B_{SO} + B_e} \right)^2. \]

And finally, we include a classical cyclotronic MR given by:

\[ \beta_c B^2 = -\mu_{\text{Mr}}^2 G_q B^2. \]

In total, all contributions yield:

\[ \Delta G(B) = -\frac{3e^2}{2\pi \hbar} \left[ \psi \left( \frac{\hbar}{4eL^2 B} + \frac{1}{2} \right) - \ln \left( \frac{\hbar}{4eL^2 B} \right) \right] + \left( \beta_q + \beta_c \right) B^2. \]

Given that we are able to resolve up at least 2 and possibly 3 channels, the WAL in unlikely to be due exclusively to bulk 2D bands. This conclusively confirms the existence of surface WAL resulting from spin-momentum locking, and additionally decouples bulk WAL from surface WAL.

**f. Summary and prospects**

In sum, we have grown Bi\textsubscript{2}Te\textsubscript{3}Se thin film on Si(111). The films were qualitatively identical to Bi\textsubscript{2}Se\textsubscript{3} films. The carrier concentration and the observed quantum coherent transport were strongly similar to what is generally reported for Bi\textsubscript{2}Se\textsubscript{3}. We observed linear magnetoresistance and provided an explanation of the phenomenon in terms of quantum coherent transport.

At low fields we demonstrated that the surface states yield WAL. The bulk may also yield WAL that turns over into WL at high fields, due to the finite spin-orbit characteristic field.
of the bulk states. This bulk contribution was extracted from using the proposed model and compared to the typical spin-orbit splitting observed in ARPES in Bi$_2$Se$_3$. A discrepancy of about a factor of 2 results. This result is not surprising as Te atoms as well as atmospheric contaminants may enhance spin-orbit splitting.

In the future, a study of the LMR versus gating voltage may shed light on the dependence of spin-split bulk states on the applied electric field. This is of some relevance, as it may tune the Rashba splitting by modifying the band-bending at the interface between the dielectric gate and the topological surface. Gating may also allow one to deplete the bulk conduction band close to the surface and study quasi-surface-only contributions.
V. **Topological Crystalline Insulator SnTe: Growth and Magnetotransport**

1. **Achieving high-quality epitaxial growth of SnTe on BaF$_2$**

   a. **MBE films of SnTe on BaF$_2$(001): background and material science**

   One of the most convenient aspects of studying SnTe to a physicist is the fact that single phase SnTe exists stoichiometrically; it is simply a rocksalt cubic structure characterized by space group Fm-3m. The lattice constant – $a = 6.327$ Å – is however somewhat difficult to match to standard substrates such as Si ($a = 5.43$ Å) or GaAs ($a = 5.65$ Å). BaF$_2$ ($a = 6.2$ Å) and KCl ($a = 6.3$ Å) both have a decent lattice mismatch of under 2% with SnTe. KCl being extremely sensitive to humidity and atmospheric contaminants may require in-situ cleaving, which is not straightforward in our MBE setup. We thus choose BaF$_2$ as the best common substrate to attempt to achieve epitaxy.

   Earlier work on IV-VI semiconductors already shows that extremely high mobilities can be obtained when PbTe films and heterostructures are grown on BaF$_2$ (111) [97, 98, 99, 100]; the quantum Hall effect is even observed in PbTe-EuTe heterostructures having $\mu \sim 10^6$ cm$^2$/Vs [100]. A study of SnTe/EuTe quantum wells also reports mobilities on the order of $10^3$ cm$^2$/Vs. [98]

   Note, however, that most of the work on (Pb,Sn)Te grown on BaF$_2$ was done on films that are several micrometers thick. The reason behind that is the fact that both PbTe and SnTe nucleate as islands that eventually coalesce at high enough thicknesses following a Volmer-Weber-like mechanism. In order to investigate the topological surface states, one would like to be able to grow films that are no thicker than 100 nm, so that the surface-to-bulk ratio is maximized, where surface states penetrate about 3 - 5 nm into the bulk. We thus have to start by optimizing the growth conditions of thin films of SnTe on BaF$_2$ (001). We choose (001) oriented
substrates as we are interested in studying the physics of the (001) topological surface states of SnTe.

b. Optimizing the growth conditions

As we have established that BaF$_2$ is the best substrate in order to grow SnTe, we next look at how substrate temperature influences film crystallinity, morphology and transport. Let us first begin by discussing the growth procedure.

First, BaF$_2$ (001) substrates are pre-annealed in a $10^{-7}$ torr load-lock chamber at 340 °C for approximately 2 hours prior to loading in the main MBE deposition chamber. The substrate preparation procedure is discussed in detail in the methods section. Once in the MBE chamber, the substrate temperature is set to the desired growth temperature (220 °C – 340 °C) and the shutter in front of the substrate is open to initiate the growth, several minutes after reaching a stable substrate temperature. No annealing is performed after the growth. Elemental high purity (99.9999%) Sn is evaporated from an e-gun source, and ultra-high purity (99.9999%) Te is evaporated from a Knudsen-cell with atomic flux ratios set to be close to Sn:Te=1:1.1. After the growth is finished and the sample is cooled down, a protective 3-4nm thick Al$_2$O$_3$ capping layer is deposited at room temperature.

We grew films that were 40 nm thick at 5 different temperatures: 220 °C, 260 °C, 290 °C, 320 °C, and 340 °C.

c. Surface topography by atomic force microscopy
Figure V-1. (a-d) AFM images (5×5μm) taken on films grown at different temperature between 220 °C and 340 °C.

Films grown at different temperatures were initially characterized by atomic force microscopy (AFM). Figure V-1(a-d) shows the evolution of the surface morphology versus growth temperature. It is evident that the film grown at 220 °C exhibits small morphological features that are less than several tens of nanometers in diameter. For growth at 260 °C, narrow stripe-like features emerge, with widths reaching no more than 100 nm, and lengths reaching 100 – 200 nm. As the temperature is increased the feature size significantly increases until reaching lengths and widths of several hundred nanometers at a growth temperature of 320 °C. The AFM image for growth at 320 °C shows flat, terrace-like features that are well connected, but slightly separated by holes that possibly extend down to the substrate. We believe the growth proceeds by a Volmer-Weber nucleation mechanism, where SnTe grows as isolated clusters that eventually nucleate as the thickness increases (illustrated in Fig. V-2). A similar growth mechanism has been reported for PbTe on BaF$_2$ [101] and also for Ag on insulating
substrates [102]. This process might be either a result of a poor wetting of the BaF$_2$ surface by Sn or SnTe, or a consequence of an unfavorable chemical termination of the substrate. Keep in mind that the (001) surface of BaF$_2$ is neutral (layers containing both Ba and F), as is that of SnTe.

![Figure V-2. Illustration of the Volmer-Weber nucleation mechanism for thin films.](image)

d. **X-ray Diffraction and TEM characterization**

Next, we carry out an X-ray diffraction (XRD) study in order to determine the crystalline orientation of our films and their crystalline quality. Let us note here that since the topological protection mechanism in SnTe is closely related to the crystal structure, it is vital for us to be able to achieve a crystalline quality that matches the ideal assumptions considered in the TCI theory as closely as possible.

A systematic improvement is seen as the growth temperature is increased. The film grown at 220 °C does not exhibit strong enough Bragg peaks to be useful. In films grown above 260 °C, well-defined (002) and (004) peaks (shown in Fig. V-3) corresponding to the rocksalt structure are observed alongside the BaF$_2$ substrate peaks. Interestingly, a 60 nm film grown at 320 °C exhibits a peak intensity that is only one order of magnitude lower than the substrate peak
intensity. This shows that the resulting film crystallinity is likely to be as good as bulk single crystals of SnTe.

Figure V-3. (004) Bragg peak of SnTe films grown at different temperatures along with the BaF$_2$ substrate (002) peak, obtained from standard XRD.

Additionally, we performed an elaborate high-resolution synchrotron XRD study at beamline 33ID/D at the Advanced Photon Source at Argonne National Laboratory. A 40 nm film grown at 320 °C was thoroughly investigated. The out-of-plane {002} Bragg series was initially probed as shown in Fig. (V-4), followed by a detailed analysis of in-plane Bragg peaks ({022} and {222} series). The (002) Bragg peaks for both SnTe and BaF$_2$ can be seen. Distinct Laue fringes can be seen around the SnTe peak, suggesting the formation of coherent stacking and a parallel surface and interface.
The in-plane and out-of-plane lattice constants can then be extracted, \( c = 6.324 \pm 0.003 \) Å and \( a = 6.299 \pm 0.006 \) Å. This shows that a slight tetragonal expansion occurs elongating the lattice in the \( c \)-direction by a small amount \( (c/a = 1.004) \). The out-of-plane lattice constant is seen to relax faster than the in-plane lattice constant.

---

Figure V-4. Reciprocal space map of the (002) Bragg peak in 40nm SnTe film on BaF\(_2\).

Figure V-5. Φ-scan of the \{022\} Bragg series showing both the substrate and SnTe peaks.
A Φ-scan (Fig. V-5) is also performed; the sample is basically rotated about the c-axis with the diffractometer aligned along a (022) Bragg peak. The SnTe {022} Bragg series is probed with respect to the BaF₂ {022} series as the sample is rotated. The scan is shown in Fig V-5. Strong peaks that are several orders of magnitude higher than the background are observed at 90° periods. Two distinct peaks corresponding to BaF₂ and SnTe can be resolved at all four periodic angles (shown in the inset of Fig. V-5). This implies an excellent cube-on-cube epitaxial match between SnTe and BaF₂. The SnTe lattice thus aligns well with the underlying substrate and is not rotated or twinned in the film plane. We have thus shown that SnTe forms ultra-high quality single crystalline films on BaF₂ (001) substrates when the substrate temperature is high enough.

Finally, cross-sectional TEM images of a film grown at 340 °C are shown in Fig. V-6. Atomic planes can be resolved in the bulk and all the way down to the interface, again confirming the highly-crystalline quality of SnTe on BaF₂. The lattice separation is extracted from the TEM image and found to be 3.18±0.05 Å, in agreement with that extracted from X-ray diffraction. An FFT-pattern (Fig. V-6b) of the interface is also shown. The pattern matches well with what is expected for a cubic crystal. No sign of spot separation is visible indicating the formation of a single phase layer at the interface. Note that the tetragonal distortion is too small to be visible in the TEM image.
Figure V-6 (a). Cross-sectional TEM view of the interface and bulk of a 40 nm SnTe film grown on BaF$_2$ (001) at 340 °C. (b) FFT pattern of the interface.

e. **Summary**

To summarize this section we can conclusively say that highly-ordered epitaxial SnTe films can be grown on BaF$_2$ (001) at 320 °C and above. No sign of any twinning or dislocations is observed in either TEM or XRD. The tetragonal distortion is probably a consequence of the slight lattice mismatch between SnTe and BaF$_2$ (1.9%). Since the SnTe film is slightly compressed in-plane, the c-axis expands in order to relieve strain. This tetragonal distortion does not however break the symmetry properties of the (001) surface, and hence conserves the topological surface states. Interestingly, the crystalline and morphological quality of the film can be tuned by changing the substrate temperature. In what comes next, this ability to tune the structural properties of the films will allow us to map out the fundamental physical behavior of SnTe surface states as a function of disorder.
2. Tuning the Fermi level by varying the growth temperature

   a. *The non-linear Hall effect in SnTe thin films*

   We then measure the Hall resistivity of the films up to fields of 5 T (9 T for a 30 nm film) and down to a temperature of 2 K using a modified probe inserted in a SQUID MPMS magnetometer [55] (and a PPMS). The Hall resistivity is linear for films grown below 320 °C and results in p-type carriers. At 320 °C and above, a non-linearity emerges in the Hall resistivity at fields above ~2 T. This is shown in Fig. V-7. A 30 nm film grown at 320 °C was measured up to 9 T at 2 K; the curvature in the Hall resistivity is strongly resolved by 9 T and is unambiguously present, even in the raw Hall effect data.

   ![Figure V-7. Hall resistivity measured at 2 K in a film grown at 220 °C and a pair of films grown at 320 °C.](image)

   In order to get more insight on the observed phenomenon, we take a look at the Hall curvature defined as the Hall resistivity minus a low-field linear slope extracted below 0.5 T. The
Hall curvature is plotted for different growth temperatures in Fig. V-8(a). There is clear evidence that the curvature depends on the growth temperature, as it is only observed when the growth temperature is greater than or equal to 320 °C. Similar behavior in the Hall effect was also reproduced in films of different thicknesses grown at 320 °C. The slight variations in the magnitude of the effect are due to small changes in mobility in films resulting from different growths. This will be discussed later. It can, however, be conclusively said that the occurrence of the non-linear Hall effect is independent of thickness.

A non-linear Hall resistivity can arise as a result of several physical effects:

- An ellipsoidal Fermi surface that has an effective mass anisotropy. [103, 104]
- Coexisting transport channels, in parallel, one of which has a high mobility. [49, 75, 105, 106]
- A single high-mobility transport channel. [3, 107]

All three are likely to arise in SnTe. We thus rely on empirical data to rule out some effects.

b. **Ruling out the effective-mass anisotropy and the dual channel explanations**

Although the anisotropic effect-mass explanation seems very plausible from a band structure perspective, it does not explain the trend observed versus temperature. According to that explanation, the film grown at 220 °C is as likely to result in a non-linear Hall resistivity as any other film. Our results show that it is clearly not the case. Additionally, we attempted to fit our data to a modified Drude model that takes into account this mass anisotropy and failed to provide decent agreement with data [103, 104].

The second explanation relies on having parallel conduction channels such as the coexistence of surface and bulk conduction channels [105, 106]. Using the conductivity tensor in the Drude model, one can derive the Hall conductivity and the longitudinal conductivity as a function of magnetic field for two parallel channels. This is gives the two-channel model:

\[
\sigma_{xx} = \frac{en_1\mu_1}{1 + \mu_1^2B^2} + \frac{en_2\mu_2}{1 + \mu_2^2B^2} \quad \text{and} \quad \sigma_{xy} = \frac{en_1\mu_1^2B}{1 + \mu_1^2B^2} + \frac{en_2\mu_2^2B}{1 + \mu_2^2B^2}
\]

Here, \(\mu_i\) and \(n_i\) are respectively, the mobility and the carrier density of the channel \(i (i=1,2)\). Both \(\sigma_{xx}\) and \(\sigma_{xy}\) are then divided by the total zero field conductivity:

\[
\sigma_0 = n_1e\mu_1 + n_2e\mu_2
\]

The resulting form is then fit to both the Hall and longitudinal conductivity:
\[
\frac{\sigma_{xx}}{\sigma_0} = \frac{1 - \alpha}{1 + \mu_1^2 B^2} + \frac{\alpha}{1 + \mu_2^2 B^2} \quad \text{and} \quad \frac{\sigma_{xy}}{\sigma_0} = \frac{(1 - \alpha) \mu_1 B}{1 + \mu_1^2 B^2} + \frac{\alpha \mu_2 B}{1 + \mu_2^2 B^2}
\]

Here, \( \alpha = \frac{\sigma_2}{\sigma_1 + \sigma_2} = \frac{n_2 e \mu_2}{n_1 e \mu_1 + n_2 e \mu_2} \), is the relative contribution of channel 2. The relative contribution of channel 1 would be \( 1 - \alpha \). Figure V-9 shows the two-channel model to the Hall and longitudinal conductivities of a 30 nm film grown at 320 °C. The resistivity data from the film is converted to conductivity by inverting the resistivity tensor.

\[
\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{xy}^2} \quad \text{and} \quad \sigma_{xy} = \frac{\rho_{xy}}{\rho_{xx}^2 + \rho_{xy}^2}
\]

The simultaneous fit to \( \sigma_{xx}(B) \) and \( \sigma_{xy}(B) \) is performed up to 9 T. Decent agreement with both experimental quantities is found. Channel 2 yields \( p \)-type carriers as expected for SnTe, with \( n_2 = 1.0 \times 10^{20} \) holes/cm\(^3\) and \( \mu_2 = 660 \) cm\(^2\)/Vs. Channel 1 surprisingly yields an \( n \)-type contribution \( n_1 = 1.3 \times 10^{21} \) electrons/cm\(^3\) and \( \mu_1 = 77 \) cm\(^2\)/Vs. It is also unusual that the \( n \)-type channel is dominant, having a 50 % larger conductivity than the \( p \)-type channel. Similar results we obtained from all films showing the non-linear Hall resistivity.
Figure V-9. Two-channel model fit for the 30nm film grown at 320 °C to the (a) Hall conductivity and (b) longitudinal conductivity. The contribution of each carrier channel is shown separately (indigo and black curves) as well as the data (red) and the fit resulting from adding the two channels (dark blue).

We shall now attempt to understand these observations in terms of the band structure of SnTe. Generally speaking, SnTe has always been seen to result in $p$-type conduction. However, it has been shown in the case of SnTe (111) grown on Bi$_2$Te$_3$ [105], that severe band-bending occurs close to the surface and moves the Fermi level into the surface conduction band, and thus enhances the surface-band contribution. In SnTe (111), this results from the fact that the (111) planes are polar. This is not the case for (001) surfaces. Moreover, band-bending as a result of adsorbents was shown to occur in Bi$_2$Se$_3$ [95, 96]. Generally, this occurs over a 10 nm distance into the sample, and results in a total Fermi level shift of 0.25 eV into the conduction band.

If this scenario were to occur and result in SnTe films having $n = 1.3 \times 10^{21}$ electrons/cm$^3$ one would need to move the Fermi level up by a total of ~1 eV over a thickness of 10-30 nm – the majority of the sample thickness. This would require an extreme amount of charging to occur. Also, there is no apparent reason why such an effect would depend on the growth temperature. We are thus inclined to reject this modeling of two-channel conduction which simultaneously fits both $\sigma_{xx}(B)$ and $\sigma_{xy}(B)$.

c. The non-linear Hall effect: the single high-mobility channel explanation

Lastly, we look at agreement between data and modeling when a standard single-channel Drude model is used to fit the Hall and longitudinal conductivity:

\[
\sigma_{xx} = \frac{n_e e \mu_c}{1 + \mu_c^2 B^2} \quad \text{and} \quad \sigma_{xy} = \frac{n_h e \mu_h^* B}{1 + \mu_h B^2}
\]
We apply this model to the 30 nm film grown 320 °C and extract the transport parameters independently from $\sigma_{xx}(B)$ and $\sigma_{xy}(B)$. This is shown in Fig. V-10.

![Graph](image)

Figure.V-10. Hall and longitudinal conductivity data (blue) of a 30 nm film versus magnetic field with corresponding fit to the single-channel Drude model (red). The fit is performed independently for $\sigma_{xx}(B)$ and $\sigma_{xy}(B)$.

The fits yield excellent agreement with the measured nonlinear Hall conductivity. We are able to extract a mobility of 716 cm$^2$/Vs and a carrier density of $7.1 \times 10^{19}$ holes/cm$^3$. Unfortunately, parameters extracted from the Hall conductivity (Fig. V-10(a)) did not match what is found when analyzing the longitudinal conductivity (Fig. V-10(b)). Additionally, the $\sigma_{xx}(B)$ curve fit does not seem to satisfy the observed resistivity trend at high field. This disagreement between the Hall and longitudinal conductivities is common in semiconductors in general, and SnTe in particular. It can arise when transport time $\tau$ is inhomogeneous. This usually introduces a multiplicative factor $r$ proportional to $<\tau^2>/<\tau>^2$ [2, 108, 109] up to first order in $(\omega \tau)^2$. [1] The measured Hall mobility would thus differ from the actual electron drift mobility, and the Hall carrier density may change as a result. Going beyond the simple Drude
an approach would introduce terms in $\sigma_{xy}$ that cannot be solved analytically. It is thus beyond the scope of our analysis [1, 109]. In reference 109, similar results are obtained and thoroughly discussed.

Fortunately for SnTe, theoretical work done in the past managed to correlate the Hall carrier density with the Fermi level by providing a proper understanding of the shape of the bulk Fermi surface of the valence band [109, 110, 111]. We are thus able to extract information that allows us to directly explain our data in terms of what band structure calculations and ARPES results predict and observe.

d. **Extracting the Fermi level from the band structure**

* Note that in the following discussions we use “Fermi level” as the magnitude of the “Fermi energy” relative to the center of the band gap, as the Fermi energy is negative and the Fermi level lies in the valence band.

Since we have performed a systematic study versus growth temperature, we shall extract the Fermi level and mobility for all samples considered here. Let us start by discussing how this is performed.
Figure V-11. (a) Valence band (VB) density-of-states (DOS) versus energy from Littlewood, et al. [111]. (b) Fermi energy versus Hall carrier density from Tsu, et al. [109].

In 2010, Littlewood et al. empirically correlated the carrier density to the ARPES measurements and \textit{ab initio} band structure calculations [111]. We thus use their results to extract the Fermi level, by self-consistently integrating the calculated carrier density per unit cell as shown in Fig. V-11(a) up to the appropriate Fermi level by iteration. Additionally, work done in 1968 [109] correlated the Hall density to the position of the Fermi level, again by taking into consideration the non-trivial shape of the bulk Fermi surface, shown in Fig. V-11(b), and by performing cyclotron resonance measurements. We also extract a Fermi level from the analysis as shown in Fig. V-11 for the samples discussed earlier. The extracted Fermi energies (measured from the center of the gap) are somewhat at odds – 0.29eV when using Littlewood, et al. [111] and –0.215eV when using Tsu, et al. [109]

Regardless of that, we shall see in the next section that when multiple samples are analyzed the extracted trends are similar regardless of which theory we use.

\textbf{e. Tuning the Fermi level and mobility with growth temperature}

We now extract the Fermi level for different samples grown at different temperatures, as discussed in the previous section. Figure V-12(a) shows the carrier density extracted from the Hall (blue) and longitudinal conductivity (red) for all samples. Note that when the Hall effect is linear the conventional approach is used to extract the transport parameters. This result is of capital importance, as it shows that SnTe having a lower carrier can be grown by increasing the substrate temperature. It also shows that one can tune the Fermi level simply by growing films at different temperatures. Finally, we see how the mobility changes versus growth temperature. The
mobility extracted from both the Hall and longitudinal conductivity is shown versus growth temperature in Fig. V-13. For films not exhibiting a non-linear Hall effect the carrier density is extracted using the conventional linear Hall effect formalism, and the mobility is deduced from the zero field conductivity. Hence, the left-most points in Fig. V-12(a) and Fig. V-13 walyasoverlap.

Figure V-12. (a) Carrier density extracted from the Hall (blue triangles) and longitudinal conductivity (red squares) versus growth temperature. For films not exhibiting a non-linear Hall effect, the carrier density is extracted from the Hall slope and the mobility is deduced from the zero-field conductivity. Solid lines are a guide for the eye. (b) Fermi level extracted from Littlewood, et al. [111] and Tsu, et al. [109] for the measured Hall carrier density.
f. Summary

In order to summarize this section, let us again highlight the importance of the trends observed versus growth temperature. Our study conclusively shows the following:

- The Fermi level moves closer to the band gap as the growth temperature is increased;
- The mobility improves significantly when films are grown at higher temperature;
- The crystalline quality and the surface morphology also improve with increasing substrate temperatures.

It is not unusual that the mobility improves when the surface morphology is smoother and when the crystalline quality of the sample improves. A reduction in the dislocation density in the film may also impact the Fermi level through the carrier density. An analysis of how dislocations induce atomic defects and vacancies is, however, not straightforward. An alternative reason for why the Fermi level is closer to the gap when the substrate temperature is increased may be found in other growth related parameters, such as the Te sticking coefficient.

Figure V-13. Mobility extracted from both the Hall and longitudinal conductivities.
As SnTe is naturally non-stochiometric as a result of Sn vacancies, $p$-type conduction is always expected. When the growth temperature is low, Te antisites replacing Sn atoms are likely to form acceptors. At higher growth temperatures a Te antisite is less stable, as the Te sticking probability is lower. We thus have a reduction in antisite defects, and hence fewer acceptor states. Thus, this speculation calls for experiments probing the antisite defect density, as well calculations that could determine the stability of a Te antisite defect versus temperature.

Let us end this section by going over the issues that were left unsolved. The disagreement between the Hall and longitudinal conductivity remains a pending issue. Magnetotransport at higher fields, exhibiting SdH oscillations may provide an answer to this issue. Also, as will be discussed in the next chapter, surface transport is present at low magnetic fields. As a result, it may influence the high field regime in a non-trivial way that we could not clarify.

Finally, keeping in mind that the disagreements we observe may result from an inhomogeneous transport time [3,108], the trend in the high-field magnetoresistance is strongly similar to what one would expect from the Parish-Littlewood model of linear MR [83, 84]. Notice in Fig. V-9 the highly sub-parabolic behavior of the conductivity at high fields. A systematic study of the MR slope at high fields may lead to some interesting findings. We now move on and study TCI physics via quantum coherent transport.

3. Multivalley weak antilocalization

a. Weak antilocalization in SnTe: a multivalley system

The physics of WAL in TCI SnTe is very subtle. In conventional TIs, a single Dirac cone on each surface contributes to WAL in addition to a trivial spin-orbit coupled bulk band. In SnTe, several complications have to be taken into account:
- Dirac cones are degenerate. One can get up to four per surface. [16, 27]

- For Fermi levels located in the bulk valence band, a Lifshitz transition may change the Fermi surface topology of the surface states. [16, 27, 46]

- Farther down in Fermi energy, the Fermi surface topology of the bulk states may also change [111]. Not much is known about the behavior of surface states in this regime.

- All of the above have to be understood in light of intervalley scattering and surface-to-bulk scattering that may couple or decouple the Dirac cones and the bulk bands. [48, 52, 112, 113, 114]

Figure V-14. (a) Lifshitz transition as seen in the Fermi surface of the surface states projected onto to (001) plane. As the Fermi level moves into the valence band, the surface carrier pockets merge. (b) Change in the bulk Fermi surface topology versus Fermi level [109].

As shown in Fig. V-14(a), the number of surface hole pockets is reduced by half through the Lifshitz transition, as the Fermi level moves down into the bulk conduction band. When the Fermi energy is below –0.05eV, one ends up with 2 surface carrier pockets instead of 4. In a similar fashion, as the Fermi energy is reduced farther, the bulk Fermi surface also undergoes a
change in topology. Instead of the small bulk-hole pockets found at low Fermi level, Fig. V-14(b) shows that one ends up with a tubular interconnect that acts as a single larger, hole pocket.

Next, let us discuss our results of WAL measurements.

b. *Weak antilocalization in SnTe thin films – a likely surface effect*

WAL is reproducibly observed in all films, regardless of the growth temperature. The strength and sharpness of the WAL cusp is however seen to change dramatically. This is shown in Fig. V-15. WAL from the film grown at 220 °C (Fig. V-15(a)) is compared to the ones grown at 290 °C (Fig. V-15(b)) and 320 °C (Fig. V-15(c)). The WAL cusp is wide and small for films grown at low growth temperatures, and gets sharper and stronger as the growth temperature is increased.

![Figure V-15. WAL cusp for films grown at 220 °C (a), 290 °C (b) and 320 °C (c). HLN model curve fits shown as solid red lines.](image)

The indisputable reproducibility of the cusp is a reliable confirmation of the contribution of surface states to the observed transport. This claim may be further supported by results observed in Sn doped-InSb films grown on GaAs(100) [115]. Spin-orbit interactions in InSb are
expected to be similar in magnitude to what one finds for SnTe. In order to get insight on the possible role of the bulk bands of SnTe in WAL, it would thus be fair to compare SnTe to InSb. In InSb although WAL is observed at low fields (<5mT), a cross-over to WL is generally observed by 10mT. This indicates that bulk bands of InSb have a finite spin-orbit length, that eventually gives rise to WL [66, 115]. One would expect an identical effect from the bulk bands of SnTe. This is clearly not the case, according to our observation as can be seen in Fig. V-16(a,b) where SnTe is compared to what is seen for InSb in reference 115. Also, keep in mind, the non-inversion-symmetric zinc-blend structure of InSb that can yield Dresselhaus spin-orbit coupling, in addition to Rashba spin-orbit interactions. In rocksalt SnTe, the Dresselhaus contribution vanishes.

In order to confirm this behavior, we calculate the expected quantum coherent behavior of SnTe by using the full HLN model considered for InSb.

\[
\Delta G(B) = -\frac{e^2}{2\pi\hbar} \left[ \psi \left( \frac{B_\phi}{B} + \frac{1}{2} \right) - \ln \left( \frac{B_\phi}{B} \right) \right] \\
-\frac{e^2}{\pi\hbar} \left[ \psi \left( \frac{B_{SO} + B_\phi}{B} + \frac{1}{2} \right) - \ln \left( \frac{B_{SO} + B_\phi}{B} \right) \right] \\
+ \frac{3e^2}{2\pi\hbar} \left[ \psi \left( \frac{(4/3)B_{SO} + B_\phi}{B} + \frac{1}{2} \right) - \ln \left( \frac{(4/3)B_{SO} + B_\phi}{B} \right) \right].
\]
Figure V-16. (a) WAL and WL observed in a Sn-doped InSb thin film [115]. (b) WAL observed in a 30 nm SnTe film. (c) Expected quantum coherent contribution from the bulk bands of SnTe.

Assuming that band bending is not significant in SnTe, one can estimate the expected quantum correction from bulk bands, by analogy to InSb. This spin-orbit characteristic field may be approximated according to the following in relation to the average atomic number $Z$:

$$\frac{B_{SO}(SnTe)}{B_{SO}(InSb)} \sim \frac{Z(SnTe)^4}{Z(InSb)^4} \approx 1.08 \cdot [116]$$
$B_{SO(InSb)} \sim 1\, \text{mT}$ is extracted from reference 115. The expected results for SnTe are shown in Fig. V-16(c). WL – not WAL – is seen to dominate the behavior of SnTe in this scenario. The observed dominant WAL behavior for SnTe has to find its origin in the surface states. Surface-to-bulk scattering is still present, and bulk bands may still yield a WAL channel that can mix surface and bulk contributions as discussed by Garate and Glazman [52].

We can now extract the number of coherent channels given by $2\alpha$, and the coherence length $L_\phi$, using the HLN model for topological systems [63]:

$$\Delta G(B) = \frac{\alpha e^2}{\pi h} \left[ \psi \left( \frac{\hbar}{4 e L_\phi B} + \frac{1}{2} \right) - \ln \left( \frac{\hbar}{4 e L_\phi B} \right) \right].$$

Both $2\alpha$ (the number of coherent channels) and $L_\phi$ are plotted in Fig. V-17 versus the Fermi level that was extracted in the previous section.

![Graphs showing $2\alpha$ and $L_\phi$ versus Fermi level](image)

Figure V-17. (a) $2\alpha$ plotted versus Fermi level. (b) Coherence length plotted versus Fermi level. The Fermi level is extracted from the Hall effect and reference 111.
Apart, from the 60 nm film being an outlier, $2\alpha$ increases from 2.4 to 3.2, with increasing Fermi level, up to the point where the Fermi level reaches ~0.45 eV. At the highest obtained Fermi levels, $2\alpha$ collapses back to below 2. Additionally, the coherence length increases for decreasing Fermi level. This trend is likely to be a direct consequence of the reduction of the inelastic scattering rate caused by electron-electron collisions at low temperature when the Fermi level is lower and film mobility is higher. There are, thus, three observations that require an explanation:

- Why is the 60 nm film an outlier?
- What causes the observed low $\alpha$-value at low Fermi energy, and the increase in $\alpha$ up to a Fermi level ~0.45 eV?
- What causes the final collapse observed in $\alpha$ at Fermi levels above 0.45 eV?

c.  Weak antilocalization and the role of surface-to-bulk and intervalley scattering

Let us begin by discussing our results in terms of how different scattering lengths may influence the number of coherent channels. Some relevant trends can be extracted if $\alpha$ is plotted versus $L_\phi$ for Fermi levels less than or equal to 0.45 eV. The reason behind this choice will become clear in the next section. $\alpha$ versus $L_\phi$ is shown in Fig. V-18.
Evidently, a larger number of coherent channels is observed for smaller $L_\phi$. This can be understood in terms of different valley coupling strengths. As long as the Fermi level is less than 0.45 eV, the Fermi surface topology is not dramatically altered \[111\]. One can thus safely assume that the intervalley scattering length $L_{IV}$ and the surface-to-bulk scattering length $L_{SB}$ are almost constant. Starting from the right most point, where $L_\phi$ is largest we have $L_\phi \gg \{L_{IV}, L_{SB}\}$. In this case, a charge carrier can scatter between different valleys and between the surface and the bulk while remaining coherent. \[48, 52, 112, 113, 114, 117, 118\] We are thus unable to resolve more than 1.6 WAL channels due to this type of coupling. As $L_\phi$ gets shorter, it starts approaching $L_{SB}$; more WAL channels emerge. Between 2 and 3 channels can be detected for the three intermediate points. This is likely to be due to two surface bulk and a third bulk channel.

It is important to note that $L_{IV}$ is expected to be the smallest of the three lengths discussed here. In analogy to graphene, achieving regimes where valley decoupling occurs is extremely difficult \[112, 113, 114\]. In comparison to graphene, SnTe is expected to host a significant
amount of impurities that give rise to intervalley scattering such as domain boundaries and charged impurities. As can be seen in our AFM images, grain boundaries are not uncommon. In sum, as intervalley scattering is strong, one channel is expected from each surface and one channel may contribute from the bulk. Finally, the left most point results in more than 3 channels while having the lowest $L_\phi$. This is the regime where $L_{SB} > L_\phi$, that fully decouples two surface channels and a possible a third bulk channel. The fact that we get a number slightly larger than 3 within error is probably due to $L_\phi$ approaching $L_{IV}$ so that coherent intervalley scattering starts to diminish and gives hints to the existence of multiple surface Dirac valleys.

[27]

A more promising explanation may be obtained if one assumes WAL to be a surface only effect. As we are always beyond the Lifshitz transition ($E_F < -0.05$ eV) [27], one expects at most 4 Dirac cone per Brillouin zone for two surfaces. A change in the number of WAL channels from $\sim 1.6$ to $\sim 3.2$ could mean a decoupling between the surfaces followed by a decoupling of the individual valleys on each surface.

Whether one or the other explanation holds better is beyond the scope or this thesis at this point. In sum, we have shown that the 60 nm film looks like an outlier in Fig. V-17 because it has the longest $L_\phi$. The change of $\alpha$ versus $L_\phi$ also explains the increase in $\alpha$ observed in Fig. V-17(a) up to 0.45eV.

WAL is strong evidence of the suppression of backscattering resulting from the combined effect of spin-momentum locking on the surface and spin-orbit coupling in the bulk.

Let us finally address the sudden collapse in the number of coherent channels at high Fermi level.
d. *Weak antilocalization in different topological Fermi surface regimes*

![Graph showing α plotted versus Fermi level with 30-40 nm outlier highlighted.](image)

Figure V-19. Figure V-17(a) α plotted versus Fermi level. (b) Shape of the Fermi surface versus Fermi level for both the surface [27] and bulk states [111].

Now that we have provided an explanation for the occurrence of the 60 nm outlier, and understood the behavior below 0.45eV, we discuss the observed decrease in α at large Fermi level. The drop in α observed for the two films having the largest carrier density or the largest Fermi level, may be a result of the changing bulk Fermi surface topology at about 0.5eV [111]. As shown by Littlewood, et al. [111] (Fig. V-19(b)), the bulk Fermi surface evolves from isolated hole pockets to a tubular network-like feature at 0.5 eV.

This change in the Fermi surface topology may have a severe effect on the surface states. Firstly, it may alter the scattering dynamics by enhancing both surface-to-bulk scattering and intervalley scattering [52]. Keep in mind that a tubular Fermi surface allows a wider spread of momentum states to exist at the Fermi energy. This would cause charge carriers to scatter more freely from and into additional available states. Both surface-to-bulk scattering and intervalley
scattering rates are increased. Different WAL valleys are thus more strongly coupled, which leads to a drop in $\alpha$.

Additionally, as of this date, no known theoretical work has given any insight on the characteristics of the surface states in SnTe when the Fermi level is that deep in the valence band [46]. Naively, one may picture the surface pockets as interconnected ellipses as shown in Fig. V-20. At the points where the individual pockets touch, backscattering may no longer be suppressed, hence reducing the number of states that would give rise to WAL. It is also possible that surface states merge with the bulk states at such large Fermi levels, hence leading to a trivial Fermi surface. In the latter case, the remaining $\alpha$ would be reminiscent of bulk WAL as a result of possible spin-orbit coupling.

![Figure V-20](image)

Figure V-20. Changes in the Fermi surface of the topological surface states as the Fermi level is varied from nearly 0 to 0.5 eV into the valence band, where 0 eV is the Dirac point. Arrows indicate points where the pockets touch. At the touching points backscattering is restored.
We would like to highlight the fact that the connections made between our observations and the Fermi surface of the topological surface states are tentative and hypothetical. They do, however, call for more theoretical work on the behavior of TCI topological surface states at deep Fermi levels, as was done for Bi$_2$Te$_3$ [119].

e. **Summary and prospect**

This section formed an essential part of this thesis. We have shown a systematic optimization of the crystalline properties and surface morphology, and related them to the transport characteristics and the quantum coherent transport of SnTe TCI films. The behavior of WAL in SnTe brings interesting answers and questions. Our Fermi level being always located deep in the valence band leads to having 2 distinct Dirac cones per surface in high-quality films. Our results do confirm that the WAL shows an interplay between 2 to 4 quantum coherent channels. Although it is likely that the bulk may be contributing to the WAL, we believe that our observations show evidence of a strong suppression of back scattering in SnTe, significantly stronger than in InSb [115], which is unexpected if only bulk bands are considered.

Finally, as films become less insulating when the Fermi level moves farther from the gap and the bulk Fermi surface became tubular, a sudden drop in the number of coherent channels is observed. These observations raise several questions concerning the behavior of surface states at elevated Fermi levels, and thus provide evidence of a reduction of WAL as a result of a partial restoration of backscattering.

Our findings call for systematic transport and STM studies versus gating voltage, as well as a proper theoretical understanding of the Fermi surface topology and the WAL behavior in TCI systems.
We shall finally move on and discuss the investigation of SnTe grown on Si (001) substrates.

4. **Heteroepitaxial growth of SnTe on Si (001)**

   a. **SnTe on Si (001): background and material science**

   The bulk lattice constant of Si is 5.431\(\text{Å}\), and thus has a 16% lattice mismatch with SnTe (6.327\(\text{Å}\)). Considering the fact that Si is one of the cheapest and most commonly available substrates, and since it is widely used in semiconductor research and industry, we grew SnTe on Si and investigated the structural and transport properties. PbSe has been shown to grow along the (001) directions on Si (001) without a buffer layer [120]. The lattice mismatch between PbSe and Si is 14%. Thus, heteroepitaxy must also be possible for SnTe.

   b. **Highly-oriented SnTe (001) films on Si (001) probed by X-ray diffraction**

   SnTe was grown on Si (001) substrates that were etched with HF prior to loading in the vacuum chamber. Elemental high-purity (99.999%) Sn was evaporated from an e-gun source, and ultra-high purity (99.999%) Te was evaporated from a Knudsen-cell with atomic flux ratios set to be close to Sn:Te=1:1.1. A protective 4 nm thick Al\(_2\)O\(_3\) capping layer was deposited at room temperature after the growth and the sample was cooled down. Some films were also grown from a single e-gun source of SnTe using MBE and by sputtering from a single source SnTe target using an Argon plasma. Interestingly, all growths on Si (001) result in highly-oriented SnTe (001) films as seen in the XRD pattern shown in Fig. V-21.
Figure V-21. XRD pattern of SnTe on Si (001) grown by MBE (blue) and sputtering (red) (Si peaks removed). Kiessig fringes can be seen around the (002) peak in the inset.

The lattice constant was found to be around 6.32±0.01 for the both films shown above which is close to the bulk value, hence indicating that the structure is relaxed. The observed fringes and peak broadening are due to finite film thickness (12-20 nm).

Additionally, we grew films of different nominal thicknesses (6-50 nm) by MBE and looked at the XRD pattern versus thickness. All films are seen to have grown along the (001) direction as only (002) and (004) Bragg peaks were observed. This can be seen in Fig. V-22(a), where a 50 nm film grown on Si (001) is compared to a polycrystalline film grown on native Si oxide. The (002) Bragg peak is then shown in Fig. V-22(b) for three film thicknesses. The lattice constant and full-width at half-maximum linewidths are extracted and plotted versus thickness in Fig. V-22(c). The lattice parameter is constant within error versus film thickness and is close to the bulk value for all three films.
Figure V-22. (a) XRD pattern comparing an oriented film grown on Si (001) and a polycrystalline film grown on the native SiO\textsubscript{x} oxide. (b) The (002) Bragg peak for different film thicknesses. (c) The lattice constant and peak full-width at half-maximum extracted from the (002) peak.

This result is surprising as SnTe is expected to undergo a large amount of compressive strain at the interface, which can expand the lattice along the growth axis. The out-of-plane lattice constant would then be expected to progressively relax to the bulk lattice constant as the thickness is reduced. We do not observe this behavior which indicates that the film is not pseudomorphic and may be fully relaxed by 6 nm. We thus take a closer look at the interface by performing cross-sectional TEM measurements.

c. *Dislocations and strain relaxation probed by cross-sectional TEM*
Cross-sectional TEM images were taken on an MBE-grown film. The TEM images shown in Fig. V-23 show a close up look at the SnTe-Si interface at several different locations in the same film. It was observed that the SnTe lattice is tilted at the interface and even in bulk for several grains. A tilt angle of about 11° off-normal can be measured. This is clearly seen in Fig. V-23(a,b). Other grains were observed to retain the cubic symmetry and are shown in Fig. 23(c).

![Cross-sectional TEM images](image)

Figure V-23. SnTe-Si interface as seen by cross-sectional TEM images showing: (a) a tilted grain, (b) a tilted interface and (c) a cubic symmetric grain and interface.
The growth of SnTe on Si (001) is dominated by dislocations, as several grains having different contrast can be resolved in TEM. As seen in Fig. V-24, in a range of about 100 nm at least 4 different grains having different crystallographic orientation can be observed, with several grain boundaries and dislocation lines in between.

![Figure V-24. Zoomed out cross-sectional TEM view showing several crystalline grains and grain boundaries.](image)

In summary, SnTe is highly (001) oriented but polycrystalline in the film plane when grown on Si (001). From a topological point of view, crystalline symmetry should be conserved within each individual grain. The effect of crystalline grain boundaries has not been studied before in a TCI and remains an open question.

\[d. \textit{Evolution of the film morphology with thickness}\]

AFM imaging was then used to probe the morphology of the SnTe films as a function of thickness. This is shown in Fig. V-25.
Figure V-25. AFM images of SnTe grown on Si(001). The *nominal* thickness is reported on the top left corner of each image.

The film in Fig. V-25(a) has a nominal thickness of 6 nm. As can be seen in the AFM image, the growth did not result in a film, but rather in an array of uniformly sized nanoparticles. The resistance of that film was $>10^7 \, \Omega$, indicating that the nanoislands do not percolate. By the 12 nm nominal thickness, a cohesive network of particles is formed (Fig. V-17(b)), as the measured resistance of the film becomes finite. At higher thicknesses – namely 25 nm and 50 nm – shown in Fig. V-25 (c,d), the morphology evolves from a series of nanoislands into a rough slab of SnTe. This result is similar to what is observed when PbTe is intercalated in a CdTe matrix [121].

Now that we have fully characterized the films grown on Si, we move on to briefly discuss the transport characteristics.
e. Basic transport characteristics

The transport characteristics of films grown on Si were similar to those grown on BaF$_2$ at low temperatures. The mobility never exceeded 100 cm$^2$/Vs, and the carrier density was typically $4\times10^{20}$ holes/cm$^3$. The Hall effect was consistently linear, indicating that the mobility does not improve significantly as was seen in the case on SnTe grown on BaF$_2$.

f. Summary

We have thus shown that SnTe may also be grown on Si(001). The resulting films have relatively poor transport characteristics compared to what was observed when SnTe is grown on BaF$_2$. Our investigation still shows that the morphology of SnTe can be tuned by growing on Si. At thicknesses < 6 nm, a systematic study of the nanoparticle size and morphology may be useful in the future. This is highly relevant for the purpose of engineering 3D confined nanostructures of TCI materials [122].

Finally, the results of this section will be used to study the proximity effect in SnTe/EuS heterostructures.
VI. Magnetism in Topological Matter

1. EuS-SnTe heterostructures

   a. The Motivation: quantum anomalous Hall edges induced by magnetic proximity

   Thus far, the main proposals and experimental realization of the quantum anomalous Hall effect (QAHE) relied on ferromagnetically-doped topological materials – both TI and TCI – in the bulk. [36, 37, 123] Experimentally, this was shown to give rise to a large QAHE that cannot be explained by the conventional theoretical formalisms of the AHE. [37, 124] The mechanism for the QAHE must thus originate from the band structure of the material.

   An alternative proposal to realize the QAHE relies on the proximity effect, whereby ferromagnetism is induced at the surface of a topological material that is interfaced with a ferromagnet. Of course, one has to overcome several obstacles. Firstly, one has to interface the TI with an appropriate insulating ferromagnet. Second, the topological material also has to be made insulating either by chemical doping or by gating. The first obstacle was overcome when Bi₂Se₃ was shown to host an AHE state and a hysteretic MR when in proximity to EuS, a ferromagnetic insulator [67,125]. Additionally, it was shown that EuS can localize the transport in the TI by breaking time-reversal symmetry at the surface. Some other works on GdN/TI interfaces reported similar results [68, 69]. Finally, the hysteretic MR observed in EuS/Bi₂Se₃ bilayers was hypothesized to be a result of QAH 1D states propagating on domain walls, where time-reversal symmetry is conserved. [67]

   In a TCI, a QAHE may be induced similar to that in a TI, either by magnetic bulk doping or by proximity [123, 126]. We thus proceed with the proximity effect by the following:

   - Grow a trilayer consisting of an EuS film interfaced between two SnTe films. This should induce ferromagnetism on the two TCI surfaces adjacent to the EuS.
- Reproduce the observations made for Bi$_2$Se$_3$-EuS bilayers. [67]

- Provide evidence of domain wall driven conduction at the SnTe-EuS interfaces as hypothesized for Bi$_2$Se$_3$, by measuring the MR in the coercive-field regime.

  This would be a first demonstration of induced magnetism on the surface of a TCI.

\[ \text{b. Growing the heterostructures} \]

As shown earlier, oriented SnTe films may be grown on Si (001). An 10 nm film is thus grown at 320 °C then capped with EuS at the same temperature, and finally the growth is completed by growing a top SnTe layer and capping with Al$_2$O$_3$. SnTe is grown from a single composite e-gun source.

EuS has a lattice constant of 5.96 Å, only 4% smaller than that of SnTe. We thus believe that heteroepitaxy may be achieved. Additionally, in order to explore the impact of roughness, as well as that of chemical diffusion, we also grew trilayers at room temperature and explored the effect of annealing at 315 °C and 410 °C.

\[ \text{c. XRD and AFM characterization} \]

The x-ray diffraction (XRD) pattern of four films – one grown at 320 °C, one grown at room temperature, and two annealed films – is shown in Fig. VI-1.
Figure VI-1. X-ray diffraction pattern taken around the (002) Bragg peak of SnTe-EuS multilayer structures grown using different conditions. The lower light blue curve shows the Bragg peak resulting from a SnTe-EuS bilayer on Si (001) grown at room temperature and annealed at 320 °C. The (002) peak is also shown for a SnTe(11 nm) – EuS (2 nm) – SnTe (11 nm) trilayer grown at 320 °C (purple), and a trilayer grown at 30 °C (dark blue), then annealed at 410 °C (black). The gray solid line is the peak position corresponding to bulk SnTe. The solid orange line corresponds to the (002) peak of EuS having a lattice constant of 5.96 Å. Kiessig fringes (black arrows) are observed around the SnTe (002) peak.

The films are highly oriented out of the film plane. Strong (002) and (004) peaks are observed for all films. Traces of a (220) and a (222) peak were seen in some cases, but their intensity was several orders of magnitude lower than the (002) peak. They might originate from the top layer grown on EuS, which is likely to exhibit some additional crystalline domains not oriented along the (002) direction, or as a result of lattice tilting along a dislocation line. Bulk lattices constants are 5.96 Å and 6.327 Å for EuS and SnTe, respectively. Additionally, Kiessig
fringes can be observed in the vicinity of the Bragg peak. The corresponding thickness is close to 22 nm, the total thickness of a trilayer.

Comparing the trilayers to a bilayer grown on Si (001) (Fig. VI-1-light blue) at room temperature and annealed at 320 °C, one can see a clear splitting of the (002) peak in the case of the trilayers, except when it is annealed at 410 °C. The peak at lower angles clearly appears when the SnTe top layer is grown. The top SnTe layer therefore has a lattice constant of 6.4 Å – larger than what is expected for bulk SnTe. The SnTe grown at the bottom has a lattice constant of 6.30 Å, slightly smaller than the bulk value.

In a control experiment, we grew a SnTe layer of varying thickness on EuS/Si (111) during a single MBE growth. We observed trends indicating that the out-of-plane lattice constant of SnTe is indeed larger than the bulk value, when grown on EuS, and relaxes to the bulk value as the SnTe layer gets thicker. The SnTe layer is thus expanded in the growth direction when grown on EuS. This is not surprising since the lattice constant of EuS is smaller that of SnTe. EuS thus compresses SnTe in the plane and elongates it along the growth axis. The major question that arises here is whether EuS diffuses into SnTe, causing SnTe grown on EuS to have a larger lattice constant. TEM images as well as SQUID magnetometry are however able to rule out this possibility.

Moreover, we do not observe any Bragg peaks corresponding to the lattice constant of EuS. The appearance of Kiessig in the vicinity of the SnTe Bragg peak makes difficult to locate peaks corresponding to EuS, as they are expected to occur on the high angle side of the SnTe (002) peak.
Lastly, AFM images were obtained for the films grown at 320 °C, room temperature, and 410 °C. Roughness was high for the film grown 320 °C compared to the other two, which showed almost identical behavior.

Interestingly, from magnetization measurements, the proximity effect was only detected in the rough film grown at 320 °C. No proximity effect was observed in the case of film annealed 410°C. This indicates the possible enhancement of the proximity-induced magnetism as a result of surface roughness. Accordingly, we can also reliably rule out interdiffusion between the layers as the mechanism giving rise to the induced magnetism onto SnTe, as interdiffusion would be enhanced at higher temperatures.

d. Observation of induced magnetism through the anomalous Hall effect

Since EuS is an insulating ferromagnet [125, 126], it should not contribute to the transport of the heterostructures. The observation of magnetism through electrical measurements is thus a definitive confirmation of induced magnetism on the SnTe surface, as long as the diffusion of Eu atoms into SnTe can be ruled out.

In the trilayer grown at 320 °C, we have observed an anomalous Hall effect below ~20 K. This is shown in Fig. VI-2. The raw data are dominantly linear, as a result of the high bulk carrier density of SnTe. After subtraction of a linear background, the obtained Hall resistivity is found to be non-linear. At 2 K, clear hysteretic behavior is observed at low fields, as shown in the inset of Fig. VI-2. The anomalous Hall resistivity becomes suppressed by 20K above the Curie temperature of EuS (14K), and thus indicates that the anomalous Hall effect finds its origin in the magnetism of the EuS layer.
Figure VI-2. Anomalous Hall resistivity measured in the SnTe – EuS – SnTe trilayer grown at 320 °C at four different temperatures between 3 K and 20 K. Inset shows hysteresis at low fields measured at 3 K.

The fact that the Hall resistivity shows hysteresis and remanence at zero-field in the perpendicular direction indicates a possible canting in the magnetic moment of EuS away from the usual in-plane direction. This is corroborated by that observed in the SQUID magnetization behavior discussed next.

e. The magnetic properties of the EuS-SnTe system

The magnetization of SnTe – EuS – SnTe trilayer structures where the anomalous Hall resistivity is observed, is shown in Fig. VI-3 for both the in-plane and out-of-plane field directions. The saturation moment is close to 5.5 $\mu_B$/Eu$^{2+}$. This is slightly lower than the expected 6.7-7$\mu_B$/Eu$^{2+}$ usually observed in EuS [125, 126]. This reduction in the saturation magnetization might be a result of tensile strain at the EuS – SnTe interface, which can reduce the strength of the exchange interaction of Eu atoms as the distance between them grows. This is
confirmed by the observation of a larger lattice constant for EuS in XRD, as discussed in section VI-1(c). Additionally, Te inclusions in EuS, although unlikely to occur, may result in puddles of EuTe that may be either antiferromagnetic or ferrimagnetic. However, the fact that we do not observe any exchange-biasing in the M(H) measurements excludes the possibility of having antiferromagnetic inclusions. It remains however likely that Te inclusions might result in regions of the EuS film that have a lower moment.

![Diagram of magnetic moment versus field](image)

Figure VI-3. Magnetic moment versus field of a SnTe – EuS – SnTe trilayer grown at 320 °C that was measured for both the in-plane and out-of-plane direction at 2.5 K. Inset shows low-field hysteresis for both directions.

The magnetic easy-axis of the film is dominantly oriented in the film plane as expected in EuS. The out-of-plane magnetization saturates at about 2 T, but shows a non-zero remanence at zero-field, indicating the existence of an out-of-plane magnetization component. The out-of-plane remanence is equal to 0.08μB/Eu2+. The in-plane remanent component is equal to 1.6 μB/Eu2+. This allows us to speculate that the moment is slightly canted at the interface.
f. *Isotropic magnetoresistance - evidence of domain wall supported conduction*

We next move on and measure the in-plane MR of the heterostructure and relate it to topological conduction in domain walls. A hysteretic MR is observed. The resistance minima correspond to the coercive fields \( H_C \) measured in EuS. The MR is measured in two geometries – both parallel and perpendicular to the driving current at 2 K. This is shown in Fig VI-4. No in-plane anisotropy is observed. We can thus rule out the effect of spin-scattering that causes anisotropic MR (AMR) in ferromagnetic metals and semiconductors [127, 128, 129].

![Figure VI-4](image)

Figure VI-4. Isotropic hysteretic magnetoresistance in the SnTe – EuS – SnTe trilayer grown at 320 °C at 2 K for in-plane magnetic fields applied parallel (orange) and perpendicular (black) to the current direction. Minima occur at the coercive field \( H_C \).

As the observed effects are isotropic in field, we hypothesize, as in the case of Eu-Bi\(_2\)Se\(_3\), that the MR results from conduction in the domain walls. In the case of a TI-EuS bilayer, the out-of-plane magnetization component at the interface breaks time-reversal symmetry inside a
magnetic domain, but not at the domain wall where the moment reverses and goes to zero. [8, 9, 35, 67] The surface states are thus gapped inside a magnetic domain, but are ungapped in a narrow path inside the domain wall. Two domains having opposite magnetization directions induce mass terms of opposite sign. Hence, a topological phase transition occurs between two oppositely oriented magnetic domains where the surface state mass goes from positive to negative. A 1D conduction state thus exists at the interface between the two magnetic domains.

In a TCI, as in a TI [8, 67], an out-of-plane magnetic moment is shown to gap the surface-states [8, 27]. Under the effect of magnetization component perpendicular to the surface, the topological surface states become massive. Two opposite domains would result in opposite Dirac masses [8, 27]. In between the domains, at a domain wall, a 1D conduction state occurs [8].

Lastly, the hysteresis seems to disappear by 5 K. This is well below the Curie temperature of EuS and is similar to what is reported in EuS-Bi$_2$Se$_3$ bilayers [67]. As the induced magnetism is due to the out-of-plane component of the magnetization, it is possible that the canted moment at the interface can only overcome the easy axis direction below 5K. Above 5K, the canting is suppressed and the hysteretic MR disappears.

We next correlate the transport to the magnetic domain structure by examining the minor loop regime in both MR(H) and m(H).

\textbf{g. Correlating the transport to the domain wall structure in the minor loop regime}

We then measured the hysteretic MR in the minor loop regime and now attempt to quantify the changes in resistance as a function of the degree of magnetic saturation. The field is
swept in a loop between $\pm H_{\text{max}}$. As $H_{\text{max}}$ is reduced, the magnetic texture of the EuS film breaks into smaller and more numerous magnetic domains. Figure VI-5(a) shows the m(H) minor loops taken for $H_{\text{max}}$ varying between 500 Oe and 150 Oe.

![Figure VI-5. m(H) (a) and MR(b) minor loops at 2K for $H_{\text{max}}$ between 500 Oe and 150 Oe.](image)

As expected for a minor loop, the coercive field and moment are reduced, indicating changes in the magnetic domain texture. The minor loop MR is shown in Fig. VI-5(b). The magnitude of the MR is reduced as the $H_{\text{max}}$ gets smaller. This is counterintuitive as one would expect an increase in the density of magnetic domains, and hence the density of domain walls would increase. It is not the case, however, as the net change in resistance is consistently smaller for smaller $H_{\text{max}}$.

We now quantify those changes by plotting the $MR(H_c)$ at the coercive field $H_c$ and $R(H=0)$ as a function of $H_{\text{max}}$. We define the change in MR at the coercive field as:

$$MR(H_c) = \frac{R(H_c) - R(0)}{R(0)}.$$
Figure VI-6. Change in transport hysteresis parameters as a function of $H_{\text{max}}$. (a) MR($H_C$): Change in MR at $H_C$ relative to $H=0$. (b) R(0): resistance at $H=0$

Figure VI-6(a) shows that the MR indeed decreases as $H_{\text{max}}$ is decreased. R(0) also decreases as $H_{\text{max}}$ is decreased. The decrease in MR results from the fact that the magnetic domain texture does not nucleate completely in a minor loop. The decrease in zero-field resistance indicates that the intrinsic resistance of the trilayer is lower when more domain walls are present. This decouples the observed effect from the effect of the applied magnetic field and clearly establishes that the transport is highly correlated with the magnetic texture of the EuS layer.

We thus provided experimental proof for the domain wall conduction hypothesis. We finally give an illustrative picture of the magnetic domain texture of the sample, by simulating the domains of a ferromagnet during demagnetization. At low remanence Fig. VI-7(a) shows that a higher density of magnetic domains exists compared to the near-saturated or remanence case shown in Fig. VI-7(b). As a result, Fig. VI-7(c) shows that the domain walls percolate at low remanence, but, as shown in Fig. VI-7(d) they get disconnected at high remanence or near-saturation.
Figure VI-7. Illustration of the magnetic domain texture of a ferromagnet at (a) low remanence and (b) high remanence or near-saturation (b). The domain walls where conduction is expected to occur are highlighted in (c) and (d).

As final check, we characterize the SnTe-EuS interface using cross-sectional TEM and X-ray absorption spectroscopy.

h. \textit{TEM and XAS studies: is the EuS layer intact?}

We found it extremely important to rule out the possibility of atomic interdiffusion at the EuS-SnTe interface. We thus performed cross-sectional TEM measurements and X-ray
absorption spectroscopy (XAS) in order to characterize the SnTe-EuS interface, and the ionization state of Eu atoms and their bonding environment.

First, a TEM image of a similar SnTe-EuS interface is shown in Fig. VI-8. The SnTe film shown in the TEM image was grown from elemental Sn and Te sources on EuS, as opposed to the trilayer which was grown using a composite SnTe source. The interface exhibits a large density of dislocations (Fig. VI-8(a)) likely to be due to the mismatch between the substrate and the EuS. The purpose of this film was to characterize the extent to which Te diffusion into EuS is likely.

Energy dispersive X-ray (EDX) map of the distribution of Te and Eu across the interface are taken and shown in Fig. VI-8 (b-d). The Te interface is not sharp as seen in the figure (Fig. VI-8(b)). It also obvious that Eu interface is not sharp either (Fig. VI-8(c)). Once the two maps are brought to together, the Eu map turns out to be complementary to the Te map, with Te inclusion filling regions were Eu seems relatively absent according to EDX. The likelihood of Te diffusion into EuS from a top SnTe layer is thus minimal even when elemental Te is used to grow SnTe. As we said earlier, the trilayer that resulted in positive observations was grown using composite source, and hence no net Te flux. We can thus confidently rule out possible Te inclusions into EuS.
Moreover, the EuS diffusion into SnTe can be refuted according to the images shown here. For the trilayer discussed earlier in this section, one thus safely claim that EuS and SnTe are both chemically intact. The observed reduction in the magnetic moment of EuS is thus not due to Te diffusion. It can either be a result of strain or a result of the presence of 3+ valent Eu atoms.
We finally performed XAS at beamline U4B of Brookhaven National Lab in order to rule out the latter possibility. Our results were directly compared to an Eu$_2$O$_3$ polycrystal that is generally used as an energy calibration standard for the beamline. The XAS spectrum resulting from our SnTe-EuS-SnTe trilayer and the standard are compared in Fig. VI-9.

![XAS Spectra](image)

Figure VI-9. XAS spectra of EuS in a SnTe-EuS-SnTe trilayer that hosts a proximity effect (blue) and an Eu$_2$O$_3$ standard (red). Gaussian fits are shown as black solid lines.

The main peaks recovered from the trilayer occur at 1128eV and 1158eV for the 5d$_{3/2}$ and 3d$_{3/2}$ peaks respectively. This is identical to what is observed for Eu$^{2+}$ in EuO [130]. Both peaks also seem to be strongly asymmetric. This asymmetry can be reliably fit with two Gaussians, for
both transition energies, as shown by the black solid lines in Fig. VI-9. Both shoulder peaks occur at an energy that is 3 eV higher than the main 3d\(_{3/2}\) and 3d\(_{5/2}\) peaks. They do not seem to originate from the presence of Eu\(^{3+}\) in the trilayer, as they occur at energies lower then what resulted from the Eu\(_2\)O\(_3\) standard.

The occurrence of such absorption peak profiles is actually common in 4f-based compounds. Many-electron processes may result in additional excitations other than the main absorption resonances. These processes are given the name “shake-up”. They originate in charge transfers that occur between the rare-earth metal and the ligand states and may yield additional information about the bonding of Eu atoms. [131, 132]

All in all, we have ruled out the presence of any noticeable amount of Eu\(^{3+}\) in EuS.

In total, we can conclude that the EuS layer is intact. No significant amount of Te inclusions and Eu\(^{3+}\) valence states can be detected. The drop in moment is thus likely to be due to strain. As the distance between Eu atoms increases in the lattice, the exchange interactions are weaker which results in a drop in the magnetic moment per Eu atom. [133] The insulating quality of EuS is also likely to be conserved. Our results are thus unlikely to be due to artifacts or impurities.

i. Summary and prospects

As discussed in this section, magnetism can be induced in SnTe by proximity to EuS. We observe an anomalous Hall resistivity as well as an isotropic hysteretic MR. Domain wall conduction is confirmed by the observation of decreasing MR and resistance by decreasing the minor loop size, and thereby increasing magnetic domain density.
It is noticeable that the changes observed are small. This is a result of the high bulk carrier density shorting the surface channel. In the future, it would be worthwhile to attempt enhancing the effect by reducing the bulk carrier density via Pb doping or electrostatic gating. It would also be of interest to characterize the domain walls that arise in the trilayer in order to determine their Bloch versus Néel character [134, 135] and how that influences the nature of the 1D proximity-induced state. This is possible in polarized TEM, but such an apparatus is not readily available. A proximity effect induced by a room temperature ferromagnetic insulator such as yttrium-iron-garnet (YIG) of would be of extreme interest in the future as it would allow one to make use of the observed behavior in a potential practical device.

Finally, we would like to point out the relevance of this realization for the prospect of realizing Majorana states in a TCI-superconductor hybrid such as Sn$_{1-x}$In$_x$Te. Sn$_{1-x}$In$_x$Te has already been thoroughly studied as a superconductor and is believed to have a T$_c$ that varies between 2K and 4K [136, 137]. Proximity induced magnetism at the interface between Sn$_{1-x}$In$_x$Te and EuS would thus be expected to yield 1D propagating Majorana modes at domain walls.

2. **Prospects on magnetic bulk-doped topological materials**

a. **Growth of Cr-Bi$_2$Te$_2$Se**

The main objective in growing magnetic topological materials is the realization of the QAHE [36, 37]. Based on the successful realization of ferromagnetism in Cr-Bi$_2$Se$_3$ [138] we attempted doping Bi$_2$Te$_2$Se with Cr in a similar fashion. Cr is co-evaporated with Bi, Te and Se. The growth is identical to what described for Bi$_2$Te$_2$Se is section IV. The X-ray diffraction pattern for Cr$_{0.08}$Bi$_{1.92}$Te$_2$Se is compared to that of standard Bi$_2$Te$_2$Se (FigVI-8). Both films are
15nm thick. A clear shift in the Bragg peak is observed upon the addition of Cr. This is good evidence that that lattice constant is smaller when Cr is doped into the film. It is this likely that Cr substitutes for Bi. Also, the fact that the intensity modulation of the \{003\} series does not change is again good evidence that the Te and Se layers are intact and Cr is substituting for Bi. Recently, however, STM [139] studies on \((\text{CrBi})_2\text{Se}_3\) has shown that Cr may in addition form metallic clusters in the form of Cr-trimers. This effect has not been studied systematically, and may be alleviated by modifying the growth conditions.

![XRD pattern](image)

Figure VI-8 (a) XRD pattern of \(\text{Cr}_0.08\text{Bi}_{1.92}\text{Te}_2\text{Se}\) (red) compared to that of \(\text{Bi}_2\text{Te}_2\text{Se}\). (b) Zoomed-in view of the \(00\ 12\), \(00\ 15\) and \(00\ 18\) Bragg peaks showing a shift in the peak positions – a sign of a smaller lattice constant in the Cr-doped compound.

Additionally, it was found that \(\text{Cr}_0.08\text{Bi}_{1.92}\text{Te}_2\text{Se}\) has an in-plane magnetic easy-axis, which is a serious obstacle to the realization of the QAHE.
b. *The crossover from weak antilocalization to weak localization*

The crossover from WAL to WL was observed at low temperature in Cr-Bi$_2$Te$_2$Se (Fig VI-9). This is a promising sign of broken time-reversal symmetry as a result of magnetism. Although several reports attempted to correlate this effect to a band gap opening at the surface no conclusive phenomenological model has provided a consistent explanation of the observed transport [40, 140]. We thus propose a procedure based of the work of Lu, Shen and Shi [53, 54] that allows one to extract band structure information directly from the observed crossover from WL to WAL.

![Graph showing weak localization and weak antilocalization versus temperature in Cr-Bi$_2$Te$_2$Se.](image)

Figure VI-10. Weak localization and weak antilocalization versus temperature in Cr-Bi$_2$Te$_2$Se.

c. *Determining the band gap from transport – a theory and a suggested experiment*
Lu, Shen and Shi, [53, 54] have developed a model that takes into account magnetic interactions that may yield WL from the topological surface states. We summarize some of the finding of Lu, Shen and Shi in bullet points:

- Magnetic doping gaps the surface state and reduces the coherence length by introducing magnetic spin-flip scattering.
- In n-type TIs, the Fermi level $E_F$ is located high up in the bulk conduction band. The transport is thus a function of $\Delta/2E_F$, where $\Delta$ is the band-gap induced unto the surface states.
- In total, the model allows one to extract $\Delta/2E_F$ from the ratio of WL to WAL observed.

The model being of extreme complexity is not convenient for experimentalists. We thus propose a simplified form of the model. Our proposed requires some additional assumptions listed below:

- Magnetic spin-flip scattering is assumed to be isotropic.
- The magnetic scattering energy $U_m$ is assumed to be comparable to the elastic scattering energy $U_0$ ($U_m \approx U_0$).
- The density of elastic scattering centers $N_0$ is assumed to be equal to the carrier density. We are thus in the limit where the density of magnetic scattering centers $N_m$ is always larger than the density of elastic scattering centers, $N_m >> N_0$.
- The bulk may be included as an additional WL channel. (not always taken into account).
We only report the final result that includes the assumptions states above.

According to Lu, Shen and Shi, the following relation allows one to extract the surface band gap from the cross-over from WAL to WL [53, 54]:

\[
\frac{\alpha(WAL)L^4(WAL)}{\alpha(WL)L^4(WL)} = f\left(\frac{\Delta}{2E_F}, N_M, N_0, U_M, U_0\right)
\]

Introducing the assumptions discussed above we find (See Appendix):

\[
\frac{\alpha(WAL)L^4(WAL)}{\alpha(WL)L^4(WL)} = f\left(\frac{\Delta}{2E_F}\right).
\]

Here \(\alpha\) and \(L\) have their usual meaning. The ratio above is equal to the ratio of the MR curvature at low fields of the WAL to the WL.

Figure VI-10. Conductance versus field at 7K in Cr-Bi\(_2\)Se\(_3\) showing parabolic curve fits (solid lines) to the WAL cusp (green) and the WL cusp (red).
Although we have not systematically tested this model, we did test its validity for a 7nm Cr$_{0.08}$Bi$_{1.92}$Se$_3$ film grown on Si (111). This is shown in Fig. VI-10. The extract surface gap divided by the Fermi energy is $\Delta/2E_f = 0.22\pm0.02$. This is in decent agreement with ARPES spectrum observed in reference [40] for a film of similar Cr-content. Beyond this basic analysis scheme, this model has to be well understood in light of both the temperature dependence of the MR and its gate voltage dependence.

d. Summary

In summary, magnetic doped Se-based TIs would not probably hold their promise as QAHE hosts, given the fact that in-plane magnetic anisotropy dominates, unlike Te-based compounds. They are still however of extreme interest to study from the point of view of quantum coherent transport. Based on what we have discussed, the appropriate model may very likely lead to a reliable extraction of band structure parameters from transport. A systematic study as a function of Fermi level, by top or back gating Cr-Bi$_2$Se$_3$ would be of some importance.

Finally, Mn-SnTe may hold some potential to the realization of a QAHE in a TCI. As discussed by Hsieh et al., magnetic TCI states where massless Dirac Fermions and ferromagnetism coexist, may also be possible in Mn-SnTe if the magnetic easy-axis is oriented perpendicular to a mirror plane.
VII – Conclusion

In conclusion, the scope of this thesis covered three fundamental topics dealing with topological materials: optimization of MBE growth; quantum coherent transport measurements; and symmetry-breaking in a TCI.

We first optimized the growth of Bi$_2$Te$_2$Se TI by MBE. The films exhibit transport properties similar to what is generally obtained in Bi$_2$Se$_3$. Most notably, quantum coherent transport was studied in detail up to magnetic fields of 14 T. Linear MR was observed above 5 T and explained with our modified HLN model. Analysis of low-field MR also yielded information about the quantum coherent transport and were able to separate the contributions of WAL resulting from surface bands from those resulting from Rashba-split bulk bands.

We grew the first high-quality thin films of the TCI SnTe. Growth on BaF$_2$ (001) led to high-quality films having a mobility of more than 700 cm$^2$/Vs. It was found that the Fermi level may be tuned simply by varying the growth temperature between 220 °C and 340 °C. Growth at high temperatures resulted in the best films. In sum, film crystallinity, film morphology as well as film mobility were improved by increasing the growth temperature.

We then studied the quantum coherent WAL that arises in SnTe films at low magnetic fields. We have shown that the bulk valence band alone does not provide a complete explanation of the observed phenomena. As SnTe is a degenerate TCI system, coupling between different Dirac and bulk valleys affects the observed number of valleys in WAL. A modulation of the number of Dirac valleys versus the Fermi level was shown to be the consequence of a change in the bulk Fermi surface topology.
We studied the effect of adjacent magnetic layers on both TI and TCI. The magnetic proximity effect was realized in TCI-EuS heterostructures. Several material characterization probes were used to determine the properties of the EuS film in proximity to the TCI. We observed a domain-wall-supported QAH-state, similar to what we reported earlier in MR measurements of Bi$_2$Se$_3$-EuS. Additionally, we have shown that the observed MR is unambiguously correlated to the magnetic domain texture of the insulating ferromagnet. This provides strong evidence of the role played by domain walls in transport.

Finally, we grew Cr-doped Bi$_2$Te$_2$Se and observed a crossover from WAL to WL. We developed a simplified phenomenological model based on the work of Lu, Shen and Shi, to describe the crossover as a function of the surface band gap and the Fermi level. The model remains untested in other systems.

Overall, our finding in the field of TI and TCI physics can be summarized as follows:

- Highly linear MR is likely due to a Rashba-split bulk conduction band yielding a WAL-WL correction. Our modified HLN model allows the separation of such a bulk contribution from the surface contribution.
- In SnTe thin films, the quantum coherent transport – assigned to a surface effect – is highly influenced by intervalley coupling, as well as the bulk Fermi surface topology.
- A proximity effect is realized in SnTe-EuS heterostructures. This is the result of a broken crystalline symmetry between magnetic domains of different orientation, but preservation of the symmetry properties in magnetic domain walls gives rise to a domain-wall-supported 1D QAH state. The transport is unambiguously correlated to the magnetic domain texture of EuS.
Finally, a simplified version of a model proposed by Lu, Shen and Shi is proposed in order to reliably quantify the crossover from WAL to WL that occurs in magnetic topological materials.

More importantly, this thesis leaves behind several open questions that should be addressed in the future.

- Can the bulk-Rashba component obtained from the modified HLN model be tuned by a dielectric gate?
- What is MR in the regime beyond 14 T and can it still be explained by the same model?
- How does the WAL change when the Fermi level is moved across the Lifshitz transition in SnTe? Chemical doping would be necessary to obtain such low carrier densities.
- What is the nature of the domain walls at the EuS-SnTe interface, are they Néel walls or Bloch walls?
- Can the domain-induced MR be enhanced by tuning the Fermi level?
- Can we reliably extract the surface-band gap in magnetic-doped TIs from the model proposed here? A systematic study versus gating voltage would be highly relevant.

Many of these questions can be answered by developing ways to achieve lower carrier concentrations, such as by proper alloying or dielectric gating.

Our work was intended as an initial fundamental study of the transport properties of unique topological materials. The potential applications promised by such materials are of tremendous importance and are crucial to sustain the current rate of development in device
technology. As most topological materials require a great deal of optimization before being readily understood and available, it is up to us to demonstrate and achieve the proper implementation of such future technological prospects.
VIII- Bibliography


[8]. M. Z. Hasan, and C.L. Kane, Rev. Mod. Phys. 82, 3045 (2010).


IX- Appendix

Extracting the surface energy gap from the crossover from WAL to WL.

Lu, Shen and Shi [53,54] proposed the following model of the conductivity to explain the crossover from WL to WAL observed in Cr-doped TI films:

$$\Delta \sigma(B) = \sum_{i=0,1} \frac{\alpha_i e^2}{\pi h} \left[ \psi \left( \frac{\hbar}{4eB} \left( \frac{1}{l_{\phi}^2 + l_i^2} \right) + \frac{1}{2} \right) - \ln \left( \frac{\hbar}{4eB} \left( \frac{1}{l_{\phi}^2 + l_i^2} \right) \right) \right],$$

where $i = 0,1$ and

$$\alpha_i = -\frac{\eta_v (1 + 2\eta_H)}{2 \left( 1 + \frac{1}{g_0} + \frac{1}{g_2} \right)} \equiv \alpha_{WL}^{i},$$

$$\frac{1}{l_i^2} = \frac{g_1}{v_F^2 \tau^2 \sin \theta \left( 1 + \frac{1}{g_0} + \frac{1}{g_2} \right)} \equiv \frac{1}{l_{WL}^2},$$

$$\alpha_0 = \frac{\eta_v (1 + 2\eta_H)}{2 \left( 1 + \frac{1}{g_1} \right)} \equiv \alpha_{WL}^{0},$$

$$\frac{1}{l_0^2} = \frac{g_0}{v_F^2 \tau^2 \sin \theta \left( 1 + \frac{1}{g_1} \right)} \equiv \frac{1}{l_{WL}^0}.$$

Recall that according to the HLN model, in the low-field limit the behavior of the conductivity is parabolic, thus:

$$\alpha \psi \left( \frac{\hbar}{4eB} \left( \frac{1}{l_{\phi}^2} + \frac{1}{l_i^2} \right) + \frac{1}{2} \right) - \ln \left( \frac{\hbar}{4eB} \left( \frac{1}{l_{\phi}^2} + \frac{1}{l_i^2} \right) \right) \rightarrow R \alpha \left( \frac{1}{l_{\phi}^2} + \frac{1}{l_i^2} \right)^2.$$

For two channels, it is convenient to look at the ratio of the parameters of the two channels.

At low enough temperature where $l_{\phi} \gg l_i$ and $l_0$, one finds $\left( \frac{1}{l_{\phi}^2} + \frac{1}{l_i^2} \right) \rightarrow l_i^{-2}$ (i=0,1). Fitting the change in the conductivity versus field with a parabola at low enough magnetic fields, allows us
to extract the curvature for both WAL and WL at temperatures where they both coexist. Interestingly according to HLN, it turns out that:

\[
\frac{\beta(WAL)B^2}{\beta(WL)B^2} = \frac{\alpha_1(l_1)^4}{\alpha_0(l_0)^4} = \frac{\alpha_{WAL}l_{WAL}^4}{\alpha_{WL}l_{WL}^4}.
\]

The problem can be narrowed down to solving the following equation in order to extract the size of the gap induced onto the Dirac cone:

\[
\frac{\alpha_{WAL}l_{WAL}^4}{\alpha_{WL}l_{WL}^4} = f(\text{surface energy gap}).
\]

In what follows we shall discuss why this equality holds.

Taking the following ratio is seen to simplify the model proposed in ref. 53 and 54 to:

\[
\left| \frac{\alpha_{1/l_{1}}}{\alpha_{0/l_{0}}} \right|^4 = \frac{\alpha_{WAL}l_{WAL}^4}{\alpha_{WL}l_{WL}^4} = \left( \frac{1 + \frac{1}{g_1}}{1 + \frac{1}{g_0} + \frac{1}{g_2}} \right)^2 \left[ \frac{g_0}{g_1} \left( \frac{1 + \frac{1}{g_0} + \frac{1}{g_2}}{1 + \frac{1}{g_1}} \right) \right]
\]

\[
\left| \frac{\alpha_{1/l_{1}}}{\alpha_{0/l_{0}}} \right|^4 = \frac{\alpha_{WAL}l_{WAL}^4}{\alpha_{WL}l_{WL}^4} = \frac{g_0^2}{g_1^2} \left( \frac{1 + \frac{1}{g_0} + \frac{1}{g_2}}{1 + \frac{1}{g_1}} \right) \quad (*)
\]

We shall now work out the ratios of the different g terms used above:
\[ g_0 = 2 \left( \frac{a^4 + b^4}{a^4 + 1/\tau_e + b^4} - 1 \right) \]
\[ g_1 = 2 \left( \frac{1/\tau}{(1/\tau_e + 1/\tau_z) \frac{2a^2b^2}{a^4 + b^4} - 2/\tau_x} - 1 \right) \]
\[ g_2 = 2 \left( \frac{a^4 + b^4}{b^4} \frac{1/\tau}{1/\tau_e + 1/\tau_z} - 1 \right) \]

with

\[ 1/\tau_e = \frac{2\pi N_F n_0 u_0^2 (a^4 + b^4)}{\hbar} \]
\[ 1/\tau_z = \frac{2\pi N_F n_m u_x^2 (a^4 + b^4)}{\hbar} \]
\[ 1/\tau_x = \frac{2\pi N_F n_m u_z^2 (2a^2b^2)}{\hbar} \]
\[ 1/\tau = \frac{1}{\tau_e} + \frac{2}{\tau_x} + \frac{1}{\tau_z} \]

\[ a = \cos(\theta/2) \]
\[ b = \sin(\theta/2) \]
\[ a^2 + b^2 = 1 \]
\[ \cos(\theta) = \frac{1}{\sqrt{1 + \left( \frac{2E_F}{\Delta} \right)^2}} \]

Assumptions

\( \tau_e \) is the elastic transport time, and \( \tau_x \) and \( \tau_y \) are the magnetic scattering times in the \( x \) and \( z \) directions. \( n_0 \) is the density of elastic scatterers, \( n_m \) is the density of magnetic scatterers, \( u_0 \) is the strength of elastic scattering collisions, and \( u_x \) and \( u_z \) are the respective strengths of the magnetic scattering collisions in the \( x \) and \( z \) directions.

We then implement the following simplifying assumptions:

\( u_0 = u_x = u_z = U \). All scattering phenomena have the same strength.
We’re in the limit where magnetic scattering is more frequent than elastic scattering, so \( n_m \gg n_0 \).

This is reasonable, as in most magnetically-doped TI systems the defect density is \( \sim 10^{19} \text{cm}^{-3} \) whereas the magnetic doping density is more than 1 atomic-% or rather close to \( \sim 10^{21} \text{cm}^{-3} \).

This simplifies the expressions for \( g_0 \), \( g_1 \) and \( g_2 \) when ratios of different scattering times are taken:

\[
g_0 = 2 \frac{a^4 + b^4}{a^4} \left( \frac{1}{\tau_e} + \frac{2}{\tau_e + \tau_s} + \frac{1}{\tau_s} \frac{1}{\tau_e + \tau_s} - 1 \right) = 2 \frac{a^4 + b^4}{a^4} \left( \frac{2}{\tau_z} + \frac{1}{\tau_e + \tau_z} \right)
\]

\[
g_0 = 2 \frac{a^4 + b^4}{a^4} \frac{n_m 4a^2b^2}{(n_m + n_0)(a^4 + b^4)} \quad (u_m = u_0)
\]

\[
g_0 = \frac{a^4 + b^4}{a^4} \frac{8a^2b^2}{(a^4 + b^4)} = \frac{8b^2}{a^2} \quad (n_m \gg n_0).
\]

\[
g_1 = 2 \left( \frac{1}{\tau_e} + \frac{2}{\tau_e + \tau_s} + \frac{1}{\tau_s} \frac{1}{\tau_e + \tau_s} - 1 \right) = 2 \left( \frac{1}{\tau_e} + \frac{1}{\tau_s} \right) \frac{2a^2b^2}{a^4 + b^4} - 2/\tau_x
\]

\[
g_1 = 2 \frac{(n_0 + n_m)(a^4 + b^4) + 4a^2b^2n_m}{(n_0 + n_m)2a^2b^2 - 4a^2b^2n_m} - 2 \quad (u_m = u_0)
\]

\[
g_1 = -\frac{(a^4 + b^4) + 6a^2b^2}{a^2b^2} \quad (n_m \gg n_0)
\]
Going back to (*) we can now plug in for $g_0, g_1$ and $g_2$:

$$g_2 = 2 \frac{a^4 + b^4}{b^4} \left( \frac{1}{\tau_e} + \frac{2}{\tau_e} + \frac{1}{\tau_e} \right) = 2 \frac{a^4 + b^4}{b^4} \left( \frac{2}{\tau_e} \right)$$

$$g_2 = 2 \frac{a^4 + b^4}{b^4} \frac{n_m 4a^2b^2}{(n_m + n_0)(a^4 + b^4)} \quad (u_m = u_0)$$

$$g_2 = 2 \frac{a^4 + b^4}{b^4} \frac{4a^2b^2}{(a^4 + b^4)} = \frac{8a^2}{b^2} \quad (n_m >> n_0)$$

$$\frac{g_0}{g_1} = -8 \frac{b^2 (a^4 + b^4) + 6a^2b^2}{a^2b^2} = -8 \frac{a^4 + b^4}{a^4} + 6a^2b^2 = -8 \frac{(a^2 + b^2)^2 + 4a^2b^2}{a^4}$$

$$\frac{g_0}{g_1} = -8 \frac{1 + 4a^2b^2}{a^4} \quad \text{(since } a^2 + b^2 = 1)$$

$$1 + \frac{1}{g_0} + \frac{1}{g_2} = 1 + \frac{a^2}{8b^2} + \frac{b^2}{8a^2} = 1 + \frac{a^4 + b^4}{8a^2b^2} = \frac{(a^2 + b^2)^2 + 6a^2b^2}{8a^2b^2}$$

$$1 + \frac{1}{g_0} + \frac{1}{g_2} = \frac{1 + 6a^2b^2}{8a^2b^2} \quad \text{(since } a^2 + b^2 = 1)$$

$$1 + \frac{1}{g_1} = 1 - \frac{a^2b^2}{(a^4 + b^4) + 6a^2b^2} = \frac{1 + 3a^2b^2}{1 + 4a^2b^2} \quad \text{(since } a^2 + b^2 = 1)$$
Putting everything together:

\[
\left| \frac{\alpha_{l_1}^4}{\alpha_{l_0}^4} \right| = \left( \frac{8 \left(1+4a^2b^2\right)}{a^4} \right)^2 \frac{1+6a^2b^2}{8a^2b^2} = \left( \frac{8 \left(1+4a^2b^2\right) \left(1+4a^2b^2\right)}{8a^2b^2} \right)^2 \frac{1+6a^2b^2}{1+3a^2b^2} = \left( \frac{8 \left(1+4a^2b^2\right) \left(1+4a^2b^2\right)}{a^4} \right) \frac{1+6a^2b^2}{1+3a^2b^2}
\]

\[
\left| \frac{\alpha_{l_1}^4}{\alpha_{l_0}^4} \right| = 8 \left(1+4a^2b^2\right)^3 \frac{1+6a^2b^2}{a^4b^4} \frac{1+3a^2b^2}{1+3a^2b^2}
\]

The analysis narrows to extracting \( \alpha \) and \( l \) for the WAL and the WL channel independently and then finding the root of a polynomial.

Or, if \( l_1 \) and \( l_0 \) can be extracted independently the problem narrows down to:

\[
\frac{\alpha_{l_1}^4}{\alpha_{l_0}^4} = f(\text{surface energy gap}).
\]

It can also be shown that
\[ \frac{\alpha_{l_1}^2}{\alpha_{l_0}^2} = \frac{\alpha_{WL}^2}{\alpha_{WL}^2} = \frac{g_0}{g_1} = \frac{1 + 4a^2b^2}{a^4} \text{ and} \]

\[
\frac{\alpha_{l_1}^2}{\alpha_{l_0}^2} = 8 \frac{1 + 4a^2 - 4a^4}{a^4}.
\]

Also, recall that:

\[ a = \cos(\theta / 2) \text{ and} \]

\[ \cos(\theta) = \frac{1}{\sqrt{1 + \left(\frac{2E_F}{\Delta}\right)^2}}. \]

The ratio of the surface band gap to the Fermi level \( \left(\frac{2E_F}{\Delta}\right) \) may then be extracted by solving for \( a \) using one of the highlighted equations.