



SPIN-TO-CHARGE CONVERSION AT THE SURFACE OF A TOPOLOGICAL INSULATOR USING A TIGHT-BINDING PLATFORM

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Internship Report

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1 Introduction

Traditionally an insulator is defined as a material that does not conduct electricity. In most insulators, the absence of electrical conduction is explained by the band theory of solids. In the past few years, a new kind of insulator has been theoretically predicted, which has a band structure that is topologically different from an ordinary insulator "Topological Insulator". Despite having an energy gap in the bulk, a topological insulator has unique gapless states bound to the sample surface as a consequence of the topological order in the bulk. Recent experimental observations of these unique surface electron states have provided direct evidence of the topological insulator phase in a number of materials.

In this thesis we present the theory and calculations of topological insulators like represented by $Bi_{1-x}Sb_x$. The outline of this thesis is as follows. In chapter 2, a brief description is presented about the laboratory where my internship took place. In chapter 4, topological surface states, which are of the spin orbit coupling, are explained, then within the same chapter an overview is given about spin to charge conversion. In chapter 5, the framework of the tight binding is provided. In addition Bismuth Antimony $Bi_{1-x}Sb_x$ alloy, a strong topological insulator and will be described in chapter 6 using a Tight binding (TB) approach. The last chapter will be about a study of Cobalt/ $Bi_{1-x}Sb_x$.

First, we present the theory and the calculations of TI surface electronic band structures. Specifically, we describe the mathematical formulation of the topological order of insulating band structures, which leads to the theoretical discovery of threedimensional topological insulator phases. We also give the physical characterization of the topological order, thereby establishing that the hallmark signatures of topological insulators are the distinctive surface states. Unlike any other two dimensional metal, the surface of a topological insulator has unique properties giving rise to unusual phases.

2 Laboratory presentation

The "Unite Mixte de Physique CNRS/Thales" (UMPhy), created in 1995, is a joint laboratory between CNRS and the industrial company Thales (previously Thomson-CSF).

UMPhy is associated to University Paris-Sud 11 since 2000. The creation of UMPhy Lab followed a longstanding collaboration between Albert Fert's team at University Paris-Sud and Alain Friederich's physics group at Thomson-CSF's Central Research Lab. This fruitful collaboration, initially centered on magnetic metal multilayers, led first of all to the discovery of the Giant Magnetoresistance effect (GMR) in 1988 whose major importance was recognized by the 2007 Physics Nobel prize. It is also considered as the birth of the field of spintronics with now major applications in everyday life.

Since 1995, UMPhy has been active in all major topics in the field of spintronics such as spin polarized tunneling, magnetic nanowires, spin injection in a variety of heterostructures based on metals, oxides, semiconductors, and spin transfer effects in nanodevices. Nowadays, the research at the laboratory is oriented towards the spinorbitronics, involving transition metals and novel high spin-orbit materials.

Initially centered on spintronics and nanomagnetism, the scientific activities at UMPhy were extended in 1996 to high-Tc superconductors (SHTC) with the arrival of Jean-Pierre Contour's team from ESPCI, and then merged in 1998 with the Superconductive Devices group at Thomson-CSF Central Research Lab to facilitate the technological transfer of SHTC research to signal processing applications. More recently, to cope with the renewal of interest in oxides' physics, a full research line on Functional Oxides was launched.

UMPhy is also hosting since 2006 the hard X-ray lithography group of Stephan Megtert previously located at the LURE synchrotron laboratory. Beside the motivation of exploring new fundamental routes, the mission of UMPhy is to propose and demonstrate innovative concepts of devices for medium and long term applications in the frame of signal processing and Beyond CMOS electronics. Today, an important part of the scientific activity of the spintronic teams resides in the research and development of a new kind of materials (heavy metals, Ferromagnets, Topological Insulators) grown for their properties of spin charge conversion and their ability to produce magnetic torques.



3 Context general of my Internship

This year I took a class about spintronics taught by Mr.JAFFRES, I liked his style of teaching and also I appreciated the field of his research.

I contacted him for an internship and I was lucky because at that time he had two offers and he accepted to attribute one of these two offers, about (Topological Insulators), to me. To be honest at the beginning I didn't have enough knowledge about the subject of my internship; it was totally new for me except the part about the "Tight Binding" platform which I have studied during my master program at the university of Paris.

I decided to continue in the subject about Topological Insulators after my interview with Mr.JAFFRES who explained me the importance of the subject in the industry, and the need to understand the theory behind the interface of a Topological Insulator. I have started my internship on the 8 of March 2021, the mission was clear in the first part, we have to see what happens at the interface of $Bi_{1-x}Sb_x$ by using a (TB) model. In the second part which I will continue till the end of JULY, it is expected to study $Co/Bi_{1-x}Sb_x$ using also the TB platform. The importance of studying Cobalt (ferromagnet) on top of a TI is that we can observe THz emission in the time domain (sub-picosecond), thanks to spin-to-charge conversion.

Due to the actual situation I was not allowed to be at the laboratory all the time, so the organisation of my work was:

- 40% to pursue and implement TB codes at distance
- 60% presence in lab, my role was to make the theory of the band structure and to fit ARPES data in order to find the correct band structure
- The connection between surface structure and surface effective Rashba and finding relevant surface Hamiltonian terms.

The first task was to calculate the electronic band structure of the TI $(Bi_{1-x}Sb_x)$ for different values of (x : Antimony concentration) and also for different film thicknesses and corroborate the calculations to the ARPES measurements.

The $Bi_{1-x}Sb_x$ material was grown in the frame of the thesis of Laëtitia Baringthon (PHD UMPHy-C2N-Soleil, 2018-2021) for their properties to be a topological insulator depending on x. The growth and in-sitee ARPES measurements were performed at the "Cassiopee line (Soleil)" displaying the exact band structure of materials along selected crystallographic directions. Some samples capped with Co/Al or Co/Au are also prepared at the same time to study spin-injection properties into BiSb thin films and for THz emission.

An important parameter to find from simulation point of view was the two surface

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"Rashba parameters" (spin-orbit parameters) able to conventionally reproduce the spin dispersion of the two surface states making the material topological or not, and this is the aim of my internship, to understand theses properties owing to TB band structure calculations.

4 Introduction to Topological Insulators

4.1 Topological surface states

The surface of a crystal is an interesting subject for many reasons. In particular, the surface breaks the three dimensional translational symmetry of the bulk, leading to the existence of physical phenomena not observable in the bulk. The lack of translational symmetry along the surface normal can result in the existence of special electronic states localized perpendicularly to the surface so-called "surface states". At the surface the inversion symmetry is broken, and this allows for a splitting of the surface state.

The spin orbit interaction (SOI) is a relativistic effect. An electron moving with a velocity (v) around the nucleus of an atom will feel an electric field $E = -\nabla V_c(r)$, $V_c(r)$ represents the colombian potential, this electric field behaves like an effective magnetic field with : $B' = \frac{-1}{c^2}(E \times v)$, where c is the speed of light. This magnetic field is Zeeman-coupled to the electron's spin, leading to an energy term

$$H_{soc} = \frac{\mu_B}{2c^2} (v \times E) . \sigma, \tag{1}$$

where σ denotes the electron spin, i.e., the Pauli matrices. To arrive at the correct Hamiltonian for quantum calculations using the Schrodinger equation (which is non relativistic) an additional energy term is needed and it is proportional to $(\nabla V \times p).\sigma$, where V is the potential in which the electrons move and p is the momentum. In band structure calculation each band is doubly degenerate (spin-up and spin-down). The time reversal symmetry leads to

$$E(k,\uparrow) = E(-k,\downarrow),\tag{2}$$

i.e. the energy of a spin-up electron with momentum, k, equals that of a spin-down electron with momentum, -k. Furthermore, if the lattice has inversion symmetry (means that the operation $r \rightarrow -r$ does not change the crystal lattice), one finds

$$E(k,\uparrow) = E(-k,\uparrow),\tag{3}$$

From these two equations, it is clear that if both time reversal and inversion are symmetri elements, the band structure must fulfil

$$E(k,\uparrow) = E(k,\downarrow),\tag{4}$$

i.e., the energy cannot depend on the electron spin, so the bulk cannot have a spin orbit split band structure (each band is doubly degenerate) if the lattice is invariant under inversion. At the surface, there is no (3D) inversion symmetry but time reversal symmetry is maintained so we can have $E(k,\uparrow) \neq E(k,\downarrow)$, i.e., it is possible for the spin degeneracy to be lifted.

The electrons are free to move in the surface plane, i.e., $V = V_{\perp}$, leading to $\nabla(V) = \frac{dV}{dz}e_z$ where z is along the surface normal, and e_z is a unit vector pointing in the z-direction. In this model, V represents the potential that confines the electrons to the solid and the gradient of this potential controls the strength of SOI. The resulting spin-orbit Hamiltonian is of the form:

$$H_{SOC} = \alpha_R(e_z \times p).\sigma,\tag{5}$$

the so called Rashba term. Here $\alpha_R = (\hbar/4m^2c^2)dV(z)/dz$, is called the Rashba parameter (strength parameter), proportional to the gradient of the potential. Typically the appearance of V(z) terms can be due to the atomic position relaxation effects or surface construction.

4.2 Conversion spin charge

In the case of the interface type Rashba, there is an alternative mechanism that converts the current of charge to spin current (and vice versa), this mechanism called Effet Edelstein (inverse). This latter can be described by Berry phase, here we give a phenomenological description of this mechanism.[1]

Let's consider a 2D electrical system with spin-orbit coupling: an electrical current can induce under some conditions an accumulation of spin (or polarisation of spin of the carriers) out of equilibrium. In the case of 2D materials like Topological Insulators or of surface Rashba, the introduction of spin-orbit coupling has the effect of locking the spin structure around the circular contour of Fermi as is presented in figure 1. This locking between the spin structure and the wave vector k, gives the possibility to have a conversion between charge current and spin current thanks to Edelstein effect (EE) and inverse Edelstein effect (IEE).

In the case of (EE), a charge current J_c applied on the 2DEG (dimensional electron gas) along x direction, causes a shift of the Fermi's contour in the reciprocal space along x direction, which lead to an increasing of the population of the spin with an orientation along y direction, we talk about spin accumulation. The efficiency of conversion from spin to charge and vice versa is characterised by the ratio of the spin current density generated (for example in a ferromagnetic material deposited on top of 2DEG) and the density of charge current applied to the same gas : $q_{EE} = \left| \frac{J_s}{J_c} \right|$ which has the dimension of the inverse of a length.

Concerning the IEE, the injection of the spin current at the surface state lead to the generation of the charge current in the 2DEG. The conversion efficiency is characterised by λ_{IEE} , and it is given by the ratio of the charge current 2D, and the spin current injected (3D) ($\lambda_{IEE} = \left| \frac{J_c}{J_s} \right|$).



Figure 1: a) Schematics of the Edelstein effect. The electron cone and the hole cone of the surface state shift in opposite directions (dotted circles) in the presence of an in-plane electric field $E \parallel x$ due to their opposite group velocities, yet result in the same spin accumulation $\langle \sigma \rangle \parallel y$, because of their opposite spin chirality (red and green arrows). b) Schematics of the inverse Edelstein effect caused by an instantaneous magnetization dynamics $\frac{dS}{dt} \parallel y$ in the FMM. The generalized spin force $\frac{dS}{dt}$ must project to the spin-momentum locked $\langle \sigma \rangle_{k\beta}$ in order to increase the population of $\langle \sigma \rangle_{k\beta}$, which yields a shift of the Fermi surface (dotted circle, assumed to be at the hole cone) and hence a charge current along x.[2]



Figure 2: Schematic illustration of THz emission from Bi2Se3 films(TI) via dynamical (time-dependent) spin-to-charge inter-conversion

The spin and momentum of the two-dimensional (2D) surface states of a threedimensional (3D) TI are helically locked in the Fermi contour. Because of spin momentum locking, a 3D spin current density injected onto the surface of a TI will produce a 2D charge current density on the surface (IEE). Due to the existence of strong spin–orbit coupling, the injected spin current generated from transferring the spin angular momentum from the processing magnetization can be converted to a charge current via the inverse Edelstein effect (IEE) on the surface.

This Spin to charge conversion process can lead to the large-amplitude THz waveforms that can be detected from the TI(Topological Insulator)/FM (Ferromagnet) heterostructure as shown in figure 2. We note that the SCC transient charge currents generated by IEE flow in the same direction—since $j_c \propto \hat{z} \times \sigma$ in IEE, where j_c is the charge current and, σ is the direction of the spin polarization, and \hat{z} is the unit vector normal to the TI/FM interface. As a result, the polarization of the emitted THz pulses from IEE also point in the same direction.

Some of these experiments and scientific activities are developed at UMPhy CNRS-Thales (PHD Enzo Rongione, 2019-2022). For instance, the generation of an ultra fast spin current (100 fs) followed by a spin relaxation into BiSb structure can be measured with a laser pulse injection. The efficiency of spin injection is then followed by measuring the THz electromagnetic wave emitted from the samples according to the following law: $E_{THz} \equiv -\frac{\partial J_c}{\partial t}$ (J_c is the ISHE or IRE charge current produced in time). Those experiments are led in the laboratory and has allowed to demonstrate the strong efficiency of $Bi_{1-x}Sb_x$ (0.07 <x< 0.3) to convert a spin into a charge current.



Figure 3: THz emission from $Co/Bi_{0.79}Sb_{0.21}$ (2.5, 5 and 15 nm structures)

5 Tight Binding Model

We present now the main formalism able to describe the surface of BiSb materials. The tight binding scheme is an extension of the method of linear combination of atomic orbitals. The empirical formulation of tight binding model was introduced by Slater and Koster and amounts to treating the matrix elements of the Hamiltonian as free parameters, to be determined by fitting energy gaps and effective masses to experimental data. This method is very popular because:

- It is fairly straightforward to implement
- It incorporates the correct space group symmetry and, hence, reproduces band mixing and inversion-asymmetry effects
- The overall accuracy in the band structure is generally acceptable, and can be improved systematically;

Many-Body-Problem is described by the following Hamiltonian:

$$H = T_e + T_c + V_{e-c} + V_{e-e} + V_{c-c}$$
(6)

where T_e , T_c , are the kinetic energies of electrons and nuclei, and V_{e-c} , represents the Coulomb interactions between electrons and nuclei, V_{e-e} is electron-electron interaction, and V_{c-c} is the nuclei-nuclei interaction term.

Born-Oppenheimer approximation is used to simplify Many-Body-Problem in which the position of the nuclei does not vary so the kinetic energy term of the nuclei in (6) is neglected, taking only into account this approximation we can not solve the Many-Body- Problem due to the presence of electron-electron interaction. By considering that each electron moves in the electrostatic potential of all other electrons, we reduce the Many-Body-Problem electron-electron interaction problem to the problem of non-interacting electrons. Within this idea, Kohn and Sham introduce the density function theory (DFT) which is implemented in the majority of ab-initio electronic structure methods. Despite providing a high accurate results, DFT required lots of computational time, to reduce the computational time but still have a quantitative behavior of the system, one can use a parametrized tight-binding (TB) method with the parameters obtained by ab-initio calculation.

5.1 Basics

In this section we present the main theoretical basis of the tight-binding method used to modelize the band structure of Topological Insulators.

The solution of one-electron Schrödinger equation in a special finite set of basis functions is searched :

$$H |\Psi\rangle = (T+V) |\Psi\rangle \tag{7}$$

where T is the one-electron kinetic energy and V is the effective one-electron potential in the mean field approximation. $|n, i, \mu\rangle$ are used as atomic-orbital-like basis functions, where n denotes the Bravais vector R_n , i is the i-th basis with its position τ_i in the unit cell and μ represents the orbital type (s,p,d).

The Schrödinger equation becomes the matrix-eigenvalue equation: $\underline{H}.c = E.\underline{S}.c$, $\underline{H}, \underline{S}$ are the Hamiltonian and the overlap matrix in the representation of the atomic orbitals, c is an eigenvector containing the coefficients for the linear expansion of the atomic orbital-like of the wave function $|\Psi\rangle$,

$$|\Psi\rangle = \sum_{n,i,\mu} c_{ni\mu} |n,i,\mu\rangle \tag{8}$$

The expression of \underline{H} and \underline{S} in the atomic orbitals representation is :

$$H_{ni\mu}^{mj\nu} = \langle n, i, \mu | m, j, \nu \rangle , \qquad (9)$$

$$S_{ni\mu}^{mj\nu} = \langle n, i, \mu | m, j, \nu \rangle , \qquad (10)$$

By taking into account the periodic structures we can introduce a new basis of Bloch-waves of the following form:

$$|\phi\rangle = \frac{1}{\sqrt{N}} \sum_{n,i,\mu} \exp(ik(R_n + \tau_i)) |n, i, \mu\rangle, \qquad (11)$$

In the representation of the Bloch-waves, the Hamiltonian H and the overlap matrix become:

$$H_{i\mu}^{j\nu} = \langle \phi_{k,i,\mu} | H | \phi_{k,j,\nu} \rangle = \sum_{n} \exp(ik(R_n + \tau_j - \tau_i)) H_{0i\mu}^{nj\nu}$$
(12)

$$S_{i\mu}^{j\nu} = \langle \phi_{k,i,\mu} | \phi_{k,j,\nu} \rangle = \sum_{n} \exp(ik(R_n + \tau_j - \tau_i)) S_{0i\mu}^{nj\nu}$$
(13)

The bloch wave are orthogonal for different k-values in the Brillouin zone so $\langle \phi_{k,i,\mu} | \phi_{k,j,\nu} \rangle$ and $\langle \phi_{k,i,\mu} | H | \phi_{k,j,\nu} \rangle$ are zero for k different from k'. The matrix elements of the Hamiltonian $H_{0i\mu}^{nj\nu}$ and those of the overlap matrix $S_{0i\mu}^{nj\nu}$ are described by slater koster parametrization.

5.2 Slater-Koster parametrization

In the case of one basis atom is considered, the element of the Hamiltonian matrix is given by:

$$H_{0\mu}^{n\nu} = \int \phi_{\mu}^{*}(r).(T+V).\phi_{\nu}(r-R_{n}).dr$$
(14)

$$H_{0\mu}^{n\nu} = \int \phi_{\mu}^{*}(r).(T + \sum_{m} v_{at}(r - R_{m})).\phi_{\nu}(r - R_{n}).dr, \qquad (15)$$

where $v_{at}(r - R_m)$ is the atomic potential of the atom in the m-th unit-cell and $\phi_{\mu}(r) = \langle r | n, \mu \rangle$. Two types of integrals can be distinguished. 1-center-integrals:

$$\int \phi_{\mu}^{*}(r).v_{at}(r).\phi_{\nu}(r).dr$$
(16)

 $\mu = \nu$: on site atomic orbital energies, ε_{mu} $\mu \neq \nu$: small contribution if overlap $\langle \phi_{\mu} | \phi_{\nu} \rangle \neq 0$ 2-center-integrals:

$$\int dr \,\phi_{\mu}^{*}\left(r\right) \cdot \sum_{n \neq 0} v_{at}\left(r - R_{n}\right) \cdot \phi_{\nu}\left(r\right) \tag{17}$$

 $\mu = \nu$: contribution to the on-site energies due to existence of other atoms $\mu \neq \nu$: hopping element on-site from $\mu \rightarrow \nu$ due to the existence of other atoms

$$\int dr \,\phi_{\mu}^{*}\left(r\right) \cdot v_{at}\left(r\right) \cdot \phi_{\nu}\left(r-R\right), \qquad R \neq 0 \tag{18}$$

typical hopping elements, which describe the electronic transition from $\phi_{\nu}(r-R)$ to $\phi_{\mu}(r)$ and it is only for the valence electrons.

3-center-integrals : are very small for atomic orbitals $\phi_{\mu}(r)$ and they are neglected

in theoretical tight-binding descriptions.

In order to simulate the system by the TB method, the on-site elements and the hopping integrals are parameterized. A common parametrization for the hopping elements is the so-called "Slater-Koster parametrization", each hopping element depends on the distance and and the direction of the bonding between the corresponding atoms. Therefore the parametrization of the hopping elements consists of a angular-dependent description and a distance-dependence parametrization.

The angular dependence of the basis function $\phi_{\nu} (r - R)$ is expressed by the s-, pand d-orbitals. These orbitals are linear combinations of the spherical harmonics. Thus, the hopping-elements contain the matrix elements of the Hamiltonian:

$$\tilde{V}_{ll'm}^{(i \to j)} = \langle n, i, l, m | H | n', j, l', m \rangle \quad (m = m')$$
(19)

where $|l, m\rangle$ is the spherical harmonic function and m is the magnetic quantum number of the orbitals, m stands for σ, π , and δ and must equal to m' due to selection rules; l is the angular quantum number of the orbitals and stands for s,p,d.

The hopping elements of the Hamiltonian in the representation $(s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{xz}, d_{xz}, d_{x^2-y^2}, d_{z^2})$ is presented in the figure 4, where $\underline{H}^{\nu}_{\mu}(R \cdot \vec{e}_z) = H^{mj\nu}_{ni\mu}$ with $R_n - R_m = R \cdot e_z (R_n \neq R_m)$ the nearest-neighbour bonding direction and i = j.

The spherical harmonic functions have an angular dependence, so all hopping elements along a bonding direction R can be expressed by linear combinations of these 10 Slater-Koster parameters. To get the matrix with the hopping elements along the R direction we have to rotate $\underline{H}(R \cdot \vec{e_z})$ from the z-axis to the direction of the bonding.

$$\underline{\mathbf{H}}(R) = \underline{\mathbf{U}}^{\dagger} \cdot \underline{\mathbf{H}}(R.e_z) \cdot \underline{\mathbf{U}}$$
(20)

where \underline{U} is the unitary matrix, which changes the representation of the s-, p-, dorbitals with the z-axis as quantization axis into the representation with the R-axis as a quantization axis.

5.3 Electronic structure properties

The eigenvalue-equation for the Hamiltonian is given by :

$$\underline{\mathbf{H}}\left(\vec{k}\right)\cdot\Psi_{i,\mu}\left(\vec{k}\right) = \varepsilon_{i\mu}\left(\vec{k}\right)\underline{\mathbf{S}}\left(\vec{k}\right)\cdot\Psi_{i,\mu}\left(\vec{k}\right)$$
(21)

$$\sum_{j\nu} H_{i\mu}^{j\nu} \left(\vec{k} \right) \cdot \left(\Psi_{i,\mu} \right)_{j\nu} \left(\vec{k} \right) = \varepsilon_{i\mu} \left(\vec{k} \right) \sum_{i\nu} S_{i\mu}^{j\nu} \left(\vec{k} \right) \cdot \left(\Psi_{i,\mu} \right)_{j\nu} \left(\vec{k} \right)$$
(22)

By solving this Hamiltonian we can find the expressions of $\varepsilon(\vec{k})$ and $\Psi_{i,\mu}(\vec{k})$, so we can calculate the Fermi energy and the density of states.

H_s^s	$=V_{ss\sigma}$
H_s^x	$= lV_{sp\sigma}$
H_x^x	$= l^2 V_{pp\sigma} + (1 - l^2) V_{pp\pi}$
H_x^y	$= lmV_{pp\sigma} - lmV_{pp\pi}$
H_x^z	$= lnV_{pp\sigma} - lnV_{pp\pi}$
H_{*}^{xy}	$=\sqrt{3}lmV_{sd\sigma}$
$H_{e}^{x^2-y^2}$	$=\frac{1}{2}\sqrt{3}(l^2-m^2)$
$H_s^{z^2}$	$= \left[n^2 - \frac{1}{2} (l^2 + m^2) \right] V_{sd\sigma}$
H_x^{xy}	$=\sqrt{3}l^2mV_{pd\sigma} + m(1-2l^2)V_{pd\pi}$
H_r^{yz}	$=\sqrt{3}lmnV_{pd\sigma}-2lmnV_{pd\pi}$
H_x^{xz}	$=\sqrt{3}l^2nV_{pd\sigma} + n(1-2l^2)V_{pd\pi}$
$H_{x}^{x^{2}-y^{2}}$	$=\frac{1}{2}\sqrt{3}l(l^2-m^2)V_{nd\sigma}+l(1-l^2+m^2)V_{nd\sigma}$
$H_{y}^{x^{2}-y^{2}}$	$=\frac{1}{2}\sqrt{3}m(l^2-m^2)V_{pd\sigma}-m(1+l^2-m^2)V_{pd\pi}$
$H_{z}^{y^{2}-y^{2}}$	$=\frac{1}{2}\sqrt{3}n(l^2-m^2)V_{pd\sigma}-n(l^2-m^2)V_{pd\sigma}$
$\tilde{H_x^{z^2}}$	$= l \left[n^2 - \frac{1}{2} (l^2 + m^2) \right] V_{pd\sigma} - \sqrt{3} l n^2 V_{pd\sigma}$
$H_{u}^{z^{2}}$	$= m \left[n^2 - \frac{1}{2} (l^2 + m^2) \right] V_{pd\sigma} - \sqrt{3} m n^2 V_{pd\pi}$
$H_{z}^{y^{2}}$	$= n \left[n^2 - \frac{1}{2} (l^2 + m^2) \right] V_{pd\sigma} + \sqrt{3} n (l^2 + m^2) V_{pd\sigma}$
\tilde{H}_{xy}^{xy}	$= 3l^2m^2V_{dd\sigma} + (l^2 + m^2 - 4l^2m^2)V_{dd\pi} + (n^2 + l^2m^2)V_{dd\delta}$
H_{xy}^{yz}	$= 3lm^2 nV_{dd\sigma} + ln(1 - 4m^2)V_{dd\pi} + ln(m^2 - 1)V_{dd\delta}$
H_{xy}^{xy}	$= 3l^2 mn V_{dd\sigma} + mn(1 - 4l^2) V_{dd\pi} + mn(l^2 - 1) V_{dd\delta}$
$H_{xy}^{x^2-y^2}$	$= \frac{3}{2}lm(l^2 - m^2)V_{dd\sigma} + 2lm(m^2 - l^2)V_{dd\pi} + \frac{1}{2}lm(l^2 - m^2)V_{dd\delta}$
$H_{uz}^{x^{y}}-y^{2}$	$=\frac{3}{2}mn(l^2-m^2)V_{dd\sigma}-mn\left[1+2(l^2-m^2)\right]V_{dd\pi}+mn\left[1+\frac{1}{2}(l^2-m^2)\right]V_{dd\delta}$
$H_{xx}^{y\tilde{2}}-y^{2}$	$=\frac{3}{2}nl(l^2-m^2)V_{dd\sigma}+nl\left[1-2(l^2-m^2)\right]V_{dd\sigma}-nl\left[1-\frac{1}{2}(l^2-m^2)\right]V_{dd\delta}$
H^{z^2}	$= \sqrt{3} lm \left[n^2 - \frac{1}{2} (l^2 + m^2) \right] V_{dd_7} - 2\sqrt{3} lm n^2 V_{dd_7} + \frac{1}{2} \sqrt{3} lm (1 + n^2) V_{dd_8}$
H_{uz}^{xy}	$= \sqrt{3}mn\left[n^2 - \frac{1}{2}(l^2 + m^2)\right]V_{dd\sigma} + \sqrt{3}mn(l^2 + m^2 - n^2)V_{dd\sigma} - \frac{1}{2}\sqrt{3}mn(l^2 + m^2)V_{dd\delta}$
H^{z^2}	$= \sqrt{3} ln \left[n^2 - \frac{1}{2} (l^2 + m^2) \right] V_{ddz} + \sqrt{3} ln (l^2 + m^2 - n^2) V_{ddz} - \frac{1}{2} \sqrt{3} ln (l^2 + m^2) V_{ddz}$
$H^{x^2-y^2}$	$= \frac{3}{2}(l^2 - m^2)^2 V_{1/2} + [l^2 + m^2 - (l^2 - m^2)^2] V_{1/2} + [n^2 + \frac{1}{2}(l^2 - m^2)^2] V_{1/2}$
$ _{L_{2}}^{T_{2}} _{L_{2}}^{T_{2}} _{L_{2}}^{T_{2}}$	$= \frac{1}{4} \begin{pmatrix} c & -m \end{pmatrix} \sqrt{dd\sigma} + \begin{bmatrix} c & +m & -(c & -m) \end{bmatrix} \sqrt{dd\pi} + \begin{bmatrix} n & +\frac{1}{4}(c & -m) \end{bmatrix} \sqrt{dd\sigma}$ $= \frac{1}{2} \sqrt{2} \begin{bmatrix} n^2 & 1/(2 + m^2) \end{bmatrix} V_{cc} + \sqrt{2} n^2 (m^2 - 1^2) V_{cc}$
$x^{2}-y^{2}$	$-\frac{1}{2}\sqrt{3(t-m)}\left[n-\frac{1}{2}(t+m)\right]\sqrt{dd\sigma} + \sqrt{3n}\left(m-t\right)\sqrt{dd\pi}$
2	$+\frac{1}{4}\sqrt{3(1+n^2)(l^2-m^2)}V_{dd\delta}$
$H_{z^{2}}^{z^{2}}$	$= \left n^{2} - \frac{1}{2}(l^{2} + m^{2})\right ^{2} V_{dd\sigma} + 3n^{2}(l^{2} + m^{2})V_{dd\pi} + \frac{3}{4}(l^{2} + m^{2})^{2}V_{dd\delta}$

Slater-Koster transformations for s, p and d-orbitals. The matrix elements $H_{\mu}^{\nu}(\boldsymbol{R}_n)$ of the real-space Hamiltonian depend on the direction cosines $l = \frac{(\boldsymbol{R}_n)_x}{|\boldsymbol{R}_n|}$, $m = \frac{(\boldsymbol{R}_n)_y}{|\boldsymbol{R}_n|}$ and $n = \frac{(\boldsymbol{R}_n)_z}{|\boldsymbol{R}_n|}$ of the bonding vector \boldsymbol{R}_n . The table is separated in *s-s*, *s-p*, *p-p*, *s-d*, *p-d* and *d-d* matrix elements by horizontal lines.

Figure 4: Slater-koster Transformations [3]

$$\underline{H}(R \cdot \boldsymbol{e}_z) = \begin{pmatrix} V_{ss\sigma} & 0 & 0 & V_{sp\sigma} & 0 & 0 & 0 & 0 & V_{sd\sigma} \\ 0 & V_{pp\pi} & 0 & 0 & 0 & V_{pd\pi} & 0 & 0 \\ 0 & 0 & V_{pp\pi} & 0 & 0 & V_{pd\pi} & 0 & 0 & 0 \\ -V_{sp\sigma} & 0 & 0 & V_{pp\sigma} & 0 & 0 & 0 & 0 & V_{pd\sigma} \\ 0 & 0 & 0 & 0 & V_{dd\delta} & 0 & 0 & 0 & 0 \\ 0 & 0 & -V_{pd\pi} & 0 & 0 & V_{dd\pi} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & V_{dd\pi} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & V_{dd\sigma} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & V_{dd\sigma} & 0 \\ V_{sd\sigma} & 0 & 0 & -V_{pd\sigma} & 0 & 0 & 0 & 0 & V_{dd\sigma} \end{pmatrix}$$

Figure 5: 10 types of Slater-Koster parameters



Figure 6: Representation of Slater-Koster parameters

• Fermi energy:

The fermi energy may be calculated from:

$$N_{e^-} = \sum_{\vec{k},n} f\left(\varepsilon_{\vec{k},n}, \varepsilon_F\right) \tag{23}$$

where

$$f(\varepsilon, \varepsilon_F) = \frac{1}{\exp(\beta \cdot (\varepsilon - \varepsilon_F)) + 1}$$
(24)

is the Fermi-Dirac distribution function for the electrons and N_{e^-} is the total number of valence electrons in the system, $\beta^{-1} = k_B \cdot T \approx 1 \text{ meV}$ (thermal smearing) is introduced to stabilize the calculation.

• Density of states:

The DOS is defined as:

$$D(\varepsilon) = \sum_{\vec{k},n} \delta(\varepsilon - \varepsilon_{\vec{k},n})$$
(25)

and the partial DOS of the j-th basis atom and the μ -th orbital is given by:

$$D_{j\nu} = \sum_{\vec{k},n} \delta(\varepsilon - \varepsilon_{\vec{k},n}) \cdot (\Psi^{\dagger}_{\vec{k},n})_{j\nu} \cdot (\underline{\mathbf{S}}(\vec{k}) \cdot \Psi_{\vec{k},n})_{j\nu}$$
(26)

In the orthogonal set of basis functions, the eigenvectors would be orthonormal : $\Psi_n^{\dagger} \cdot \Psi_m = \delta_{nm} \forall n, m$. In the case of non-orthogonal set, $\Psi_n^{\dagger} \cdot \underline{S} \cdot \Psi_m = \delta_{nm} \forall n, m$. Thus the total DOS is:

$$D(\varepsilon) = \sum_{\vec{k},n} \delta(\varepsilon - \varepsilon_{\vec{k},n})$$
(27)

• Band energy:

The band energy is defined by :

$$E_{band} = \sum_{\vec{k},n} \varepsilon_{\vec{k},n} \cdot f(\varepsilon_{\vec{k},n}, \varepsilon_F)$$
(28)

5.4 Stoner model-Exchange Hamiltonian

In the magnetic system, the spin dependence causing exchange splitting between the electronic majority-band (spin up band) and the minority-band (spin down band) is explained by Stoner model (figure 5). The exchange splitting is described by :

$$\varepsilon_{i\mu}^{exc} = I_{i\mu} \cdot m_i^d. \tag{29}$$

where $I_{i\mu}$ is the Stoner parameter depends on materials and $m_i^d = N_{i,d}^{\uparrow} - N_{i,d}^{\downarrow}$ stands for magnetic d-moment for collinear magnets, $N_{i,d}^{\sigma}$ ($\sigma = \uparrow, \downarrow$) the number of electron in the majority and minority bands. We note that the Stoner parts are used only for d-orbitals since the magnetism originate mainly from the d-electrons. The exchange Hamiltonian elements are given by:

$$[H_{mag}]_{i\mu}^{j\nu} = \begin{pmatrix} -\frac{I_{i\mu}}{2} \cdot m_i^d & 0\\ 0 & +\frac{I_{i\mu}}{2} \cdot m_i^d \end{pmatrix} \cdot \delta_{ij}\delta_{\mu\nu} .$$
(30)

5.5 Spin-orbit coupling

This section on the description of the spin-orbit coupling is very important owing to the specific role of the spin-orbit coupling in the spin-orbitronics effects and in particular to its role in the various spin-to-charge conversion effects (spin-Hall effect, inverse Edelstein effect). The spin-orbit coupling is the relativistic effect arising from the Dirac equation. The SOC Hamiltonian is expressed as:

$$H_{SOC}\left(\Delta V(\vec{r}) \times \vec{p}\right) \cdot \vec{\sigma} \tag{31}$$

Where $V(\vec{r})$ is the electrostatic potential, $\vec{\sigma}$ is the vector containing the Paulimatrices and \vec{p} stands for the momentum of the electron. Using spherical potential approximation: $V(\vec{r}) = V(r)$, the SOC Hamiltonian can be simplified as:

$$H_{SOC} = \xi \left(r \right) \cdot \vec{L} \cdot \vec{S} \tag{32}$$



Figure 7: a) Stoner criteria for the appearance of spin-split band and ferromagnetism of transition metals (real band structure of Cobalt), b) Co band structure (DFT formalism)

with $\vec{L} = \vec{r} \times \vec{p}$ the angular momentum and $\vec{S} = \frac{\hbar}{2} \cdot \vec{\sigma}$ the spin of the electron and the radial-dependent function $\xi(r) = \frac{1}{2m^2c^2} \cdot \frac{1}{r} \cdot \frac{\partial V(r)}{\partial r}$. The SOC Hamiltonian matrix now can be represented on the atomic-like orbitals basis as:

$$(H_{SOC})^{j\nu\sigma'}_{i\mu\sigma} = \langle i, \mu, \sigma | \xi \cdot \vec{L} \cdot \vec{S} | j, \nu, \sigma' \rangle = \xi_{i\mu,j\nu} \cdot \langle \mu, \sigma | \vec{L} \cdot \vec{S} | \nu, \sigma' \rangle$$
(33)

where $\xi_{i\mu,j\nu} = \frac{\hbar}{2} \left[dr \cdot r^2 \xi(r) R_{i\mu}^*(r) \cdot R_{j\nu}^*(r) \right]$ and $\langle \mu, \sigma | \vec{L} \cdot \vec{S} | \nu, \sigma' \rangle = \int_0^{2\pi} \int_0^{2\pi} d\Theta d\phi \sin \Theta \cdot \left[Y_{\mu}^{(i)} \right]^*(\Theta, \phi) \cdot \left[Y_{\nu}^{(j)} \right]^*(\Theta, \phi) \cdot \langle \sigma | \vec{L} \cdot \vec{S} | \sigma' \rangle$ represents the radial and angular dependence parts The SOC exist only for p-, d-, f-orbitals since l = 0 for s-orbital. The angular moment \vec{L} in the atomic orbitals basis is written as $L_{\mu}^{\nu} = \langle \mu | \vec{L} | \nu \rangle$. Finally, the SOC Hamiltonian matrix elements of the atomic orbitals in the spin-representation with the z-axis as quantization axis are given by:

$$(H_{SOC})_{i\mu}^{j\nu} = \xi_{i\mu} \cdot \begin{pmatrix} (L_z)_{\mu}^{\nu} & (L_x)_{\mu}^{\nu} - i \cdot (L_y)_{\mu}^{\nu} \\ (L_x)_{\mu}^{\nu} + i \cdot (L_y)_{\mu}^{\nu} & - (L_z)_{\mu}^{\nu} \end{pmatrix} \cdot \delta_{ij}$$
(34)

where $(L_{\alpha})^{\nu}_{\mu}$ are the angular momentum components in the atomic orbital representation.

5.6 Green function

Green functions G(E) can defined as solutions of inhomogeneous Schrödinger equation of the type:

$$\left(z - \hat{H}\right)\hat{G}\left(z\right) = \hat{I} \tag{35}$$

where $z = E \pm i\xi$ is a complex number; ξ stands for energy broadening and \hat{H} is the Hamiltonian of the system. The Green function then can be expressed as: $\hat{G}(z) = \left(z - \hat{H}\right)^{-1}$ or $\hat{G}(z) = \frac{1}{z - \hat{H}}$. In the eigenvectors of the Hamiltonian basis, the Green function is written by:

$$\hat{G}(z) = \sum \frac{\left|\Psi^{(n)}\right\rangle \left\langle\Psi^{(n)}\right|}{z - E^{(n)}} \tag{36}$$

To avoid the singularity of the Green function when E equals the eigenvalue of \hat{H} we introduce the retarded and advanced Green function depending on the sign of the imaginary part of z :

$$\hat{G}^{R}(z) = \lim_{\xi \to 0^{+}} \left(E + i\xi - \hat{H} \right)^{-1}$$
(37)

$$\hat{G}^{A}(z) = \lim_{\xi \to 0^{+}} \left(E - i\xi - \hat{H} \right)^{-1}$$
(38)

Now, we define a new Green function for the system $\hat{G}'(z) = \hat{G}^R(z) - \hat{G}^A(z)$. The density of state then is given by:

$$D(E) = -\frac{1}{2\pi} ImTr \sum_{n} \hat{G}'(z)$$
(39)

where Tr denotes the trace of matrix and Im stands for imaginary part of the matrix. The DOS for spin up electron and spin down electron are expressed as follows:

$$DOS^{\uparrow}(E) = -\frac{1}{2\pi} ImTr \sum_{n} U \cdot \hat{G}'(z)$$
(40)

$$DOS^{\downarrow}(E) = -\frac{1}{2\pi} ImTr \sum_{n} D \cdot \hat{G}'(z)$$
(41)

where U and D are the block diagonal matrix of $(I_2 + \hat{\sigma}_z)$ and $(I_2 - \hat{\sigma}_z)$ with I_2 is the 2-dimension identity matrix.

6 Bismuth Antimony $Bi_{1-x}Sb_x$

6.1 From bulk crystal structure to slab structures

Bulk Bi and Sb are group-V semimetals. They have a weak overlap between the valence and the conduction bands, which leads to a small number of free electrons and holes. Connected with these properties are high carrier mobilities, small effective masses, and a large characteristic length, which makes Sb and Bi ideal for studying and employing quantum confinement effects.

Bulk Bi and Sb have the rhombohedral A7 structure as shown in figure 9.a, which is composed of two interpenetrating, trigonally distorted face-centered-cubic lattices with two atoms per unit cell. The x, y-directions represent the binary and bisectrix axes respectively, while z-direction represents the trigonal axes. The three primitive translation vectors of the lattice are:

$$a_1 = (-1/2a, -\sqrt{3/6a}, 1/3c) \tag{42}$$

$$a_2 = (1/2a, -\sqrt{3}/6a, 1/3c) \tag{43}$$

$$a_3 = (0, \sqrt{3}/3a, 1/3c) \tag{44}$$

the three corresponding reciprocal-lattice vectors, defined by

$$b_i.a_j = 2\pi\delta_{ij} \tag{45}$$

are given by:

$$b_1 = (-1, -\sqrt{3}/3, b)g \tag{46}$$

$$b_2 = (1, -\sqrt{3}/3, b)g \tag{47}$$

$$b_3 = (0, 2\sqrt{3}/3, b)g \tag{48}$$

where b = a/c and g is the reciprocal-lattice constant.

The Brillouin zone is shown in figure 9.b, it contains eight special points which are invariant under inversion and time reversal, denoted by Γ , T, and three equivalent L and X points.

The semimetals Bi and Sb have a negative indirect gap since the conduction-bandminima at the L points lie at (40 meV for Bi, 180 meV for Sb) lower than the valence-band maxima (at the T point for Bi, and H points for Sb), figure 8.

The ensemble of parameters that describes pure Bismuth (Bi) and pure Antimony (Sb) for the bulk can be found in [5], which is the reference for all the TB calculations, in this article we find also the expression of the Hamiltonian that describes bulk Bismuth versus the wave vector (k_x, k_y, k_z) , which is a matrix (16×16) that contains 2 atoms per unit cell and four orbitals (sp^3) and the spin σ .



Figure 8: Band structure of Bi (a) and Sb (b) along various symmetry lines

In order to describe thin film $Bi_{1-x}Sb_x$, it is necessary to generalize the TB approach used in the case of pure Bi, by linearizing the hopping potentials for $x \neq 0$ and $x \neq 1$. This work was done by proposing equations 2.4 and 2.5 in [8]. For thin film structures, it is necessarily to introduce the terms of spin-orbit at the interface of type "Rashba surface" and describing the effects of the electric field and the transfer of charge at the upper and lower surfaces.

6.2 Involvement of Rashba terms

The Rashba effect, which is caused by the strong spin-orbit coupling in the two dimensional surface or interface, is one of the most important physical phenomena which can be applied to the development of next-generation spintronic devices, since it enables the generation and manipulation of spin-polarized electrons solely by an electric field.

In nonmagnetic solids, the electronic states with opposite spin have the same energy (Kramers' degeneracy) because of the time-reversal and the space-inversion symmetries. [7]

More specifically, the following relation is requested from the space-inversion symmetries.

$$E(k,\uparrow) = E(-k,\uparrow),\tag{49}$$



Figure 9: a)-Crystal structure of Bi and S, showing first and second neighbors (labeled 1 and 2) to the central atom represented by an open circle. The bisectrix (C1), binary (C2) and trigonal (C3) axes ,b)-(3D) Brillouin zone and its projection onto the (111) surface, z is along the (111) direction, y is along the $\overline{\Gamma}$ to \overline{M} direction

In addition, the following is also requested from the time-reversal symmetries.

$$E(k,\uparrow) = E(-k,\downarrow),\tag{50}$$

These two equations (49) and (50) finally result in the following relation.

$$E(k,\uparrow) = E(k,\downarrow),\tag{51}$$

On the other hand, the relation (1) is not satisfied under the absence of the spaceinversion symmetries such as surface or interface.

$$E(k,\uparrow) \neq E(k,\downarrow) \tag{52}$$

Therefore the spin degeneracy is lifted by the spin-orbit interaction, resulting in the splitting of energy bands. Now we explain an electronic spin state for free electron model as a simple example of a broken space-inversion symmetry system. The Hamiltonian which takes into account the spin-orbit interaction term is expressed as

$$H = H_0 + H_{SO} = -\frac{\hbar^2}{2m} \nabla^2 + \frac{\hbar}{4m^2 c^2} \sigma \cdot (\nabla V \times p)$$
(53)

where \hat{V} is the crystal potential, p is the momentum operator, c is the velocity of light, and σ is the spin operator. The potential in the presence of the space inversion



Figure 10: Relationship between momentum and surface potential at surface



Figure 11: Spin polarization vector expected for the Rashba effect at normal Fermi surface

asymmetry can generate a net electric field.

If the term $\nabla V \times \hat{p}$ is considered as a magnetic field (effective magnetic field), the spin splitting arises because of the finite H_{SO} . When an electron moves with momentum p, the electron feels potential gradient $\nabla V = (0, 0, E_z)$ along the surface normal.

 $\nabla V \times p$ term acts as an effective magnetic field B_{eff} which is parallel to surface and orthogonal to $p = \hbar k$. As a result, the electron spin is quantized along the direction perpendicular to the wave vector k in the surface plane. The energy of free electron gives the following eigenvalues,

$$E(k) = \frac{\hbar^2}{2m}k^2 \pm \frac{\hbar^2 E_z}{4m^2 c^2}k = \frac{\hbar^2}{2m}k^2 \pm \alpha_R k$$
(54)

which is well known as Rashba effect, where α_R is a so-called Rashba parameter. This equation means that the free-electron-like parabolic band (Fig.11) splits into two bands along the k_{\parallel} -direction, and the positive term in the equation provides an inner state, while the negative term gives an outer one. There is a band crossing at $k_{\parallel} = 0$, and spins are anti-symmetric with respect to $k_{\parallel} = 0$ as required by the time-reversal symmetry.

The magnitude of the spin splitting by the Rashba effect depends on the strength

of the atomic spin-orbit coupling, namely, the Rashba splitting becomes larger for heavier atom which has a strong spin-orbit coupling. Here, Rashba parameter α_R is given by

$$\alpha_R \propto \frac{\partial V}{\partial z} |\psi|^2 d\tau \tag{55}$$

where $E_z = \frac{\partial V}{\partial z}$ is the potential gradient perpendicular to the surface, and Ψ is the wave function of the surface band. Since the E_z value becomes maximum around the nucleus, the α_R value becomes large when the electron wave function of surface band is concentrated around the nucleus. Moreover, since the potential around the nucleus is nearly anti-symmetric along the z-axis, it is required that $|\Psi|^2$ has to be also asymmetric with respect to the z-axis when α_R becomes large in Eq.7 so the size of the Rashba spin splitting highly depends on the asymmetry of the wave function at the heavy nucleus around the surface.

This indicates that the size of the band splitting by the Rashba effect is affected not only by the spin-orbit interaction, but also by the distortion of the wave function along the surface vertical direction owing to the structure and chemical bonding characteristics.[9]

6.3 Tight binding model for $Bi_{1-x}Sb_x$

The alloy Bi_xSb_{1-x} retains the rhombohedral A7 crystal structure. As x increases from zero two things happen. First, the small gap at L closes and then reopens. The L_s (even-parity) and L_a (odd parity) bands switch places, and the mass of the three dimensional Dirac point changes sign. Second, the top of the valence band at T descends below the bottom of the conduction band, resulting in a semi metalsemiconductor transition.

 Bi_xSb_{1-x} thin film is obtained by stacking BLs along the (111) direction, such as the z-axis depicted, the surface is thus parallel to the xy plane and the uppermost and lowermost BLs are in contact with a vacuum.

We first construct a Hamiltonian model for the $Bi_{1-x}Sb_x$ thin film, for this purpose, the sp^3 tight-binding model proposed for the bulk Bi crystal used in [5] is adapted to the $Bi_{1-x}Sb_x$ thin film. There are s, p_x , p_y , p_y with spin index σ on each atom and the hopping terms among the atomic orbitals are decomposed into inter- and intra-BL hopping terms.

There is a surface potential gradient on the surface BL along the z axis between the surface $Bi_{1-x}Sb_x$ and the vacuum, the surface Rashba effect is induced by the contribution of this potential gradient originating from atomic position relaxation or surface reconstruction. In terms of the sp^3 tight-binding model, this is described by the following spin independent hopping terms between the nearest-neighbor sites, R_i and R_j :

$$t_{\alpha\beta} = \gamma_{pp} \cos(\theta_{ij}), (\alpha, \beta) = (p_x, p_z) or(p_z, p_x)$$
(56)

$$t_{\alpha\beta} = \gamma_{pp} \cos(\theta_{ij}), (\alpha, \beta) = (p_x, p_z) or(p_z, p_x)$$
(57)

$$t_{\alpha\beta} = \gamma_{sp}, (\alpha, \beta) = (p_x, p_z) or(p_z, p_x)$$
(58)

where θ_{ij} is the azimuthal angle between $R_i - R_j$ and the x axis, and γ_{pp} and γ_{sp} are the hopping terms, in the bulk BiSb crystal model and due to the inversion symmetry $\gamma_{pp} = \gamma_{sp} = 0$. It is assumed that the surface hopping terms appear only on the first atomic layer of the uppermost BL and the lowermost atomic layer with $-\gamma_{sp/pp}$, the sign minus here is due to the fact that the surface field points in the opposite direction at the lowermost layer, the values of γ_{sp} and γ_{pp} remain to be determined at this stage.[4]

6.4 Implementation of the Hamiltonian

The Hamiltonian that we employ can be divided into three different contributions:

$$H = H^{tb} + H^{SOC} + H^z \tag{59}$$

The first term is the tight-binding Hamiltonian describing the band structure in the linear combination of atomic orbitals (LCAO) approximation. In this part about $Bi_{1-x}Sb_x$ we will consider only s and p orbitals with on-site contributions E_s and E_p , respectively. The tight binding parameters describing the orbital overlap from neighboring atoms are $V_{ss\sigma}, V_{sp\sigma}, V_{pp\sigma}$ and $V_{pp\pi}$. Here in our model we consider first, second and third neighbors so in total we have twelve parameters that describe the orbital overlap. The corresponding matrix is then

$$H_{o,o'}^{tb} = E_o \delta_{o,o'} + \sum_i \exp\{ikR_i\} E(o,o',R_i)$$
(60)

Here o and o' are the orbitals (s, p_x, p_y, p_z) in the tight binding matrix and $\delta_{o,o'}$ is the Kronecker. $E(o, o', R_i) = \langle o | H^{tb} | o', R_i \rangle$ is an element from the table in figure 2, i denotes the sum over neighboring atoms with R_i being the vector connecting two neighboring atoms.[8]

In our model that we have developed to reproduce the band structure, DOS and Spin texture, the Hamiltonian in equation 61 represents the kinetic energy term and it is denoted by H_k and contains 4 sub-matrices and each one of these four sub-matrices is 8-by-8.

The first sub-matrice of H_k is H_1 , it contains the on-site energies E_s and E_p and the in-plane terms due to the presence of the third neighbors. The nearest neighbors and second nearest neighbours which represent plane to plane terms contribute to

 H_k through H_{2-1} and H_{2-2} respectively. The off-diagonal term H_2 is the sum of H_{2-1} and H_{2-2} , so the total kinetic terms H_k can be presented as follows:

$$H_k = \begin{pmatrix} H_1 & H_2 \\ H_3 & H_4 \end{pmatrix} \tag{61}$$

where $H_3 = H_2^{\dagger}$ and $H_3 = H_1$. The term H^{SOC} in Equation 62 is the atomic spin-orbit interaction and it is expressed by the following Hamiltonian in the basis $(p_{x\uparrow}, p_{y\uparrow}, p_{z\uparrow}, p_{x\downarrow}, p_{y\downarrow}, p_{z\downarrow})$:

$$H^{SOC} = \frac{\lambda}{3} \begin{pmatrix} 0 & -i & 0 & 0 & 0 & 1\\ i & 0 & 0 & 0 & 0 & -i\\ 0 & 0 & 0 & -1 & i & 0\\ 0 & 0 & -1 & 0 & i & 0\\ 0 & 0 & -i & -i & 0 & 0\\ 1 & i & 0 & 0 & 0 & 0 \end{pmatrix}$$
(62)

where λ is the spin-orbit coupling parameter ($\lambda_{Bi} = 1.5eV$ and $\lambda_{Sb} = 0.6eV$), $\lambda_{Bi_{1-x}Sb_x}$ can be given by a linear combination of λ_{Sb} and λ_{Bi} , $\lambda_{Bi_{1-x}Sb_x} = (1 - 1)$ $x_{\lambda} \lambda_{Bi} + x_{\lambda} \lambda_{Sb}$. The SOC term is labeled in our codes as H_{SO} and it contains four sub matrices with H_{s11} has the form of H^{SOC} in 62, the remaining 3 sub-matrices are: $H_{s22} = H_{s11}$ and $H_{s12} = H_{s21} = 0_{8,8}$, so the final expression of H_{SO} is represented in equation 63:

$$H_{SO} = \begin{pmatrix} H_{s11} & H_{s12} \\ H_{s21} & H_{s22} \end{pmatrix}$$
(63)

We can decomposed the Hamiltonian formed by H_k and H_{SO} into two parts: the first part is the intra terms: $H_{intra} = H_1 + H_{s11}$, and the second one is the inter terms : $H_{inter} = H_{1-inter} + H_{2-inter} = H_{2-1} + H_{2-2}$.

The third contribution H^z in equation 60 takes into account the potential gradient ξ in the z direction perpendicular to the 2D electronic structure, which resides in the xy plane.

The contribution of H^z can be divided into two contributions an on-site part and another part coming from neighboring atoms. The on-site contribution is characterized by γ_{sp} which is given by $\gamma_{sp} = \langle s | z | p_z \rangle$, where $z = rcos(\theta)$ and r is the radial component in spherical coordinates, γ_{sp} serves as an empirical parameter in the TB platform and it becomes more important for heavier atoms and this can be understood by the increasing of the spatial extension of the wave function, so that it becomes more sensitive to the effects of potential gradient.

The second contribution comes from the nearest-neighbour and it is characterized by γ_{pp} and it is defined by $\langle p_n | z | p_z, de_n \rangle$, where n denotes x,y and it depends on the distance (d) between neighboring atoms and it reaches its maximum for optimal



Figure 12: $Bi_{1-x}Sb_x$ thin film

overlap.

Once we define all the three contributions to the Hamiltonian H now we proceed to the construction of our thin film $Bi_{1-x}Sb_x$. We grow bilayer by bilayer along the (111) direction as shown in figure 12, the multi-layer Hamiltonian contains a diagonal part, an upper and lower diagonal elements due to plane to plane terms. The Rashba terms appear only on the top block and on the lower block since in the bulk we have inversion symmetry. The total Hamiltonian has the following form :

$$H = \begin{pmatrix} H_{11s} & H_{12}^{(1)} & 0 & 0 & \dots & 0 \\ H_{21}^{(1)} & H_{11} & H_{21}^{(2)} & 0 & \dots & 0 \\ 0 & H_{12}^{(2)} & H_{11} & H_{12}^{(1)} & \dots & 0 \\ \vdots & & & & \vdots \\ 0 & \dots & 0 & H_{12}^{(1)} & H_{11} & H_{12}^{(1)} \\ 0 & \dots & 0 & 0 & H_{12}^{(2)} & H_{11s}' \end{pmatrix}$$
(64)

6.5 Results and discussions

6.5.1 Comparaison to pure Bi

To see the validity of the model that we have constructed, first we compare our results to those obtained in [4] for Bismuth thin film, so in this part the value of x which represents Antimony concentration is 0. The values of γ_{sp} and γ_{pp} are taken to be 0.45 and -0.27 respectively which are the same values used in [4]. We plot the energy band structure and the density of state for a number of bilayers equals 16 $(n_b = 16)$. In figure 13 we present the results of our calculation and those obtained in [4], in our calculation the Fermi level is at 0 eV.

From the band structure in figure 13-a) we see two surface states that arise from



Figure 13: a) Band structure of thin film (16 BLs) Bismuth (our model), b) Saito's model, c) DOS at the surface of pure Bi thin film, d) Saito's model.

 $\overline{\Gamma}$, the upper surface state represents the electron surface state while the lower one represents the hole surface state, the two surface states have the large separation energy at \overline{M} , the two surface states cross the Fermi level which will give the possibility to see the electron and hole pockets in the DOS. By comparing our results to those in [4] we can see that the band structure that we have obtained is the same as the one found in [4].

The DOS is represented in figure 11.c) and it contains an hexagonal electron pocket at $\overline{\Gamma}$ then followed by six hole lobes due to the intersection of the hole surface sate with the Fermi level, then we see six extra electron lobes.

By comparing our results (13.c) to those of [4] (13.d) we see that they are similar, in (13-d) we see also an hexagonal electron pocket designed by the intersection of S1 (electron surface state) with the Fermi surface, and six hole lobes designed by S2 (hole surface state), then followed by six electron lobes, which probe that our model works very well to describe thin film pure Bismuth.

Now we can use our model to generate the band structure and DOS of thin film $Bi_{1-x}Sb_x$ and it will be the subject of the next section.

As we see before, the Rashba terms play an important role in describing the behaviour of the band structure obtained experimentally, so our goal in the next section when we will deal with thin film $Bi_{1-x}Sb_x$ is to find the best Rashba terms at the surface, this is can be done by fitting the band structure to the ARPES measurements.

6.5.2 Electronic band structure and DOS of $Bi_{1-x}Sb_x$

In this part we will reproduce the electronic band structure and DOS for x = 7%, 15%, 21% and 30%, compared to ARPES experiments. In our model we have the possibility to control the thickness of $Bi_{1-x}Sb_x$ thin film via controlling the number of bi-layers, we choose $n_b = 40, 13$ and 7 bi-layers which equivalent to thickness 15, 5, 2.5 nm respectively.

The values of x and n_b were not taken arbitrary but we choose them according to the ARPES measurements that have been grown at "SOLEIL" Synchrotron by Laëtitia Baringthon.

To construct the band structure first we solve the Hamiltonian, then it is diagonalized. The multilayer Hamiltonian in our model has a dependence on x, n_b , $\lambda_{Bi_{1-x}Sbx}$, so each time we vary these three parameters to obtain the band structure. The most important two parameters that affect the surface states are γ_{sp} and γ_{pp} which play the role of fitting parameters, in order to find the best values of these two parameters we compare our results to what obtained in ARPES measurements.

The energy band structure plotted are classified according to the number of bilayers, in figure.14 for $n_b = 13$, in figure.15 $n_b = 7$, and figure.16 $n_b = 40$. To find the

best fitting parameters and the position of the Fermi level as found in ARPES, we compare our results to ARPES measurements in figure.17, since we have only the binding energy for only a thickness of (5nm) so we fit only the electronic band structure corresponding to 13 BLs.

The energy band structure in figures:14, 15, 16 is along $\overline{\Gamma} \cdot \overline{M}$ line $(k_x = 0)$, as in the case of Bismuth thin film what we see from the energy band structure that two surface bands emerge from the bulk valence band near $\overline{\Gamma}$, these two bound surface states are due to the presence of the surface terms.

The passage from 7 BLs to 40 BLs increases the number of electronic states in the bulk, while increasing the concentration of Sb, the gap between the two maxima of electron and hole surface states around $k_y = 0.2A^{-1}$ decreases, and they start to be close to each other at $k_y \approx 0.4A^{-1}$.

The surface states appear clearly in the ARPES measurements, normally they rise close to $\overline{\Gamma}$ then they disappear when we go towards the bulk.

The density of states and the band structure of the thin film is obtained from the retarded Green's function matrix $G(E,k_x,k_y)$, E denotes the energy:

$$G(E, k_x, k_y) = [E + i\delta - H(k_x, k_y)]^{-1}$$
(65)

with $\delta = 1 \times 10^{-2}$ in the numerical calculations. the DOS in the sd defined by:

$$\rho(i, E, k_x, k_y) = -\frac{1}{\pi} \operatorname{Tr} \operatorname{Im} G(E, k_x, k_y)$$
(66)

where Tr represents the trace over the orbitals. The results are presented in figures 18 and 19, in figure 18 as in the case of pure Bismuth thin film we have an hexagonal electron pocket followed by six hole lobes then six more electron lobes, the most important result is that the hole lobes do not change when we increase the number of BLs (thickness), in the other hand the electron lobes are affected by increasing the thickness of the film, we go from a small lobes in 7 BLs to big ones when $n_b = 40$, in figure 18.d) we have the ARPES measurement in which we see the hexagonal electron pocket and electron-hole lobes. In figure 19 we have plotted DOS for x=0.21 and x=0.3 and the observations are the same as those for x=0.07.



Figure 14: The energy band structure of $Bi_{1-x}Sb_x$ for BLs=13 and a) x=0.07, $\lambda = 1.437$, b) x=0.15, $\lambda = 1.365$, c) x=0.21, $\lambda = 1.311$, d) x=0.3, and $\lambda = 1.23$. the values of $\gamma_{sp} = (0.2, 0.11, 0.14, 0.19)$ and $\gamma_{pp}(-0.6, -0.73, -0.64, -0.23)$ for x(0.07, 0.15, 0.21, 0.3), respectively.



Figure 15: The energy band structure of $Bi_{1-x}Sb_x$ for BLs=7 and a) x=0.07, $\lambda = 1.437$, b) x=0.15, $\lambda = 1.365$, c) x=0.21, $\lambda = 1.311$, d) x=0.3, and $\lambda = 1.23$. γ_{sp} and γ_{pp} are the same for BLs=13.



Figure 16: The energy band structure of $Bi_{1-x}Sb_x$ for BLs=40 and a) x=0.07, $\lambda = 1.437$, b) x=0.15, $\lambda = 1.365$, c) x=0.21, $\lambda = 1.311$, d) x=0.3, and $\lambda = 1.23$



Figure 17: ARPES band structure (March 2021) for 5nm of $Bi_{1-x}Sbx$ and x(0.07, 0.15, 0.21, 0.3)

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Figure 18: Density of states at the fermi energy for x=0.07, a)7BLs, b)13 BLs, c)40BLs,d)ARPES measurement for x=0.07 and



Figure 19: Density of states at the Fermi energy for x=0.21, a) 7BLs, b) 13 BLs, c) 40BLs, and for x=0.3, e) BL=13, d) and f) ARPES measurements (March 2021)

6.5.3 Spin-texture and spin resolved DOS

The spin-resolved DOS ($\rho_{\sigma\alpha}(i = 1, E = 0 \text{ eV}, k_x, k_y)$) at the Fermi energy ($E_F = 0$) and on the top BiSb surface plane and mapped onto the 2D Brillouin zone are shown on Fig. 20a. This displays the in-plane σ_y spin component for $S_{1,2}$ projected on the 2D Fermi surface. The plots evidences the symmetry of the corresponding spinsplitting near the Γ point (the yellow color represents a positive projection of the spin whereas a red color represents a negative projection of the spin). Near Γ , along the $\Gamma \overline{M}$ direction represented by k_x , the spin is mainly oriented along $\pm y$ whereas the opposite holds for the k_y direction (not shown).

The spin-splitting onto S1 is then observed to be rather similar to what is expected from a pure 2×2 Rashba model except the reminiscence of the hexagonal symmetry away from the Γ point. In details, on S1, σ lies mainly along the pocket structure, while on the S2 hole pocket, the direction of σ is opposite to that on S1. Note moreover that the in-plane σ_k component along the lobe on S2 is almost constant.

These numerical observations are consistent with previous experimental results obtained on Bi. One also observes that is not always perpendicular to the wavevector k on S2, and this originates from the nonparabolic band structure. These indicate that the spin structure cannot be fully described by a simple 2 band Rashba model and this makes tight-binding modelling essential by involving the p^3 orbital degree of freedom.

The surface spin texture at the Fermi energy; is presented in figure 20.b), where the direction of spin is switched to the other direction when going from electron pocket to hole lobes and the same thing when going from hole lobes to the electron ones. This behaviour is explained by the presence of the Rashba term in the Hamiltonian H as it is explained before. The best selection of γ_{sp} and γ_{pp} that matches the ARPES measurements is presented in the table below and we present also the position of the Fermi level.

X	$\gamma_{sp}(eV)$	$\gamma_{pp}(eV)$	$E_f(eV)$
0.07	0.2	-0.6	0
0.15	0.11	-0.73	0.04189
0.21	0.14	-0.64	0.099
0.3	0.19	-0.23	0.198



Figure 20: Surface DOS S_y (a), b) spin surface texture. Spin Resolved DOS without additional Rashba surface terms (c), with additional surface Rashba terms (d)

7 Cobalt/Bismuth-Antimony $Co/Bi_{1-x}Sb_x$

One of the application of Topological insulators is THz emission as it is discussed previously, in which a ferromagnetic material is deposited on the top of a Topological insulator and benefiting from the inverse Edelstein effect we can obtain a THz emission.(see part 4.2).

The aim of this part is to see what occurs to the surface states at the interface between Cobalt (ferromagnetic material) and $Bi_{1-x}Sb_x$ (topological insulator). Here in this part We use the same platform (Tight Binding) as we did for $Bi_{1-x}Sb_x$.

The main difference between $Co/Bi_{1-x}Sb_x$ and $Bi_{1-x}Sb_x$ is that in Cobalt we have also d-orbitals which complicate our system so instead of having a TB model containing only s, p_x, p_y, p_z we have to use a model that contains 10 orbitals s, $p_x, p_y, p_z, d_{xy}, d_{yz}, d_{x^2-y^2}, d_{z^2}$. We use the Slater-koster transformations given in figure 2 but here we do not have all the entries so to find the missing entries one has to do a cyclic permutation of the coordinates and direction cosines.[3]

The tight Binding parameters of Cobat are taken from [10] and the parameterization of $Bi_{1-x}Sb_x$ is given in [5]. The possible possible crystal structure of Cobalt is hexagonal close-packed structure with lattice constant $a_{Co} = 2.5 * 2 = 5A$ while Bismuth has a lattice constant $a_{Bi} = 4.5A$ so to grow cobalt on the top of $Bi_{1-x}Sb_x$ we have to apply a strain and since the hopping parameters depend on the distance between the different neighbours so To take this fact in consideration we can use the following formula that gives the variation of the hopping parameters as a function of the distance:

$$V_{\gamma}(R) = (e_{\gamma} + f_{\gamma}R)exp(-g_{\gamma}^2R)F_c(R), \qquad (67)$$

where γ indicates the type of interaction (e.g $ss\sigma, pd\pi, \text{etc.}$), R is the distance between atoms and $F_c(R)$ is a smooth cutoff-function and it is given by :

$$F_c(R) = (1 + exp[(R - R_0)/l])^{-1},$$
(68)

where $R_0 = 14$ Bohr and l = 0.5 Bohr. For neighbors with R > 16.5 Bohr all interactions are effectively zeros.

To construct the Hamiltonian of this system we use the Hamiltonian of $Bi_{1-x}Sbx$ in equation 66 as a lower part, then we add on top of it the cobalt part. We divide the cobalt part into four planes and we denote them as Co_1, Co_2, Co_3 and Co_4 , as we did with BiSb by classifying the contributions to the Hamiltonian H into an intra and inter parts, we follow the same strategy here. The on-site terms contain E_s, E_p and E_d in addition to spin-orbit coupling while the inter terms contain the contribution from the hopping between the different orbitals. The form of the Hamiltonian that we are working on it is represented below:

$$H = \begin{pmatrix} Co_1 & V_{12} & V_{13} & V_{14} & V_{BiSb/Co_1} \\ V_{12}^* & Co_2 & V_{23} & V_{24} & V_{BiSb/Co_2} \\ V_{13}^* & V_{23}^* & Co_3 & V_{34} & V_{BiSb/Co_3} \\ V_{14}^* & V_{24}^* & V_{34}^* & Co_4 & V_{BiSb/Co_4} \\ V_{BiSb/Co_1}^* & V_{BiSb/Co_2}^* & V_{BiSb/Co_3}^* & V_{Bi/Co_4}^* & BiSb \end{pmatrix}$$
(69)

where V_{ij} contains the inter terms due to the hopping between the different planes, and the Co_i contains the on site elements.

The next stage after the construction of this Hamiltonian is to solve it in order to obtain the band structure and Density of states which can help us to understand the evolution of the surface terms at the interface with a ferroelectric materials such as Cobalt.

8 Conclusion

In this master thesis we have investigated the surface states of $Bi_{1-x}Sb_x$ with varying x and the thickness(number of slabs), and the important of Rashba terms to obtain a Topological Insulator instead of trivial phase. We used the TB platform in order to reproduce the electronic band structure and DOS, the results that we have obtained match perfectly the experimental results, this gives more importance to this platform comparing to DFT for reproducing the electronic properties of a crystal, since it does not take much time technique as in the case of DFT.

As we discussed in 4.2 One of the main application of TIs is that the ability of using their properties in converting spin to charge taking advantage of the Inverse Edelstein Effect (IEE) which give the possibility to THz emission.

In the next future, I propose to carry on the calculations by implementing the electronic band structure of Co/BiSb bi-layers for their properties of spin-charge inter-conversion.

The difficulties lie here in the determination of Co(111)/BiSb(111) hopping parameters from the ferromagnetic d-band of Co into the sp^3 orbitals of BiSb systems. The remaining part of the work would consist in calculating the spin-dependent quantum transport properties (spin Hall Effect, Rashba Edelstein Effect) at the surface of $Bi_{1-x}Sb_x$. In particular, we have to investigate the dependent surface and volume contributions to SCC which would require a high computational effort.

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