Institute of Physics
Polish Academy of Sciences

Doctoral Thesis

THE PROPERTIES OF THE TOPOLOGICAL CRYSTALLINE INSULATOR SURFACE STATES – THEORETICAL ANALYSIS

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A thesis submitted in fulfillment of the requirements for the degree of Ph.D.

November 2015
To my parents for their endless love.
Acknowledgements

It is my radiant sentiment to place on record my deepest sense of gratitude and regards, first and foremost, to my supervisor Prof. Ryszard Buczko for his continuous support throughout the course of my Ph.D. study. I appreciate all his aspiring guidance, precious advice, immense knowledge, encouragement and on top of all his patience during these years. I am thankful of Prof. Perła Kacman for her friendly advice and invaluably constructive criticism. Many thanks to Prof. Tomasz Story for his intelligent and significantly helpful comments on many parts of my work.

I would like to thank my office-mates Dr. Marta Galicka and Mr. Dinh Quoc Huy Pham who have been true friends and remarkable collaborators, and other members of group ON4.6. Also, many thanks to Acta Physica Polonica A editorial staffs, particularly Ms. Katarzyna Filipiak, and to my friend Mr. Zbigniew Piotrowski.

This journey would not have been possible without the effort of many individuals from Institute of Physics, Polish Academy of Sciences who provided a great environment for an ever-growing science, thanks them all.

I owe a debt of sincere gratitude to Prof. Witold Daniel Dobrowolski for being not only my mentor and one of my best friends, but also an excellent adviser of life and science. My life in Poland would not ever go through without him, his family and friends who always treated me like one of themselves.

A special wholehearted thanks to my sisters NilooAR and Shima, my brother Ali and brother-in-law Aram, whose loving care have given me strength and enthusiasm. I genuinely appreciate their belief in me to overcome setbacks.

Last but not least, I am profoundly and forever indebted to my parents for their unconditional support and affection throughout my entire life. Words alone cannot express my heartfelt gratitude to such incredible parents, and how proud of them I am.
Abstract

Topological insulators (TIs) represent a new state of matter, whose bulks are insulating whereas they have gapless edge or surface states that are protected by the time-reversal symmetry. Having inverted band gaps due to the strong intrinsic spin-orbit coupling, they are topologically distinct from conventional insulators by a $Z_2$ topological invariant, and thus they cannot be adiabatically connected to each other. Recently a new class of topological materials emerged which are similar to TIs characterized by helical edge states inside the bulk band gap, however the role of time-reversal symmetry in insuring topological protections is replaced by crystal symmetries, and therefore, they are referred to as topological crystalline insulators (TCIs). In this regard, SnTe with space group symmetry Fm$ar{3}$m and the inverted band gap is the first TCI prototype whose experimental approval has provoked vast investigations insofar. To be concise, in this dissertation apart from SnTe and its substitution crystal Pb$_{1-x}$Sn$_x$Te for $x \gtrsim 0.38$, it will be established that the rock salt Pb$_{1-x}$Sn$_x$Se for $x \gtrsim 0.19$ also renders the TCI phase. The band gap of these materials is simultaneously located at four L valleys. Depending on whether the projection of these L points onto the surface are coincided where the mirror plane symmetries {110} are projected, the protected surface states may exist. Due to the fundamental role of crystal symmetry in TCIs, the expectation of surface states for major crystallographic directions will be explicitly analysed. The tight binding and DFT calculations have been performed to prove that not only (100) but also (110) and (111)-oriented slabs exhibit robust Dirac-like edge states which are verified experimentally as well. Furthermore, it will be demonstrated that (111)-oriented ultrathin films of SnTe and SnSe harbour the quantum spin Hall phase. Within the particular thicknesses e.g., $\sim 3 - 6$ nm, the intersection of the valence and conduction bands, that occurs at the odd number of L points, provides the 2D TI state, in which the edge channels are protected by both time-reversal and mirror symmetries. Hence, unlike (100) ultrathin film which could be tuned form a trivial insulator to the TCI, for (111) ultrathin film the topological phase transition to the QSH phase is anticipated.
Publications

* Spin-polarized (001) surface states of the topological crystalline insulator Pb$_{0.73}$Sn$_{0.27}$Se
  B. M. Wojek, R. Buczko, S. Safaei, P. Dziawa, B. J. Kowalski, M. H. Berntsen,
  T. Balasubramanian, M. Leandersson, A. Szczerbakow, P. Kacman, T. Story,
  and O. Tjernberg

* Topological crystalline insulator (Pb,Sn)Te: Surface states and their spin polariza-
  tion
  S. Safaei, P. Kacman, and R. Buczko

* Observation of topological crystalline insulator surface states on (111)-oriented
  Pb$_{1-x}$Sn$_x$Se films
  C. M. Polley, P. Dziawa, A. Reszka, A. Szczerbakow, R. Minikayev, J. Z.
  Domagala, S. Safaei, P. Kacman, R. Buczko, J. Adell, M. H. Berntsen, B. M.
  Wojek, O. Tjernberg, B. J. Kowalski, T. Story, and T. Balasubramanian

* Quantum Spin Hall Effect in IV-VI Topological Crystalline Insulators
  S. Safaei, M. Galicka, P. Kacman, R. Buczko

* Quantum spin Hall effect in strained (111)-oriented SnSe layers
  S. Safaei, M. Galicka, P. Kacman, R. Buczko
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Introduction

In the last century, one of the greatest triumphs of physics was classifying distinctive phases of matter by the principle of spontaneous symmetry breaking. This pattern led to a unique order parameter, which provided a universal description of different states. In 1980s, the quantum Hall effect was discovered, in which, the bulk of two-dimensional sample is insulating, whereas the current is carried along the edges [1]. The flow of this unidirectional current suppresses any dissipation and gives rise to a quantized conductance. Phenomenologically, this dual behaviour does not fit into the simple paradigm of symmetry breaking classification, and therefore, the ability of conducting electric current to define a conductor over an insulator is no longer credible as once it was thought to be. Thereafter, the inquiries of a new definition for materials as being whether conductor or insulator, were triggered.

Ever since this breakthrough the notion of topological field theory has been introduced in physics, to enhance the classification of materials based on their typologies. In mathematics this concept refers to the geometrical properties of objects that are preserved under continuous deformations, regardless of their shapes. For instance the surface of a perfect sphere is topologically equivalent to the surface of an ellipsoid as they can smoothly transform to each other without creating any holes or tears, as well as, a coffee cup to a torus, since both of them contain a single hole. In other words, the continuity of objects under smooth deformation operation sorts them into topological equivalence classes, that can be characterized by their Genus which is the Gaussian curvature over the entire surface. The key link between such a determination and physics is the “smooth deformation” of the many-particle Hamiltonian which preserves the bulk gap order. According to this general definition, one gapped state
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cannot be deformed to another gapped state in a different class unless a topological phase transition occurs where the system becomes gapless, i.e., two systems are topologically equivalent if their Hamiltonians can be smoothly transformed to each other without closing the gap [2]. This topological concept can be applied to both insulators and superconductors with a full energy gap, but not to gapless states such as metals, doped semiconductors, or nodal superconductors. In general, it can be applied to a condensed matter system with an energy gap, where the notion of the smooth deformation can be defined.

In this regard, numerous theoretical and experimental research has now determined that band insulators - based on their topology - can actually be divided into two classes. The first one describes the “ordinary” band insulators, in which electrons fully occupy the valence bands, while all available conduction states are well-separated by an energy gap. Since there are no low-energy excitations, the system is trivially insulating. The second class however, delineates the “topological” insulators, in which the states in the vicinity of the energy gap between the occupied and empty bands are fundamentally modified due to spin-orbit interactions of relativistic origin. In topological insulators (TIs), the coupling of the spin and orbital angular momentum of an electron causes an inversion of the band gap, thus, those states lying above the gap in ordinary insulators are now below, and vice versa. They are called topological because the wave functions describing their electronic states span a Hilbert space that has a non-trivial topology. Similar to the Möbius strip, this twist in the electronic band structure cannot be simply unwound. An ordinary insulator and TI can be distinguished by a topological invariant, $Z_2$, which can be perceived as an order parameter counterpart in a topological phase transition. In TIs, a consequence of the winded band structure is the appearance of metallic states at the edges or surfaces, which in general, do not exist in the ordinary band insulators (Fig. 1.1). These gapless states are essentially robust and protected against arbitrary perturbations of the Hamiltonian as long as, (i) time-reversal invariant is preserved and (ii) the bulk band gap is not closed. Theoretically, those topological surface states have been predicted to show a linear energy-momentum relation resembling the massless Dirac fermions, and an unusual spin texture due to a locking of spin and momentum.

Chronologically, study of TIs were initiated after the discovery of the integer quantum Hall effect which shows a quantized Hall conductivity when the 2D system is
in a perpendicular magnetic field. Such an observation spurred a large activity to establish a time-reversal preserving system which renders the same properties. In 1988, Haldane realized that the quantum Hall effect may also occur in systems without an external magnetic field, and proposed a model for spinless fermions on the two-dimensional honeycomb lattice under the influence of a fictitious inhomogeneous magnetic field. By including the spin degree of freedom and making the magnetic field spin-dependent, in 2005, Kane and Mele restored the time-reversal symmetry of the Haldane model. They suggested that the single-layer graphene sheet with intrinsic spin-orbit interactions, indeed offers a new quantum phase of matter which is called the quantum spin Hall insulator or the two-dimensional TI. Though this predication gave a big boost in this field, it was not successful for graphene, as its spin-orbit interactions is negligible. Soon after, in 2006, the quantum spin Hall effect was experimentally observed in quantum wells HgTe whose spin-orbit coupling is much larger than that of graphene, due to its heavier constituent elements. In 2007, by the discovery of three-dimensional TI in Bi$_{1-x}$Sb$_x$, which in contrast to two-dimensional ones can be observed at the room-temperature without magnetic fields, a whole new era opened up in topological physics that led to a surge of research in discovering other types of topological order in three-dimensions.

Moving forward, in 2011, Liang Fu predicted a new class of topological materials, in which space group symmetry, instead of the time-reversal symmetry, protects metallic surface states, and it is referred to as a “topological crystalline insulator” (TCI) [3]. It was primarily suggested that a TCI phase might be obtained in materials with fourfold
(C_4) or sixfold (C_6) rotational symmetries, and without (or with) spin-orbit coupling whose electron’s orbital degrees of freedom play a role similar to spin. Progressing in this field, now it is already known that the scope of TCI can be extended to many point group symmetries \[4\]. So far, SnTe, Pb_{1-x}Sn_xTe and Pb_{1-x}Sn_xSe are experimentally confirmed to be TCIs, whose metallic surface states are protected by their mirror plane symmetry \[5, 6\]. It has been theoretically proposed that TCI phase can be realized in antiperovskite material family \[7\], transition metal oxides \[8\], TiBiS_2 and TiSbS_2 \[9\] systems as well.

The focus of this thesis is the theoretical exploration throughout the novelty of the topological class of materials. Henceforth, in Chapter 2, progressive investigations, which led to the discovery of TI will be reviewed. Then in order to characterize TIs, by outlining the first model, the experimental evidence and deriving the \( \mathbb{Z}_2 \) invariant, a conceptual framework will be presented. The first prediction of TCIs along with its experimental realization will be explained at the end.

The tight binding model following by the basis of the DFT method which have been utilized as the essential theoretical tools for the calculations will be described in Chapter 3.

In Chapter 4 the main results of this thesis will be presented. Summarizing the most important features of PbTe, SnTe and their substitutitional compounds, occurrence of a topological phase transition for Pb_{1-x}Sn_xTe by changing the composition will be explained. Due to the crucial crystallographic symmetry dependence of TCIs, studying the major surfaces, [001], [110] and [111] is tremendously appealing, which will be illustrated next. In a close analogy, after a brief recap of PbSe and SnSe properties, experimental counterpart calculations for both [110] and [111]-oriented Pb_{1-x}Sn_xSe that exhibit the temperature dependent transition to the TCI phase will be represented.

Eventually, in a comprehensive survey, [111]-oriented SnTe and SnSe ultrathin films will be scrutinized. It will be shown that these films within particular thicknesses undergo a topological phase transition not to the TCI but to the 2D TI. Such predictions will be verified by the energy gap evolution versus thickness of the films, and ultimately will be endorsed by the \( \mathbb{Z}_2 \) invariant and the spectral function calculations. The application of this result in the case of SnSe might be slightly despairing since strong bands overlapping diminishes the energy gap. To solve this problem, in the last part, a strain induced band gap alignment will be delineated.
2
Topological insulator materials

2.1 Quantum Hall effect

The quantum Hall effect (QHE) is one of the most remarkable condensed matter phenomena that provides the first example of a topologically non-trivial state \[1\]. QHE occurs at low temperatures and high magnetic field and exhibits a quantized conductivity, \( \sigma = \nu e^2/h \) (where \( e \) is the elementary charge, \( h \) is the Planck constant and \( \nu \) is the filling factor and can take on integer values) which is no longer a direct function of magnetic field. Such a quantization is a universal hallmark, i.e., it is independent of the particular properties of the sample, such as its geometry, the host materials used to fabricate the 2D electron gas, and even more importantly its impurity concentration or distribution. Indeed, the Hall conductance at the plateaus has a topological significance, which can be understood in terms of topological invariants known as Chern numbers. In the following after some preliminaries, Chern numbers and how they relate to the quantum Hall effect will be explained.

2.1.1 Landau levels

A charged particle which is moving perpendicular to a static uniform magnetic field will be acted on by the Lorentz force \( \mathbf{F} = q \mathbf{v} \times \mathbf{B} \), perpendicular both to the velocity of the particle and the magnetic field. This results in circular cyclotron orbit path with angular frequency \( \omega_c = qB/m \) and the radius \( r_c = mv/qB \). When the temperature is low and the magnetic field is high enough \( (\hbar \omega_c \gg k_B T) \), these orbits are quantized with their energies acquiring discrete values. In a semi-classical view of QHE, this
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Figure 2.1: Illustration of skipping orbits. (a) In a finite size system, the boundaries prevent electrons from completing full revolutions, leading the chiral edge states [11]. (b) The trajectory of electron while facing a localized impurity. Backscattering over distances sufficiently larger than \( r_c \) is suppressed [12].

Quantization forces the electrons to move into circular orbitals (Fig. 2.1), and leads to an energy gap separating the occupied and empty states, just like an ordinary insulator [10]. However, at the boundary of the system where the electrons confront the edges, they cannot complete their revolutions and they bounce off instead. Such a motion which is also known as skipping orbitals, obligates the electrons to bounce to the next circular path to satisfy the energy level that they are allowed and also to conserve their velocities. Facing electrons at the boundaries give rise to a uni-directional motion in one side and opposite motion in the other side of the Hall sample. Fig. 2.1a shows a schematic illustration of the electrons propagations at two edges.

In order to verify the described picture above, the expectation value of charge current inside and on the edges of the sample should be calculated [11]. The energies of a 2D electron gas system which is subjected to a magnetic field \( B = B_0 \hat{z} \) oriented along \( z \) axis that restricts the motion of electrons in \( x-y \) plane, are given by solving the Schrödinger equation

\[
E \psi = \frac{1}{2m} (p - qA)^2 \psi
\]  

(2.1)

with \( q \) as charge of the electron and \( A \) the magnetic vector potential \( B = \nabla \times A \). Choosing

\(^1\)A gas of electrons free to move in two-dimensions, but tightly confined in the third
Landau gauge

$$A = B_0x\hat{y}$$  \hspace{1cm} (2.2)

for the vector potential the Eq. 2.1 yields

$$E\psi = \frac{1}{2m}(p_x\hat{x} + p_y\hat{y} - qB_0x\hat{y})^2\psi = \frac{1}{2m}(p_x^2 + (p_y - qB_0x)^2)\psi.$$  \hspace{1cm} (2.3)

Since the Hamiltonian is independent of y, it can be expressed separately by its certain coordinates. In y direction the solution is that of a free particle, and therefore, the momentum operator can be replaced by its eigenvalue $\hbar k_y$. The resulting equation for x-dependence will be

$$E\phi(x)e^{ik_yy} = \left(\frac{p_x^2}{2m} - \frac{1}{2}m\omega_c^2(x - \frac{\hbar k_y}{m\omega_c})^2\right)\phi(x)e^{ik_yy} $$  \hspace{1cm} (2.4)

and $\omega_c$ is the angular frequency equals to the classical one $\omega_c = qB_0/m$. Eq. 2.4, is the equation for a quantum harmonic oscillator centred at

$$\frac{\hbar k_y}{m\omega_c} = x_{k_y},$$  \hspace{1cm} (2.5)

hence, the solutions in x are ordinary harmonic oscillator functions $\varphi_n(x)$ shifted in x by $x_{k_y}$. The complete solution ends up

$$\psi_{n,k_y}(x,y) = \phi_{n,k_y}(x)e^{ik_yy} = \varphi_{n,k_y}(x - x_{k_y})e^{ik_yy}$$  \hspace{1cm} (2.6)

where energies are the energies of the harmonic oscillator

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega,$$  \hspace{1cm} (2.7)

and are independent of quantum number $k_y$. The corresponding quantum states of these energy levels are called Landau levels. The current in y direction is given by,

$$I_{n,k_y}^y = q\langle v_y \rangle = \frac{q}{m} \int_0^L dx \varphi_{n,k_y}^*(p_y - qA_y)\varphi_{n,k_y}$$

$$= \frac{q^2B_0}{m} \int_0^L dx |\varphi_{n,k_y}|^2(x_{k_y} - x),$$  \hspace{1cm} (2.8)

where $v_y = (p_y - qA_y)/m$ is the y component of velocity operator in y direction. Because the modulus square of the harmonic oscillator wave function is an even function, the
integral becomes odd around $x_{k_y}$ when multiplied by $x_{k_y} - x$. The state in the interior of the system are ordinary harmonic oscillator wave functions. There, the integrated value is zero. However, for the edge states due to the boundary conditions, the wave function is not symmetric around $x_{k_y}$, and the integral is non-zero. Moreover, $x_{k_y} - x$ changes the sign from one edge to the other, so the currents will run in the opposite directions on the opposite edges. The notable conclusion is that there are currents running at the edges without any external field propelling them.

The current carrying edge states are quite robust. When the Fermi energy lies in between two Landau levels they are immune to elastic scattering since there are no locally available states to scatter into \cite{13}. Therefore, at $T = 0$ K backscattering is completely forbidden, and edge states must take detour around impurities, as it is schematically shown in Fig \ref{fig:2.1b}. Low temperature is a crucial requirement of QHE to compensate the random thermal energy for the separation of the Landau levels, $\hbar \omega_c \gg k_B T$, otherwise the Landau levels cannot form discrete energy band \cite{12, 13}.

\subsection{Berry phase}

The quantum Hall phase can be distinguished from an ordinary insulator by its non-trivial topological invariant which is called Chern number (also known as TKNN invariant). It is equal to the Berry phase of the Bloch wave function calculated around the Brillouin zone (BZ). Before proceeding further, it is important to clarify the meaning of Berry phase as the basis in the discussion of topological materials.

Assume that the time dependence of a Hamiltonian is represented by a vector of parameter $R(t)$ and its $n$th eigenstate as $|n, R(t)\rangle$. The Schrödinger equation for this system is

$$H[R(t)]|n, R(t)\rangle = E_n[R(t)]|n, R(t)\rangle.$$  \hfill (2.9)

Suppose that $R$ is changing adiabatically from $t = 0$ value $R_0$. The time evolution of the states follows

$$H[R(t)]|n, t\rangle = i \hbar \frac{\partial}{\partial t} |n, t\rangle$$  \hfill (2.10)

and the state at time $t$ is given by

$$|n, t\rangle = \exp \left( \frac{i}{\hbar} \int_0^t dt' L_n[R(t')] \right) |n, R(t)\rangle,$$  \hfill (2.11)
2.1 Quantum Hall effect

where

\[ L_n[R(t)] = i\hbar \dot{R}(t) \cdot \langle n, R(t) | \nabla_R | n, R(t) \rangle - E_n[R(t)]. \quad (2.12) \]

This can be easily confirmed by putting Eq. 2.11 into the Eq. 2.10. Using \( L_n[R(t)] \) given in Eq. 2.12, the time dependent state can be expressed as

\[ |n, t\rangle = \exp \left\{ - \int_0^t dt' \dot{R}(t') \langle n, R(t') | \nabla_R | n, R(t') \rangle \right\} |n, R(t)\rangle \exp \left\{ i \frac{\hbar}{\hbar} \int_0^t dt' E_n[R(t')] \right\}. \quad (2.13) \]

In this expression of \( |n, t\rangle \), the first exponential term represents the non-trivial effect of quantum mechanical phase accumulated during the time evolution, and the last exponential term is the trivial one called dynamical term. In an adiabatic cycle, when \( R \) moves on a closed loop \( C \) from \( t = 0 \) and returns to the original position at \( t = T \), i.e., \( R(t) = R_0 \), the non-trivial phase \( (\text{Berry phase}) \) is

\[ \gamma_n[C] \equiv \oint_C dR \cdot i\langle n, R | \nabla_R | n, R \rangle = \oint_S dS \cdot B_n(R), \quad (2.14) \]

where the last equality comes from the Stokes’ theorem. The Berry connection, \( \mathcal{A}_n(R) \), is defined as

\[ \mathcal{A}_n(R) = -i\langle n, R | \nabla_R | n, R \rangle \quad (2.15) \]

and its rotation is Berry curvature

\[ B_n(R) = \nabla_R \times \mathcal{A}_n(R). \quad (2.16) \]

Eqs. 2.15 and 2.16 show that the Berry phase is determined by the “flux” of a generalized field throughout a surface \( S \) bounded by circuit followed by \( R(t) \) over a complete cycle. The same phase \( \gamma_n \) should be obtained as long as one encounters the same total flux, regardless of the actual path followed by \( R(t) \). The Berry connection corresponds to the gauge field defined on that parameter space, similar to the vector potential for the electromagnetic fields in the real space \([14, 15]\).
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2.1.3 TKNN invariant

In solid state physics different phases of matter can be classified by the spontaneous symmetry breaking principle, but the quantum Hall state does not fit into this paradigm. In other words, an order parameter which defines the phase transition from an ordinary insulator state to the quantum Hall state cannot be expressed based on this principle [2]. Indeed, the quantum Hall state is topologically distinct from an insulator, and it can be perceived by a topological invariant concept within a topological framework.

In mathematics Genus number is introduced as the topological invariant to classify different geometrical objects based on continuous deformations (including stretching and bending, but not tearing and pasting). The surface of a perfect sphere and an ellipsoid, a coffee cup and a doughnut are topologically equivalent instances, since they can be smoothly deformed to one another [2]. Topological materials in general, and the topological insulators (TIs) in particular, can be characterized by physically measurable topological invariants, that essentially remains unchanged when the Hamiltonian varies smoothly, and the bulk gap is not closed.

Topological invariant of the integer quantum Hall system, the first Chern number \( \nu \in \mathbb{Z} \) [16], is analogous to an order parameter which identifies the quantum Hall insulator phase from a normal insulator. It is equal to the pre-factor \( \nu \) in the Hall conductance \( \sigma = \nu e^2/h \), and was first explained by Thouless, Kohmoto, Nightingale, den Nijs (TKNN) [17].

It can be derived by calculating the Hall conductivity of a 2D electron system of size \( L \times L \) in perpendicular magnetic fields, where the electric field \( E \) and the magnetic field \( B \) are applied along the \( y \) and \( z \) axes, respectively. By treating the effect of the electric field \( E \) as a perturbation potential \( V = -eEy \), the perturbed eigenstate \( |n\rangle_E \) yields

\[
|n\rangle_E = |n\rangle + \sum_{m(\neq n)} \frac{<m|(-eEy)|n \rangle}{E_n - E_m} |m\rangle + \cdots.
\]

Using this perturbed eigenstate, the expectation value of the current density along the \( x \) axis, \( j_x \), in the presence of the \( E \) field along the \( y \) axis is

\[
\langle j_x \rangle_E = \sum_n f(E_n) |n\rangle_E \left( \frac{e v_x}{L^2} \right) |n\rangle_E
\]

\[\text{(2.17)}\]

\[\text{(2.18)}\]

\[\text{\footnote{\( \mathbb{Z} \) denotes the integers}}\]
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\[ \langle j_x \rangle_{E=0} = \frac{1}{L^2} \sum_{n} f(E_n) \sum_{m \neq n} \left( \frac{\langle n|\mathbf{ev}_x|m\rangle\langle m|-eEy|n\rangle}{E_n - E_m} + \frac{\langle n|-eEy|m\rangle\langle m|\mathbf{ev}_x|n\rangle}{E_n - E_m} \right), \]  

(2.19)

where \( \mathbf{v}_x \) is the electron velocity along the x direction and \( f(E_n) \) is the Fermi distribution function. The Heisenberg equation of motion \( dy/dt = v_y = 1/i\hbar [y, H] \) leads to

\[ \langle m|v_y|n \rangle = \frac{1}{i\hbar} (E_n - E_m) \langle m|\mathbf{v}y|n \rangle, \]  

(2.20)

from which

\[ \sigma_{xy} = \frac{\langle j_x \rangle_E}{E} = \frac{i\hbar e^2}{L^2} \sum_{n,m} f(E_n) \left( \frac{\langle n|\mathbf{v}_x|m\rangle\langle m|v_y|n \rangle - \langle n|v_y|m\rangle\langle m|\mathbf{v}_x|n \rangle}{(E_n - E_m)^2} \right). \]  

(2.21)

Considering the system in a periodic potential and its Bloch states \( |u_{nk}\rangle \) as the eigenstates, the identity

\[ \langle u_{nk}|v_{nk}|u_{nk} \rangle = \frac{1}{\hbar} (E_{nk} - E_{mk}) \langle u_{nk}|\frac{\partial}{\partial k_{\mu}}|u_{nk} \rangle \]  

(2.22)

allows to rewrite Eq. 2.21 into the form

\[ \sigma_{xy} = \frac{-ie^2}{\hbar L^2} \sum_{k} \sum_{n \neq m} f(E_n) \left( \frac{\partial}{\partial k_x} \langle u_{nk}|\frac{\partial}{\partial k_y} u_{nk} \rangle - \frac{\partial}{\partial k_y} \langle u_{nk}|\frac{\partial}{\partial k_x} u_{nk} \rangle \right). \]  

(2.23)

Since the Berry connection defined in Eq. 2.15 is written for Bloch states as

\[ \mathbf{A}_n(k) = -i(u_{nk}|\nabla_k|u_{nk}) = -i \langle u_{nk}|\frac{\partial}{\partial k}||u_{nk} \rangle, \]  

(2.24)

the Hall conductivity reduces to

\[ \sigma_{xy} = \nu \frac{e^2}{h} \]  

(2.25)

with

\[ \nu = \sum_n \int_{\text{BZ}} \frac{d^2k}{2\pi} \left( \frac{\partial A_{n,y}}{\partial k_x} - \frac{\partial A_{n,x}}{\partial k_y} \right). \]  

(2.26)

This \( \nu \) can be expressed as \( \nu = \sum_n \nu_n \) with \( \nu_n \) the contribution from the nth band. It can be easily seen that \( \nu_n \) is related to the Berry phase, namely

\[ \nu_n = \int_{\text{BZ}} \frac{d^2k}{2\pi} \left( \frac{\partial A_{n,y}}{\partial k_x} - \frac{\partial A_{n,x}}{\partial k_y} \right) = \frac{1}{2\pi} \oint_{\partial \text{BZ}} dk \cdot \mathbf{A}_n(k). \]  

(2.27)
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Because the BZ has no boundaries, it forms a torus, hence, integral above is equal zero if \( \mathcal{A}_n(k) \) is well defined in the whole BZ. Whereas, a non-zero value of the integral is the consequence of the non-trivial structure of the Berry connection, which can be ascribed to its singularities at points in the BZ. It represents an obstruction to the application of Stokes’ theorem over the entire BZ [18].

Thus Eq. 2.27 is shorten to

\[
\nu_n = \frac{1}{2\pi} \gamma_n \left[ \partial \text{BZ} \right] = m \ (m \in \mathbb{Z}). \tag{2.28}
\]

\( \nu_n \) can only take an integer value, and hence \( \sigma_{xy} \) is quantized to integer multiples of \( e^2/h \). The integer \( \nu \) is called TKNN invariant, and it plays the role of the topological invariant of the quantum Hall system, which is a time-reversal symmetry breaking TI. A zero TKNN invariant corresponds to zero conductivity and consequently defines an ordinary insulator, while non-zero TKNN invariant shows a non-trivial phase, i.e., the system becomes topological. Recognition of the Hall conductance as topological invariant is not only a mathematical formality, but also of physical relevance as it explains the robustness of quantization of the Hall conductance against many kinds of perturbation [15].

2.2 Quantum spin Hall effect

The quantum Hall state, which is an insulating in its interior but supports the flow of electrons on its edges, can be observed only when the external magnetic field is applied. Henceforth, there were many efforts to establish another system which offers the same properties, but does not require the magnetic field.

In this regard, first Haldane proposed that a QHE can be observed in a system of spinless fermions with any net magnetic flux, but with a broken time-reversal symmetry [19]. Although this model satisfies the condition of no needs for a magnetic field, the physical implementation is considered unlikely. Afterwards, Kane and Mele suggested a more general version of Haldane model, which includes the spin of electrons, and the spin-orbit coupling plays the role of the spin-dependent effective magnetic field. This model, the quantum spin Hall (QSH), can be realized as a superposition of two quantum Hall subsystems with opposite spins, the spin up subsystem with \( \sigma_{xy} = e^2/h \), and the spin down subsystem with \( \sigma_{xy} = -e^2/h \). The QSH or 2D TI, was
2.2 Quantum spin Hall effect

primarily predicted for graphene [20, 21] and then experimentally observed in mercury telluride quantum well [22], which shed a new light to the field of topological materials.

In the following, after describing the initial model of QSHE, the $Z_2$ invariant and the first experimental evidence of 2D TIs will be reviewed.

### 2.2.1 Kane and Mele model

In 2005, Kane and Mele introduced a generalized Haldane model for the graphene lattice by involving the spin of the electrons. Here the periodic magnetic flux is replaced by the spin-orbit coupling consideration between spin and momentum. Spin-orbit inclusion preserves the time-reversal symmetry, since the momentum $p \rightarrow -p$ and spin $\sigma \rightarrow -\sigma$ under the time-reversal. In the system with time-reversal symmetry, the electrons with spin up in the edge channel flow in one direction, while electrons with spin down in the edge channel flow in an opposite direction, $I^\uparrow = -I^\downarrow$. The net charge current in two edge channels is zero, $I_c \equiv I^\uparrow + I^\downarrow = 0$, as a non-zero net charge current breaks the time-reversal symmetry. Instead, a pure spin current circulates around the boundary of system, $I_s \equiv \hbar/2e(I^\uparrow - I^\downarrow)$.

Thus, the QSHE can be regarded as the combination of two independent QHE for spin up and spin down which becomes doubly degenerate if there is no coupling between electrons with spin up and spin down. When the interaction between spins is negligible they can be treated as if each of them has its own TKNN integer $\nu^\uparrow$ and $\nu^\downarrow$, which corresponds to a counterclockwise chiral edge channel flow around the boundary for $\nu^\uparrow$ and a clockwise one for $\nu^\downarrow$. Moreover, $\nu^\uparrow + \nu^\downarrow = 0$ but the difference $\nu^\uparrow - \nu^\downarrow$ is non-zero and defines a quantized spin Hall conductivity. Unlike TKNN invariant, $\nu^\uparrow - \nu^\downarrow$ is not always quantized and breaks down when spin non-conserving terms are presented, hence, it cannot always be a good parameter to characterize the QSH phase. Alternatively, for such a time-reversal system a topological index, $Z_2$, has been established which is the analogous to the Chern number classification of QHE, and distinguishes the QSH phase from an ordinary insulator [20].

The Kane and Mele model for QSHE is a graphene model with the time-reversal invariant spin-orbit coupling, whose Hamiltonian can be written as

$$H = t \sum_{\langle i,j \rangle} c_i^\dagger c_j^\uparrow + i \lambda_{SO} \sum_{\langle\langle i,j \rangle\rangle} \tau_{ij} c_i^\dagger s_y c_j^\uparrow + i \lambda_R \sum_{\langle i,j \rangle} c_i^\dagger (s \times d_{ij})_z c_j^\uparrow + \lambda_v \sum_i \xi_i c_i^\dagger c_i^\uparrow$$

(2.29)
where the first term denotes the nearest neighbour hopping term on graphen honeycomb lattice, with suppressed spin index on the electron operator, $c_i^\dagger = (c_i^\dagger, c_i^\dagger, c_i^\dagger, c_i^\dagger, c_i^\dagger)$ (i and j label different unit cells). The second term is a mirror symmetric spin-orbit interaction, that involves spin dependent next nearest neighbour hopping. Here

$$\tau_{ij} = \frac{2}{\sqrt{3}}(d_i \times d_j)_z = \pm 1$$

in which $d_i$ and $d_j$ correspond to two unit vectors along the two bonds the electron traverses going from site j to i. The Pauli matrices $s_i$ represent the electron spin. The third term that explicitly violates the $z \rightarrow -z$ mirror symmetry, indicates the nearest neighbour Rashba term. It is stemming from a perpendicular electric field or interaction with a substrate. Adding this term makes the system more sophisticated since $s_z$ is no longer conserved and the electron with spin up and spin down are coupled together. The last term is a staggered sublattice potential, $\xi_i = \pm 1$ that is included to delineate the transition between the QSH and the normal insulator.

$H$ is diagonalized in the basis written as $u_\alpha(k)e^{ik \cdot R}$, with $s$ is the spin and $R$ is a bravais lattice vector, and $\alpha = 0, 1$ is the sublattice index since the unit cell consists of two atoms. For each $k$ the Bloch wave function is a four component eigenvector $|u(k)\rangle$ of the Bloch Hamiltonian matrix $\mathcal{H}(k)$ which can be expressed in term of Dirac matrices $\Gamma^a$ and their commutators $\Gamma^{ab} = 1/2[\Gamma^a, \Gamma^b]$,

$$\mathcal{H}(k) = \sum_{a=1}^5 d^a(k) \Gamma^a + \sum_{a<b=1}^5 d^{ab}(k) \Gamma^{ab}. \quad (2.30)$$

The presentation of Dirac matrices is chosen as

$$\Gamma^a = (\sigma_x \otimes s_0, \sigma_z \otimes s_0, \sigma_y \otimes s_x, \sigma_y \otimes s_y, \sigma_y \otimes s_z) \quad (a = 1, 2, 3, 4, 5) \quad (2.31)$$

where the Pauli matrices $\sigma_i$ and $s_i$ stand for sublattice and spin indices respectively. This choice of representation organizes the matrices according to time-reversal whose operator is given by $\Theta \equiv (\sigma_0 \otimes s_y)\mathcal{K}$, with $\mathcal{K}$ is the complex conjugation. The five Dirac matrices are even under time-reversal,

$$\Theta \Gamma^a \Theta^{-1} = \Gamma^a, \quad (2.32)$$

while the ten commutators are odd,

$$\Theta \Gamma^{ab} \Theta^{-1} = -\Gamma^{ab}. \quad (2.33)$$

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Time-reversal operator changes \( k \rightarrow -k \), thus, in order to have a time-reversal invariant Hamiltonian, the coefficients should fulfill the relations,

\[
d_a(-k) = d_a(k), \quad (2.34a)
\]

\[
d_{ab}(-k) = -d_{ab}(k). \quad (2.34b)
\]

The non-zero coefficient in Eq. 2.30.

| \(d_1\) | \(t(1 + 2\cos \frac{k_x}{2}\cos \frac{\sqrt{3}k_y}{2})\) | \(d_{12}\) | \(-2t\cos \frac{k_x}{2}\sin \frac{\sqrt{3}k_y}{2}\) |
| \(d_2\) | \(\lambda_{v}\) | \(d_{15}\) | \(\lambda_{SO}(2\sin k_x - 4\sin \frac{k_x}{2}\cos \frac{\sqrt{3}k_y}{2})\) |
| \(d_3\) | \(\lambda_{R}(1 - \cos \frac{k_x}{2}\cos \frac{\sqrt{3}k_y}{2})\) | \(d_{23}\) | \(-\lambda_{R}\cos \frac{k_x}{2}\sin \frac{\sqrt{3}k_y}{2}\) |
| \(d_4\) | \(-\sqrt{3}\lambda_{R}\sin \frac{k_x}{2}\sin \frac{\sqrt{3}k_y}{2}\) | \(d_{24}\) | \(\sqrt{3}\lambda_{R}\sin \frac{k_x}{2}\cos \frac{\sqrt{3}k_y}{2}\) |

The Eq. 2.30 gives four energy bands, of which two are fully occupied. If there is an energy gap between two upper bands and lower ones the system becomes insulating. As the whole system does not break time-reversal symmetry, the Chern number is always zero. When \(\lambda_{R} = 0\), the Hamiltonian can be split into two independent parts,

\[
H = \sum_{s=\uparrow,\downarrow} H_s \quad (2.35)
\]

at which

\[
H_s = t \sum_{\langle ij \rangle} c^\dagger_{i,s} c_{j,s} + i s \lambda_{SO} \sum_{\langle ij \rangle} \tau_{ij} c^\dagger_{i,s} c_{j,s} + \lambda_{v} \sum_{i} \xi_{i} c^\dagger_{i,s} c_{i,s}. \quad (2.36)
\]

Accordingly, in this case, there is an energy gap with the magnitude \(|6 \sqrt{3}\lambda_{SO} - 2\lambda_{v}|\). For \(\lambda_{v} > 3 \sqrt{3}\lambda_{SO}\) the gap is dominated by \(\lambda_{v}\), while for \(3 \sqrt{3}\lambda_{SO} > \lambda_{v}\), the gap is dominated by \(\lambda_{SO}\). For each \(H_s\), one can define a spin dependent Chern number. For \(\lambda_{v} > 3 \sqrt{3}\lambda_{SO}\), the corresponding Chern number is zero for both \(H_{\uparrow}\) and \(H_{\downarrow}\). However, for \(3 \sqrt{3}\lambda_{SO} > \lambda_{v}\) the corresponding Chern number becomes non-zero,

\[
\nu_{s} = \text{sgn}(s\lambda_{SO}). \quad (2.37)
\]

Although the total Chern number \(\nu = \nu_{\uparrow} + \nu_{\downarrow} = 0\) their difference is \(\pm 2\). Thus, \(3 \sqrt{3}\lambda_{SO} > \lambda_{v}\), is a combination of two independent quantum Hall phases with different chirality, that is, the quantum spin Hall system. In Fig. 2.2 energy band structures of a zigzag strip obtained by solving the lattice model, show these two distinct phases. Each of
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![Energy band structures for a one-dimensional stripe with the zigzag boundary condition in (a) the quantum spin Hall phases with $\lambda_\nu = 0.1t$ and (b) an insulating phase with $\lambda_\nu = 0.4t$ (In both cases $\lambda_{SO} = 0.06t$ and $\lambda_R = 0.05t$) [23].](image)

Figure 2.2: Energy band structures for a one-dimensional stripe with the zigzag boundary condition in (a) the quantum spin Hall phases with $\lambda_\nu = 0.1t$ and (b) an insulating phase with $\lambda_\nu = 0.4t$ (In both cases $\lambda_{SO} = 0.06t$ and $\lambda_R = 0.05t$) [23].

them has both gapped bulk energy band structure and edge states, in Fig. 2.2a, for the quantum spin Hall phase a pair of edge states connects the conduction and valence bands, whereas in Fig. 2.2b no edge states connect the two bands. At the transition between insulator to QSHE, the energy gap closes, allowing the edge states to “switch partners” [20].

For a more general case, when $\lambda_R \neq 0$ the electron with spin up and spin down are mixed together and therefore, the Hamiltonian cannot be divided into two independent parts, and the Chern number definition as described above is no longer valid. As a consequence of Chern number’s lack of credibility a new parameter, $Z_2$ invariant, were introduced which will be described in the next section.

While this model provided a simple description to study the QSHE, it was not however a successful prediction for graphene to be the first evident quantum spin Hall system. Because the model relied on an estimate of magnitude of spin-orbit interaction which turned out to be too small [23].

2.2.2 $Z_2$ invariant

Over the last couple of years, a large number of equivalent mathematical formulations of the $Z_2$ invariant have been developed [24, 25, 26, 27]. It was originally formulated by Kane and Fu in terms of the occupied Bloch states $|u_{n,k}\rangle$ [28]. In the QSHE, the value of the spin Hall conductance is not quantized in general [27], thus, unlike the
QHE, the spin conductance cannot be used to classify different phases. Instead, they introduced the time-reversal polarization, which is related to the Berry phase of each occupied state. Such a determination can be applied for any Bloch insulator which preserves the time-reversal symmetry.

In this section, by recalling the significance of time-reversal operator, first $Z_2$ invariant for a simple two-band system will be derived. Then in the following, it will be generalized for a multi-band system. This realization can be implemented for both two and three-dimensional systems.

### 2.2.2.1 Time-reversal polarization

Starting with a time-reversal symmetry preserving insulator, it is worth mentioning important properties of the time-reversal operator for the Bloch Hamiltonian. The anti-unitary operator $\Theta$ for a spin $1/2$ particle takes the form $\Theta = -is_y K$. $s_\mu$ ($\mu = x, y, z$) stands for the spin operator given by Pauli matrices. Taking the eigenstates of $s_z$ as the basis set $|\sigma\rangle$, one can get the following features;

$$\Theta^2 = -1,$$

$$\langle \psi | \Theta | \phi \rangle = -\langle \phi | \Theta | \psi \rangle,$$

$$\langle \Theta \psi | \Theta \phi \rangle = \langle \phi | \psi \rangle.$$

More broadly, for any arbitrary linear operator $A$

$$\langle \Theta \psi | \Theta A \Theta^{-1} | \Theta \phi \rangle = \langle \phi | A^\dagger | \psi \rangle.$$  

For a periodic system with the total Hamiltonian $H$ states can be expressed as

$$H|\psi_{nk}\rangle = E_{nk}|\psi_{nk}\rangle$$

applying the Bloch theorem leads to the separation of $|\psi_{nk}\rangle$ into

$$|\psi_{nk}\rangle = e^{ik_r} |u_{nk}\rangle$$

where $|u_{nk}\rangle$ is the cell-periodic eigenstate of the Bloch Hamiltonian

$$\mathcal{H}(k) = e^{-ik_r} He^{ik_r}$$
and $|u_{nk}\rangle$ fulfills the reduced Schrödinger equation

$$\mathcal{H}(k)|u_{nk}\rangle = E_{nk}|u_{nk}\rangle.$$  

(2.45)

The time-reversal symmetry preservation of $H$, $[H, \Theta] = 0$ implies

$$\mathcal{H}(-k) = \Theta \mathcal{H}(k) \Theta^{-1}.$$  

(2.46)

The equation above indicates that the energy bands of a time-reversal symmetric system come in pairs, i.e., $+k$ state and $-k$ state are at the same energy, and they are referred to as Kramers pairs. Naturally, Kramers pairs are degenerate at the time-reversal invariant momentum (TRIM) where $+k$ becomes equivalent to $-k$ due to the periodicity of the BZ (Fig. 2.3). A convenient representation of the time-reversal operator in the Bloch wave function basis is defined as

$$w_{\alpha\beta}(k) = \langle u_{\alpha, -k}\Theta|u_{\beta, k}\rangle,$$  

(2.47)

where $\alpha$ and $\beta$ indicate band indices. These two Bloch states can be related to each other via

$$|u_{\alpha, -k}\rangle = \sum_{\beta} w^*_{\alpha\beta}(k) \Theta |u_{\beta, k}\rangle.$$  

(2.48)

Furthermore, it is a unitary matrix, i.e.,

$$\sum_{\alpha} w^*_{\alpha\beta}(k) w_{\alpha\gamma}(k) = \langle u_{\beta, k}|u_{\gamma, k}\rangle = \delta_{\beta\gamma},$$

(2.49)

and it has the following property;

$$w_{\beta\alpha}(-k) = -w_{\alpha\beta}(k).$$

(2.50)

This equation denotes that at a time-reversal invariant momenta (TRIM) $\Lambda$, the $w$ matrix becomes antisymmetric

$$w_{\beta\alpha}(\Lambda) = -w_{\alpha\beta}(\Lambda).$$  

(2.51)

For instance, if there are only two occupied bands, $w_{\alpha\beta}$ becomes a $2 \times 2$ matrix and at $\Lambda$ it can be explicitly written as

$$w(\Lambda) = \begin{pmatrix} 0 & w_{12}(\Lambda) \\ -w_{21}(\Lambda) & 0 \end{pmatrix} = w_{12}(\Lambda) \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}.$$  

(2.52)
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Yet another convenient matrix worth considering for a time-reversal symmetric system is the U(2) Berry connection,

$$\mathcal{A}_{\alpha\beta}(k) = -i \langle u_{\alpha,k} | \nabla_k | u_{\beta,k} \rangle$$ (2.53)

where $\mathcal{A}$ is a set of three matrices. Substituting Eq. 2.48 and using Eq. 2.40 the relation between $\mathcal{A}_{\alpha\beta}(k)$ and $\mathcal{A}_{\alpha\beta}(-k)$ is

$$\mathcal{A}(-k) = w(k) \mathcal{A}^\dagger(-k) w^\dagger(k) + iw(k) \nabla_k w^\dagger(k),$$ (2.54)

whose trace gives

$$\text{tr}[\mathcal{A}(-k)] = \text{tr}[\mathcal{A}^\dagger(k)] + \text{itr}[w(k) \nabla_k w^\dagger(k)].$$ (2.55)

Because $\mathcal{A}_{\beta\alpha} = \mathcal{A}_{\alpha\beta}^\dagger$, $\text{tr}[\mathcal{A}] = \text{tr}[\mathcal{A}^\dagger]$ and $w\nabla w^\dagger = -(\nabla w)w^\dagger$ since $ww^\dagger = 1$, therefore, the replacement of $-k \rightarrow k$ ends up to

$$\text{tr}[\mathcal{A}(k)] = \text{tr}[\mathcal{A}^\dagger(-k)] + \text{itr}[w^\dagger(k) \nabla_k w(k)],$$ (2.56)

that is the essential relation to calculate the $Z_2$ invariant as proceeding.

In order to derive the $Z_2$ invariant, based on Kane and Fu argument [28], consider a one-dimensional system with length $L$ and lattice constant $a_0 = 1$. Here, for simplicity only two bands from Kramers pairs, denoted by $|u_1(k)\rangle$ and $|u_2(k)\rangle$, are taken into account. The general formulation of the entire system will be expounded in the next step. Assume that band parameters change with time and return to the original value at $t = T$, and also the Hamiltonian satisfies these conditions

$$H[t + T] = H[t]$$ (2.57a)

$$H[-t] = \Theta H[t] \Theta^{-1}.$$ (2.57b)

From the modern theory of ferroelectricity, it is known that charge-polarization $P_\rho$ can be calculated by integrating the Berry connection of the occupied states over the BZ. For such a 1D two-bands system, it can be expressed as

$$P_\rho = \int_{-\pi}^{\pi} \frac{dk}{2\pi} \mathcal{A}(k),$$ (2.58)
where

\[ A(k) = -i(u_1(k)|V_k|u_1(k)) - i(u_2(k)|V_k|u_2(k)) \]  
\[ = A_{11}(k) + A_{22}(k) \]  
\[ = \text{tr}[A]. \] (2.59)

Partial polarization associated with each band contribution is

\[ P_i = \frac{\pi}{2\pi} \int_{-\pi}^{\pi} dk A_{ii}(k) \] \( (i = 1, 2) \) (2.60)

that gives the total charge-polarization \( P_\rho = P_1 + P_2 \). The time-reversal polarization however, is defined as \( P_\theta = P_1 - P_2 = 2P_1 - P_\rho \), which intuitively is the difference in charge-polarization between spin up and spin down bands.

From Eq. 2.57a and Eq. 2.57b it is clear that the system is time-reversal symmetric at \( t = 0 \) and \( t = T/2 \). Thus, at these times the Kramers degeneracy must be observed at any \( k \), which requires that the time-reversed version of \( |u_2(k)\rangle \) (\( \Theta |u_2(k)\rangle \)) being equal to \( |u_1(-k)\rangle \) except for a phase factor. Hence at time-reversal invariant points

\[ \Theta |u_2(k)\rangle = e^{-i\chi(k)} |u_1(-k)\rangle \] (2.62)
\[ \Theta |u_1(k)\rangle = e^{-i\chi(-k)} |u_2(-k)\rangle \] (2.63)

therefore,

\[ w(k) = \begin{pmatrix} 0 & e^{-i\chi(k)} \\ -e^{-i\chi(-k)} & 0 \end{pmatrix}. \] (2.64)

Starting from Eq. 2.63, \( P_1 \) can be calculated at the time-reversal symmetric times

\[ A_{11}(-k) = A_{22}(k) - \frac{\partial}{\partial k} \chi(k) \] (2.65)

which leads to

\[ P_1 = \frac{1}{2\pi} \left( \int_0^{\pi} dk A_{11}(k) + \int_{-\pi}^0 dk A_{11}(k) \right) \]
\[ = \frac{1}{2\pi} \int_0^{\pi} dk \left( A_{11}(k) + A_{22}(k) - \frac{\partial}{\partial k} \chi(k) \right) \]
\[ = \frac{\pi}{2\pi} \int_0^{\pi} \frac{dk}{2\pi} A(k) - \frac{1}{2\pi} [\chi(\pi) - \chi(0)]. \] (2.66)
2.2 Quantum spin Hall effect

Since \( w_{12}(k) = e^{-i\chi(k)} \), \( \chi(k) \) can be represented as

\[
\chi(k) = i \log w_{12}(k)
\]

which reduces Eq. 2.66 to

\[
P_1 = \int_0^{\pi} \frac{dk}{2\pi} A(k) - \frac{i}{2\pi} \log \frac{w_{12}(\pi)}{w_{12}(0)}.
\]

Substituting latter equation in \( P_\theta \), it can be expressed as

\[
P_\theta = 2P_1 - P_\rho = \int_0^{\pi} \frac{dk}{2\pi} [A(k) - A(-k)] - \frac{i}{\pi} \log \frac{w_{12}(\pi)}{w_{12}(0)}.
\]

Noticing \( A(k) = \text{tr}[A(k)] \) and using Eq. 2.56, it follows

\[
P_\theta = \int_0^{\pi} \frac{dk}{2\pi} - \frac{i}{\pi} \log \frac{w_{12}(\pi)}{w_{12}(0)}
\]

Eventually as \( \det[w] = w_{12}^2 \) for this case, \( P_\theta \) reduces to

\[
P_\theta = \frac{1}{i\pi} \log \left( \frac{\sqrt{w_{12}(0)^2}}{w_{12}(0)} \cdot \frac{w_{12}(\pi)}{\sqrt{w_{12}(\pi)^2}} \right).
\]

Since \( \log(-1) = i\pi \), the argument of \( \log \) above is either +1 or -1, therefore, \( P_\theta \) is equal to 0 or 1 (mod 2). These two values of \( P_\theta \) corresponds to two different polarization states which the present 1D system can take at \( t = 0 \) and \( t = T/2 \). Now consider the change of \( P_\theta \) from \( t = 0 \) and \( t = T/2 \). The wave function \( |u_0(k, t)\rangle \) can be viewed as a map from the 2D phase space \((k, t)\), which forms a torus due to the periodic boundary conditions, to the Hilbert space. This Hilbert space can be classified into two groups depending on the difference in \( P_\theta \) between \( t = 0 \) to \( t = T/2 \),

\[
\Delta = P_\theta(T/2) - P_\theta(0).
\]
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![Diagram of TRIMs for a 2D square BZ and a time-reversal symmetric 1D system.]

**Figure 2.3:** Time-reversal invariant momentas (TRIMs). (a) There are four TTRIMs for a 2D square BZ. (b) The TRIMs for a time-reversal symmetric 1D system. Identifying \( t \to k_y \) maps the periodic \((k, t)\) space to the ordinary 2D BZ as shown in (a) [15].

This \( \Delta \) is specified only in mod 2, so it gives a \( \mathbb{Z}_2 \) topological invariant to characterize the Hilbert space. Intuitively, when \( P_\theta \) changes between \( t = 0 \) to \( t = T/2 \), the Hilbert space is “twisted” and \( \Delta = 1 \), while the Hilbert space is trivial (\( \Delta = 0 \)) when there is no change in \( P_\theta \). Ultimately using Eq. 2.73, this criterion can be expressed in terms of

\[
(-1)^\Delta = \prod_{i=1}^{4} \frac{w_{12}(\Lambda_i)}{\sqrt{w_{12}(\Lambda_i)^2}}
\]

(2.75)

where \( \Lambda_1 = (k, t) = (0, 0) \), \( \Lambda_2 = (\pi, 0) \), \( \Lambda_3 = (0, T/2) \), \( \Lambda_4 = (\pi, T/2) \), as depicted in Fig. 2.3b.

The physical consequence of a cycle with \( \Delta = 1 \) is spin pumping from one end of the 1D system to the other [28].

### 2.2.2.2 General formula of the \( \mathbb{Z}_2 \) invariant

Extending the latter argument to a multiband system will generalize the formula of \( \mathbb{Z}_2 \) invariant. Let’s assume that the Hamiltonian still fulfils Eq. 2.57a and Eq. 2.57b, and also for simplicity \( T = 2\pi \). Suppose that 2N bands are occupied and forming N Kramers pairs. For each Kramers pair \( n \), at the time-reversal symmetric times \( t = 0 \) and \( \pi \) wave functions are related by

\[
\Theta |u_2^n(k)\rangle = e^{-i\chi_n(k)}|u_1^n(-k)\rangle
\]

(2.76)

\[
\Theta |u_1^n(k)\rangle = e^{-i\chi_n(-k)}|u_2^n(-k)\rangle
\]

(2.77)
therefore, the w matrix becomes

\[
w(k) = \begin{pmatrix}
0 & e^{-i\chi_2(0)} & 0 & 0 & \cdots \\
-e^{-i\chi_1(-k)} & 0 & e^{-i\chi_2(0)} & 0 & \cdots \\
0 & 0 & 0 & e^{-i\chi_2(0)} & \cdots \\
0 & 0 & -e^{-i\chi_2(-k)} & 0 & \cdots \\
\vdots & \vdots & \vdots & \vdots & \ddots
\end{pmatrix}.
\]

Thus, at \( t = 0 \) and \( \pi \), \( w(0) \) and \( w(\pi) \) turn antisymmetric, then

\[
w_{12}(\Lambda_i)w_{34}(\Lambda_i)\ldots w_{2N-1,2N}(\Lambda_i) = e^{-i\sum_{n=1}^{N} \chi_n(\Lambda_i)}
= \text{Pf}[w(\Lambda_i)],
\]

where \( w \) is a function of \( k \) and \( t \), and the Pfaffian considered for a \( 2N \times 2N \) skew-symmetric matrix with \( 2 \times 2 \) blocks on the diagonal. In general Pfaffian is defined for an antisymmetric matrix and is related to determinant by

\[
\text{Pf}[A]^2 = \det[A].
\]

Now it is quite straightforward to develop the previous calculations for the time-reversal symmetric times \( t = 0 \) and \( \pi \) to obtain

\[
P_1 = \int_0^\pi \frac{dk}{2\pi} d(k) - \frac{1}{2\pi} \sum_{n=1}^{N} [\chi_n(\pi) - \chi_n(0)]
= \int_0^\pi \frac{dk}{2\pi} d(k) - \frac{1}{2\pi} \log \left( \frac{\text{Pf}[w(\pi)]}{\text{Pf}[w(0)]} \right),
\]

which leads to

\[
P_\theta = \frac{1}{2\pi} \log \left( \frac{\sqrt{\det[w(0)]}}{\text{Pf}[w(0)]} \cdot \frac{\text{Pf}[w(\pi)]}{\sqrt{\det[w(\pi)]}} \right).
\]

Consequently, the \( Z_2 \) topological invariant \( \nu \) is given by

\[
(-1)^\nu = \prod_{i=1}^{4} \frac{\text{Pf}[w(\Lambda_i)]}{\sqrt{\det[w(\Lambda_i)]}}
\]

that essentially classifies the Hilbert space into twisted (\( \nu = 1 \)) and trivial (\( \nu = 0 \)) ones.

If the crystal has inversion symmetry, there is another shortcut to computing \( \nu [29] \).

At the time-reversal invariant points the Bloch states are also parity eigenstates with
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eigenvalue $\pm 1$. As a result, the $Z_2$ becomes the product over the parity of the Kramers pairs of occupied bands. Therefore, when the band inversion occurs at an odd number of time-reversal invariant points $\nu$ is equal to 1, which corresponds to a topological phase, whereas the band inversion at an even number of time-reversal invariant points ($\nu = 0$) give rise to a trivial phase [15].

2.2.3 Experimental evidence of 2D TIs

The first experimentally identified 2D TI was CdTe/HgTe/CdTe quantum well, i.e., a thin layer of HgTe sandwiched with CdTe [30]. Both HgTe and CdTe have strong spin-orbit coupling and crystallize in zinc blend structure. CdTe has a band structure similar to other semiconductors. The conduction band is an s-like state while the valence band is a p-like state. On the other hand, in HgTe, the p-levels rise above the s-levels, leading to an inverted band structure. Therefore, HgTe is a good starting material for conceiving a TI phase. However, in bulk HgTe, a crystal-symmetry-protected-degeneracy at the $\Gamma$ point makes the system to be intrinsically a zero-gap, which means that there is no band gap between the p- and s-orbital bands and the system is not qualified as an insulator. Nevertheless, by sandwiching HgTe with CdTe, which has a slightly larger lattice constant, the epitaxial strain exerted on HgTe breaks the cubic lattice symmetry and leads to a gap opening, and hence the system can become a genuine insulator. When the thickness of the HgTe layer is $d < d_c = 6.3$ nm, due to confinement effect the ordering of the band gap is dominated by the neighboring CdTe barriers thus, the 2D electronic states bound to the quantum well have the normal band gap. For $d > d_c$, however, the confinement effect is weak and the 2D bands invert, therefore, the sample shows a quantized conductance $2e^2/h$ in a zero magnetic field.

Recently, another 2D TI system, AlSb/InAs/GaSb/AlSb quantum well, was theoretically predicted [31] and experimentally confirmed [32]. The valence band top of GaSb lies above the conduction band bottom of InAs. Hence, when InAs and GaSb are in direct contact and they are both quantum confined, the resulting hole subband in GaSb may lie above the electron subband in InAs, and therefore, the band order of this quantum well is inverted. The band gap in this quantum well arises from anticrossing of the two subbands at finite momentum and hence is very small ($\sim 4$ meV), which makes clean observation of the helical edge state very difficult. Recently, direct
observation of the conductance quantization to $2e^2/h$ has been achieved by introducing disorder to the InAs/GaSb interface by Si doping to localize the unwanted bulk carriers.

2.3 Topological crystalline insulators

Extremely fascinating studies of the topology of band structures and also the discovery of topological insulators inspired physicists to extend this field to other discrete symmetry classes, such as particle-hole symmetry which leads to a rich family of topological phases like topological superconductors, and the classification of magnetic insulators ushered by a certain magnetic translation symmetry. Recently a new class of topological insulator is introduced by Liang Fu [3], which is the counterpart of TIs in materials without (or with) spin-orbit coupling. It crucially depends upon the crystal point group symmetry and hence, it is called “Topological Crystalline Insulator” (TCI). Establishment of this new class of materials has been attracting interests of both fundamentalists and experimentalists to prove and dig into its new hallmarks.

In this section the very first hypothetical model which predicted and explained the entity of TCIs will be surveyed. The experimental evidence which was pursued after theoretical predictions of SnTe family of materials as the TCIs, will be explained in the next following section.

As it was previously stated the time-reversal invariant and strong enough spin-orbit coupling play the key roles of having TI state. In the primary prediction of TCI

![Figure 2.4: (a) Tetragonal lattice with two atoms A and B along the c axis in the unit cell. (b) The Brillouin zone and four high symmetry points [3].](image)
2. Topological insulator materials

however, there is no necessity for spin-orbit coupling. Instead, this role can be replaced by the electron’s orbital degree of freedom. The first and foremost condition to obtain TCI is that the system should have a certain point group symmetry. Nevertheless, crystal symmetry which protects the metallic surface states can be broken by the sample surfaces and consequently a low symmetric TCI does not preserve any robust surface state. Therefore, to eliminate this fault the threshold of this investigation commenced from the most symmetric crystals which have fourfold (C$_4$) or sixfold (C$_6$) rotational symmetry.

To prove the existence of gapless surface states on (001) face of a hypothesis crystal with C$_4$ symmetry, consider a tetragonal lattice with two inequivalent atoms A and B along the c axis in its unit cell, as depicted in Fig. 2.4a. Stacking such bilayer square lattices in ab-plane creates the 3D crystal. To describe the band structure of an electron’s p-orbitals (particularly the energy bands derived from p$_x$ and p$_y$ orbitals) one can introduce a tight binding model. It is assumed that the bands do not overlap with the p$_z$ bands, and construct a tight binding from the Wannier functions with the same symmetry as p$_x$ and p$_y$ orbitals. The Hamiltonian consists of hopping within the layers $H^A$ and $H^B$, as well as hopping between the layers $H^{AB}$ terms;

$$
H = \sum_n H^A_n + H^B_n + H^{AB}_n,
$$

$$
H^A_n = \sum_{i,j} t^a(r_i - r_j) \sum_{\alpha,\beta} c^\dagger_{A\alpha}(r_i, n) \epsilon^i_j c_{\beta\alpha}(r_j, n),
$$

$$
H^{AB}_n = \sum_{i,j} t'(r_i - r_j) \left( \sum_{\alpha} c^\dagger_{A\alpha}(r_i, n) c_{B\alpha}(r_j, n) + H.c. \right) + t'_z \sum_i \sum_{\alpha} \left( c^\dagger_{A\alpha}(r_i, n) c_{B\alpha}(r_i, n + 1) + H.c. \right).
$$

Here each site is specified by (n, r, a), where n designates the bilayer unit cell along c axis, r = (x, y) coordinates ab-plane, a = A, B stands for the sublattices and $\alpha, \beta$ label the p$_x$ and p$_y$ orbitals. Electron’s spin index is deliberately omitted based on the assumption that the spin-orbit coupling is negligible. The form of Eq. 2.84 is entirely determined by the crystal symmetry. Since d$_{xz, yz}$ orbitals transform in the same way as p$_x, y$ orbitals do under C$_4$, Eq. 2.84 can be applied to a broader range of materials included those with d shells. Thus, this discussion is potentially relevant to transition metal compounds with t$_{2g}$ orbitals near Fermi energy, as well.
Simplifying Eq. 2.84, the nearest and next nearest neighbour intralayer hoppings in $H^a$ with amplitude $t_1^a$ and $t_1'^a$, and the nearest and next nearest neighbour inter-layer hoppings in $H^{AB}$ with amplitude $t_1'$ and $t_2'$, are taken into account. The Bloch Hamiltonian $\mathcal{H}(\mathbf{k})$ is obtained by Fourier transform:

$$
\mathcal{H}(\mathbf{k}) = \begin{pmatrix}
\mathcal{H}^A(\mathbf{k}) & \mathcal{H}^{AB}(\mathbf{k}) \\
\mathcal{H}^{AB+}(\mathbf{k}) & \mathcal{H}^B(\mathbf{k})
\end{pmatrix},
$$

$$
\mathcal{H}^a(\mathbf{k}) = 2t_1^a \begin{pmatrix}
\cos k_x & 0 \\
0 & \cos k_y
\end{pmatrix}
+ 2t_1'^a \begin{pmatrix}
\cos k_x \cos k_y & \sin k_x \sin k_y \\
\sin k_x \sin k_y & \cos k_x \cos k_y
\end{pmatrix},
$$

$$
\mathcal{H}^{AB}(\mathbf{k}) = [t_1' + 2t_2'(\cos k_x + \cos k_y) + t_2'e^{i k_z}] I.
$$

For this set of parameters: $t_1^A = -t_1^B = 1$, $t_1^A = -t_1^B = 0.5$, $t_1' = 2.5$, $t_2' = 0.5$, $t_2' = 2$ the calculated band structure is shown in Fig 2.5a. As long as the energy gap does not close, the system remains in the same topological class within a finite parameter range. Solving $\mathcal{H}$ in a slab geometry reveals that the existence of surface states crucially

Figure 2.5: (a) Bulk band structure of the tight binding model along high symmetry lines. (b) Surface states with quadratic band touching exist on (001) face [3].
depends on the surface termination. In Fig 2.5b, the (001) surface which preserves $C_4$ symmetry exhibits the surface states (red lines). These surface states which are doubly degenerated at $\bar{M} = (\pi, \pi)$, one in $p_x$ orbital and the other one in $p_y$ orbital, transverse the whole energy gap leading to a 2D surface metal. The $p_x$ and $p_y$ orbitals of the doublet can be represented as pseudospin $\sigma = \pm 1$. In such a basis, $C_4$ rotation is expressed as $e^{i\pi y/4}$ and time-reversal operator for spinless fermions is a complex conjugation.

To study band dispersion near $\bar{M}$ one can consider the $k.p$ form of Hamiltonian which is dictated by symmetry

$$H(k_x, k_y) = \frac{k_x^2}{2m_0} + \frac{k^2 - k_y^2}{2m_1} \sigma_z + \frac{k_x k_y}{2m_2} \sigma_x. \quad (2.86)$$

Perturbations that can open up an energy gap and destroy the protected surface states in this model are either $C_4$ breaking terms or time-reversal breaking terms. This can be explicitly seen by adding respectively $M_1 k_x \sigma_y + M_2 \sigma_z$ or $M_1 \sigma_y$ to the Hamiltonian. Indeed, the preservation of the time-reversal symmetry together with $C_4$ symmetry is the guarantee that the shown surface states are topologically protected [3].

### 2.3.1 SnTe class of materials

The entity of TCI was proposed for a hypothetical material with $C_4$ or $C_6$ crystal point group symmetry which supports the expected surface states [3]. Afterwards, SnTe with the intrinsic inverted band gap became the first experimentally proven TCI prototype, in which the surface states are protected by its mirror plane symmetry [6]. SnTe is a simple rock salt structure, whose fundamental band gaps are located at four $L$ points of the FCC BZ. It has been long discovered that these gaps are inverted, but since these inversions occur at an even number of points, SnTe cannot be regarded as the TI. However, due to the mirror symmetry of this crystal, it is a good candidate for being TCI.

Consider the $\Gamma L_1 L_2$ plane, which is denoted by $\Gamma$, $L_1$ and $L_2$ in the FCC BZ of SnTe (Fig 2.6). Crystal momenta on this plane are invariant under the reflection about [110] mirror plane in the real space. This allows one to label the Bloch wave functions on this plane by their eigenvalues $\pm i$ under the mirror operation $M^1$. Each class of $M = \pm i$

\footnote{Mirror operator satisfies $M^2 = -1$ for spin 1/2 electrons.}
mirror eigenvalues has an associated Chern number $n_{\pm i}$, and the mirror Chern number is defined by $n_M = (n_{+i} - n_{-i})/2$ [33]. Provided that mirror symmetry is present, $n_M$ is an integer topological invariant. A non-zero mirror Chern number characterizes a TCI with mirror symmetry. To establish the TCI phase of SnTe, it is relevant to find the difference of its mirror Chern number from that of a reference material which is a trivial insulator, for instance PbTe. Indeed the mirror Chern number of SnTe should vary by two from PbTe one, if it is truly a TCI. This will be proven by considering the band inversion between them, which is captured by k.p theory at the L point

$$\mathcal{H} = m \sigma_z + v (k_1 s_2 - k_2 s_1) \sigma_x + v_3 k_3 \sigma_y,$$  \hspace{1cm} (2.87)

where $k_1$, $k_2$ and $k_3$ form an orthogonal system with $k_3$ along $\Gamma - L$ and $k_1$ along (110), $\sigma_z = \pm 1$ corresponds to p-orbital on the cation (Pb or Sn) and anion (Te) respectively, and $s_3 = \pm 1$ labels the total angular momentum projection $j_z = \pm 1/2$ along $\Gamma - L$ [34]. A positive m means the conduction and valence bands at L are derived from the cation and anion respectively, and vice versa for negative m. Here, in particular, reflection about the [110] mirror plane is represented by $M = -is_1$. The Hamiltonian in Eq. 2.87 reduces to $H_0 = m \sigma_z - v k_2 s_1 \sigma_x + v_3 k_3 \sigma_y$, on the mirror invariant plane $\Gamma L_1 L_2$ ($k = 0$). Due to mirror symmetry, $H_0$ can be decomposed into the $s_1 = 1$ ($M = -i$) and $s_1 = -1$ ($M = i$) subspaces

$$\mathcal{H}^\pm_0 = m \sigma_z \mp v k_2 \sigma_x + v_3 k_3 \sigma_y,$$ \hspace{1cm} (2.88)

each of which describes a 2D massive Dirac fermions.

By changing the composition in Pb$_{1-x}$Sn$_x$Te, the valence and conduction bands will be switched at L point that is compatible to $m \rightarrow -m$ in the k.p theory. Reversing the
Figure 2.7: The band structure of (a) SnTe and (b) PbTe. Highlighted area mathematically signifies the intrinsic band inversion of SnTe [6].

The non-zero $n_M$ in SnTe dictates the existence of surface states on any crystal surface which is symmetric about the \{1\bar{1}0\} mirror planes.
A common surface termination satisfying this condition is [001]. For this surface, the plane ΓL₁L₂ in the bulk BZ projected onto the symmetry line \(\bar{\Gamma} - \bar{X}_1\) in the surface BZ, with both \(L_1\) and \(L_2\) projecting onto \(\bar{X}_1\). \(|n_M| = 2\) indicates that there must be two pairs of counter-propagating chiral surface states with opposite mirror eigenvalues along \(\bar{X}_1 - \bar{\Gamma} - \bar{X}_1\) line. By rotational symmetry, such surface modes also appear along \(\bar{X}_2 - \bar{\Gamma} - \bar{X}_2\). But they are absent along any other mirror-invariant line. As the crossing of two mirror branches creates a Dirac point, the [001] surface states have four Dirac points on the four equivalent \(\bar{\Gamma} - \bar{X}\) (Fig. 2.8).

Similar prediction can be applied to the [111] surface, where the \(\Gamma L_1L_2\) plane projects onto the high symmetry line \(\bar{\Gamma} - \bar{M}\). Accordingly, two surface modes must exist along three equivalent lines \(\bar{M} - \bar{\Gamma} - \bar{M}\).

To conclude it should be emphasized that, unlike TIs, here the Dirac points are located at an even number of non-time-reversal invariant momenta and are protected by the mirror plane symmetry [6].

**Figure 2.8:** The predicted (001) surface states of SnTe: (a) band dispersion and (b) Fermi surface. Between \(\bar{\Gamma}\) and \(\bar{X}\) two surface bands with opposite mirror eigenvalues cross the Fermi energy, is consistent with \(|n_M| = 2\) [6].
3 Methodology

Arguably, there are various methods to calculate electronic states in crystals, depending upon their structures and how the electrons are bound to the nuclei. In this essence, systems can be approached by many extreme ways, from the nearly free electron approximation to the tight binding one, that intuitively are corresponding to the more itinerant and localized electrons respectively. To this end, the tight binding model proved to be a reliable method that provides a reasonable description of occupied states in many type of crystals (e.g., semiconductors and insulators), and often also of the lowest lying conduction states [35]. In the following section, a brief scrutiny of the tight binding method, as the most prominent tool for determining properties of studied materials, will be presented. Afterwards, DFT methods which were particularly utilized to find SnSe band structure, will be explained.

3.1 Tight binding method

The tight binding method, suggested by Bloch in 1928, is the approach to calculate electronic band structure based on the simple assumption that electrons in the crystals are tightly bound to the atom to which they belong and have limited interaction with states and potentials on surrounding atoms of the solid. Thus the wave function of the electron will be rather similar to its atomic orbital, and as a result the total wave function can be expressed by a linear combination of the atomic orbitals (LCAO). Therefore, if $\varphi_i(\mathbf{r})$ indicates an atomic orbital of quantum numbers $i$ and energy $E_i$ of an atom centred in the reference unit cell, and $\varphi_i(\mathbf{r} - \mathbf{R}_m)$ the same orbital of the atom
3.1 Tight binding method

in the unit cell \( R_m \), the Bloch sum of \( k \) wave vector can be written as

\[
\phi_i(k, r) = \frac{1}{\sqrt{N}} \sum_{R_m} \exp(i k \cdot R_m) \varphi_i(r - R_m),
\]

(3.1)

where \( N \) is the number of unit cells of the crystal. In a solid, eigenfunctions \( \psi_i(k, r) \) are defined as a linear recombination of Bloch functions

\[
\psi(k, r) = \sum_i c_i(k) \phi_i(k, r)
\]

(3.2)

where the coefficients \( c_i(k) \) are to be determined by standard variational methods. The eigenvalues of the system described by the Hamiltonian \( H = \frac{\hbar^2}{2m} + V(r) \) are given by

\[
E(k) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\int \psi^*(k, r) H \psi(k, r) \, dr}{\int \psi^*(k, r) \psi(k, r) \, dr}
\]

(3.3)

Substituting Eq. 3.2 in the latter leads to

\[
E(k) = \frac{\sum_{ij} c^*_i c_j \langle \psi_i | H | \psi_j \rangle}{\sum_{ij} c^*_i c_j \langle \psi_i | \psi_j \rangle} = \frac{\sum_{ij} \mathcal{H}_{ij}(k) c^*_i c_j}{\sum_{ij} \mathcal{S}_{ij}(k) c^*_i c_j}
\]

(3.4)

in which \( \mathcal{H}_{ij}(k) \) and \( \mathcal{S}_{ij}(k) \) are transfer and overlap matrices and are defined by

\[
\mathcal{H}_{ij}(k) = \langle \phi_i | H | \phi_j \rangle,
\]

(3.5a)

\[
\mathcal{S}_{ij}(k) = \langle \phi_i | \phi_j \rangle.
\]

(3.5b)

For a given \( k \) value, the coefficient \( c_i^*(k) \) is optimized so as to minimize \( E(k) \)

\[
\frac{\partial E(k)}{\partial c_i^*(k)} = 0
\]

(3.6)

that can be readily simplified as

\[
\sum_j \mathcal{H}_{ij}(k) c_j(k) - E(k) \sum_j \mathcal{S}_{ij}(k) c_j(k) = 0.
\]

(3.7)

Putting in the matrix form will proceed

\[
[[H] - E(k)[S]]c_j(k) = 0.
\]

(3.8)
If the matrix \([\mathcal{H}] - E(k)[\mathcal{S}]\) has an inverse, the vector \(\{c_j(k)\}\) will be identically zero and this gives rise to the trivial solution. Hence, non-trivial solutions require

\[
\left| [\mathcal{H}] - E(k)[\mathcal{S}] \right| = 0. \tag{3.9}
\]

This equation is called the secular equation, whose eigenvalues \(E(k)\) give the energy band structure \([36]\).

To unravel sophistications, for atomic-like functions one can use the Wanier functions which are orthonormal and their overlap on different atoms are negligible. Thus, the overlap matrix \(\delta_{ij}(k)\) in Eq. 3.5b is now the unitary matrix \(\delta_{ij}\) and Eq. 3.5a is

\[
\mathcal{H}_{ij}(k) = \frac{1}{N} \sum_{R_m,R_n} \exp(ik.(R_n - R_m)) \langle \phi_i(r - R_m)|H|\phi_j(r - R_n) \rangle, \tag{3.10}
\]

because of translational invariance of \(H\), in the expression above, \(R_m\) can be chosen as zero. By dropping the sum over \(R_m\) and the factor \(1/N\), then it can be rewritten as

\[
\mathcal{H}_{ij}(k) = \sum_{R_n} \exp(ik.R_n) \langle \phi_i(r)|H|\phi_j(r - R_n) \rangle. \tag{3.11}
\]

For such evaluations, it is convenient to express the crystal potential as the sum of spherically symmetric atomic-like potentials \(V_a(r - R_n)\), centred at the lattice positions. Therefore, by substituting the approximated crystal Hamiltonian in the form,

\[
H = \frac{p^2}{2m} + \sum_{R_n} V_a(r - R_n) \tag{3.12}
\]

in the Eq. 3.11,

\[
\mathcal{H}_{ij}(k) = \sum_{R_n} \exp(ik.R_n) \int \phi_i^*(r) \left[ \frac{p^2}{2m} + V_a(r) + V'(r) \right] \phi_j(r - R_n) dr, \tag{3.13}
\]

where \(dr\) is the volume element in the direct space, and \(V'(r)\) denotes the sum of all the atomic potentials of the crystal, except the contribution \(V_a(r)\) of the atom at the origin. Based on the premises of orthogonality of the Wanier functions, and regarding \(\phi_i(r)\) as eigenfunction of the atomic Hamiltonian with energy \(E_i\), Eq. 3.13 will be shortened to

\[
\mathcal{H}_{ij}(k) = E_i \delta_{ij} + \sum_{R_n} \exp(ik.R_n) \int \phi_i^*(r)V'(r)\phi_j(r - R_n) dr. \tag{3.14}
\]
3.1 Tight binding method

The tight binding parameters

<table>
<thead>
<tr>
<th></th>
<th>SnTe</th>
<th>PbTe</th>
<th>PbSe</th>
<th></th>
<th>SnTe</th>
<th>PbTe</th>
<th>PbSe</th>
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<tr>
<td>$E_{s_i}$</td>
<td>-6.578</td>
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<td>-7.010</td>
<td>$V_{p,s}$</td>
<td>-0.198</td>
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</tr>
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<td>7.73</td>
<td>8.72</td>
<td>$V_{p,d}$</td>
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<td>7.73</td>
<td>11.95</td>
<td>$V_{d,p}$</td>
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<td>-1.59</td>
<td>-1.09</td>
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<td>$\lambda_c$</td>
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<td>1.693</td>
<td>$V_{d,p}$</td>
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Table 3.1: The nearest neighbour tight binding parameters of SnTe, PbTe, PbSe in [eV], based on Ref. [37]

If $\mathbf{R}_n = 0$ the second term in Eq. 3.14 becomes a constant diagonal matrix, which produces a rigid shift of the whole band structure but does not influence on the dispersion curves, whereas $\mathbf{R}_n \neq 0$ indicates the interactions between neighbours. Once again invoking the localized nature of the Wanier functions, the sum in the Eq. 3.14 can be limited to a small number of neighbours, commonly up to the nearest neighbour contributions (two-center approximation). The integrals involving further neighbours are negligible.

The two-center integrals can be expressed in terms of independent parameters called overlap parameters, whose magnitudes are determined by how they are bound together. They are evaluated either analytically, or numerically, or semi-empirically. Table 3.1 shows sets of tight binding parameters for SnTe, PbTe and PbSe, which are taken from literature and will be used in Chapter 4. The independent integrals are labelled as $V_{s,s}$, etc. The convention for the notation is that $s,p$ or $d$ specify the angular momentum of the orbitals while $\sigma, \pi$ and $\delta$ denote that the angular part with respect to the axis of quantization (along the two-centres) is characterized by $\exp(im\varphi)$ with $m = 0, \pm 1, \pm 2, \ldots$.
3. Methodology

3.2 Density functional theory

In solid state physics, density functional theory (DFT) is one of the widely utilized methods to investigate electronic structures, in particular ground state of many-electron systems, by using functionals\(^1\). In this theory, the emphasize is narrowed down from the ground state wave function \(\psi(r_1, r_2, \ldots, r_N)\) to the more manageable ground state of one-body-electron density \(\rho(r)\), i.e., spatially dependent one-electron density, instead of dealing directly with all electrons. Principally, DFT shows that the ground state of a many-particle system can be expressed as a functional of one-body density, whose minimization will determine the actual ground state density and energy. The success of this theory is to provide a reasonable approximation of the functional to be minimized.

3.2.1 Hohenberg-Kohn theorem and Kohn-Sham equation

The DFT was put on a firm theoretical footing by the Hohenberg-Kohn theorem\(^3\). This theorem originally held only for non-degenerate ground states in the absence of a magnetic field, although newer versions encompass these.

Consider a system of \(N\) electrons, described by the standard many-electron Hamiltonian \(H\), which can be decomposed into the sum of an internal and external part,

\[
H = H_{\text{int}} + V_{\text{ext}}
\]

where

\[
H_{\text{int}} = T + V_{\text{ee}} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|r_i - r_j|}
\]

and

\[
V_{\text{ext}} = \sum_i v_{\text{ext}}(r_i), \quad v_{\text{ext}}(r) \equiv v_{\text{nuc}} = -\sum_i \frac{z_i e^2}{|r - R_i|}.
\]

Clearly, \(H_{\text{int}}\) is identical for all electronic systems, since the mass of electrons, their charge, their number \(N\) and the form of interactions are supposed to be fixed. They differ only in the matter of external potential \(v_{\text{ext}}(r)\). Thus the ground state \(\psi(r_1, r_2, \ldots, r_N)\) and the ground state energy depend upon the chosen external potential \(v_{\text{ext}}(r)\),

\[
H[\psi[v_{\text{ext}}]] = E[v_{\text{ext}}] \langle \psi[v_{\text{ext}}] | \psi[v_{\text{ext}}] \rangle.
\]

\(^1\)Function of another function
3.2 Density functional theory

As the theorem states, there is a one-to-one correspondence between ground state density of the N electron system and the external potential acting on it,

\[ v_{\text{ext}}(r) \leftrightarrow \rho(r), \] (3.19)

one can deduce uniquely the external potential (to within a non-essential additive constant) from the knowledge of the ground state density, and vice versa. Therefore, the ground state energy functional becomes

\[ E_{\text{HK}}[\rho] = \langle \psi[\rho]|T + V_{\text{ee}} + V_{\text{ext}}|\psi[\rho]\rangle \] (3.20)

\[ = \langle \psi[\rho]|T + V_{\text{ee}}|\psi[\rho]\rangle + \int v_{\text{ext}}(r)\rho(r)\,dr, \] (3.21)

with \( F_{\text{HK}}[\rho] = \langle \psi[\rho]|T + V_{\text{ee}}|\psi[\rho]\rangle \), is the universal Hohenberg-Kohn functional. It is universal in the sense that the \( F_{\text{HK}} \) does not include the system dependence external potential. Eq. 3.21 is minimal at the ground state energy, or in other words, the exact ground state energy of many body electron system is given by minimization of Eq. 3.21 with respect to \( \rho(r) \), which is called the Kohn-Sham equation.

To carry out explicitly the variational procedure, the ground state density \( \rho(r) \) of an interacting electron system can be decomposed the sum of N independent orbital contributions of the form

\[ \rho(r) = \sum_i \phi_i^*(r)\phi_i(r), \] (3.22)

where \( \{\phi_i(r)\} (i = 1, 2, \ldots, N) \) are orthonormal orbitals. For convenience Eq. 3.21 can be rewritten as the sum of non-interacting and interacting terms

\[ E_{\text{HK}}[\rho] = T[\rho] + V_H[\rho] + \int v_{\text{ext}}(r)\rho(r)\,dr + E_{\text{xc}}[\rho] \] (3.23)

where

\[ T[\rho] = \sum_i \langle \phi_i(r)|-\frac{\hbar^2}{2m}\frac{\nabla^2}{2m}|\phi_i(r)\rangle \] (3.24)

is the non-interacting kinetic energy,

\[ V_H[\rho] = \frac{1}{2} \int \rho(r)\frac{e^2}{|r - r'|}\rho(r')\,dr\,dr' \equiv \frac{1}{2} \sum_{ij} \langle \phi_i|\phi_j|\frac{e^2}{r_{ij}^2}|\phi_i\phi_j\rangle \] (3.25)

is the inter-electron Coulomb interaction (Hartree potential), and \( E_{\text{xc}}[\rho] \) is the exchange-correlation function defined as

\[ E_{\text{xc}}[\rho] = T[\rho] - T[\rho] + V_{\text{ee}}[\rho] - V_H[\rho]. \] (3.26)
3. Methodology

The function Eq. 3.23 can be recast in the form

\[
E_{HK}[\rho] = \sum_i \langle \phi_i(r) - \frac{\hbar^2 V^2}{2m} + v_{\text{excl}} \phi_i(r) \rangle + \frac{1}{2} \sum_{ij} \langle \phi_i \phi_j \rangle \frac{e^2}{r_{ij}^2} \phi_i \phi_j \rangle + E_{xc}[\rho].
\]  (3.27)

According to the standard variational procedure, the \(N\) contributing orbitals \(\phi_1, \phi_2, \ldots, \phi_N\) can be varied so to make stationary the energy functional Eq. 3.27, under the constraint of orthonormalization of the wave function \(\{|\phi_i\rangle\}\). A straightforward variational calculation of the functional Eq. 3.27 leads to the Kohn-Sham equations

\[
-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{nucl}}(r) + V_{\text{coul}}(r) + V_{xc}(r) \phi_i(r) = \varepsilon_i \phi_i(r),
\]  (3.28)

where \(V_{\text{nucl}}(r)\) is the external potential, \(V_{\text{coul}}(r)\) is the Hartree potential and \(V_{xc}(r)\) is a functional derivation of \(E_{xc}[\rho]\) which can be found as follows,

\[
\delta E_{xc}[\rho] = \int V_{xc}(r) \delta \rho(r) dr = \int V_{xc}(r) \delta \sum_i \phi_i'(r) \phi_i(r) dr,
\]  (3.29)

\[
V_{xc}(r) \equiv \frac{\delta E_{xc}[\rho]}{\delta \rho(r)}.
\]  (3.30)

Once the Kohn-Sham orbitals and energies have been established, the exact total ground state energy Eq. 3.27 of the electronic system can be expressed as:

\[
E_0 = \sum_i \varepsilon_i - \frac{1}{2} \sum_{ij} \langle \phi_i \phi_j \rangle \frac{e^2}{r_{ij}^2} \phi_i \phi_j \rangle + E_{xc}[\rho] - \int V_{xc}(r) \rho(r) dr.
\]  (3.31)

Despite the remarkable achievement of the DFT in finding the exact ground state and energy of the electronic systems, there are some limitations that need to be cautiously considered in application. For instance, for a strongly correlated system, where an independent particle picture breaks down, this method is very inaccurate. More importantly, the exact exchange-correlation functionals \(E_{xc}[\rho]\) are not known except for the free electron gas. However, approximations exist which permit the calculation of certain physical quantities quite accurately. Among them, the most popular is the local density approximation (LDA), which is particularly justified in systems with reasonably slowly varying spatial density \(\rho(r)\).

Overall, experience shows that the calculations, performed within one version or another of this method, tend to underestimate the energy band gap in semiconductors and insulators, however, the general trend of dispersion of the valence and conduction bands is often represented to be decently rigorous [35].
Results

4.1 Pb\textsubscript{1−x}Sn\textsubscript{x}Te

IV-VI semiconductors are among the most attractive materials for their broad range of applications. Comprehensive investigations over a long time, at least made many of their salt band structures considered as being established [37]. Pb\textsubscript{1−x}Sn\textsubscript{x}Te, a ternary solid solution of these groups, is a famous narrow-gap semiconductor which has been vastly used in laser devices and was subjected to extensive studies. Apart from this significance, this material can be focalized from the band topology perspective.

In the following section, after outlining basic features of its binary compounds, the expectancy of a topological phase for Pb\textsubscript{1−x}Sn\textsubscript{x}Te will be discussed.

4.1.1 Basic properties of the bulk

Tin telluride (SnTe) is a rock salt structure crystal (Fig. 4.1) with the room-temperature lattice constant $a_0 = 6.327$ Å [39] and space group symmetry Fm\overline{3}m. It belongs to IV-VI narrow-gap semiconductors group with $E_g \approx 0.33$ eV [40]. It is one of the earliest known

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**Figure 4.1:** Red balls represent Sn/Pb and gray balls represent Te; halite crystal structure of SnTe and PbTe
inverted band gap materials which is discovered more than half a century ago [41]. Its fundamental band gaps are located at four equivalent valleys in the face-centred cubic (FCC) Brillouin zone, where the valence band is an $L^{-}_6$ and the conduction band is an $L^{+}_6$ state. To survey the semiconducting properties of SnTe, its band structure is primarily required. Here the band structure is calculated (Fig. 4.2a) with the tight binding method, including interactions of the nearest neighbours, consist of 18 orbitals of s, p$^3$ and d$^5$ with spin degrees of freedom. The set of parameters, which gives the energy gap value consistent with experiment and proves its proper dependence on solid solutions, is taken from the literature [37] (Table 3.1).

Likewise SnTe, lead telluride (PbTe) is a rock salt crystal structure (Fig. 4.1) with space group symmetry Fm$\overline{3}$m and a slightly different room-temperature lattice constant $a_0 = 6.464$ Å [42]. It is also one of the very well-known IV-VI narrow-gap semiconductors with $\varepsilon_g \approx 0.19$ eV [43]. It is often alloyed with Sn, based on its variety of applications e.g., in photovoltaic and thermoelectric devices.

Despite similar band structure of PbTe (Fig. 4.2b) and SnTe (Fig. 4.2a) in which the band gaps are located at L points, their orderings are the opposite of each other. In PbTe the valence band is an $L^{+}_6$ state and conduction band is an $L^{-}_6$, whereas as it mentioned, in the case of SnTe they are reversed.

Since both PbTe and SnTe are crystallized in cubic structure, practically their solid solutions can be easily obtained. However there is a minor difference in their lattice constants, that can be solved by implementing the virtual crystal approximation (VCA). With this approach, on each potentially distorted cation site there is a virtual atom that interpolates between the behaviour of the actual compounds. Hence the local distortion in the system can be ignored.

Thereby, finding hopping integrals for the tight binding Hamiltonian of the mixed crystal Pb$_{1-x}$Sn$_x$Te is straightforward. They can be directly determined by product of each compounds contribution $x$, that varies from 0 to 1, corresponds to changing from pure PbTe to pure SnTe receptively. Schematic diagram in Fig. 4.3 illustrates the linearity of the mixed crystal energy gap versus composition ($x$), and shows the exact composition ($x_c = 0.38$) where the band gap is closed. In Pb$_{1-x}$Sn$_x$Te alloy sample, with increasing Sn content the energy gap initially decreases, as $L^{+}_6$ and $L^{-}_6$ states approach each other, then at an intermediate composition $x = x_c$ closes (here two states become degenerate), and finally at $x > x_c$ reopens, with the $L^{+}_6$ state now forming the conduction
4.1 Pb$_{1-x}$Sn$_x$Te

**Figure 4.2:** Bulk energy band structure of (a) SnTe and (b) PbTe throughout high symmetrical points in the Brillouin zone.

band and L$^{-}_6$ state forming the valence band [44]. Transformation of the Pb$_{1-x}$Sn$_x$Te energy gap from normal (PbTe) to the inverted one (SnTe) with developing composition can qualitatively be expounded in terms of the difference between the relativistic effect in Pb and Sn, which is an extremely significant correction in determining the position
4. Results

Figure 4.3: Red line; schematic representation of the valence and conduction bands for Pb$_{1-x}$Sn$_x$Te and its constituent compounds

of energy bands. Such a relativistic correction can be referred to the spin-orbit coupling and the Darwin term [23].

The major aftermath of SnTe’s band gap being inverted relative to that of PbTe, is that they have different band topologies, or in another word, their band gaps cannot smoothly convert to each other unless one is closed and reopened again. Notwithstanding their distinct topology, neither of them is a topological insulator. It is because the band inversion occurs at four equivalent valleys and number of the surface states is even. Therefore, according to topological classifications based on the time-reversal symmetry, both PbTe and SnTe are regarded as trivial insulators [29, 45].

However as it is explained previously [§. 2.3], in some non-time-reversal invariant class of materials, robust surface states exist which are protected and crucially depended upon their particular crystal symmetries. According to what has been predicted [6] and discussed (§. 2.3.1), the band topology distinction of SnTe characterises this material as a topological crystalline insulator type, as its surface states are supported by the mirror plane symmetry, and not by the time-reversal one. Due this, its substitutional solid solutions with PbTe, Pb$_{1-x}$Sn$_x$Te, ought to be TCI provided that x is high enough to have the band gap order dominated by Sn content.

In the following section appearing of (001) surface states in the course of composition evolution for Pb$_{1-x}$SnSe will be analysed.
4.1 Pb\textsubscript{1-x}Sn\textsubscript{x}Te

4.1.2 Trivial to topological crystalline insulator phase transition

Clarifying a detached topology of PbTe and SnTe, and the sketch of closing and reopening the energy gap by developing the composition, are the hints to a plausible phase transition. Each thermodynamic phase transition follows by drastic changes in an order parameter, which is varying from zero to non-zero values throughout the transition process. Analogously, observing the metallic surface or edge states for an insulator is a credible criterion to perceive that insulator is a topological one. Here for the purpose of illustrating the topological phase transition, (001) surface is considered to be examined. Nonetheless, it is not impossible to carry out the same consideration for other crystallographic directions, as will be described soon after. Based on Fig. 4.3 diagram, after a critical composition the band gap is inverted, therefore, in order to prove that a topological phase transition occurs in the system, the absence and existence of the Dirac-like surface states for \( x < x_c \) and \( x > x_c \) must be upheld.

![Figure 4.4: The Brillouine zone of FCC structure projected onto (001) surface (2D BZ), is represented by the green plane. The [110] mirror planes are highlighted in yellow, and mirror plane symmetry lines mapped on 2D BZ in black lines through \( \bar{X} - \Gamma - \bar{X} \).](image)

The first Brillouine zone of FCC structure of Pb\textsubscript{1-x}Sn\textsubscript{x}Te, a truncated octahedron with six square faces and eight hexagonal faces, is shown in Fig. 4.4. As it was mentioned before the Pb\textsubscript{1-x}Sn\textsubscript{x}Te band gap is simultaneously located at four L points in BZ, which are at the center of eight hexagonal faces. Each L points and their diametrically opposite partners of BZ are completely equivalent. Hence there are four distinct L
point momentas, whose projections onto (001) two-dimensional BZ (green plane) are indicated by $\bar{X}$. The other points in this 2D BZ, $\bar{M}$ and $\bar{\Gamma}$ correspond to the projection of $X$ and $\Gamma$ respectively.

**Figure 4.5:** Generic view of a miniature (001) slab unit cell; red balls stand for cation (Pb/Sn) and gray balls for anion (Te).

The tight binding calculated band structures throughout 2D BZ, of a 280 monolayers ($\sim 90$ nm) (001)-oriented slab, for a low-to-high range of compositions are presented in Fig. 4.6. The slab geometry with periodic boundary conditions imposed in two directions parallel to its surfaces, is utilized to minimize the interaction between surfaces. Miniature structure of such a slab along (001) direction is shown in Fig. 4.5. The energies are calculated versus k-values along $\bar{\Gamma} - \bar{X} - \bar{M}$, in which k is the wave vector of electron given in the $2\pi/a_0$ scale, with $a_0$ is the rock salt lattice constant. Yellow and blue color lines stand for the cation and anion p-type orbitals dominant contribution to the state’s wave function.

In Fig. 4.6a $x = 0.2$, as $x < x_c$ noticeably there is no surface state connecting the valence and conduction bands, and the open gap indicates the trivial insulator phase. At the critical composition $x = x_c = 0.38$, Fig. 4.6b, the band gap must supposedly be closed, but it is slightly open. This can be referred to the finite thickness of the slab, that causes minor interaction between surfaces and consequently opens the energy gap. This effect is highly suppressed with increasing the slab thickness, i.e., for a 160 nm slab the gap is likely to be less than $10^{-2}$eV. Above the critical composition $x = 0.6$, Fig. 4.6c, due to domination of Sn content, the band gap is inverted, and thus the protected gapless surface states exist along $\Gamma - \bar{X}$ line, where is the projection of the mirror symmetry plane. Whereas along the $\bar{X} - \bar{M}$, there is no protected surface state, since no mirror plane symmetry is projected. Clearly the Dirac point is situated not in the $\bar{X}$ point but is moved toward $\bar{\Gamma}$ in the projected $\{110\}$ mirror planes. The reason is the interaction between L valleys, those that are projected in pairs on the $\bar{X}$. They repel each other, and ultimately shift the Dirac point along $\bar{\Gamma} - \bar{X}$.
Figure 4.6: The band structure of a 280 monolayers (~ 90 nm) (001)-oriented slab of Pb$_{1-x}$Sn$_x$Te for different compositions; (a) $x = 0.2$ trivial insulator, (b) $x = 0.38$ closed bulk band gap, (c) $x = 0.6$ TCI and (d) $x = 1.0$ pure SnTe TCI. Yellow and blue lines respectively represent the cation and anion p-type orbitals dominant contribution to the state’s wave function, which is exchanged for $x > x_c$ due to the inversion of band gap. $k = 0$ corresponds to L points projection (shown in Fig. 4.4). Dense packed lines show the bulk states, whereas surface states are the ones that are significantly separated from bulk states. Appearing of the gapless surface states for $x > x_c$ indicates occurrence of the topological phase transition.
4. Results

Finally $x = 1.0$, Fig. 4.6d, corresponds to the pure SnTe with stronger yet similar properties to Pb$_{0.4}$Sn$_{0.6}$Te (Fig. 4.6c). The appearance of a Dirac crossing along the high symmetric line corroborates with what has been predicted before [6] and current investigations. For this material a recent experiment has been performed which confirms and is in agreement with the phenomena of the topological phase transition versus composition [46].

At last it is worth mentioning, switching the order of band gap from a normal to an inverted one with any other accessible parameters may lead to the similar transition, for instance by changing temperature [5, 47], pressure [48] and the thickness of thin film [49].

4.1.3 Surface states of other crystallographic oriented Pb$_{0.4}$Sn$_{0.6}$Te

Inspired by the fundamental role of crystal symmetry in TCI, which protects surface states, other crystallographic directions with their corresponding symmetries are also attractive to be examined. In the next two following sections the speculation through actuality of TCI state for two other major directions, [110] and [111]-oriented Pb$_{0.4}$Sn$_{0.6}$Te slabs will be scrutinized.

In order to study the Dirac-like surface states, as they occur for well above critical composition ($x > x_c$), hereafter it is considered to be $x = 0.6$ (Pb$_{0.4}$Sn$_{0.6}$Te), which assures the alloy already is in TCI region.

4.1.3.1 [110]

In Fig. 4.7 the Brillouin zone of the FCC structure with the [110] mirror symmetry planes (in yellow), projected onto [110] surface (2D BZ) is shown. The projection of L$_1$ and L$_2$ are represented as $\bar{Y}$ and L$_3$ and L$_4$ are as $\bar{S}$. The calculated band structure of a 315 monolayers (~ 70 nm) Pb$_{0.4}$Sn$_{0.6}$Te for k wave vector along $\bar{\Gamma} - \bar{Y} - \bar{S} - \bar{\Gamma}$ in 2D BZ is presented in Fig. 4.9. Fig. 4.9b and Fig. 4.9c correspond to the more precise calculations performed for a thicker slab, 365 monolayers (~ 80 nm) in the vicinity of $\bar{Y}$ and $\bar{S}$ points respectively.

It can be clearly observed around $\bar{Y}$ (along $\bar{\Gamma} - \bar{Y}$) the surface states cross the band gap, likewise that of (001) surface around $\bar{X}$ point. This is due to the same fact that L$_1$ and L$_2$ which are doubly projected onto $\bar{Y}$ point, are located on (110) mirror plane of the
Figure 4.7: The Brillouin zone of (110)-oriented rock salt crystal with corresponding 2D BZ shown in green. The [110] mirror planes are highlighted in yellow.

(110) surface (Fig. 4.7). Therefore, as it is anticipated, there ought to be a topologically protected Dirac point along this symmetry line.

In the vicinity of \( \bar{S} \) however, there is no Dirac point, since there is no symmetry line neither along \( \bar{Y} - \bar{S} \) nor \( \bar{S} - \bar{\Gamma} \), or in another words \( L_3 \) and \( L_4 \) are not situated on \( \bar{(110)} \) plane. Fig. 4.9c shows a close-up calculated band structure for a thicker slab. Using the thick enough slab proves that the gapped states around \( \bar{S} \) are undoubtedly the result of lack of symmetry and not the interaction of surfaces.

And yet similar to the (001) scenario, the Dirac point is not exactly in the point where \( L \) valleys are projected, instead it is shifted (here along \( \bar{Y} - \bar{\Gamma} \)), which is based on the interaction between pair of \( L_1 \) and \( L_2 \) that are projected on the same point.

Figure 4.8: Generic view of a miniature (110) slab unit cell; red balls stand for cation (Pb/Sn) and gray balls for anion (Te).
4. Results

Figure 4.9: (a) The calculated band structure of a 315 monolayers (110)-oriented Pb$_{0.4}$Sn$_{0.6}$Te slab. The zoomed view in the vicinity of (b) $\bar{Y}$ and (c) $\bar{S}$ points of 2D BZ have been obtained for a thicker Pb$_{0.4}$Sn$_{0.6}$Te slab (356 monolayers).
4.1.3.2 [111]

Unlike two previous cases, namely [001] and [110] directions, each layer of [111]-oriented slab unit cell consists of only one single atom (Fig. 4.11). Therefore, for this direction the crystal surfaces are exclusively composed of either anions or cations. As a result, there are two distinct types of slabs where their surfaces confront anion-anion or cation-cation interactions, provided that the number of layers is odd. However, since here the slabs are thick enough, an even or odd number of layers does not make a very pronounced difference. In this section, the band structure of anion-terminated and cation-terminated cases will be discussed, and the study of an even number of layers [111]-oriented films, in particular, is postponed to the latter sections.

Figure 4.10: The Brillouin zone of (111)-oriented rock salt crystal with corresponding 2D BZ shown in green. The [110] mirror planes are highlighted in yellow.

Figure 4.11: Generic view of a miniature (111) slab unit cell; red balls stand for cation (Pb/Sn) and gray balls for anion (Te).
Figure 4.12: (a) The calculated band structure of a 451 monolayers, anion-terminated (111)-oriented Pb$_{0.4}$Sn$_{0.6}$Te slab, for the $k$ wave vectors of the 2D BZ along the $\bar{K} - \bar{\Gamma} - \bar{M} - \bar{K}$ pass. The zoomed view in the vicinity of $\bar{\Gamma}$ and $\bar{M}$ are shown in (b) and (c) respectively. (The blue to yellow color coding indicates the contributions of the cation (yellow) and anion (blue) p-orbitals)
Figure 4.13: (a) The calculated band structure of a 451 monolayers, cation-terminated (111)-oriented $\text{Pb}_{0.4}\text{Sn}_{0.6}\text{Te}$ slab, for the $k$ wave vectors of the 2D BZ along the $\overline{K} - \Gamma - \overline{M} - \overline{K}$ pass. The zoomed view in the vicinity of $\Gamma$ and $M$ are shown in (b) and (c) respectively. (The blue to yellow color coding indicates the contributions of the cation (yellow) and anion (blue) p-orbitals)
4. Results

As it is depicted in Fig. 4.10 there are four non-equivalent L points located in three mirror planes, whose projection onto 2D BZ are \( \bar{\Gamma}, \bar{M}_1, \bar{M}_2 \) and \( \bar{M}_3 \) where four single topologically protected Dirac cones are anticipated. Fig. 4.12 and Fig. 4.13 show the calculated band structures along \( \bar{K} - \bar{\Gamma} - \bar{M} - \bar{K} \), presenting one pair of Dirac cones, for a 451 monolayers anion-terminated and cation-terminated slabs respectively. Fig. 4.12b, Fig. 4.12c and Fig. 4.13b, Fig. 4.13c correspond to the more precise calculations to enlarge the crossing regions around \( \bar{\Gamma} \) and \( \bar{M} \) points for anion-terminated and cation-terminated cases.

The Dirac points for (111) cation surface states appear in the energy gap close to the top of the valence band, whereas for the anion surface states the Dirac points are situated just below the the conduction band. It can be roughly understood from the higher contribution of anion or cation orbitals of surface states.

Essentially it should be pointed out that here, in contrast to the (001) and (110) surfaces, all the Dirac points are well separated and placed exactly at the commensurate projection of single L points. Moreover, as shown in Fig. 4.10, for the (111) surface all L points belong to the three \( \{110\} \) mirror planes of the (111) surface and, thus, all Dirac points should be topologically protected.

At this point it is worth mentioning that in this study the polarity of the cation-terminated and anion-terminated surfaces is not taken into account. The extra confinement related to the charges on the surfaces can lead to additional Rashba splittings, as shown for instance, for Bi\(_2\)Se\(_3\) in Ref. [50].

4.1.4 Spin textures

It has been quite well-known that for Pb\(_{1-x}\)Sn\(_x\)Te, electron states at the high symmetry L points are not the eigenstates of spin but of the total angular momentum projection \( j_z = \pm 1/2 \) operator. Thus, neither the surface states in the vicinity of L point projections are the eigenstates of spin. They are composed mostly of the p-orbitals and the spin. Nevertheless these non-degenerate surface states are spin-polarized.

In order to replicate what experimentalists may observe in SRPES\(^1\) measurements, only the expectation value of spin components are necessary to be calculated, which has been performed here for (001), (011) and (111)-oriented slabs of Pb\(_{0.4}\)Sn\(_{0.6}\)Te (high

\(^1\)Spin Resolved Photo Emission Spectroscopy
above critical content $x > x_c$). In the following “spin” term stands for a vector defined by these expectation values.

The calculated spin textures of states above and below the Dirac points are presented in Fig. 4.14, Fig. 4.15 and Fig. 4.16 for (001), (011) and (111) directions respectively, where the arrows represent the vectors of the expectation values of in-plane spin components and their length shows the degree of spin-polarization. The blue to yellow color indicates the contributions of the cation (yellow) and anion (blue) p-orbitals to the wave functions, as it is shown by the side bar. These spin-polarized states have chiral spin texture for all of the surfaces.
For energies above the Dirac points of the (001)-oriented surface, and wave vectors $k$ between the Dirac points (inner vortex) the spin rotates counterclockwise about $X$. Outside this region (outer vortex) the rotation is reversed (clockwise). In the local environment of each Dirac point a small left-handed chiral structure is obtained, as predicted in Ref. [6] and observed in the case of Pb$_{0.6}$Sn$_{0.4}$Te [46]. For energies below the Dirac point all the chiralities are reversed as compared to those obtained for the band above the Dirac point. The clockwise (counterclockwise) chirality is related to...
the cation (anion) p-type orbitals. This spin texture leads to the conclusion that the mirror Chern number of Pb$\text{1}_x\text{Sn}_x\text{Te}$ is $|n_M| = 2$ [6, 51].

For (110) surface states the spin pattern around the $\bar{Y}$ projection point has also a multivortical structure (Fig. 4.15a and Fig. 4.15c), similar to that of (001) surface states around the $\bar{X}$ point, in which the rotation in the outer vortex is opposite to that in the inner vortex. Although a multivortical structure is also obtained for (110) surface states around the $\bar{S}$ projection, the spin texture in this case looks much more intricate. Here, instead of two local vortices around the Dirac points, four local vortices along the $\bar{S} – \bar{\Gamma}$ lines are obtained (Fig. 4.15b and Fig. 4.15d). These local vortices are related to the four energy gaps in the surface states.

The spin texture of (111) cation surface states only above the Dirac points and anion surface states only below the Dirac points (upper and lower rows respectively), at $\bar{\Gamma}$ and $\bar{M}$, are presented in Fig. 4.16. For the cation case below the Dirac points the surface states are hybridized with the valence band and similarly for the anion case the surface states above the Dirac points enter the conduction band.

Around $\bar{\Gamma}$ point, for both anion and cation cases there is a single vortex, where spins in the upper and lower Dirac cone rotate clockwise and counterclockwise. It should be emphasized that these chiralities are the same as those predicted in Ref. [52] and observed in the 3D TIs Bi$_2$Se$_3$ and Bi$_2$Te$_3$ [53]. The same chirality was also predicted in the case of the PbTe/Pb$_{1-x}$Sn$_x$Te (111) interface [54].

Around $\bar{M}$ point, resemble the $\bar{\Gamma}$ point, there is a single vortex, in which spins rotate conversely in the upper and lower Dirac cone. However, due to anisotropy of this point, it is stretched and forms an oblong chiral shape.

Eventually, for the (001) surface, it has been shown that, by symmetry, the perpendicular to the surface spin component is equal to zero in the whole Brillouin zone [51]. It is checked here that this is also the case for the (110) surface, where the same symmetry reasons are valid. Thus, in the spin texture calculations for both (001) and (110) surfaces a zero out-of-plane component of the spin has been obtained. In contrast, for the (111) surface the symmetry requires that the spin component normal to the surface equals zero only along the three high-symmetry $\bar{\Gamma} – \bar{M}$ lines. While in the vicinity of the $\bar{\Gamma}$ point, where these lines intersect, the normal spin component vanishes, in the Dirac cones around the $\bar{M}$ points (crossed by only one such line) the out-of-surface spin component appears. The same different behaviour of the out-of-(111)-surface spin
4. Results

Figure 4.16: Contour plots of the constant-energy lines of the (111) surface states of Pb$_{0.4}$Sn$_{0.6}$Te, around the $\bar{\Gamma}$ (a) above and (c) below the Dirac point) and $\bar{M}$ ((b) above and (d) below the Dirac point). In the upper panel the results obtained for the cation-terminated slab are shown, while the lower panel shows the results for the anion-terminated slab.

component at the $\bar{\Gamma}$ and $\bar{M}$ points has been also predicted for the PbTe/Pb$_{1-x}$Sn$_x$Te interface [54]. Moreover, the symmetry requires opposite signs of the components of the spin parallel to the mirror plane for a given $k$ vector and its mirror reflection. Therefore, on the mirror symmetry lines ($\bar{\Gamma} - \bar{X}$ for the (001) surface, $\bar{\Gamma} - \bar{Y}$ and $\bar{Y} - \bar{S}$ for the (110) surface, and $\bar{\Gamma} - \bar{M}$ for the (111) surface) the spins are perpendicular to the appropriate mirror planes.
4.2 Pb$_{1-x}$Sn$_x$Se

Pb$_{1-x}$Sn$_x$Se, is a ternary solid solution of group IV-VI and a narrow-gap semiconductor. Aside from SnTe and its substitutional solid solution Pb$_{1-x}$Sn$_x$Te for $x > x_c$, which are verified to be TCIs and proven to exhibit the Dirac-like helical states on [001] [3, 46],
4. Results

[110] and [111] [55] surfaces, another TCI candidate is Pb$_{1-x}$Sn$_x$Se for high enough content of Sn, where the band gap is inverted [56]. In the following section, this possibility will be theoretically surveyed.

4.2.1 Basic properties of the bulk

Lead selenide (PbSe), is a rock salt crystal structure, with space group symmetry Fm̅3m and the room-temperature lattice constant $a_0 = 6.12$ Å [57]. Like other lead chalcogenides, PbSe is a well-established direct narrow-gap semiconductor with $E_g \approx 0.165$ eV [58].

Tin selenide (SnSe) though, has a distorted lattice and unlike PbSe, naturally crystallizes in the orthorhombic structure with space group symmetry Pnma [59]. It only can be transformed to a rock salt structure at high temperatures [60]. As a result, Pb$_{1-x}$Sn$_x$Se in contrast with Pb$_{1-x}$Sn$_x$Te does not form a complete series of pseudobinary solid solutions. However, it has been reported that the rock salt Pb$_{1-x}$Sn$_x$Se can be obtained within particular compositions $0 \leq x \leq 0.4$ [56], where the energy gap is linearly proportional to the composition $x$.

In order to describe Pb$_{1-x}$Sn$_x$Se within the virtual crystal approximation, the tight binding parameters for its constituent compounds, PbSe and SnSe are needed. Similar to SnTe and PbTe cases, these parameters for PbSe can be taken from the literature [37]. The calculated band structure of PbSe, utilizing the tight binding Hamiltonian including the nearest neighbour interactions and s, p$^3$ and d$^5$ orbitals is shown in Fig. 4.18b.

However, since the pure SnSe is orthorhombic, any set of tight binding parameters for a cubic SnSe is not available and therefore, they are required to be derived. So as to find them, first by using standard ab-initio methods, i.e., DFT-LDA$^1$, a qualitative electronic band structure for such a hypothetical structure is calculated. Afterwards, by applying the simulated annealing method [61], a set of tight binding parameters for SnSe is contrived.

To verify the accuracy of these parameters, its resulting energy gap should be compared with the experimental counterpart. One rational way to estimate the energy gap of rock salt SnSe is a linear extrapolation of the band gap exchange of Pb$_{1-x}$Sn$_x$Se

$^1$Density-Functional Theory with Local-Density Approximation
with Sn content. Accordingly, at T = 4K by knowing $\varepsilon_g = 0.165$ eV for $x = 0$, $\varepsilon_g = 0$ for $x \approx 0.19$ and $\varepsilon_g = -0.129$ eV for $x \approx 0.33$, the “experimental” energy gap for the rock salt SnSe ($x = 1$) can be deduced as $\varepsilon_g = -0.725$ eV (Fig. 4.19). Although, the energy difference between the conduction and valence band in the L point obtained...
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Figure 4.19: Red line; schematic representation of the valence and conduction band for Pb$_{1-x}$Sn$_x$Se and constituent compounds. Extrapolation to pure rock salt SnSe represented with dashed line.

by the DFT-LDA method is equal to $-0.981$ eV, it can be ultimately rescaled to the “experimental” value by an appropriate rescaling of the tight binding parameters. Thus, the commensurate $E_g(x)$ dependence for Pb$_{1-x}$Sn$_x$Se with the energy gap sign change occurring at $x_c = 0.19$, is achieved.

The credible band structure, which is calculated by using the acquired tight binding parameters (Table 4.1), is shown in Fig. 4.18a. The tight binding Hamiltonian of SnSe, akin to that of PbSe, consists of the s, p$^3$, and d$^5$ orbitals and the nearest neighbour interactions.

By the same token that expounded for Pb$_{1-x}$Sn$_x$Te, also Pb$_{1-x}$Sn$_x$Se undergoes a topological phase transition by changing the composition, since SnSe and PbSe belong to different topological classes. Presuming the mixed crystal symmetry remains unchanged, for $x > x_c$, Pb$_{1-x}$Sn$_x$Se can be regarded as TCI. Such a phase transition can be achieved not always by changing composition, but also by other means that can impact the band gap and its order. In the following section, a temperature dependent phase transition for Pb$_{1-x}$Sn$_x$Se will be discussed.

4.2.2 Temperature dependent phase transition

The energy gaps of the studied mixed crystals depend not only on their composition contents, but also depend on the temperature $E_g(x, T)$. A direct energy gap tends to
Table 4.1: The nearest neighbour tight binding parameters of SnSe found by using DFT-LDA calculated band structure (Fig. 4.18a).

decrease as the temperature increased. This can be roughly understood based upon the inter-atomic space expansion when the amplitude of the atomic vibrations increases due to the increased thermal energy, which shields the potential seen by the electrons in the material, and in turn reduces the size of the energy gap. For an inverted energy gap however, this dependence is opposite, since the sign of gap is opposite \[56\].

Comparable to the flipping of the order of Pb\(_{1-x}\)Sn\(_x\)Te energy gap by varying the composition that led to a TCI phase transition, here, the order of Pb\(_{0.73}\)Sn\(_{0.27}\)Se energy gap turns inverted while the temperature decreases (Fig. 4.20a), and therefore, a TCI phase transition is expected.

The effect of temperature on the energy gap is more likely dominated by the change in the lattice constant \(a_0\). Thus, by rescaling the tight binding parametrization with the proper ratio of the lattice constant according to the Harrison rules \[62\], temperature variability is introduced to the calculations. Based on the Harrison rules the tight binding integrals at \(T \neq 0\) are related to the ones at \(T = 0\) K by the following ratios

\[
\begin{align*}
V_{s,s} \& V_{s,p} \& V_{p,p} \propto (a_0^*/a_0)^2 \\
V_{p,d} \propto (a_0^*/a_0)^4 \\
V_{s,d} \& V_{d,d} \propto (a_0^*/a_0)^5,
\end{align*}
\]

where \(a_0^*\) and \(a_0\) are the lattice constants at \(T = 0\) K and \(T \neq 0\) respectively. It is assumed that the lattice constant \(a_0\) for any Sn content diminishes by the same amount
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with decreasing temperature as for PbSe [63]. However this assumption becomes less accurate with increasing Sn content. The linear evolution of the energy gap versus temperature \(E_g(T)\) for \(\text{Pb}_{0.73}\text{Sn}_{0.27}\text{Se}\) (Fig. 4.20a) differs from the results given in Ref. [56] by less that about 15 \%, whereas it is much higher for \(\text{Pb}_{0.64}\text{Sn}_{0.36}\text{Se}\) (Fig. 4.20b). As a result \(x = 0.27\) is a more reliable composition for the temperature dependent transition.

![Figure 4.20: Temperature dependence of energy gap for (a) \(\text{Pb}_{0.73}\text{Sn}_{0.27}\text{Se}\) and (b) \(\text{Pb}_{0.64}\text{Sn}_{0.36}\text{Se}\)](image)

Taking the room-temperature lattice constant \(a_0\) from x-ray-diffraction experiments [64], the calculated band structures for (001) surface of a 180 monolayers (~78 nm) \(\text{Pb}_{0.73}\text{Sn}_{0.27}\text{Se}\) at \(T = 300\) K and \(T = 80\) K, are shown in Fig. 4.21a and Fig. 4.21b respectively.

Based on Fig. 4.20a, \(T = 300\) K is high enough that yields a non-inverted energy gap, thus at this temperature there is no gapless state (Fig. 4.21a). Nevertheless, the lowest (\(\text{i}\)) and the highest (\(\text{ii}\)) states of the conduction and valence band are localized at the surface. Whereas, at \(T = 80\) K the band gap is inverted and analogous to the situation in SnTe, surface states are found to cross the bulk gap along the symmetry line, \(\Gamma - \bar{X}\) (Fig. 4.21b).

The substantiated spin texture of \(\text{Pb}_{0.73}\text{Sn}_{0.27}\text{Se}\) for two latter temperatures, above
4.2 Pb$_{1-x}$Sn$_x$Se

and below the Dirac points are presented in Fig. 4.23. Clearly, these states in both cases are spin-polarized and have chiral spin textures. The clockwise and counterclockwise chiralities are related to the cation and anion p-type orbitals respectively. While at the high temperature single vortices are anticipated, the spin pattern for the low temperature consist of a double vortical structure (Fig. 4.23c and Fig. 4.23e). For the band above and wave vector $k$ between the Dirac points (inner vortex), spin rotates counterclockwise about $\bar{X}$, however outside this region (outer vortex) the rotation is reversed (clockwise). Hence, in the local environment of each Dirac point the same left-handed chiral structure is obtained, as predicted in Ref. [6]. For the energies below the Dirac point, i.e., for band $\overline{\text{II}}$ all the chiralities are reversed as compared to band $\overline{\text{I}}$.

Moreover, it is noticeable that the polarization is expected to be slightly larger for the anions than for the cations. In contrast, the spin texture of the next higher ($\overline{\text{III}}$)
and lower (IV) bands (Fig. 4.23d and Fig. 4.23f) have the form of single vortices, which is due to two additional Dirac points at X. These Dirac points are not topologically protected, but still have an impact on the overall spin structure. The spins in the anion (cation) Dirac cones of the III (IV) bands are rotating in the opposite direction as compared to the anion (cation) spins in the I (II) bands.

In a parallel experiment, the chiral spin texture of metallic surface states in the TCI phase of Pb_{0.73}Sn_{0.27}Se have been observed, as well as the gapped spin-polarized normal-insulator states [47]. The SRPES measurements provides the conclusive evidence for the realization of the chiral spin texture in both cases, which is perfectly consistent with these calculations. The spin-polarization seems to be inherent to surface states in narrow-gap IV-VI semiconductors influenced by very strong spin-orbit coupling. Nonetheless, the spin-polarized normal-insulator has not been yet reported in either Pb_{1-x}Sn_xTe system [46] or in TIs [65].

**Figure 4.22:** The three-dimensional view of the band structures in the vicinity of the X (a) at T = 300 K (b) at T = 80 K.
Figure 4.23: Contour plots of the constant energy lines of the (001)-oriented Pb\textsubscript{1-\textalpha}Sn\textsubscript{\textalpha}Se\textsubscript{1-\textalpha} for (a) the lowest state of conduction band and (b) the highest state of valence band, at $T = 300$ K. At $T = 80$ K (c) and (d) represent the first two bands above the Dirac point and (e), (f) the first two bands below the Dirac point.
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4.2.3 (111)-oriented surface of Pb$_{1-x}$Sn$_x$Se

From the perspective of potential device applications, and advancing fundamentals of TCIs research, it is yet appealing to survey the existence of metallic states on (111) surface for Pb$_{1-x}$Sn$_x$Se.

Using the same set of tight binding parameters which were previously developed by DFT-LDA method, and taking the lattice constant $a_0$ from x-ray diffraction experiments [64], the band structure of a 451 monolayers ($\sim$ 80 nm) (111)-oriented cation-terminated Pb$_{1-x}$Sn$_x$Se for $x = 0.27$ and $x = 0.36$ at $T = 300$ K, are calculated and presented in Fig. 4.24a and Fig. 4.24b respectively. From Fig. 4.20a, it is evident that at the room-temperature the order of energy gap of Pb$_{0.73}$Sn$_{0.27}$Se is normal, even while $x > x_c \approx 0.19$. This is stemming from the high temperature effect, which causes flipping the order of gap to the normal one.

Whereas at this temperature the energy gap of Pb$_{0.64}$Sn$_{0.36}$Se remains inverted since $x = 0.36$ is high enough above the critical composition that compensates the high temperature turndown. Therefore, this slab has the Dirac-like surface states at high symmetrical points, $\bar{\Gamma}$ and $\bar{M}$. Observing these states for Pb$_{0.64}$Sn$_{0.36}$Se but not for Pb$_{0.73}$Sn$_{0.27}$Se, is another intuitive verification of the topological phase transition occurring by increasing the constituent content towards the inverted band gap.

Additionally, the corresponding spin textures for each slabs around $\bar{\Gamma}$ are depicted in Fig. 4.25. Fig. 4.25a and Fig. 4.25b indicate the states at the bottom of the conduction band and the top of the valance band for Pb$_{0.73}$Sn$_{0.27}$Se. Although Pb$_{0.73}$Sn$_{0.27}$Se is not a TCI at the room-temperature, noticeably these states are spin-polarized with clockwise and counter-clockwise chiralities which are related to the cation and anion p-type orbitals.

Fig. 4.25c and Fig. 4.25d represent the state above and below the Dirac point for Pb$_{0.64}$Sn$_{0.36}$Se. As it is anticipated the spin textures are polarized, however the polarization of states below the Dirac point are less pronounced as compared to above ones. This is due to the position of the Dirac point which is closer to the valence band (for anion-terminated case it is opposite) and thus can be slightly mixed with the bulk states.
Figure 4.24: The calculated band structure of a 451 monolayers (~ 80 nm) (111)-oriented cation-terminated Pb$_{1-x}$Sn$_x$Se, for (a) $x = 0.27$ and (b) $x = 0.36$. 

Pb$_{1-x}$Sn$_x$Se, $x = 0.27$ & $T = 300$ K 

Pb$_{1-x}$Sn$_x$Se, $x = 0.36$ & $T = 300$ K
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Figure 4.25: Spin textures of Pb_{1-x}Sn_xSe around $\bar{\Gamma}$ point for $x = 0.27$ (a) at the bottom of the conduction band, (b) at the top of the valence band, and for $x = 0.36$ (c) above the Dirac point, (d) below the Dirac point.

These calculations have been performed solely to endorse the parallel experimental results accomplished by photo-emission spectroscopy [66]. The ARPES\textsuperscript{1} spectra found for Pb_{0.64}Sn_{0.36}Se is in agreement with Fig. 4.24b, and approves both the dispersion anisotropy and the difference between the $\bar{\Gamma}$ and $\bar{M}$ Dirac points binding energies [66].

\textsuperscript{1}Angle Resolved Photo Emission Spectroscopy
4.3 Quantum spin Hall effect in topological crystalline insulators

The quantum spin Hall (QSH) phase is the very first experimentally exemplified two-dimensional topological insulator (2D TI), which has distinctive metallic edge states protected by the time-reversal symmetry. The edge states come in Kramers doublet and are helical as two states with the opposite spin-polarizations counter propagate at a given edge. Time-reversal symmetry ensures their protection against the backscattering, thus these spin-polarized channels can flow without dissipation. Such a feature makes QSH state in particular and TIs in general, extremely appealing for the spintronic device usage that could operate with low power consumptions and perform reversible quantum computations [67, 68].

Subsequently, soon after the QSH breakthrough, an ever-growing quest has been arisen to find the system with topologically non-trivial edge states. Chronologically, the earliest effort due to establishment of QSH effect in graphene was not promising, since the intrinsic spin-orbit coupling, which opens the band gap at the Dirac points, is very weak, therefore, it could only occur at unrealistically low temperatures. Afterwards, HgTe/HgCdTe quantum well for the thickness above the critical width (d_{QW} > 6.3 nm) [30], verified to show QSH behaviour and have a plateau of residual conductance close to 2e^2/h, which indicated the edge states [69]. Another experimentally proved QSH state came off in hybridized InAs/GaSb quantum well [32], which undergoes a transition from insulating to conducting phase with conductivity close to 2e^2/h, by tuning the gate voltages. Nonetheless the spin-polarized nature of the edge states have been observed only in HgTe-based structures [70]. It should be pointed out that, all these observations are provided when the temperature is very low (below 10 K), in order to sustain the energy gap inverted.

Based on the property of such prototypes many theoretical predictions have been made in which various, sometimes exotic, chemical classes of 2D materials were considered. These include slightly buckled honeycomb lattice of Si atoms (silicene) [71], Bi bilayers on different substrates [72], Ge(Bi_xSb_{1-x})Te_4 with various Bi concentrations [73] and functionalized ultrathin Sn films (stanene) [74]. Recently, it has also been shown that 2D transition metal dichalcogenides MX_2 (M = (W, Mo) and X = (Te, Se, S)) should form a new class of large-gap QSH insulators [75]. Finally, a 2D TI with energy
gap as large as 0.8 eV has been proposed for an overlayer of Bi grown on semiconductor Si(111) surface functionalized with one-third monolayers of halogen atoms [76]. Despite all these theoretical predictions, up to now, no stand-alone thin film or a thin film supported on a suitable substrate has ever been experimentally demonstrated to harbour a QSH state.

Ultimately, in this essence, thin films of well-known IV-VI semiconductors SnSe and SnTe can be considered as optimistic candidates. As it has been mentioned at length in previous sections, these materials belong to the TCI class and have metallic surface states which are protected by crystal symmetry rather than time-reversal symmetry since the band inversion happened simultaneously at an even (four) number of L points in the Brillouin zone. Moreover a prominent factor which makes them more facile to use is that they can be easily grown on BaF$_2$ substrate by molecular beam epitaxy, and also in this way, control over counting the number of layers is straightforward.

Because TCIs substantially depend upon their crystallographic symmetries, it is natural that their thin films grown in different directions show different behaviour. It has been lately reported that in (001)-oriented thin film of SnTe, above the particular thickness (over 5 monolayers), hybridization leads to an inversion of the energy gap and consequently a new 2D TCI phase [77, 49]. The edge states of such a 2D TCI are protected solely by mirror symmetry, and the topological phase is indexed by the mirror Chern number $|n_M| = 2$. Whereas, as it will be scrutinized in this section, in an ultrathin TCI film grown along (111) direction, the QSH state can be obtained. The reason is that the projection of four L points onto the 2D Brillouin zone of a (111)-oriented thin film ($\bar{\Gamma}$, $\bar{M}_1$, $\bar{M}_2$, and $\bar{M}_3$) are not equivalent (Fig. 4.31d). While the energy structures at the three $\bar{M}$ projections are the same by symmetry, the energy structure at the fourth projection at the $\bar{\Gamma}$ point is different. As a result, if the band inversion takes place at either of these points, since they are odd (one or three) and the TI prerequisite is fulfilled therefore, a QSH can be anticipated.

Furthermore, it should be reminded that a typical (111)-oriented slab of rock salt structure (Fig. 4.11) is composed of (111) planes which are consist of either anions or cations. Thus, for such a slab two qualitatively different cases must be distinguished, an even number of monolayers, in which one surface is cation-terminated and another is anion-terminated, and in contrast, an odd number of monolayers whose both surfaces are the same (either anion-anion or cation-cation terminated). For the significance of
4.3 Quantum spin Hall effect in topological crystalline insulators

Inversion symmetry which is preserved in an odd number of monolayers but not in even ones, these cases will be taken into account separately.

In the following sections, to prove the possibility of QSH phase for (111)-oriented ultrathin films of SnTe and SnSe, a complete survey of these materials will be presented.

4.3.1 SnTe thin films; evolution of the energy gap vs. thickness

As it was revealed earlier, for a (111)-oriented thick (∼ 80 nm) film of SnTe, at four non-equivalent L points projected onto 2D BZ (one in $\bar{\Gamma}$ point and three in $\bar{M}$ point) there are topologically protected Dirac cones, since all these L points belong to the $\{110\}$ mirror planes of (111) surface. Nevertheless, it is provided that the film is thick enough to keep the surface states at the top and bottom layers well-separated. Otherwise interaction of surfaces for a less thick TCI film opens the gap where the Dirac cones used to be. It is because, when the thickness of the ultrathin film is comparable with the decay length of the surface states into the bulk, the wave functions of the top and bottom surface states start to hybridize with each other, which ends up to create the gap. It is analogous to the splitting of the bound and antibound orbitals in a double-well potential.

The calculated band structure instances for ultrathin films of SnTe (∼ 3 nm), performed by the tight binding method are shown in Fig. 4.26. Similar to thick film SnTe, the band structure around $\bar{\Gamma}$ is isotropic, whereas it is highly anisotropic for $\bar{M}$, which arises from the different orientation of constant energy ellipsoids around their corresponding L points. The $L_1$ ellipsoid is projected on $\bar{\Gamma}$ along its long axis, though the ellipsoids for other three L points are inclined away from the projection direction. Additionally the yellow to blue lines, still stand for the cation and anion p-type orbitals contribution to the state’s wave function.

Evidently due to the mentioned interaction of thin film surfaces, at $\bar{\Gamma}$ and $\bar{M}$ the states are gapped for both odd number of monolayers, and even ones. Moreover, for a slab consisting of an even number of monolayers, energy gaps are not located at the time-reversal invariant points, instead they are doubly shifted to the either sides. This is because in the slab with an even number of monolayers the inversion symmetry is not preserved.

For the finite thickness (111)-oriented thin films of SnTe, it is shown in Fig. 4.27 how the energy gaps at $\bar{\Gamma}$ and $\bar{M}$ points depend upon the thickness. On the left column of
4. Results

Figure 4.26: The band structure of (111)-oriented thin films of SnTe (~ 3 nm)
4.3 Quantum spin Hall effect in topological crystalline insulators

Figure 4.27: The 2D states band gap (right column) and the associated valence and conduction bands extrema (left column) versus the thickness of (111)-oriented SnTe slabs, (a), (b) for anion-terminated, (c), (d) for cation-terminated and (e), (f) for even numbers of monolayers.
Fig. 4.27, black lines represent the energy gap magnitude in the $\Gamma$ point versus number of monolayers in the film, while red lines depict this in $\bar{M}$ point. As it can be noticed from Fig. 4.26c, for the even numbers of monolayers the energy gap splits, so these gaps can be labelled as $\bar{\Gamma}_1$ and $\bar{\Gamma}_2$ around $\bar{\Gamma}$, and $\bar{M}_1$ and $\bar{M}_2$ around $\bar{M}$. Unlike $\bar{\Gamma}_1$ and $\bar{\Gamma}_2$ which are equal in both directions due to isotropy, $\bar{M}_2$ along $\bar{M} - \bar{\Gamma}$ is much larger than $\bar{M}_1$ along $\bar{M} - \bar{K}$ and are plotted in gray and red lines respectively. The energy gap in $\bar{M}_2$ is incompatibly big as compared to the others, and therefore, it can simply be ignored.

On the right column of Fig. 4.27 the valence and conduction energies related to the energy gaps on the left side versus thickness, are presented.

Noticeably, for odd (both anion-terminated and cation-terminated) and even numbers of monolayers, the energy gap at $\bar{M}$ point decreases monotonically with the decrease of the film thickness. At $\bar{\Gamma}$ point however, damped oscillations of the energy gap with the number of monolayers can be observed. Such oscillations are stemming from $k^2$ correction term to the Dirac-like effective mass Hamiltonian in the direction perpendicular to the surface, and have been already predicted for thin films of 3D TIs, like Bi$_2$Se$_3$ or Bi$_2$Te$_3$ [78, 79]. Correspondingly, where the oscillation reaches to negative magnitude of the energy gap, the valence and conduction bands intersect, which leads to the energy gap inversion within a significant thickness interval. The first and biggest energy gap inversions take place for anion-terminated film consisting of 13–19 monolayers, for cation-terminated 15–33 and for the film with even numbers of monolayers 14–28, where are highlighted in green shade.

Here for the odd number of layers, the inverted energy gap happens at $\bar{\Gamma}$ which is the projection of only $L_1$ (the odd number of time-reversal invariant point), hence, it specifies a topological insulator phase. For the even number of layers though, the gap is broken into two, and the inverted energy gap comes at $\bar{\Gamma}_1$ and $\bar{\Gamma}_2$. As it has been shown in Ref. [80], for inversion-asymmetric systems in general, the existence of a topological insulator phase is plausible if the band inversion occurs in an odd number of such pairs, therefore, thin films with even numbers of monolayers can also offer the topological insulator phase.

Resultantly, it can be perceived, that (111)-oriented thin film of SnTe renders the topological phase transition, from trivial insulator not to TCI for the threshold thickness
of (001)-oriented Pb$_{1-x}$Sn$_x$Te thin film [77], but to 2D TI. The same transition to 2D TI is also predicted for Bi$_2$Se$_3$ or Bi$_2$Te$_3$ thin film [79].

The $\mathbb{Z}_2$ invariant, which distinguishes between the trivial and QSH phase with $\nu = 0, 1$ respectively, is the approval to the statement above. For systems with inversion symmetry, i.e., for films consisting of odd numbers of monolayers, the parity of the occupied bands eigenstates at the four time-reversal momenta points in the BZ (one $\bar{\Gamma}$ and three $\bar{M}$) determines the $\mathbb{Z}_2$ topological invariant [29]. However, for even numbers of layers, there is no inversion symmetry, hence, $\mathbb{Z}_2$ invariant cannot be found by the same method. Instead an adopted method proposed by Fukai and Hatsugai has been utilized [81]. In this method the improvements to computing Chern numbers in a lattice BZ, enable the tight binding calculations of $\mathbb{Z}_2$ based on the formula derived by Fu and Kane in Ref. [28].

The $\mathbb{Z}_2$ invariant is calculated for different thicknesses and marked on Fig. 4.27. $\nu = 1$ is perfectly consistent with the regions where the energy gap is negative and identified as QSH phase, as well as $\nu = 0$ elsewhere.

4.3.2 SnTe thin films; density of states

The hallmark of a topologically non-trivial insulator phase, is the existence of gapless helical edge states inside the bulk gap [16]. Here at $\bar{\Gamma}$ where the energy gap falls to the negative region, such doubly degenerate edge states are expected. They are necessarily robust against arbitrary perturbations since they are protected by both time-reversal and mirror symmetry.

To endorse the predictions discussed in the previous section, the explicit analysis of [1$\bar{1}$0] edge spectral function of (111) SnTe, which have been carried out by recursive Green’s function method, will be presented henceforth. Fig. 4.28, Fig. 4.29 and Fig. 4.30 represent the density of states around projection of $\bar{\Gamma}$ (right column) and $\bar{M}$ (left column) onto the edge, for the instantiated non-trivial and trivial phases of sequentially, anion-terminated, cation-terminated and even numbers of monolayers films. Solid black lines through the figures imply and enhance the border of bulk states projection onto the edge. The 2D BZ zone of the (111)-oriented film and 1D BZ of the [1$\bar{1}$0] edge are depicted in Fig. 4.31d. As shown in the latter, the $\bar{\Gamma}$ and $\bar{M}_1$ points project onto the edge at $k_x = 0$ ($\bar{\Gamma}$), while $\bar{M}_2$ and $\bar{M}_3$ at $k_x = \pm \sqrt{2}\pi/a_0$ ($\bar{M}$).
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The bulk density of states for a 19 monolayers anion-terminated film at $\bar{\Gamma}$ and $\bar{M}$ are shown in Fig. 4.28a and Fig. 4.28b respectively. Associated with these bulks, their edge states are shown in Fig. 4.28c and Fig. 4.28d. The results for another film consisting of 11 monolayers at $\bar{\Gamma}$ and $\bar{M}$ are presented in Fig. 4.28e and Fig. 4.28e. In agreement with the $Z_2$ invariant calculations, the linear-dispersion gapless state is obtained for 19 monolayers at $\bar{\Gamma}$ point, but neither at $\bar{M}$ point where the band gap is not inverted, nor for 11 monolayers which is presumed to be a trivial insulator with $\nu = 0$. Similarly a set of calculations has been done for cation-terminated film (Fig. 4.29). Appearing the Dirac crossing at $\bar{\Gamma}$ point for a 19 monolayers film, additionally verifies that $\nu = 1$ corresponds to QSH phase, whereas gapped state for 13 monolayers indicates a trivial insulator.

Eventually, the bare bulk and QSH states related to an 18 monolayers film, and a trivial insulator phase for a 10 monolayers film are displayed in Fig. 4.30. From Fig. 4.30c, it is quite clear, that the whole inverted energy gap for states in the vicinity of $\bar{\Gamma}$ is situated inside the large gap between the conduction and valence bands close to the $\bar{M}$ point. The largest value of the inverted gap, about 75 meV, is achieved for the 18 – 20 monolayers thick SnTe film. The obtained results support the formalism developed in Ref. [80]. A similar result has been reported for graphene [21], in which a single edge state with a Dirac node appears at $\bar{\Gamma}$ (time-reversal invariant point), despite the energy gaps happen in two points $K$, where time-reversal is not preserved.

Ultimately, $G_{\uparrow}$ and $G_{\downarrow}$, the contributions of the spin up and spin down (111) projections in the edge spectral function have been calculated. The sign of $G_{\uparrow} - G_{\downarrow}$ difference corresponds to spin-polarization of the edge states. As expected for the 2D TI in the QSH state, the acquired edge states are spin-polarized and the spin-polarizations in the two branches of the Dirac cones are always opposite (denoted by red and green colours in Fig. 4.31). These spin-polarizations in all studied cases are about 80%, in other words the contribution of the dominant spin configuration surpasses about 8 – 10 times the opposite spin orientation.
4.3 Quantum spin Hall effect in topological crystalline insulators

**Anion-terminated SnTe**

Figure 4.28: The spectral function in the vicinity of $k_x = 0$ (right column) and $k_x = \sqrt{2\pi}/a_0$ (left column) for anion-terminated (111)-oriented SnTe films.
4. Results

Figure 4.29: The spectral function in the vicinity of $k_x = 0$ (right column) and $k_x = \sqrt{2\pi/a_0}$ (left column) for cation-terminated (111)-oriented SnTe films.
4.3 Quantum spin Hall effect in topological crystalline insulators

Even numbers of layers SnTe

Figure 4.30: The spectral function in the vicinity of \( k_x = 0 \) (right column) and \( k_x = \sqrt{2}\pi/a_0 \) (left column) for even numbers of monolayers (111)-oriented SnTe films.
4. Results

Figure 4.31: The spin density in the vicinity of $k_x = 0$, (a) for 19 monolayers anion-terminated, (b) 19 monolayers cation-terminated and (c) for 18 monolayers (111)-oriented SnTe films.
(d) The 2D BZ of (111)-oriented film (green hexagon) and 1D BZ of its [110] edge (red line).
4.3 Quantum spin Hall effect in topological crystalline insulators

4.3.3 SnSe thin films; evolution of the energy gap vs. thickness

By the same token, that manifested a (111)-oriented SnTe ultrathin film as being 2D TI, in this section such an expectation for SnSe will be perused. Likewise the thick film of SnTe, that of SnSe has four non-equivalent L points whose projections onto (111) surface, one in $\bar{\Gamma}$ and three in $\bar{M}$ form the Dirac cones which are protected by the $\{1\bar{1}0\}$ mirror planes. By reducing the thickness, and thus hybridizing the top and bottom surfaces, the Dirac cones open. This can be seen for the ultrathin ($\sim 3.3$ nm) slabs of (111)-oriented SnSe for 19 monolayers anion-terminated, 23 monolayers cation-terminated and 20 monolayers, in Fig. 4.34a, Fig. 4.34b and Fig. 4.34c respectively.

The energy gap diagram versus the number of monolayers for each of these cases are presented in Fig. 4.35. In contrast to SnTe, for SnSe films the energy gap at $\bar{\Gamma}$ decreases monotonically, while the one at $\bar{M}$ point oscillates with the thickness of the film.

This difference can be ascribed to the quadratic corrections ($k^2$) to the Dirac-like Hamiltonian. As it was mentioned before, damp oscillations of the energy gap result from $k^2$ term, and since in SnTe and SnSe the $k^2$ terms are highly anisotropic, their oscillations take place at different points. In SnTe the $k^2$ term moves the energy gap from L towards the $\Gamma$ point (Fig. 4.32a), whereas in SnSe, in directions perpendicular to the $L-\Gamma$ line (Fig. 4.32b). Indeed, as shown in the BZ (Fig. 4.33) for $L_1$ the direction perpendicular to the (111) surface follows the $L_1-\Gamma$ line, while for the other $L$ points it is inclined at a small angle to the $W-L-K$ plane.

Apart from this contradiction, phenomenologically SnSe can also host the QSH phase since the inverted energy gap occurs at three (odd) time-reversal invariant points ($\bar{M}_1, \bar{M}_2, \bar{M}_3$) for the odd number of monolayers, and three pairs for the even number of monolayers.

Green foregrounded area in both columns of Fig. 4.35, identifies where the conduction and valence bands intersect, and hence, the energy gap is negative. The first and biggest band inversion is between 15 – 33 monolayers for anion-terminated, 19 – 39 for cation-terminated and 14 – 40 for even numbers of monolayers slabs. The broader range of cation wave functions lingers its negative energy gap to the thicker films as compared to the anion one.
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Figure 4.32: The band structure of (a) bulk SnTe and (b) bulk SnSe crystal along $P - L - \Gamma$ line. The $P$ point is not a high symmetry point of the Brillouin zone, it is only chosen to show the direction perpendicular to (111) surface.

4.3.4 SnSe thin films; density of states

Featurewise SnTe, the inverted energy gap of SnSe occurs at the odd number of time-reversal invariant points, therefore, the existence of helical edge states inside the bulk gap is anticipated. To establish these states, a similar set of calculations in the vicinity of $k_x = 0$ and $k_x = \sqrt{2}\pi/a_0$ have been performed and exhibited in Fig. 4.36 for anion-terminated, Fig. 4.37 for cation-terminated and Fig. 4.38 for even numbers of monolayers.
4.3 Quantum spin Hall effect in topological crystalline insulators

![Diagram](image)

**Figure 4.33:** The Brillouin zone for (111)-oriented rock salt crystal with the corresponding 2D BZ (in green). The dashed lines show the perpendicular directions between the L valleys and the (111) surface. P is an arbitrary chosen point along such a line from the L$_2$ valley.

Fig. 4.36a and Fig. 4.36c represent the bulk and edge states of a 21 monolayers anion-terminated film at $\tilde{\Gamma}$ and $\tilde{\Gamma}$, and on the right side Fig. 4.36b and Fig. 4.36d the bulk and edge states of the same configuration at $\tilde{M}$ and $\tilde{M}$. For this thickness $\nu = 1$ and intuitively at $\tilde{M}$ point, where the energy gap is negative, the gapless edge states can be observed. The Dirac point corresponds to $\tilde{M}$ projected onto $k_x = \sqrt{2}\pi/a_0$ ($\tilde{M}$) is distinctively located within the bulk gap, whereas due to the strong band overlapping the one projected onto $k_x = 0$ ($\tilde{\Gamma}$) is buried among the valence band. Manipulating a selected substrate or overlay material, e.g., Pb$_{1-x}$Eu$_x$Se$_{1-y}$Te$_y$, would allow to tune the height of the energy barriers by biaxial strain in the structure [82]. Applying tensile strain can align the gaps at $\tilde{\Gamma}$ and $\tilde{M}$ and solve the latter issue. Such a consideration for the SnSe thin film will be fully discussed in the next section. The results of a 13 monolayers anion-terminated film around these two points are shown in Fig. 4.36e and Fig. 4.36f, which gapped states at either points indicate a trivial insulator phase with $\nu = 0$, in agreement with the $\mathbb{Z}_2$ calculations.

With the same arrangement of the result, Fig. 4.37 represents in the first two rows the bulk and edge states of a 23 monolayers cation-terminated film with $\nu = 1$, and in the last row a 15 monolayers film with $\nu = 0$. The crossings of edge states which connect the conduction and valence bands could verify a more ideal QSH phase (Fig. 4.37d), if the valence band at $\tilde{\Gamma}$ did not overspread the gap at $\tilde{M}$ (Fig. 4.37c).
4. Results

Figure 4.34: The band structure of (111)-oriented thin films of SnSe (∼ 3.3 nm)
Figure 4.35: The 2D states band gap (right column) and the associated valence and conduction bands extrema (left column) versus the thickness of (111)-oriented SnSe slabs, (a), (b) for anion-terminated, (c), (d) for cation-terminated and (e), (f) for even numbers of monolayers.
4. Results

Finally the edge spectral of a 20 monolayers (111)-oriented SnSe film at \( k_x = 0 \) and \( k_x = \sqrt{2\pi/a_0} \) are depicted in Fig. 4.38c and Fig. 4.38d respectively. A pair of edge states can be seen near the top of the valence band at \( \Gamma \) even though the gap is very small. At \( \bar{M} \) point however, the edge states which form the two Dirac cones do not crossover the band gap to connect the valence and conduction bands. Instead, the upper and lower edge states repel each other and an anticrossings appear.

In contrast to the result obtained for films with the odd number of monolayers, where two Dirac cones intersect, there is no crystal symmetry, which can protect such additional Dirac points. They cannot be explained by the inversion symmetry, which distinguishes the two cases, because an edge in the semi-infinite sample breaks this symmetry. Surprisingly enough, the same difference between the odd and even cases can be obtained within a simple effective mass model presented below. The Hamiltonian \( \hat{H}_0 = v_1 k_x \hat{s}_y - v_2 k_y \hat{s}_x \) proposed in Ref. [83] is used to describe the surface states. For two surfaces of a thick film the Hamiltonian has the form,

\[
\hat{H} = (\hat{H}_0 + \Delta) \hat{\tau}_z
\]  

(4.1)

where \( \tau_z = \pm 1 \) describes the upper and lower surface, respectively and \( s_z = \pm 1 \) denotes a Kramers doublet. \( 2\Delta \) is the energy difference between the Dirac point positions for anionic and cationic surfaces and equals zero when the upper and lower surfaces are the same. For films with the odd number of monolayers this effective Hamiltonian is invariant not only against the crystalline symmetries of the system but also against reflection from the mirror plane situated in the middle of the film, \( \hat{M}_z = -i\hat{s}_z \hat{\tau}_x \). When the thickness of the film decreases the states of the two surfaces start to interact, but this interaction does not break the mirror symmetry. The conclusion is valid for any L point projection. The [110] edge mixes \( \bar{\Gamma} \) with \( \bar{M}_1 \) and \( \bar{M}_2 \) with \( \bar{M}_3 \), but also does not destroy the mirror plane symmetry. In case of films with the odd number of monolayers this symmetry protects the Dirac cone intersections. Moreover, it provides additional protection of Dirac points in the time-reversal invariant momenta. However, such a symmetry does not exist in films consisting of an even number of layers, with two different surfaces, i.e., with a non-zero \( \Delta \hat{\tau}_z \) term in the Hamiltonian \( \hat{H} \). Thus, for such SnSe films instead of additional Dirac points anticrossings appear (Fig. 4.39f).

Eventually, spin-polarization of edge states are represented in Fig. 4.39. As it is mentioned for SnTe case, spin-polarization corresponds to the difference in the
contribution of spin up and spin down (111) projections in the edge spectral function \((G \uparrow - G \downarrow)\). Right and left columns in Fig. 4.39 show the spin density at the edge around \(\tilde{\Gamma}\) and \(\tilde{M}\) points respectively. At \(\tilde{\Gamma}\), where \(\tilde{M}_1\) projects onto 1D BZ, there should exist one Dirac point. But due to the aforementioned overlapping such crossings are totally (Fig. 4.39a) or partially (Fig. 4.39c and Fig. 4.39e) covered by the bulk states. At \(\tilde{M}\) (projection of \(\tilde{M}_1\) and \(\tilde{M}_2\)) two Dirac points are anticipated, which can be seen for a 21 monolayers anion-terminated film (Fig. 4.39b). For a 23 monolayers cation-terminated case, although there are two branches connecting the valence and conduction bands, one of the Dirac points is mixed with the conduction band (Fig. 4.39d). Ultimately, based on the discussion above, for an even number of monolayers there are two anticrossings at \(\tilde{M}\), which is due to lack of protecting symmetry (Fig. 4.39f).
4. Results

Anion-terminated SnSe

Figure 4.36: The spectral function in the vicinity of $k_x = 0$ (right column) and $k_x = \sqrt{2}\pi/a_0$ (left column) for anion-terminated (111)-oriented SnSe films.
Figure 4.37: The spectral function in the vicinity of \(k_x = 0\) (right column) and \(k_x = \sqrt{2\pi/a_0}\) (left column) for cation-terminated (111)-oriented SnSe films.
4. Results

Even numbers of layers SnSe

![Graphs showing band structures](image)

**Figure 4.38:** The spectral function in the vicinity of $k_x = 0$ (right column) and $k_x = \sqrt{2}\pi/a_0$ (left column) for even numbers of monolayers (111)-oriented SnSe film
4.3 Quantum spin Hall effect in topological crystalline insulators

Figure 4.39: The spin density in the vicinity of $k_x = 0$ (right column) and $k_x = \sqrt{2}\pi/a_0$ (left column), (a), (b) for 21 monolayers anion-terminated, (c), (d) for 23 monolayers cation-terminated and (e), (f) 20 monolayers (111)-oriented SnSe films.
4. Results

4.4 Quantum spin Hall effect in strained (111)-oriented SnSe film

It was determined in previous sections, that (111)-oriented ultrathin films of SnTe and SnSe, within the particular thicknesses, render 2D TI phase. They belong to the TCI class and exhibit four Dirac cones at $\bar{\Gamma}$ and $\bar{M}$ points when the surfaces of the layer are well-separated, otherwise, in ultrathin films, the surface states of top and bottom surfaces hybridize and therefore, energy gaps open the Dirac cones. As a consequence of the quadratic correction term to the Dirac-like Hamiltonian, these energy gaps oscillate with the film thickness and reach to negative magnitudes at $\bar{\Gamma}$ for SnTe and at $\bar{M}$ for SnSe. Therefore, both of these two materials can be regarded as 2D TIs, since their band inversions take place in the odd numbers of time-reversal invariant points. Calculated $Z_2$ invariants and spin-polarized edge states completely corroborate with this prediction.

Yet, as it was discussed, QSH effect would be difficult to observe in SnSe, due to impairment of the band gap at $\bar{\Gamma}$ and one of the $\bar{M}$ points, which are projected on the same point $\tilde{\Gamma}$ ($k_x = 0$) in the 1D BZ of the [110] edge. Overlap of these two projections considerably diminishes the band gap by mutual shadowing. As a result the edge states appear either against the background of the bands or within a very small energy gap. In the following, the possibility of reducing such a band gap screening in (111)-oriented SnSe films by applying the biaxial strain will be scrutinized.

It is well known that strain changes the electronic properties of the materials. It can shift and split the degeneracy of energy levels. In heterostructures strain affects also the staggered band offsets and is considered as a powerful tool to engineer alternative routes for enhancing semiconductor structures [84]. To investigate the effect of biaxial tensile strain on the energy gap of (111)-oriented SnSe films, suppose that the film lays in the $x-y$ plane and the $z$ direction is chosen along [111] crystallographic axis. For a homogeneous semiconductor, the variation of energy gap as the function of the imposed strain is qualified in terms of deformation potentials tensor ($D$) and strain component ($\epsilon$). When the deformation is not very strong and the distance between atoms is still close to the equilibrium lattice constant $a_0$, $D$ can be treated as a constant and hence, the change of the energy with strain is approximately linear.
4.4 Quantum spin Hall effect in strained (111)-oriented SnSe film

Under an isotropic biaxial strain in x−y plane, the longitudinal $\varepsilon_\parallel$ and transverse $\varepsilon_\perp$ strain components are expressed as

$$\varepsilon_\parallel = \varepsilon_{x,y} = \frac{a_{x,y}}{a_0} = \frac{a_D}{a_0} \quad (4.2)$$

$$\varepsilon_\perp = \varepsilon_z = \frac{a_z}{a_0} \quad (4.3)$$

where $a_D = a_0(1 + \text{deformation}_{x,y})$, $a_z = a_0(1 + \text{deformation}_{z})$ and $a_0$ is the relaxed lattice constant. The longitudinal and transverse strain components are related through the Poisson ratio $\nu$ that characterizes the elasticity of a crystal, and is equal to

$$\nu = -\frac{\varepsilon_\perp}{\varepsilon_\parallel} \quad (4.4)$$

The Poisson ratio of rock salt SnSe is presumed to be similar to the one for PbSe, and it is taken from Ref. [85] to be equal to 1.16 at low temperature, $T \approx 4$ K. The lattice constant $a_0 = 5.97\text{Å}$ of the relaxed cubic SnSe is obtained by the first principle calculations.

4.4.1 Strain induced band gap alignment

To illustrate how implementing strain can align the energy gaps, a 17 monolayers (111)-oriented anion-terminated SnSe, whose energy gap is almost covered with a very strong overlapping, is chosen to be examined. By rescaling the tight binding integrals due to changing of the lattice constant according to the Harrison rules, the effect of strain is involved in the calculations.

Dependence of the valence and conduction bands placement on the percentage of in-plane deformation for $\Gamma$ and $\bar{M}$ are shown in Fig. 4.40. Clearly, in the relaxed layer the energy gap at $\bar{M}$ is completely shielded by the valence band in the vicinity of $\Gamma$ point. When the deformation increases, the energy gap at $\Gamma$ point is shifted down in energy, whereas the band gap at $\bar{M}$ point is moving upward. This is due to different deformation potential coefficients which are stemming from the difference between the effective masses in the vicinity of these two points of the Brillouin zone. For deformation $\sim 1.1445\%$, the tops of the valence band at $\Gamma$ and $\bar{M}$ have the same energy and the two energy gaps are aligned.

In Fig. 4.41 the band structure of the 17 monolayers anion-terminated (111)-oriented SnSe slab, for strained (1.1445% deformed) and fully relaxed structures are depicted as
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Figure 4.40: The dependence of the energy gap of a 17-monolayers anion-terminated SnSe under biaxial strain, on the percentage of deformation. The extrema of the valence band at $\bar{\Gamma}$ and $\bar{M}$ are at the same energy level when the structure is $\sim 1.1445\%$ deformed. ($\bar{\Gamma}_v$, $\bar{\Gamma}_c$, $\bar{M}_v$ and $\bar{M}_c$ stand for the valence and conduction energy magnitudes at $\bar{\Gamma}$ and $\bar{M}$ points respectively)

a solid blue line and dotted red line respectively. It is evident (as compared to Fig. 4.40) that for a relaxed structure the band gap at $\bar{\Gamma}$ and $\bar{M}$ are impaired, whereas for a strained structures bands are lined up. As a result the band gap in the 2D spectrum of such a slab opens, and the final total energy gap is $\mathcal{E}_g \sim 0.57$ meV, which is shown in Fig. 4.41 by the green strap.

The lattice constant $a_D$ associated with the optimal deformation, which aligns the energy gaps in this case, is equal to 6.04 Å. Thus, the epitaxial growth of SnSe layers on a substrate whose lattice constant is equal to 6.04 Å would lead to the desired deformation.

4.4.2 Edge states and their spin-polarization

According to what has been predicted in § 4.3.3, the 17 monolayers anion-terminated SnSe film should be a non-trivial insulator in which the band gap inversion occurs at three $\bar{M}$ points. Therefore, at the projections of the $\bar{M}$ points on the [110] edge, i.e., one at $\bar{\Gamma}$ ($k_x = 0$) and two at $\bar{M}$ ($k_x = \pm \sqrt{2}\pi/a$) points of the 1D BZ, three Dirac nodes are expected. However, the observation of these edge states would not be possible in the
4.4 Quantum spin Hall effect in strained (111)-oriented SnSe film

Figure 4.41: The band structure of the relaxed (red dotted lines) and 1.14% deformed (solid blue lines) 17 monolayers anion-terminated (111)-oriented SnSe slab.

relaxed structures due to the above mentioned problem of strong shadowing of the band gap in such layers.

Here, to endorse the proposed strain-induced alignment solution, the [110] edge spectral functions for both relaxed and deformed, (111)-oriented anion-terminated SnSe films consisting of 17 monolayers, are calculated and presented in Fig. 4.43. Notably, at \( \tilde{\Gamma} \) for the relaxed structure (Fig. 4.42b), the band gap is covered by the 2D valence band from \( \tilde{\Gamma} \) point. In turn, Fig. 4.42d shows the edge states of the same film, which is now 1.14% stretched. Therefore, the edges state with a Dirac node can be clearly seen within the energy gap. This verifies that applying appropriate strain removes the casting of the gap.

Finally, the spin up (\( G^{\uparrow} \)) and spin down (\( G^{\downarrow} \)) contributions in the edge spectral function of the 17 monolayers anion-terminated SnSe film for the relaxed structure at \( \tilde{\Gamma} \) and 1.14% deformed at \( \tilde{\Gamma} \) and \( \tilde{M} \), are shown in Fig. 4.43. The spin-polarization of the edge states is defined as \( G^{\uparrow} - G^{\downarrow} \). As expected all three Dirac crossings with opposite
4. Results

Relaxed vs. strained SnSe

Figure 4.42: The calculated spectral function of the 17 monolayers anion-terminated SnSe film, (a),(b) for the relaxed structure at \(k_x = 0\), (c),(d) 1.14% deformed structure at \(k_x = 0\) and (e),(f) 1.14% deformed structure at \(k_x = \sqrt{2}\pi/a_D\). (The black solid lines denote the projection of the 2D bands boundaries)
spin-polarizations in the two branches are now located inside the band gap, which enables their observation.

At the end, it should be emphasized that similar to this studied case, appropriate tensile strains can pair the gaps at \( \bar{\Gamma} \) and \( \bar{M} \) for other SnSe films as well. For instance, 19 monolayers cation-terminated, requires 1.07\% deformation to achieve an optimal alignment of the gaps, while 0.8\% deformation is needed to cause the same in a 20 monolayer SnSe film. This means that the in-plane lattice constant of the film should be expanded to the value of about 6.02 – 6.04 Å depending on the number of monolayers. The films can be thus stretched by using a substrate with such lattice constants. The substrate should be also a trivial insulator with a wide band gap to ensure that the interface between the SnSe layer and the substrate simulates as much as possible a free surface. It seems that the best candidate for the substrate is PbS\(_x\)Te\(_{1-x}\) with \( x \approx 0.8 \) or PbS\(_x\)Se\(_{1-x}\) with \( x \approx 0.46 \) for films with an odd number of layers and with \( x \approx 0.56 \) for 20 monolayer SnSe film. The energy gaps in the mentioned above compounds are ca 2 – 2.5 times bigger than in the film with odd numbers of monolayers, i.e., the band gap in the 17 monolayer SnSe slab is equal to −0.1 eV while for PbS\(_{0.46}\)Se\(_{0.54}\) \( \varepsilon_g = 0.21 \) eV and \( \varepsilon_g = 0.27 \) eV in PbS\(_{0.8}\)Te\(_{0.2}\). In the even number of SnSe monolayers case the difference between energy gaps of the film and substrate is larger – for 20 monolayers the gap is equal ca −0.04 eV, which means that the energy gap 0.27 eV of PbS\(_{0.56}\)Te\(_{0.46}\) is nearly 7 times bigger. It should be noted, however, that sulfur is usually not allowed in MBE\(^1\) systems and to grow such substrates other methods have to be applied. Finally, it is worth mentioning that the appropriate strain can be further adjusted by using the difference in thermal expansion coefficients of the SnSe and the used substrate. Of course one can think also about the possibility to obtain the needed deformation, i.e., the biaxial in-plane extension, by applying mechanically uniaxial pressure perpendicular to the (111) surface of the layer.

\(^1\)Molecular Beam Epitaxy
4. Results

Figure 4.43: The spin density of the 17 monolayers anion-terminated SnSe film, (a) for the relaxed structure at $k_x = 0$, (b) 1.14\% deformed structure at $k_x = 0$ and (c) 1.14\% deformed structure at $k_x = \sqrt{2}\pi/a_D$. (Red and green lines denote the spin down and spin up polarization, respectively)
Throughout this thesis, within a theoretical framework, new significant aspects of topological materials have been surveyed. It has been discussed primarily that, TIs are new quantum states which act as insulators inside their bulks whereas they have time-reversal protected conducting surface (or edge) states. Such a dual behaviour is stemming from their non-trivial band topology. In a TI the energy bands above and below the gap swap places, and thus, there is a gap between the valence and conduction bands which makes the material an insulator but with a different topology. It is shown that the TI phase can be obtained in materials with strong spin-orbit coupling and inverted band gap which occurs at an odd number of time-reversal invariant points. QSHE is a 2D TI which is experimentally realized in the CdTe/HgTe/CdTe quantum well. TCIs however, have similar properties, but their surfaces are protected not by the time-reversal symmetry but by their crystal symmetries. Unlike TIs, in TCIs band inversion does not necessarily need to take place at an odd number of time-reversal invariant points. SnTe with the intrinsic inverted band gap at four L points, is established as the TCI prototype, whose surface states are protected by the mirror plane symmetry.

Inspired by this discovery, it has been demonstrated here that, Pb$_{1-x}$Sn$_x$Te and Pb$_{1-x}$Sn$_x$Se, when their band gaps are inverted, are also TCI materials. In Pb$_{1-x}$Sn$_x$Te, by increasing Sn content, after a critical composition the band gap flips and becomes inverted. Slab of Pb$_{1-x}$Sn$_x$Te for $x > 0.36$ exhibits the Dirac-like metallic states on (001), (110) and (111) surfaces where the mirror planes are projected onto 2D BZ. Parallel to an experimental counterpart, it has been proved that Pb$_{1-x}$Sn$_x$Se slab also has metallic states on (001) and (111) surfaces. Spin texture calculations for both Pb$_{1-x}$Sn$_x$Te and...
Pb$_{1-x}$Sn$_x$Se reveal the existence of helical surface states not only for TCI phase but also, surprisingly, for the normal-insulator phase of Pb$_{0.63}$Sn$_{0.27}$Se. Indeed, Pb$_{0.63}$Sn$_{0.27}$Se undergoes a topological phase transition from a trivial insulator at room-temperature to a TCI at T = 80 K. Temperature is involved in the calculations by varying the lattice constant based on the Harrison rules, as the dominant effect of temperature is the expansion of interatomic space. These investigations have been performed by using the tight binding method. Moreover the DFT method is utilized to build a set of tight binding parametrization for a cubic SnSe which is not available.

Apart from studies of 3D TCIs, ultrathin films of these materials were explored. It was explicitly determined that within the particular thicknesses, (111)-oriented thin films of SnTe and SnSe experience a topological phase transition from trivial insulator not to the TCI phase but to the TI one. The reason is that, due to the intersection of the valence and conduction bands in the specific thicknesses, each of these films acquires an odd number of band inversions at the time-reversal invariant points, therefore, a TI phase is plausible. Such a possibility has been scrutinized and verified for both SnTe and SnSe. Additionally the $Z_2$ invariant, which distinguishes the TI phase from an ordinary insulator, has been calculated for all studied cases and was in perfect agreement with the results.

In the case of SnSe ultrathin films, due to the strong band overlapping at the projection of $\bar{\Gamma}$ and $\bar{M}$ points onto the edge ($k_x = 0$) the final gap is diminished, and thus the resulting QSH phase is shattered. It has been suggested in the present work, that applying the proper biaxial tensile strain can align the gaps and hence solve the screening problem. The required biaxial strain which leads to adjusting the gap can be implemented by using the appropriate substrate with a different lattice constant. The exact magnitude of lattice constant needed for instantiated SnSe 17 monolayers anion-terminated film is $\sim 6.04$ Å, which can be provided by PbS$_{0.8}$Te$_{0.2}$ or PbS$_{0.46}$Se$_{0.54}$ substrates. Concisely, it would seem legitimate to posit that both SnTe and SnSe are promising candidates which can harbour QSH state.

To sum up, this theoretical study elucidates the anticipation of TCI and 2D TI phases in IV-VI semiconductors. Furthermore, it presents a concrete qualitative analysis, which can be used for compatible experimental investigations.
Nomenclature

■ Abbreviations

ARPES  angle resolved photo emission spectroscopy
BZ    Brillouin zone
DFT   density functional theory
QHE   quantum Hall effect
QSHE  quantum spin Hall effect
SO    spin-orbit
SRPES spin resolved photo emission spectroscopy
TCI   topological crystalline insulator
TI    topological insulator
VCL   virtual crystal approximation

■ Symbols

A    Berry connection
B    Berry curvature
ν    Chern number
σ    conductivity
D    deformation potential
ρ    density of state
eg   energy gap
a0   lattice constant
mM   mirror Chern number
M    mirror operator
P    polarization
ε    strain component
Θ    time-reversal operator
Z2   topological invariant
References

REFERENCES


