

Faculty of Physics and Applied Computer Science

Doctoral thesis

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Dopants, non-stoichiometry and defects versus topologically non-trivial surface electronic states in Bi_2Se_3 and Bi_2Te_3

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Streszczenie

Mimo, że izolatory topologiczne (ang. topological insulators, TI) takie jak monokrystaliczne Bi_2Se_3 i Bi_2Te_3 posiadają unikalne właściwości metalicznych stanów powierzchniowych posiadających strukturę stożka Diraca, które otwierają drogę do zaawansowanych technologii, ich praktyczne zastosowania są wciąż słabo rozwinięte. Jednym z czynników ograniczających jest niedostateczna kontrola detali struktury elektronowej takich jak położenie poziomu Fermiego względem stanów elektronowych powierzchni i objętości. Prowadzi to do niepożądanego przewodnictwa objętościowego, które dominuje właściwości powierzchniowe TI.

W pracy zaproponowano kilka metod oddziaływania na strukturę elektronową TI w celu poprawy ich charakterystyk. Wpływ wprowadzonych zmian na szereg parametrów zbadano technikami charakteryzującymi się wysoką czułością powierzchniową takimi jak skaningowa mikroskopia i spektroskopia tunelowa (STM/STS), kątowo-rozdzielcza spektroskopia fotoelektronów (ARPES), dyfrakcja elektronów o niskiej energii (LEED) czy spektroskopia elektronów Auger'a (AES). Pomiary eksperymentalne zostały skonfrontowane z obliczeniami według teorii funkcjonału gęstości (DFT). Badania uzupełniły pomiary magnetotransportu w temperaturach poniżej 1 K umożliwiające obserwacje oscylacji kwantowych Shubnikov–de Haas'a.

Badania Bi₂Se₃ domieszkowanego atomami Mg i Fe wykazały, że obie domieszki modyfikują stany powierzchniowe o strukturze stożka Diraca, co powoduje zmianę takich parametrów jak promień powierzchni Fermiego czy masa efektywna nośników. Wykazano, że domieszkowanie atomami Fe powoduje znaczące przesuniecie poziomu Fermiego w głąb objętościowego pasma przewodnictwa. Topologiczne stany na powierzchni okazały się odporne na wprowadzenie domieszek Mg i Fe. W szczególności na magnetyczną domieszkę Fe, gdyż domieszki magnetyczne mogą mieć tendencję do niszczenia nietrywialnej topologii układu.

Odstępstwa od idealnej stechiometrii związku Bi₂Te₃ okazały się mieć istotny wpływ na charakter przewodnictwa materiału jak i dystrybucję występujących w związku defektów strukturalnych. Seria próbek zsyntetyzowana w funkcji warunków koncentracji Te wykazuje zmianę przewodnictwa typu p występującego dla związku stechiometrycznego na typ n dla wyraźnie nad-stechiometrycznych koncentracji Te. Najważniejszym uzyskanym wynikiem jest wykazanie, że zmiana charakteru przewodnictwa odbywa się poprzez płynne przesuwanie położenia poziomu Fermiego w funkcji stężenia Te, od objętościowego pasma walencyjnego, poprzez przerwę dla stanów objętości aż do objętościowego pasma przewodnictwa. Wykazano ponadto, że powierzchniowe stany o liniowej dyspersji są obecne we wszystkich próbkach o zawartości Te z badanego zakresu. Oznacza to, że istnieją takie stężenia Te, w których poziom Fermiego może być położony w przerwie dla stanów objętości, gdzie występują wyłącznie topologicznie chronione stany powierzchni.

Jednym z wyników uzyskanych w pracy jest zależność właściwości stanów elektronowych powierzchni od statystycznego rozkładu defektów w sieci krystalicznej Bi₂Te₃. Obróbka termiczna Bi₂Te₃ została zastosowana jako metoda wzbudzania dyfuzji defektów strukturalnych materiału mogącej prowadzić do znacznych zmian w statystyce ich rozkładu w próbce, jak na przykład aglomeracji w warstwach przypowierzchniowych. W pomiarach bezpośrednio zaobserwowano wspomnianą dyfuzję, jednak stwierdzono, że finalnie nie prowadzi ona do drastycznych zmian statystyki defektów przy powierzchni, ani tym samym struktury elektronowej. Po przekroczeniu określonej temperatury zaobserwowano powstawanie nowej fazy pokrywającej fragmenty powierzchni Bi₂Te₃ o lokalnie innej strukturze elektronowej niż powierzchnia wyjściowego materiału, nawet po wygrzewaniu. Globalny charakter przewodnictwa próbki, której duże obszary powierzchni pokryte są nową fazą okazuje się niezaburzony. Co więcej uzyskano potwierdzenie,że topologiczne stany powierzchni są odporne na częściowe pokrycie powierzchni inną fazą i są obecne na wygrzewanej próbce w obszarach, których konfiguracja atomowa nie uległa zmianie.

Abstract

Although topological insulators (TI) such as single-crystalline Bi_2Se_3 and Bi_2Te_3 possess unique properties of metallic surface states having a Dirac cone structure, which pave the way for advanced technologies, their practical applications are still limited. One of the factors that restrict their practical use is the insufficient control over the details of the electronic structure details, such as the position of the Fermi level relative to the electronic states of the surface and volume. This leads to unwanted bulk conductivity, which dominates the surface properties of TIs.

The thesis proposes several methods for manipulating the electronic structure of TIs in order to improve their characteristics. The impact of these methods on a range of parameters was investigated using high-sensitivity surface characterization techniques such as scanning tunneling microscopy and spectroscopy (STM/STS), angle-resolved photoelectron spectroscopy (ARPES), low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES). The experimental measurements were compared to calculations based on density functional theory (DFT). The studies were complemented by magnetotransport measurements at temperatures below 1 K, allowing for observations of Shubnikov–de Haas quantum oscillations.

Studies on Bi_2Se_3 doped with Mg and Fe atoms have shown that both dopants modify the surface states with Dirac cone structure, affecting parameters such as the radius of Fermi surface and effective mass of carriers. It has been demonstrated that doping with Fe atoms causes a significant shift of the Fermi level deep into the volume conduction band. Interestingly, the topological states on the surface were found to be resistant to the introduction of these dopants. In particular, on the magnetic dopant of Fe, as magnetic dopants may tend to destroy the non-trivial topology of the system.

Deviations from the perfect stoichiometry of Bi_2Te_3 has been found to have a significant impact on the conductivity character of the material and the distribution of structural defects. A series of samples synthesized as a function of Te concentration conditions show a change from p-type conductivity for the stoichiometric compound to n-type conductivity for clearly over-stoichiometric Te concentrations. The most important result obtained is the demonstration that the change in conductivity character occurs through a smooth shift of the Fermi level position as a function of Te concentration, from the volume valence band to the gap for the volume states and finally to the volume conduction band. It was also shown that surface states with linear dispersion are present in all samples within the investigated range of Te concentrations. This means that there are Te concentrations at which the Fermi level can be located in the gap for volume states where only topologically protected surface states exist. One of the results obtained in the study is the dependence of the properties of the surface electronic states on the statistical distribution of defects in the crystal lattice of Bi_2Te_3 . Thermal treatment of Bi_2Te_3 was used as a method to excite the diffusion of structural defects in the material, which can lead to significant changes in the statistics of their distribution in the sample, such as agglomeration in near-surface layers. The mentioned diffusion was directly observed in the measurements, but it was found that it does not ultimately lead to drastic changes in the defect statistics near the surface, nor therefore in the electronic structure. Upon reaching a certain temperature, the formation of a new phase was observed, covering fractions of the surface of Bi_2Te_3 with a locally different electronic structure than the surface of the initial material, even after annealing. The global nature of the conductivity of the sample, whose large surface areas are covered by the new phase, remains undisturbed. Furthermore, it was confirmed that topological surface states are resistant to partial coverage of the surface with another phase and are present in annealed samples in areas where the atomic configuration has not changed.

Contents

1	Qua	antum	topological matter in solid state physics	15					
	1.1	.1 Topology of electronic states							
	1.2	Bulk -	- edge correspondence in quantum Hall system	17					
		1.2.1	Drude model of diffusive transport	17					
		1.2.2	Integer quantum Hall effect	19					
		1.2.3	Bulk - edge correspondence	21					
		1.2.4	Hall conductance as a topological invariant	25					
2	Top	ologic	al insulators	28					
	2.1	Band	structure of the topological insulators	28					
	2.2	3D to	pological insulators: Bi_2Se_3 and Bi_2Te_3	29					
		2.2.1	Crystal structure	29					
		2.2.2	Band structure	30					
		2.2.3	Ways of identifying the topological surface states	34					
	2.3	The a	im of the study	35					
3	Exp	Experimental methods 36							
	3.1	UHV	set-up including STM and preparation chamber	39					
		3.1.1	Scanning tunnelling microscopy (STM)	41					
		3.1.2	Scanning tunnelling spectroscopy (STS)	43					
		3.1.3	Low-energy electron diffraction (LEED)	44					
		3.1.4	Auger electron spectroscopy (AES) with retarding field analyser						
			(RFA)	45					
	3.2	Electronic transport and magnetotransport at sub-Kelvin temperatures 4							
	3.3	Angle	-resolved photoemission spectroscopy	48					
	3.4	Samples							
		3.4.1	Synthesis	50					
		3.4.2	Samples preparation for the UHV measurements	51					
		3.4.3	Basic characteristics of starting materials: pristine Bi_2Se_3 and Bi_2Te_3	52					
4	Tuning the Fermi level by introducing magnetic and non-magnetic do-								
	pan	ts of a	low concentrations to Bi_2Se_3	56					
	4.1	Basic	characteristics of doped crystals	57					
		4.1.1	Crystallographic structure	57					
		4.1.2	Chemical composition	58					
	4.2	Surfac	ce topography of doped crystals with respect to Bi_2Se_3	60					
	4.3	Electr	onic structure as seen locally by STS	61					
	4.4	Electronic structure as seen globally by ARPES							
	4.5	Electr	onic structure as seen by electronic transport	65					

	4.6	Special role of magnetic dopants in relation to non – trivial topology in Bi So	70		
Б	Tur	big the Formi level by a neg steichiometric composition in Bi . To	10		
0		The regime even by a non-storemometric composition in $B_{2-x} + R_{3+x}$	73		
	51	Initial characterization of Bio. Teas. samples	73		
	0.1	5.1.1 Crystallographic structure of samples	74		
		5.1.2 Synthesis conditions versus Te content in samples	75		
	5.2	Surface defects and carrier density influenced by small changes of Te con-			
	centration		75		
		5.2.1 Surface morphology and defect density as seen by STM	76		
		5.2.2 Carrier transport measurements	78		
		5.2.3 Model of defect distribution in samples	82		
	5.3	Electronic structure of Bi_2Te_3 affected by small changes of Te concentration	85		
		5.3.1 Local surface electronic structure	85		
		5.3.2 Quantum oscillations of magnetoresistance in sub-Kelvin temperature	88		
	5.4	4 Thermoelectric properties of crystals			
6	Tur	ning the Fermi level by native point defects	97		
	6.1	Native point defects on surfaces of Bi_2Se_3 and Bi_2Te_3	98		
		6.1.1 Imprint of defects at the surface as seen by STM	98		
		6.1.2 Imprint of defects at surface calculated by DFT	02		
	6.2 Local electronic states at the surfaces resulting from structural defect				
		6.2.1 Local disturbance of electronic structure by defects as calculated by			
		DFT	05		
		6.2.2 Local disturbance of electronic structure by defects as measured by			
		STS	06		
	6.3 Influencing electronic structure through heat treatment of crystals .		08		
		6.3.1 Surface crystallographic structure and chemical composition as a			
		function of temperature in global description	09		
		6.3.2 Surface morphology as a function of temperature	11		
	6.4	Local results of annealing: a new phase	13		
		6.4.1 Topography after annealing	15		
		6.4.2 Local electronic structure after annealing	17		
	6.5	.5 Electronic structure as seen by electron transport			
	6.6	Attempts to identify a new phase			
7	Cor	nclusions 12	27		

Introduction

In recent years, the study of topological solid matter has been one of the main areas of research in solid state physics. The subject of topology in the context of quantum mechanics, theoretically described as early as the early 1980s, returned to the center of attention after experimental realization of topologically non-trivial systems, first in quantum wells, and then in bulk materials. This interest resulted in the 2016 Nobel Prize in Physics for Thouless, Haldane and Kosterlitz for "theoretical discoveries of topological phase transitions and topological phases of matter". The topological properties of electronic states in materials have been shown to have a profound impact on their electronic, magnetic and transport properties. The topological invariants in these materials are related to the geometrical and topological properties of their electronic states, and are robust against many types of perturbations, making them an ideal candidate for next-generation electronic devices with high stability and precision. Among the many types of materials exhibiting a non-trivial topology of electronic states, topological insulators constitute an important group.

Topological insulators (TI) are a class of materials that exhibit insulator characteristics within their volume while exhibiting metallic states on their surfaces. These unique electronic properties are due to their non-trivial topology, which leads to the creation of robust surface states that are protected from backscattering. The canonical examples of TIs are the monocrystalline compounds Bi_2Se_3 and Bi_2Te_3 . This Thesis aims to contribute to the growing field of topological materials and establish how its properties can be enhanced by various modifications. The dissertation is organized as follows:

Section 1 presents a general description of topological quantum matter, emphasizing the theoretical description of the formation of boundary states on the edge of a system with a non-trivial topology.

Section 2 describes the details of the general band structure of the TIs with respect to the studied Bi_2Se_3 and Bi_2Te_3 . At the end of this Section, the main aim of the Thesis is formulated.

Section 3 provides a description of the techniques and experimental methods used to investigate a wide range of physicochemical properties of the TIs in question. The basic characteristics of pristine Bi_2Se_3 and Bi_2Te_3 as the starting materials for further research are also presented.

The following Sections are the substantive part describing the TIs and their modifications. Section 4 discusses the studies on the effect of doping on the electronic structure of the Bi_2Se_3 , combining observations of the surface topography, as well as local and global electronic structure with measurements of electron transport.

Section 5 presents the study of the effect of deviations from the initial Bi_2Te_3 stoichiometry on the local and global surface properties of the compound, such as defect density, local electronic structure, electron transport and thermoelectric properties. Experiments are supported with DFT calculations.

Section 6 aims to identify and explain the defects found in crystals and how they affect their electronic structure. This was achieved through a combination of STM and STS experiments and computer simulations. The Section describes then how the properties of Bi_2Te_3 can be manipulated by changing the density of these defects in thermal processes. Finally, this Section discusses the observed new Bi_2Te_3 surface phase resulting from these processes and analyzes its non-obvious electronic structure.

The conclusions of this Thesis are summarized in Section 7.

1 Quantum topological matter in solid state physics

The period from the 1980s to the beginning of the 21st century for solid state physics initiated the questioning of one of the most basic classifications of materials. It was then understood that this distinction based on the ability to conduct electricity is not as uniform as it has been believed over the years. Overall, based on band theory, solid materials are divided into three categories: conductors, semiconductors and insulators. A conductor is a material in which the bulk conduction band (BCB) and the bulk valence band (BVB) overlap, resulting in the presence of free electrons in the BCB. The free electrons can move through the material without having to pass the band gap, and as a result are well conductive. In insulators, on the other hand, there is a wide band gap between the BCB and BVB. The valence electrons must obtain enough energy to cross the band gap and transfer into the conduction band. This is unlikely to happen under normal conditions and therefore the insulators are not electrically conductive. Semiconductors are an intermediate case between conductors and insulators. There is an energy gap in their band structure, but it is so narrow that electrons from the valence band can be easily excited into the conduction band and the material can conduct under the influence of external bias voltage.

In 1980, however, von Klitzing discovered experimentally a new quantum state of matter, the so-called integer quantum Hall effect, which occurs only in some insulators and some semiconductors and cannot be classified into any of the above groups [1]. In a nutshell, the basic observation was that the two dimensional electron gas subjected to a strong perpendicular magnetic field exhibits an almost vanishing longitudinal conductance σ_{xx} , while the transversal (Hall) conductance σ_{xy} is an integer multiple of the conductance quantum $\sigma_{xy} = C_1 \frac{e^2}{h}$, $C_1 = 1, 2, 3...$. Further works of Thouless et al. [2, 3] describe Hall conductance as a topological invariant and the parameter C_1 in the expression for quantized conductivity is a Chern number, specifying the topological order. Thus, historically the quantum Hall state is the first example of topological quantum matter to manifest in metallic states at the edge between systems with different topologies.

As a consequence of the above statements, attempts were made to find a system in which the edge conductivity would occur spontaneously, regardless of the external field. The breakthrough came after proposing the quantum spin Hall effect (QSHE) by Kane and Mele [4, 5] based on the topological order of a Z_2 class, in which a number from a set of integers characterizes a given topology. In this model, the role of the external magnetic field is assumed by the internal spin-orbit coupling (SOC) effect. In the next breakthrough it was theoretically predicted [6], and then it was confirmed experimentally [7] that CdTe/HgTe/CdTe quantum wells should give rise to the QSH effect. Due to the strong SOC, quantization of $\sigma_{xx} = \frac{2e^2}{h}$ was observed in the zero magnetic field when the chemical potential is tuned into the bulk band gap, thus proving the formation of metallic

edge states despite the insulating nature of the material itself.

It was soon predicted that this topological classification can be extended to 3D systems in the context of which the term topological insulator (TI) was coined. Fu and Kane predicted [8] that $Bi_{1-x}Sb_x$ alloy in the insulating composition should be a TI. Mapping the surface states of this compound in angle-resolved photoemission spectroscopy (ARPES) experiments showed that it is indeed 3D TI [9]. Due to the complicated surface-state structure this system turned out to be not very good for detailed studies of the topological state of the surface. The simplest system with a single Dirac cone located in the gap for volume states and centered at the Γ point of the surface Brillouin zone was reported in 2009 for Bi_2Se_3 [10] and for Bi_2Te_3 [11, 12]. The simplicity of the topological surface state and the absence of non-topological states overlapping the DC structure make these materials well suited both for experimental research on unique phenomena related to its non-trivial topology and for potential applications in modern electronics.

1.1 Topology of electronic states

Topological insulators represent a class of materials with unique quantum-mechanical properties, the correct description of which required taking into account new aspects of quantum mechanics, i.e. topology of the Hilbert space. Remember, quantum-mechanical wave functions are described by linear combinations of orthonormal vectors forming a basis set. The abstract space spanned by this orthonormal basis is called Hilbert space, which is the space of states of a given quantum system. Wave functions of some quantum systems such as TIs span the Hilbert space with non-trivial topology. An important consequence of the non-trivial topology of insulator states is the gapless interface at the physical boundary where it meets an ordinary insulator (e.g. vacuum).

This Section begins with a brief overview of the classical and quantum Hall effect, discussing in particular the emergence of chiral edge states in the quantum Hall state. Then these findings are linked to the approach of Thouless *et.al.* describing Hall conductivity as a topological invariant. The purpose of this Section will therefore be to familiarize the reader with a specific example of a quantum Hall state along with a description of quantum systems in which boundary states fundamentally different from those in the volume of the system must occur, and to show that it is directly related to the topology of electronic states of these systems. The reasoning carried out can be qualitatively easily extrapolated to the case of 3D systems and will facilitate the understanding of problems related to the effects on the surface of 3D TIs discussed later in the Thesis.

1.2 Bulk - edge correspondence in quantum Hall system

The quantum Hall effect appears in a two-dimensional electron gas subjected to a low temperature and a strong perpendicular magnetic field. The diagram of the measurement system is shown in Figure 1.1. The electrical contacts (1)-(6) enable the electric field to be applied between contacts (1)-(2), while the potential drops along the longitudinal and transverse directions are measured between contacts (4)-(6) and (3)-(4), receptively.



Figure 1.1: Schematic view of a typical four-point setup for Hall measurement. A 2D electron gas is subjected to an electric field $\mathbf{E} = \mathbf{E} \boldsymbol{e}_{\boldsymbol{x}}$ and a perpendicular magnetic field $\mathbf{B} = \mathbf{B} \boldsymbol{e}_{\boldsymbol{z}}$. The voltage drop in longitudinal direction V_{xx} is measured between contacts (4) and (6), while the Hall voltage V_{xy} is measured between contacts (3) and (4).

In a two-dimensional electron gas in the xy plane the application of an electric field $\mathbf{E} = E_x \mathbf{e_x}$ leads to current density $\mathbf{j} = \mathbf{j_x} \mathbf{e_x}$. However, in perpendicular magnetic field $\mathbf{B} = B\mathbf{e_z}$, the Lorenz force deflects electrons into the y direction. As a result of the accumulating charge at the surfaces, an electric field $\mathbf{E} = E_y \mathbf{e_y}$ builds up in y direction so that in equilibrium this electric field will balance the Lorentz force, and the current will flow again only in the x direction. Ohm's law written for directions of interest is as follows:

$$\boldsymbol{j} = \sigma \boldsymbol{E} = \frac{1}{\rho} \boldsymbol{E} \Longrightarrow \rho_{ij} = \frac{E_i}{j_j}.$$
 (1.1)

1.2.1 Drude model of diffusive transport

In terms of Drude theory of the diffusive transport of non-interacting electrons with charge q = -e and mass m, we can write the equation of motion:

$$\dot{\boldsymbol{p}} = q\left(\boldsymbol{E} + \frac{\boldsymbol{p}}{m} \times \boldsymbol{B}\right) - \tau^{-1}\boldsymbol{p}.$$
 (1.2)

The first terms in brackets correspond to the classical electric force and the Lorentz force acting on a particle of charge q placed in an electric field \mathbf{E} and a magnetic field \mathbf{B} . The last term is responsible for interactions with the atoms of the crystal lattice and describes the

momentum relaxation due to scattering of the charge carriers on lattice imperfections with a characteristic relaxation time τ . In stationary state, the forces acting on the electron are balanced and $\boldsymbol{p}(t) = \text{const.}$

$$\begin{cases} 0 = qE_x + \frac{q}{m}(p_yB_z) - \tau^{-1}p_x \\ 0 = qE_y + \frac{q}{m}(p_xB_z) - \tau^{-1}p_y \end{cases}.$$
 (1.3)

By introducing the parameters of the cyclotron frequency $\left(\omega_c = \frac{qB}{m}\right)$ we can convert to the following form:

$$\begin{cases}
0 = qE_x - \omega_c p_y - \tau^{-1} p_x \\
0 = qE_y + \omega_c p_x - \tau^{-1} p_y
\end{cases}$$
(1.4)

By multiplying these equations by $\frac{n_qq\tau}{m},$ where n_q is a density of charged particles, we can find that:

$$\begin{cases} \sigma_0 E_x = -\omega_c \tau j_y + j_x \\ \sigma_0 E_y = \omega_c \tau j_x + j_y \end{cases}$$
(1.5)

Here we have introduced the current density $\mathbf{j} = \frac{qn_q\mathbf{p}}{m}$, and the Drude conductivity given by $\sigma_0 = \frac{n_qq^2\tau}{m}$. Using matrix notation we can write:

$$\sigma_0 \begin{bmatrix} E_x \\ E_y \end{bmatrix} = \begin{bmatrix} 1 & -\omega_c \tau \\ \omega_c \tau & 1 \end{bmatrix} \begin{bmatrix} j_x \\ j_y \end{bmatrix} \iff \rho = \frac{1}{\sigma_0} \begin{bmatrix} 1 & \omega_c \tau \\ -\omega_c \tau & 1 \end{bmatrix}.$$
(1.6)

An interesting properties of these expressions are revealed if we consider a limit of a clean system, i.e. $\tau \to \infty$. In this case the resistivity and conductivity tensors read:

$$\rho = \frac{m}{nq^{2}\tau} \begin{bmatrix} 1 & -\omega_{c}\tau \\ \omega_{c}\tau & 1 \end{bmatrix} \xrightarrow{\tau \to \infty} \rho = \frac{B}{nq} \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} .$$

$$\sigma = \frac{nq}{B} \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} .$$
(1.7)

Considering the clean system limit it is obvious that the matrix structure is important. In this limit, the longitudinal components of both the resistivity and conductivity tensors vanish, although this is not a result that would seem logical if we considered only the longitudinal components, as resistivity and conductivity are inverses of each other. And although we are considering a clean system limit here, where one would intuitively expect perfect conductivity. The explanation for this seemingly unexpected result is that charged particles move in closed orbits in an external magnetic field, leading to finite values of the off-diagonal elements of resistivity and conductivity tensors. The classical image of this situation is presented in Figure 1.2(a). In a static limit an electric field E_y will balance the Lotentz force acting on electrons in magnetic field so that in equilibrium the condition $j_y = 0$ must be met:

$$\sigma_0 E_y = \omega_c \tau j_x \Longrightarrow E_y = \frac{\omega_c \tau}{\sigma_0} j_x, \qquad (1.8)$$

$$E_y = \frac{B}{nq} j_x. \tag{1.9}$$

One can easily read-off the Hall resistance as:

$$\rho_{xy} = -\rho_{yx} = -\frac{E_y}{j_x} = -\frac{B}{nq},$$
(1.10)

and the The Hall coefficient is defined:

$$R_H = \frac{1}{nq}.\tag{1.11}$$

A number of things is worth noting here. First, within this semi-classical limit, the Hall resistance ρ_{xy} is completely independent of microscopic details of the material, like for example the relaxation time τ which strongly depends on type and quality of the material used. Second, Equation 1.10 shows that the Hall resistance increases linearly with the applied magnetic field B. The slope of this relationship gives access to the microscopic nature of the carriers as their concentration and charge. If the dominant carriers are electrons, then the Hall resistance R_H is negative, and the slope of $\rho_{xy}(B)$ is negative for low magnetic fields, corresponding to the regime where the motion of the carriers is dominated by their cyclotron orbits. This behavior is known as the negative magnetoresistance. Conversely, if the dominant carriers are holes, then R_H is positive, and the slope of $\rho_{xy}(B)$ is positive for low magnetic fields. This behavior is known as the positive magnetoresistance.

1.2.2 Integer quantum Hall effect

The semi-classical linear bahavior of the Hall resistivity as a function of applied magnetic field was observed experimentally in two - dimensional electron gases at weak magnetic fields. In 1980 von Klitzing discovered that when it is subjected to strong magnetic fields (of about 15 - 20 T) and very low temperature (of about 1.5 K), the Hall resistance spreads plateau structures. This phenomenon, being an extension of a classical picture is known as the integer quantum Hall effect, and was recognized with a Nobel Prize in Physics in 1985.

To gain a basic understanding of the quantum Hall effect the following reasoning is based on the work of Altland and Fritz [13]. Let us consider a free electron gas confined to the two-dimensional system in xy plane. Let us then apply perpendicular magnetic field $\mathbf{B} = B\mathbf{e}_{\mathbf{z}}$. In order to gain the proper description the electrons in a wider range of the magnetic field, the momentum should be replaced by its gauge-invariant form:

$$\boldsymbol{p} \longrightarrow \boldsymbol{\Pi} = \boldsymbol{p} + e\boldsymbol{A}(\boldsymbol{r}), \quad \boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{r})$$
 (1.12)

Let us introduce a convenient Landau gauge potential $A_L(\mathbf{r}) = [By, 0, 0] = -By \mathbf{e}_{\mathbf{x}}$, that leads to a magnetic field $\mathbf{B} = \nabla \times \mathbf{A}_L(\mathbf{r}) = B\mathbf{e}_{\mathbf{z}}$. As the Landau gauge potential vector points the x direction, but varies only with the y position, it is particularly suited for the band structure calculations, because it possesses translational invariance in the x direction and the corresponding momentum \mathbf{k}_x remains a good quantum number which can be used to calculate the band structure below. In other words the wave-functions can be written in form $\Psi_{n,\mathbf{k}_x}(\mathbf{x},\mathbf{y}) \propto e^{i\mathbf{k}_x\mathbf{x}}\phi_{n,\mathbf{k}_x}(\mathbf{y})$. In terms of the gauge - invariant momentum the Hamiltonian can be written as:

$$\hat{H} = \frac{\left[\boldsymbol{p} + e\boldsymbol{A}(\boldsymbol{r})\right]^2}{2m} = \frac{\Pi^2}{2m} = \frac{1}{2m} \left[\Pi_x^2 + \Pi_y^2\right].$$
(1.13)

By introducing the parameter of magnetic length $l_B = \sqrt{\frac{\hbar}{eB}}$, we can define the ladder operators:

$$a = \frac{l_B}{\sqrt{2\hbar}} \left(\Pi_x - i\Pi_y \right), \quad a^+ = \frac{l_B}{\sqrt{2\hbar}} \left(\Pi_x + i\Pi_y \right). \tag{1.14}$$

Then the Hamiltonian can be rewritten as:

$$\hat{H} = \frac{\hbar^2}{4ml_B^2} \left[(a^+)^2 + a^+a + aa^+ + a^2 - \left((a^+)^2 - a^+a - aa^+ + a^2 \right) \right].$$
(1.15)

Taking into account the commutation rule of the form $[a, a^+] = 1$, and introducing the cyclotron frequency $\omega_c = \frac{\hbar}{ml_B^2}$, we can derive:

$$\hat{H} = \hbar\omega_c \left(a^+ a + \frac{1}{2}\right). \tag{1.16}$$

The obtained result can be recognized a Hamiltonian of harmonic oscillator.

As in the case of one-dimensional harmonic oscillator the eigenstates of Hamiltonian 1.16 are those of the number operator, which is defined:

$$a^{+}a\left|n\right\rangle = n\left|n\right\rangle.\tag{1.17}$$

We obtain the energy eigenvalues labelled by the integer n:

$$\epsilon_{n,k} = \hbar\omega_c \left(n + \frac{1}{2}\right). \tag{1.18}$$

Those energy levels are commonly known as Landau levels of the two-dimensional electron gas. By choosing the suitable (Landau) gauge the second quantum number can be interpreted as e.g. the conserved momentum k along the x direction. This allows to plot the bad structure as a function of k presented in Figure 1.2(b). Landau levels form a completely flat, dispersion-less bands.



Figure 1.2: (a) classical picture of free electrons in E and B fields move on closed orbits and do not contribute to the current in the direction of the E field, (b) schematic band structure obtained for homogeneous quantum Hall system. Landau levels form a completely flat bands in function of momentum k

Quantum Hall system thus exhibits the characteristics of an insulator. In general the chemical potential lies in between the Landau levels implying that the quantum Hall system is a true bulk insulator. When the chemical potential is fine-tuned to coincide with one of the Landau levels, the system becomes metallic, leading to sharp steps in the Hall conductance σ_{xy} . Those steps are, however, slightly broadened in a real sample due to disorder effects in the bulk of the sample, which is beyond the scope of this Section. As a consequence, in general the chemical potential is placed in between individual Landau levels and one would not expect to observe any sort of conductivity in the system, i.e., $\sigma_{xx} = \sigma_{xy} = 0$. Nonetheless, the experimentally observed quantization of the Hall conductance is not carried by the bulk states of the sample, but rather edge states present at the sample boundaries, as we show below.

1.2.3 Bulk - edge correspondence

Up to this point the reader has been convinced that the quantum Hall system is an insulator. Now an attempt will be undertaken to convince him that this is not the case! Understanding the occurrence of finite and quantized Hall conductivity goes beyond the analysis of a homogeneous system resulting in dispersionless Landau levels. Hall conductivity is guided by the states occurring at the edges of the system, which we will introduce in this Paragraph.

Let us look at the classical picture first. Classically in magnetic field we expect closed orbits. However, the introduction of borders, which every real physical system has, results in a clear change of this picture, schematically presented in Figure 1.3. Far from the edges, the closed-orbit interpretation remains valid, and the quantum Hall system is a good bulk insulator. However near the boundaries electrons cannot complete revolutions which forces them to bouncing along the boundaries. This picture is usually referred to as the skipping orbit picture and it is simply a consequence of magnetic field and boundaries.



Figure 1.3: Illustration of skipping orbits formation. In homogeneous system in magnetic field electrons move on closed orbits. However the boundaries prevent electrons from completing classical revolutions and introduces edge channels due to bouncing along the sample boundary

Let us now look at the quantum mechanical problem modelling the notion of boundaries by adding into the Hamiltonian the confinement potential in y direction in the form [13]:

$$V_{conf} = \frac{1}{2}m\omega_{conf}^2 y^2, \qquad (1.19)$$

where the confinement frequency $\omega_{conf} \ll \omega_c$ vary slowly of the scale of magnetic length. Assuming the vector potential $\mathbf{A} = -By\mathbf{e}_{\mathbf{x}}$, the Hamiltonian can be written as:

$$\hat{H} = \frac{\Pi^2}{2m} + V_{conf}(y) = \frac{1}{2m} \left[\left(p_x - eBy \right)^2 + p_y^2 \right] + \frac{1}{2} m \omega_{conf} y^2.$$
(1.20)

As before, the translational symmetry in x - direction is preserved, that allows us to choose eigenfunctions which take the following form:

$$\Psi_k(x,y) = e^{ikx} \Phi_k(y). \tag{1.21}$$

The one - dimensional Schrödinger equation can be written:

$$h_k \Phi_k(y) = \epsilon_k \Phi_k(y), \tag{1.22}$$

with

$$h_k = \frac{p^2}{2m} + \frac{1}{2}m\omega_c^2 \left(y - kl_B^2\right)^2 + \frac{1}{2}m\omega_{conf}^2 y^2.$$
 (1.23)

Introducing the parameters $\bar{Y}_k = -k l_B^2 \frac{\omega_c^2}{\omega_c^2 - \omega_{conf}^2}$, and $\bar{\omega}_c = \sqrt{\omega_c^2 - \omega_{conf}^2}$, the Hamiltonian takes the following form:

$$h_{k} = \frac{p^{2}}{2m} + \frac{m\bar{\omega_{c}}^{2}}{2} \left(y + \bar{Y}_{k}\right)^{2} - \frac{\omega_{conf}^{2}}{\omega_{c}^{2} - \omega_{conf}^{2}} \frac{\hbar^{2}k^{2}}{2m}.$$
 (1.24)

We obtained a Hamiltonian of a displaced harmonic oscillator with the displacement parameter \bar{Y}_k . The eigenenrgies can be easily derived as:

$$\epsilon_{n.k} = \hbar \bar{\omega}_c \left(n + \frac{1}{2} \right) + \frac{\hbar^2 k^2}{2m'},\tag{1.25}$$

with the effective mass $m'=\frac{\omega_c^2-\omega_{conf}^2}{\omega_{conf}^2}$



Figure 1.4: Classical picture and electronic structure of (a) homogeneous quantum Hall system where electrons move on closed orbits, which leads to an electron structure in the form of completely flat Landau levels. (b) in a presence of boundaries, modelled in calculations by confinement potential in y direction $V_{conf} = \frac{1}{2}m\omega_{conf}^2 y^2$, electrons move on skipping orbits along the edges and Landau levels become square functions of momentum k. For any chemical potential (dash line) there is an even number of points of intersection with Landau levels, which leads to the opening of the corresponding number of conductive channels, in contrast to panel (a)

Figure 1.4 presents the comparison of classical picture and electronic structure of the homogeneous quantum Hall system (Fig. 1.4(a)) to that with boundaries modelled at quantum mechanical picture with confinement potential V_{conf} (Fig. 1.4(b)). In the latter case the Landau levels are no longer flat, but a square function of the wave vector k. However, the Landau levels are independent of the dispersive part $\frac{\hbar^2 k^2}{2m'}$ at k = 0. Therefore we describe the chemical potential with respect to the sequence of Landau levels at k = 0. For example, the dashed line in Figure 1.4(b) represents chemical potential in between the first and second Landau level. As the Fermi level crosses the Landau levels, we can find

an even number of dispersive modes depending on exact position of chemical potential in the quantum Hall system. Especially, between the first and second Landau level we find a single dispersive mode with positive group velocity:

$$\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar} \frac{\partial \epsilon_{\mathrm{n,k}}}{\partial \mathrm{k}} \mathbf{e}_{\mathbf{x}} = \frac{\hbar \mathrm{k}}{\mathrm{m}'} \mathbf{e}_{\mathbf{x}}, \qquad (1.26)$$

and another dispersive mode with negative group velocity $-\mathbf{v}_{\mathbf{k}}$. These modes correspond to the chiral edge channels with the first one running along one edge in x direction, the other mode running along the opposite edge in $-\mathbf{x}$ direction.



Figure 1.5: Illustration of chiral states with positive and negative group velocity located at the boundaries of the sample in case of chemical potential crossing only one Landau level. For larger magnetic fields higher Landau levels are populated and more edge states are created

In order to calculate the Hall current let us consider a finite Hall voltage $V_{\rm H}$ across the quantum Hall sample in y direction, corresponding to the difference in the chemical potential between the two edges, $eV_{\rm H} = \mu_{\rm R} - \mu_{\rm L}$ (see Fig. 1.5). To calculate the Hall current we have to sum up the current densities of all occupied states in the quantum Hall sample [13]:

$$I_{x} = e \sum_{m=1}^{v} \int \frac{dk}{2\pi} \left(v_{k}^{R} n_{F} \left(\epsilon_{m,k} - \mu_{R} \right) + v_{k}^{L} n_{F} \left(\epsilon_{m,k} - \mu_{L} \right) \right)$$
(1.27)

where $v_k^{R,L}$ denotes the group velocity of right - and left - moving chiral edge states, and $n_F(\epsilon)$ is the Fermi distribution function. We have assumed that there are v Landau levels occupied in the bulk of the sample. In the zero temperature limit, only states below the chemical potential are occupied, i. e., $n_F(\epsilon - \mu) \rightarrow \Theta(\mu - \epsilon)$, and we can rewrite the integrand as a total derivative of the energy eigenvalues:

$$I_x = e \sum_{m=1}^{v} \int \frac{dk}{2\pi} \left(\frac{1}{\hbar} \frac{\partial \epsilon_{n,k}}{\partial k} \Theta(\mu_R - \epsilon_{m,k}) - \frac{1}{\hbar} \frac{\partial \epsilon_{n,k}}{\partial k} \Theta(\mu_L - \epsilon_{m,k}) \right),$$
(1.28)

$$I_x = \frac{e}{\hbar} \sum_{m=1}^{v} \int_{\mu_L}^{\mu_R} d\epsilon = v \frac{e}{\hbar} (\mu_R - \mu_L), \qquad (1.29)$$

$$I_x = v \frac{e^2}{h} V_H. \tag{1.30}$$

As a consequence, we immediately see that the Hall conductance $\sigma_{xy} = \frac{I_x}{V_H}$ is quantized:

$$\sigma_{xy} = v \frac{e^2}{h},\tag{1.31}$$

with $v \in \mathbb{Z}$. Hall conductance is an integer multiple of the conductance quantum $G_0 = e^2/h$. As mentioned before, this result does not depend on microscopic details of the sample such as the type of semiconducting material used or the quality of the crystal. This is merely a consequence that there is an integer number of conducting edge channels, substantially different from the bulk of the sample.

1.2.4 Hall conductance as a topological invariant

In this Paragraph, we review the original version of the argument for a quantized Hall conductance which was given by Thouless et al. in 1982 [2]. The following discussion is due to Watson [14].

Let us start by considering a system of non - interacting electrons moving in the xy plane on a square lattice and subject to a uniform perpendicular magnetic field. We can describe the system with a following Hamiltonian:

$$\hat{H} = \frac{\left[\boldsymbol{p} + e\boldsymbol{A}(\boldsymbol{r})\right]^2}{2m} + U(\boldsymbol{r}), \qquad (1.32)$$

with U(x, y) = U(x + a, y) = U(x, y + a). $\mathbf{A}(\mathbf{r})$ is the vector potential, and the potential $U(\mathbf{r})$ simply represents the periodic potential of the square lattice. The Hall conductance can be written as an integral over the magnetic Brillouin zone of occupied subbands:

$$\sigma_H = \frac{ie^2\hbar}{A_0} \sum_{E_\alpha < E_F} \sum_{E_\beta > E_F} \frac{v_x^{\alpha\beta} v_y^{\beta\alpha} - v_y^{\alpha\beta} v_x^{\beta\alpha}}{\left(E_\alpha - E_\beta\right)^2}.$$
(1.33)

Parameters α and β label single - particle states, $v^{\alpha\beta}$ are matrix elements of the particle velocity operator and A_0 is the area of the system. The expression comes from second-order perturbation theory, in calculating the response of the system to a small perturbing electric field.

As discussed above, the single - particle states $\Psi_{n\mathbf{k}}(\mathbf{r})$ can be labelled by a discrete band index n together with a wave vector k in the so - called magnetic Brillouin zone. The corresponding magnetic Bloch functions take the form:

$$u_{n\mathbf{k}}(\mathbf{r}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\psi_{n\mathbf{k}}(\mathbf{r}).$$
(1.34)

In terms of those Bloch functions, the matrix elements of the particle velocity operator

can then be written as:

$$\hbar v^{\alpha\beta} = (E_{\beta} - E_{\alpha}) \left\langle u_{\alpha} \middle| \frac{\partial u_{\beta}}{\partial \boldsymbol{k}} \right\rangle = (E_{\alpha} - E_{\beta}) \left\langle \frac{\partial u_{\alpha}}{\partial \boldsymbol{k}} \middle| u_{\beta} \right\rangle.$$
(1.35)

The next step is to substitute the formula 1.35 into the Hall conductance form 1.33, after rewriting the sum over states β as $\sum_{E_{\beta}>E_{F}} = \sum_{E_{\beta}} - \sum_{E_{\beta}<E_{F}}$, that the second term gives a vanishing contribution to the conductance, as may be verified by interchanging the α and β indices in the sum. We obtain:

$$\sigma_{xy} = -i \frac{e^2}{\hbar A_0} \sum_{E_\alpha < E_F} \left(\left\langle \frac{\partial u_\alpha}{\partial k_x} \middle| \frac{\partial u_\alpha}{\partial k_y} \right\rangle - \left\langle \frac{\partial u_\alpha}{\partial k_y} \middle| \frac{\partial u_\alpha}{\partial k_x} \right\rangle \right).$$
(1.36)

The next assumption is that the chemical potential lies in a subband gap, so that the sum extends over a set of filled bands α which can be rewritten as a momentum integral as follows:

$$\sum_{E_{\alpha} < E_F} \rightarrow \int d^2 r \int \frac{1}{4\pi^2/qa^2} dk_x dk_y.$$
(1.37)

Due to the translational invariance of the magnetic Bloch functions, the matrix elements take values proportional to $A_0/(qa^2)$ times the integral over the magnetic unit cell. Hence, the area prefactor A_0 cancels, and we obtain the following momentum - space integral over magnetic Bloch functions as a result for the Hall conductance:

$$\sigma_{xy} = \frac{e^2}{h} \sum_{n_{occ.}} \int \frac{d^2k}{2\pi i} \left(\left\langle \frac{\partial u_{nk}}{\partial k_x} \middle| \frac{\partial u_{nk}}{\partial k_y} \right\rangle - \left\langle \frac{\partial u_{nk}}{\partial k_y} \middle| \frac{\partial u_{nk}}{\partial k_x} \right\rangle \right).$$
(1.38)

The sum runs over occupied Landau levels, and the momentum integral is taken over the magnetic Brillouin zone. The formula 1.38 for Hall conductance was given by Thouless et. al. in [2], proofing that the integral only takes integer quantities. Mathematically, the integral appearing in Equation 1.38 was first recognized as topological invariant by Avron *et.al.* in 1983 [15]. This integral is the first Chern class of a so-called U(1) fiber bundle on the base manifold of a torus T^2 [16].

This Section has explored the conductivity of quantum Hall systems and has found that it is influenced by boundary states that differ fundamentally from those found within the system. The quantization of Hall resistance is linked to a topological invariant known as the Chern number. This invariant characterizes the electronic wave functions in the presence of a magnetic field and is topologically protected, meaning it cannot change unless the topology of electronic wave functions changes. The unique nature of this effect makes it an essential system for the study of topological phases of matter.

Similar effects occur in some 3D systems known as TIs. These materials possess a insulating gap for volume states but exhibit conducting surface states that are topologically protected. The surface states in topological insulators are similar to the edge states in the quantum Hall effect and are also protected by a topological invariant, which in this case is the so-called Z_2 invariant. This invariant characterizes the electronic wave functions in the material's volume and determines the number and nature of the conducting surface states. The Z_2 invariant is also topologically protected, meaning that the surface states are robust and resistant to scattering by disorder and impurities. In the next Section, the properties of 3D TIs will be discussed starting from a general description of their electronic structure, followed by specific examples of compounds well established as 3D TIs.

2 Topological insulators

2.1 Band structure of the topological insulators

Analogous to the 2D QHE system discussed earlier, 3D TIs are characterized by conductive states occurring on their surfaces, while the volume of material remains an insulator. The surface states of a TI are often referred to as Dirac surface states because they have a linear dispersion relation similar to that of massless Dirac fermions. This linear dispersion relation gives rise to a conical shape in the band diagram known as a Dirac cone (DC). The DC is a hallmark feature of the band structure of a topological insulator and it is a consequence of the topological protection of the surface states. A schematic picture of the 2D and 3D cases is shown in Figure 2.1.



Figure 2.1: Edge and surface states of topological insulators. (a) Schematic real-space picture of the 1D helical edge state of a 2D TI. (b) Energy dispersion of the edge state of a 2D TI forming a 1D Dirac cone. (c) Schematic real-space picture of the 2D helical surface state of a 3D TI. (d) Energy dispersion of the surface state of a 3D TI forming a 2D Dirac cone. From [17].

In the case of 2D TI, conductive edge states appear on the edge of the system (Fig. 2.1(a)), as shown in detail in Paragraph 1.2.3. Consequently, the energy gap between BVB and BCB is filled by surface bands forming a 1-dimensional DC (Fig. 2.1(b)). In 3D TI conductive states appear on surfaces (Fig. 2.1(c)) forming a 2-dimensional DC in momentum space (Fig. 2.1(d)). The surface states of a topological insulator are protected by time-reversal symmetry, which ensures that the electrons traveling in opposite directions have opposite spin. Namely, due to the strong SOC, the wave vector \mathbf{k} is related to the spin and is perpendicular to it (shown schematically by arrows in Fig. 2.1). This protection prevents backscattering of the electrons and makes the surface states robust against disorder and impurities.

Dozens of materials have been tested and classified as topologically non-trivial materials [17]. Metallic states in the form of a DC with a linear dispersion relation on the TI surface are located in the energy gap of the material's volume states, between the BVB and BCB. Although this picture seems simple, in reality the electronic structure of TI is usually very complex. In many materials there are multiple DCs located in different places of the Brillouin zone and the edges of the bulk bands often overlap the surface bands. One of the simplest band structures is demonstrated by the canonical examples of 3D topological insulators: Bi₂Se₃ and Bi₂Te₃ single crystals. They exhibit a single DC centered at Γ point of a Brillouin zone and the surface linear states are at least partially undisturbed by the volume states, and occur exclusively in the volume band gap. Furthermore, Bi_2Se_3 and Bi_2Te_3 are experimentally well-established as topological insulators, with their topological properties having been confirmed by a variety of experimental techniques. This makes them excellent candidates for studying the properties of topological surface states in a controlled and reproducible manner. Thanks to our cooperation with the Purdue University in West Lafayette, Indiana in the USA, we also had access to the highest quality pristine and doped Bi_2Se_3 and Bi_2Te_3 single crystals [18]. Later, establishing cooperation with the group of prof. Wojciechowski at the Faculty of Materials Science and Ceramics (WIMiC) of the AGH University of Krakow, we started to produce single crystals of the Bi_2Te_3 series almost on site. Therefore, they were chosen as the main material for our research, the aim of which will be formulated at the end of this Section. The following Paragraphs will be referring to TIs in the context of the studied single crystals of Bi₂Se₃ and Bi_2Te_3 .

2.2 3D topological insulators: Bi_2Se_3 and Bi_2Te_3

2.2.1 Crystal structure

The studied materials crystallize in the rhombohedral structure with the space group D_{3d}^5 [19]. Materials exhibit hexagonal surface symmetry and a layered crystal structure along the z axis, as shown in Figure 2.2.



Figure 2.2: Bi_2Se_3 and Bi_2Te_3 crystal structure is shown, with highlighted primitive unit cell in which there are five atoms (two Bi atoms and three Se/Te atoms, depending on which crystal is considered), each in a separate layer. Bi atoms are located at two equivalent positions Bi(1) and Bi(1'). Se/Te are also located in two equivalent positions Se(1)/Te(1) and Se(1')/Te(1'), and also in position Se(2)/Te(2) not equivalent to the previous one. These layers form a quintuple-layer (QL) with the arrangement Se(1)/Te(1)-Bi(1)-Se(2)/Te(2)-Bi(1')-Se(1')/Te(1'). Figure from [19].

The primitive rhombohedral unit cell marked by red square in Figure 2.2 contains five atoms (two Bi atoms and three Se/Te atoms), each in a separate layer. Together, these layers form a structure known as the quintuple layer (QL). Covalent-ionic chemical bonds within single QL are very strong, while adjacent QLs are related to a weak van der Waals interaction [18]. The vdW gap in Bi₂Se₃ is 2.54 Å and is 0.64 - 0.95 Å larger than the distance between individual layers in QL [20]. Conductive layer on the surface of studied TI is limited to a thickness of one QL [21].

Table 2.1: List of crystal lattice parameters for Bi_2Se_3 and Bi_2Te_3 single crystals in hexagonal and rhombohedral lattice.

	a_{hex} [Å]	c_{hex} [Å]	a_{rh} [Å]	α [°]
$\operatorname{Bi}_2\operatorname{Se}_3$	4.138	28.64	9.84	24.27
$\mathrm{Bi}_{2}\mathrm{Te}_{3}$	4.384	30.49	10.47	24.17

The weak bond between the individual QLs allows the crystal to break easily, so that it is possible to remove the surface with an adhesive tape-scotch, thanks to which the obtained surface is atomically clean (no dirts). The method of obtaining clean surface of studied single crystals is described in Paragraph 3.4.2. The synthesis of single crystals by the Bridgman method is described in Paragraph 3.4.1.

2.2.2 Band structure

The electronic structure of the tested materials is well known and described in the literature [10, 22, 23, 24, 25]. However, due to the diverse research conducted in our group and the desire to perform calculations of various TI configurations, we also conducted

theoretical calculations of the electronic structure of the investigated pristine materials, Bi_2Se_3 and Bi_2Te_3 . These calculations, presented in Figures 2.3 and 2.4, were performed in cooperation with dr inż. Michał Jurczyszyn. The band structures have been calculated by means of *ab initio* calculations based on the density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP). The electron–ion interaction was described by the projector-augmnented wave (PAW) [26, 27] method.

Surface states are of particular importance for our research, therefore Figure 2.3 presents the calculated projection of the electronic structure of Bi_2Se_3 from the entire slab to the first (upper) atomic layer. The band structure reveals that volume band gap is fulfilled with linearly dispersed surface states forming a single DC centered at Γ point of the Brillouin zone. The E_F is located near the DC center. Right panel shows the calculated density of states (DOS) of the surface which can be calculated from the band structure by integrating over all wave vectors in the Brillouin zone, and summing the contributions from all occupied bands. This integral takes into account the density of states for each energy level in the material, weighted by the occupation probability of the corresponding electron states. The zoomed area presented in the insert enables to distinguish the DP position and linear segment of the DOS of the surface.



Figure 2.3: DFT calculated electronic structure and DOS of Bi_2Se_3 along K- Γ -M direction in reciprocal space. Left panel presents projection of the Bi_2Se_3 band structure from the entire slab onto the first (top) atomic layer. Right panel presents DOS for the surface of Bi_2Se_3 . The insert shows the zoom to the violet-marked area close to the E_F (dashed line).

Figure 2.4 shows the calculated projection of the electronic structure of Bi_2Te_3 from the entire slab to the first (upper) atomic layer. Analogous to the previous case of Bi_2Se_3 , the volume band gap is fulfilled by surface states forming a single DC centered at the Γ point, with the E_F located at DP. However, an important difference is that the DC in Bi_2Te_3 is partially latent with the volume bands. The BVB overlaps DP and part of the range of linear surface states, which makes this electronic structure more difficult to interpret experimental results. It is sufficient to trace the DOS of the surface in the right panel to notice the range of surface states with linear dispersion relation is much shorter than in the case of Bi_2Se_3 , and the determination of the position of DP requires extrapolation of the linear dispersion relation to the position of E_F , as it is overlapped by the valence states.



Figure 2.4: DFT calculated electronic structure and DOS of Bi_2Te_3 along K- Γ -M direction in reciprocal space. Left panel presents projection of the Bi_2Te_3 band structure from the entire slab onto the first (top) atomic layer. Right panel presents DOS for the surface of Bi_2Te_3 . The insert shows the zoom to the violet-marked area close to the E_F (dashed line).

The above calculation results are proven in numerous experimental works in which the surface states with the linear dispersion relation are directly imaged [28, 29, 30, 31, 32]. The studied crystals have an energy gap of the volume states with values of approximately 0.3 eV in case of Bi₂Se₃ and 0.17 eV for Bi₂Te₃.

The calculated electronic structure at the surface assuming an ideal (in terms of atomic arrangement) slab shows the E_F located close to the center of the DC for both Bi_2Se_3

(Fig. 2.3) and Bi_2Te_3 (Fig. 2.4). Experimental works, however, show that the E_F is located deep in the BCB in the case Bi_2Se_3 and within the BVB in case of Bi_2Te_3 . For illustrative purposes, Figure 2.5 shows the electronic structure of Bi_2Se_3 as measured by the ARPES technique. In this measurement the volume and the surface bands are resolved along with the position of E_F that is clearly different that showed by calculations. This discrepancy between calculations and experiment is due to defects naturally occurring in these crystals, e.g. in the form of selenium vacancies, or by the excess atoms. These defects are of course not taken into account in the calculations presented above as the design slab may contain only a limited number of atoms, where the introduction of a defect would disturb the entire simulated structure. The in-band localization of the E_F revealed in the real crystals results in the fact that the pristine materials are usually conductive not only on the surface, but also in their volume. However, this does not change the topology, so the DC is still present in the electronic structure. As a result of overlapping of the volume and surface DC bands near the E_F , it is not possible to simply distinguish between the electron bands of surface states and volume states of the material [33].



Figure 2.5: Electronic band structure of undoped Bi_2Se_3 measured by ARPES. (A) The bulk conduction band (BCB), bulk valence band (BVB), and surface-state band (SSB) are indicated, along with the Fermi energy (E_F), the bottom of the BCB (E_B), and the Dirac point (E_D). (B) Constant-energy contours of the band structure show the SSB evolution from the Dirac point to a hexagonal shape (green dashed lines). (C) Band structure along the K – Γ – K direction. (D) Photon energy–dependent Fermi surface maps. From [34].

2.2.3 Ways of identifying the topological surface states

The basic experimental technique for determining the existence of surface states with a linear dispersion relation is ARPES. ARPES provides a unique way to directly observe the momentum-dependent band structure of the electronic states near the E_F while sampling the entire Brillouin zone. This method works by shining a beam of photons onto a sample, which causes electrons to be emitted from the surface of the material. The energy, momentum angle of the emitted electrons are then measured, allowing the band structure of the material to be determined. The information received originates from a surface area with the size of the incident beam spot, which can be as large as 1 mm square. The method allows clearly distinguish between volume bands and surface states with linear dispersion forming DC as shown in Figure 2.5.

Also scanning tunneling spectroscopy (STS) is a method of checking the metallicity of surface states. This method provides information on the density of electronic states as a function of energy, and therefore proportional to the DOS presented in Figures 2.3 and 2.4. STS is a strictly surface imaging method and can be used to observe states with a linear dispersion relation and to determine the Dirac point.

The distinguishing feature of TI surface states is the lack of backscattering. Such effect and the resulting surface localization of electrons can also be studied by STS. If a material with surface defects is observed by STM and dI/dV is continuously measured, characteristic modulations can be obtained which are the result of scattering of electrons (or actually quasiparticles) to different surface states observed as characteristic patterns of quasi particle interference (QPI) [35, 36]. Achieving the required resolution to record QPI shapes, however, requires sophisticated measurements in which the sample and most often also the STM tip are stably cooled to 4.2 K or lower. In our apparatus, we attempted to measure QPI patterns using liquid He cooling, but we could not achieve the required resolution. It's important to note that the STM microscope we used do not have the ability to cool the tip.

Another method of determining topological surface states is determination of the Berry phase based on the Schubnikov de Haas (SdH) quantum oscillations of magnetotransport analysis. SdH quantum oscillations can be revealed in magnetoresistance measurements carried out at extremely low temperatures in strong magnetic field. The reason for using ultra-low temperatures is to minimize thermal broadening of the energy levels, which would obscure the quantum effects of interest. On the other hand, high magnetic fields are necessary to achieve a large separation between energy levels, which enhances the visibility of the quantum oscillations. Fourier analysis (FFT) is performed to distinguish various frequencies of measured magnetoresistance oscillations. On this basis, a Landau fan diagram is created by transforming the magnetoresistance ρ_{xx} to conductivity σ_{xx} and assigning the integer value to the position of the successive σ_{xx} maxima of the SdH oscillations, and the value of N + 1/2 to the position of σ_{xx} minima as a function of B⁻¹. The linear function is fitted to the assigned values. The diagram typically shows a series of straight lines whose extrapolations intersect the 0-frequency axis at integer or half-integer values, depending on the topology of the material. By analyzing the Landau fan diagram, it is possible to determine the area enclosed by the electron orbits, which is related to the Berry phase through a geometric formula known as the Onsager relation [37]. Therefore, by analyzing the Landau fan diagram and determining the area closed by electron orbits, one can calculate the Berry phase for a given frequency of quantum oscillations and thus distinguish between oscillations originating from topologically trivial and non-trivial states.

2.3 The aim of the study

As shown in the previous Paragraphs TIs have a unique electronic structure where the volume is insulating, but the surface is conducting due to the presence of topologically protected surface states. The electronic properties of the volume and surface states in TIs are fundamentally different. The surface states are conducting and exhibit a unique Dirac-like dispersion relation. These surface states are topologically protected, meaning that they are robust against disorder and backscattering, which makes them useful for applications in modern electronics. The presence of surface states in TIs arises from the band inversion near the E_F , which causes the topologically protected states to emerge at the surface of the material. Therefore, the E_F position plays a critical role in determining the electronic properties of the surface states. Generally, to take full advantage of the topologically protected surface states in topological insulators, the E_F should be positioned within the volume band gap, possibly close to the DP where the surface states the surface states in topological protected states to emerge the highest carrier mobility and exhibit the most robust spin-momentum locking.

The aim of this Thesis is to explore different approaches to control the position of the E_F in relation to the unique electronic properties resulting from the non-trivial topology of Bi_2Se_3 and Bi_2Te_3 . These approaches include doping with foreign elements, changing stoichiometry of compound, and manipulating of native defects of the materials. Systematically characterizing the electronic properties of such modified materials in comparison to pristine samples using a range of experimental techniques allows to study the effect of the discussed modifications on a wide range of parameters including surface topography and electronic structure in relation to local and global properties. Ultimately, these research may contribute to the development of a relatively easy method of adjusting the position of the Fermi level in topological insulators depending on the needs which may turn out to be essential for realizing their full potential for future technologies.

3 Experimental methods

From the preceding Sections, particularly from the Paragraph 2.3, it is evident that the research focuses on the non-trivial electronic states present on the surfaces of the tested materials: Bi_2Se_3 and Bi_2Te_3 . To achieve the stated research objectives, advanced measurement techniques are employed to confirm the quality of the single-crystalline samples and to conduct surface-sensitive tests. The initial step is to ensure that the tested samples are high-quality single crystals, as only they exhibit the properties of a TI. To accomplish this, X-ray diffraction (XRD) tests were conducted on the samples to determine the material's lattice constants and ordering. Additionally, the surface's long-range ordering was analyzed using the low-energy electron diffraction (LEED) technique. Finally, the atomic purity and chemical composition of the surface was determined using the Auger electron spectroscopy (AES) technique.

Subsequent research was directed towards investigating the surface's morphology and local electronic structure with spatial resolution capable of detecting single structural defects or dopants. This was accomplished by utilizing the scanning tunneling microscope (STM) and it's STS (scanning tunneling spectroscopy) mode. However, during the advanced stage of research, it became evident that operating solely in the STM microscopy and spectroscopy domain was insufficient in fully elucidating the physical problems under investigation. Difficulties in interpreting results arose due to the overlapping of bands in the electronic structure, necessitating the use of additional research techniques.

To overcome this limitation, further insights were gained through the utilizing the synchrotron technique ARPES (angle-resolved photoemission spectroscopy) to provide a more comprehensive visualization of the electronic structure. Furthermore, collaborations were established with groups of theoreticians to perform *ab-initio* simulations and DFT (Density Functional Theory) calculations aimed at resolving the fundamental problems. The research was complemented by measurements of magnetotransport at sub-Kelvin temperatures and the analysis of observed quantum oscillations.

The combination of the aforementioned techniques enabled to conduct a comprehensive investigation into the physical problems posed in the Thesis. These methods are well described in the literature: STM and STS [38, 39], LEED [40], AES [41], ARPES [42]. Therefore, there will be just a brief characterization of them, spending more time on the description of the UHV setup which was originally designed in our group with the active involvement of the author of the Dissertation at all stages of designing and commissioning the system.

The starting point for the work was the STM microscope, transferred to a newly organi-
zed laboratory intended to enable comprehensive examination of the surface of materials. The STM microscope system itself allowed for sample insertion and surface analysis in the STM/STS mode under UHV conditions. In the era of more and more widespread access to sophisticated methods of surface testing, these possibilities gave quite a limited room for maneuver for preparing samples for measurements and complex characterization of the surface from the point of view of chemical purity, crystallographic structure and electronic structure under the same conditions. Each analysis involved transferring the sample to a different laboratory, the surface of which had to be protected, e.g. by covering it with a protective layer or transferring it in a vacuum suitcase, or taking into account the inevitable contamination of the surface by contact with the atmosphere. A big step forward was therefore the commissioning of an additional UHV chamber connected to the existing STM system. This preparation chamber allowed for a better and more controlled surface cleaning and preliminary crystallographic and chemical analysis of the surface. After the chamber was designed by our group with the authors participation, including examining the component arrangement and generating preliminary CAD designs, subsequently shared to the system contractors, the next stage involved installing the preparation chamber. During this stage, the author participated in carrying out extensive service works to initiate and synchronize all the components that had been installed. These works continued for a considerable period, lasting until around the end of 2019. Following this stage, the focus of the work shifted more from maintenance to scientific activities, with the developed system facilitating the generation of the first meaningful experimental outcomes.

The final, while this Work is in the final stage, view on the arrangement on the vacuum system in the STM laboratory is presented in Figure 3.1. The undoubted advantage of the preparation chamber connected to the STM system is that all the above-mentioned analyzes can be performed *in situ* one after another, ensuring a wide and comprehensive characteristic of the tested materials. The presented UHV system serves as the starting point for our modern materials science studies.



Figure 3.1: STM laboratory UHV setup including STM chamber (1), preparation chamber (2), and rack with control electronics (3)

Within the preparation chamber, it is possible to:

- 1. Obtain an atomically clean surface of substrate by:
 - UHV (10^{-10} mbar) cleaving of samples at various temperatures
 - annealing to a temperature of 1200°C
 - Ar⁺ ion sputtering
- 2. Characterize the surface by:
 - analysis of the crystallographic structure at the surface by the diffraction of low-energy electrons (LEED)
 - analysis of the chemical composition at the surface by measuring the energy spectrum of Auger electrons (AES)
- 3. Produce samples on a previously prepared substrate (see 1.) by:
 - deposition of single atomic layers (or multilayer systems) of selected materials by molecular bram epitaxy (MBE). Thin layers are deposited from molecular beams, the source of which are effusion cells. The amount of applied material is precisely controlled with a quartz microbalance (QCM). The produced samples can also be characterised as listed in 2.

3.1 UHV set-up including STM and preparation chamber

The vacuum system in the STM Laboratory is characterized by a very compact design which allows easy handling of the samples by one person as well as a series of in-situ measurements that will be described in detail in the following Paragraphs. A photo and schematic drawing of STM setup and the preparation chamber is presented in Figure 3.2 where all principal tools are visible: STM chamber, load-lock chamber, LEED/Auger spectrometer, MBE evaporation source, 5-axis manipulator, and the pumping stage. In order to reach the UHV regime $(10^{-9} - 10^{-11} \text{ mbar})$ several pumping stages are necessary. In this case a pre-vacuum is obtained in load-lock chamber using a pumping stage made of rotary and turbo molecular pump. This system is capable of reaching a pressure of about 10^{-7} mbar in about half an hour. All the remainder of the system is continuously pumped by ion pumps mounted in both STM and preparation chamber which maintain UHV conditions. It is worth adding that these chambers are separated by a plate valve and they have separate vacuum environments. A load-lock chamber is also separated from the rest of the system by a valve that is opened only when the load-lock chamber is pumped down. This solution allows to introduce and extract samples without significant deterioration the vacuum of the whole system.

Vacuum recovery in the entire system is carried out after service works, then the loadlock pumping system is used to achieve the initial vacuum. Then an ion pump coupled with a Ti-sublimation pump is used to reach a pressure of about 10^{-8} mbar, typically overnight. At this point a bake-out is necessary to reach lower levels of vacuum. During this process the whole chamber is heated in a special thermal cover up to a temperature of about 120°C (STM chamber) and 160°C (preparation chamber). The bake-out is carried out for an entire day (or more if necessary) in order to remove water vapour and other gases from all inner walls of the chamber. After that the system is cooled down and the pressure finally reaches the UHV regime of $10^{-10} - 10^{-11}$ mbar. This procedure is very time consuming, and it is necessary to reduce as much as possible the number of times it is needed.

Sample preparation combined with initial surface characterization and STM/STS measurements generate the need for moving the sample from one ultra-high vacuum location to another. Also the possibility of changing the sample orientation, for example tilting around some axis is necessary. For these aims we use five-axis manipulator and linear transfer mounted in preparation chamber. The sample can be picked up from the loadlock chamber directly on the manipulator, which will adjust the sample position to the analysis that we want to conduct. Then the sample can be picked up by linear transfer and transported to the STM chamber for further analysis, or it can be led back to the load-lock chamber as needed.



Figure 3.2: (a) self-prepared schematic diagram of the vacuum system configuration at the stage of designing the preparation chamber for the STM microscope, (b) the corresponding photo of the finished assembled UHV system in the STM laboratory

In general, the five-axis manipulator enables both cooling using liquid nitrogen and heating of the sample in resistive mode as well as electron beam (EB) mode. Therefore, all actions available in the preparation chamber (Ar^+ etching, cleavage, LEED, AES, MBE deposition) can be performed in the temperature range from 40 K to 700 K (at resistive heating). Flashing the sample up to 1400 K is possible in EB mode.

3.1.1 Scanning tunnelling microscopy (STM)

The STM was developed by G. Binnig and H. Rohrer at IBM Research Lab in Zurich, Switzerland in early 1980s [38, 39]. The microscope uses the probe in the form of a needle with an extremely sharp tip, usually made by electrochemical etching of tungsten rod, mechanical cutting the rod of platinum-iridium alloy. The tip is mounted on a piezoelectric element that controls its position in three dimensions, that the movements induced by the voltage may be smaller than a tenth of a nanometer (Figure 3.3). When the tip is brought at a distance of the order of one nanometer above the sample surface, the quantum effects such as tunneling of electrons through the potential barrier can occur, which in this system is the vacuum region between the sample and the tip. Applying a potential difference between the tip and the sample results in an ordered tunneling direction. The result is a small but detectable current that is exponentially dependent on the distance between the tip and the surface. Since the current increases rapidly as the distance decreases, very small changes in the position of the tip with respect to the surface can be detected.



Figure 3.3: Schematic of the STM imaging principle. The microscope probe is placed in a piezoelectric tube with electrodes enabling the tip to be moved in the (x, y) directions of the sample plane and movements in the z direction, mapping the surface topography when the tip maintains a constant distance from the sample during scanning.

To generate an image, the tip is moved back and forth across the sample at very small

intervals. Two operating modes can be distinguished as the needle tip scans the surface: the constanc current mode and the constant height mode. In constant current mode the position of the tip in z direction above the surface is continuously adjusted to keep the tunneling current constant. As the tip rises to glide over hills and sinks down into hollows, the vertical movements of the tip map the topography of the surface. In constant height mode the position of tip in z direction is kept constant. The changes in distance to the surface as the tip is scanning make the tunneling current rise on hills and lower at hollows, thus mapping the surface morphology. These adjustments are used to generate an atomic-scale topographic map of the surface.

The theoretical basis for the general description of the tunneling phenomenon in STM, known as the transfer Hamiltonian approach is given by Bardeen [43]. Tersoff and Hamann applied this approach to a model of a flat surface and a spherical tip of the needle, thus creating the first quantitative model for the tunneling current in STM. As a result, one gets the following expression for the tunneling current I in the limit of zero temperature and very low voltages:

$$I = 32\pi^{3}\hbar^{-1}e^{2}V\varphi^{2}D_{t}(E_{F})R^{2}k^{-4}e^{2kR} \times \sum_{v}|\Psi_{v}(r_{0})|^{2}\delta(E_{v}-E_{F}).$$
(3.1)

In this equation, I depends on the average work function $\varphi = (\varphi_t + \varphi_s)/2$ of tip and sample and on the density of states D_t of the tip at the Fermi level. The sample properties are represented by the value of the sample wave functions Ψ_v with an energy E_v at the center of of the probe tip curvature r_0 (Fig. 3.3), constituting the $LDOS \equiv \rho(r_0, E) = \sum_v |\Psi_v(r_0)|^2 \delta(E_v - E_F)$. The LDOS thus represents the charge density per unit energy at E_F at a certain point at the surface. Following the argumentation in [44], one can derive from Eq. 3.1 an important relation between the tunneling current at very small bias, i.e. around E_F the local DOS at the surface (LDOS):

$$dI/dV \propto LDOS(E_F).$$
 (3.2)

Based on the above arguments from Equations 3.1 and 3.2, it can be concluded that the STM result is not strictly the topography of the tested sample, but its convolution with the LDOS surface map.



Figure 3.4: Schematic picture of the tip-sample tunneling geometry. Although tunneling takes place between the surface of the sample and the protruding tip atom, the tip is modelled here as a locally spherical potential well where it approaches closest to the surface. Based on figure in [44].

Despite all its capabilities, the STM also has very real limitations that I should mention. Since its operation depends on the flow of current, it can only be used to image conducting materials. Although it probes the electron cloud structure of the surface with a great precision, it cannot distinguish well, if at all, between atoms of different elements within a compound material. Nevertheless, the possibilities offered by the STM technique, such as atomic resolution of imaging and simultaneous access to the study of surface topography and electronic states, perfectly correspond to the objectives of this Thesis. Therefore, the STM technique combined with the STS mode have become the leading techniques used in my research.

All the STM/STS results were obtained using a variable-temperature scanning tunneling microsope (VT STM) with a Beetle scan head controlled by R9 SPM (by RHK) control system. The STM and STS measurements were carried out in UHV under a base pressure of 10^{-10} mbar at room temperature.

3.1.2 Scanning tunnelling spectroscopy (STS)

The STM microscope offers the possibility to study with atomic spatial resolution not only the topography of a conductive sample, but also the electronic properties of such a sample with comparable lateral resolution. For this purpose, scanning tunneling spectroscopy (STS) mode is used to obtain information about the local density of electronic states (LDOS) of the surface [46]. In this mode, the STM tipsample separation is kept constant, at a given (x, y) location on the surface. The device then sweeps a predetermined voltage range, which effectively allows sampling of the electronic structure of the surface (Fig. 3.5). The collected relationship $I(V_{\text{bias}})$ is then differentiated, obtaining the STS spectrum in the form of dI/dV which, according to Equation 3.2, is proportional to LDOS. Exploiting the ultra-high resolution capabilities of STM, this in-



Figure 3.5: Schematic of tip-sample tunneling. Energy is along the vertical axis, and density of states of the tip and sample are shown along the horizontal axes. Filled states are shown in colors. In this case, a positive bias voltage V has been applied to the sample, which effectively lowered its Fermi level by eV with respect to the Fermi level of the tip. This allows for filled states on the left (tip) to tunnel into empty states on the right (sample). Figure from [45].

formation can in principle be obtained at a very local scale. This is a critical feature for these research that aim to study nano-scale properties such as the effect of single structural defects or dopants. In order to correctly interpret the STS spectra, the consequences resulting from Equation 3.1 should be taken into account. According to it, the tunneling current depends both on the electron states at the surface being tested and on the states at the needle tip, which are generally unknown (Fig. 3.5). Two different approaches to the interpretation of the STS spectra can be found in literature: either the directly measured differential conductivity dI/dV or the differential conductivity normalized by the total conductivity (dI/dV)/(I/V) as argued by Tersoff and Hamann [44] or Feenstra *et. al.* [47]. The later approach should make the result independent of the unknown states at the tip of the needle and ensure that the measured STS spectrum is proportional to the LDOS at the tested surface.

These research aimed at direct comparison of the STS spectra of various features at the surfaces of different samples. In these long studies, it was inevitable to use a large number of needles to obtain the final result. This, of course, introduces undesirable degrees of freedom in interpretation related to unacquaintance of the states at the tips of different needles. Therefore, for the correct interpretation of the results of this study, the approach of normalization by dividing the differential conductance dI/dV by the total conductance I/V, i.e., (dI/dV)/(I/V) was considered more appropriate. The divergence problem at small bias voltages in the case of (dI/dV)/(I/V) was overcome by broadening ΔV up to 1.2 V [48]. All the STS spectra were acquired via the standard *lock-in* technique with a 20 mV modulation amplitude and 12.3 kHz frequency.

3.1.3 Low-energy electron diffraction (LEED)

The experimental setup for the LEED experiment consists of a gun that produces a beam of electrons with a primary energy in the range of 20-300 eV. This beam is focused on the sample surface by a series of lenses. The elastically scattered electrons produce a diffraction pattern which is visualized on a fluorescent screen. Observation of the LEED pattern allows the determination of the symmetry and size of a surface unit cell and, as with all surface diffraction techniques, the analysis is based on the reciprocal lattice [49]. It should be emphasized that the average free path of an electron is not larger than a few angstroms in this energy range. This means that only those electrons that do not penetrate more than a few atomic layers below the surface can contribute to the diffraction pattern. LEED is therefore a surface-sensitive technique which makes it compatible with other techniques available in the laboratory and is also important for these studies. The lateral size of the surface area from which the LEED image is created corresponds to the macroscopic spot size of the primary beam of the order of 1 mm². From the point of view of local measurements like STM, LEED has to be considered a global technique.

In these studies, LEED patterns were taken using the SPECTALEED retarding field

analyzer by Omicron showed in Figure 3.6(b). Tungsten filament was used with filament current $I_{fil} = 1.75$ A and emission current $I_E = 0.3$ mA.

3.1.4 Auger electron spectroscopy (AES) with retarding field analyser (RFA)

The Auger effect is an atomic process of non-radiative emission. When an atom is irradiated by high-energy photons or electrons and then creates a hole in the core levels, it changes its electronic structure in such a way that the initial hole in the deep electron shells is filled with an electron from one of the outer shells. This transition may be accompanied by the emission of a characteristic X-ray photon or, alternatively, by the process of the non-radiative Auger transition. In the latter case, the excess energy is transferred to another electron, which is ejected from the atom with a well-defined kinetic energy, directly related to the differences of energy levels that participated in the transition. Each chemical element, therefore, has a characteristic set of available Auger electron energies.

In a typical AES experiment, a primary electron beam with an energy of a few keV (3.0 keV in our system) is focused on the sample surface, while the backscattered electrons are collected and analyzed for energy. For this purpose, various electron energy analyzers are often used. An alternative implementation of the AES is the retarding field analyzer (RFA) used in our system. This design operates using the same optic system as to observe low energy electron diffraction (see Paragraph 3.1.3). During



Figure 3.6: LEED/AES apparatus with retarding field analyzer. (a) LED optics diagram with signature of functional elements. The primary electron beam from the gun is modelled by an electric lens system. Diffracted electrons reach the fluorescent screen, creating a surface diffraction pattern. (b) image of the Omicron SPECTALEED apparatus, from Ref. [50]

the measurement, increasing electron retarding potential is applied to the optics grids. The collector of electrons that have passed through the energy filter is the screen of the LEED optics. The collector current, which determines the electron energy distribution, allows the measurement of AES spectra. The RFA configuration has a slightly lower energy resolution of the electron collector than systems with dedicated energy analyzers, but the big advantage of this system is that it shares the optics system with the LEED module, which is important in the case of such compact vacuum systems as used here.

A typical Auger spectrum contains a series of peaks with very precise energy values corresponding to de-excitation processes. Therefore, this technique is very sensitive to different elements as each element has its own easily identifiable Auger peaks. An important feature of AES measurements is that only Auger electrons coming from a sample depth of up to 2-3 atomic layers of the material have a chance to leave the material and participate in the measured spectrum. Therefore, AES is a technique focused on examining only the surface layers of materials, which is of key importance in the context of these research on TIs.

Apart from the standard measurement of the AES spectrum of a sample, which allows to study the chemical composition of the surface, there is an alternative measurement mode that is used to continuously determine the ratio evolution of certain elements of a complex material during a dynamic process, such as thin layer deposition or annealing. This so-called AES peak-to-peak method consists in continuously measuring the height of a selected peak or several peaks of the Auger spectrum. However, the standard version of the Omicron software does not allow measurements in this mode. Therefore, due to the important information provided in the measurement, I prepared my own version of the device software in the LabView environment. The front panel of the program with a graphical user interface is shown in the Figure 3.7.



Figure 3.7: Self-prepared software program to control AES setup. (a) panel used to measure the AES spectrum within the specified energy range, points density and *lock-in* parameters. (b) panel controlling the the peak-to-peak mode, specifying the energies of the peaks of interest and the measurement parameters.

The prepared program works in several modes, so that it provides all the options of the original Omicron software, and also extends the device's capabilities with peak-topeak measurements. The panel in Figure 3.7(a) is used to measure the AES spectrum. On the left, the user sets the energy range, density of points and *lock-in* parameters, and the large panel on the right shows the real-time AES spectrum. Figure 3.7(b) shows the peak-to-peak mode. The user specifies the energies of the peaks of interest and the measurement parameters, and after starting the measurement the intensity of up to four peaks are treated separately and presented in the panels on the right. Hopping between peaks with significantly different energies may pose some problems with the *lock-in* relaxation time. In order for the measurement results to be reliable, it would be necessary to set a suitably short time constant to *lock-in*, or to enter a sufficiently large dead time between measurements of successive peaks. In such a mode, a lot depends on the ability of the operator, so here the problem is solved by automatic stepwise transitions between the energies of the individual peaks, so that the influence of relaxation time is less dependent on the parameters entered.

3.2 Electronic transport and magnetotransport at sub-Kelvin temperatures

Electronic transport properties of the tested materials were investigated using the Triton Dilution Refrigerator by Oxford Instruments, which uses a ${}^{3}\text{He}/{}^{4}\text{He}$ mixture in a closed circuit to achieve and stabilize temperatures in the range of 10 mK to 30 K. The integrated superconducting magnet allows for the creation of a magnetic field up to 14 T. Triton is equipped with a Nanonis Tramea measurement system for electrical transport and specific heat measurements that immediately converts signals from analog to digital, minimizing measurement noise. The system can generate and read signals with high accuracy and very low noise at a speed of up to 20,000 readings per second on each channel. It also includes two *lock-in* phase sensitive detectors, a high-resolution oscilloscope, and an FFT spectrum analyzer. With the Triton dilution refrigerator and Nanonis Tramea measurement system, the following electrical transport measurements were performed using the 2- and 4-point methods at temperatures ranging from 100 mK and in magnetic fields up to 14 T:

- 1. The most basic measurement that can be performed is to measure the resistance of the sample as a function of temperature. This can be done by measuring the voltage drop across the sample as a known current is passed through it, and then using Ohm's law to calculate the resistance. By varying the temperature of the sample using the cryostat, it is possible to observe how the resistance changes with temperature. This information can be used to determine the nature of the electronic states in the material.
- 2. Hall Effect measurement. The Hall effect is a phenomenon in which a magnetic field perpendicular to the flow of current induces a voltage across the sample. This effect can be used to measure the carrier concentration and mobility of the sample. To measure the Hall effect, a magnetic field is applied perpendicular to the sample

and a current is passed through it. The voltage generated across the sample is then measured and used to determine the carrier concentration and mobility.

3. Magnetoresistance and Shubnikov–de Haas (SdH) quantum oscillations measurements. Magnetoresistance is the change in the resistance of a material in the presence of a magnetic field. By applying a magnetic field in different directions and measuring the change in resistance, it is possible to obtain information about the energy levels and the density of states in the material. In the presence of a magnetic field in the plane perpendicular to the field B, the energy states are quantized. Instead of a quasi-continuous energy spectrum as a function of the wave vector k, discrete energy levels appear: Landau levels. A very large number of states are concentrated at the Landau levels, and there are relatively few of these states between the levels. By increasing the magnetic field, we can bring the next Landau level to the $E_{\rm F}$. Since only carriers with energies close to $E_{\rm F}$ can participate in transport, a rapid increase in the density of states by the Landau level will cause a rapid increase in conductivity. Further growth will cause the Landau level to pass E_F and conductivity to drop rapidly. In this way, as the E_F passes through the Landau levels, we will observe oscillations in conductivity or resistance as a function of the magnetic field, known as Shubnikov-de Haas quantum oscillations.

Thermoelectric effect measurements were conducted in cooperation with Thermoelectric Research Laboratory at WIMiC AGH. The thermoelectric effect is the generation of a voltage when there is a temperature gradient in a material. This effect can be used to measure the thermoelectric properties of the sample, such as the Seebeck coefficient and the figure of merit. These properties are important for applications in thermoelectric power generation and cooling.

3.3 Angle-resolved photoemission spectroscopy

With the capability of directly visualizing band dispersions and Fermi surfaces, angleresolved photoemission spectroscopy (ARPES) has emerged as one of the most versatile methods for studying the electronic structure of materials. ARPES is an experimental method based on photoelectric effect. In a typical ARPES experiment a sample is placed close to an electron analyzer under ultra-high vacuum conditions, as shown in Figure 3.8(a). When light of a primary beam is incident on the sample, the electrons in the material absorb the photons. If the energy of the photons is greater than the material's work function, the electrons can escape into the vacuum. These emitted electrons, known as photoelectrons, are then collected and analyzed by a spectrometer for their kinetic energy and emission angle. The energy and momentum of the photoelectrons are directly related to those of the electrons within the sample through the conservation of energy and momentum parallel to the sample surface. The momentum perpendicular to the surface



Figure 3.8: (a) diagram of the principle of ARPES operation form [53], (b) the terminal station of the UARPES beamline of the Solaris synchrotron in Kraków with the ARPES apparatus and fittings.

is not conserved, however can still be extracted by using the nearly free-electron approximation for the final states. The basics of ARPES have been describe in detail in many literature positions [42, 51, 52].

Importantly from the point of view of this Thesis, ARPES has played and still plays a key role in the study of materials exhibiting surface states such as TIs. A review of these examples can be found in references [53, 54]. ARPES is a surface-sensitive technique and using the ability to directly distinguish overlapping volume and surface bands, AR-PES is useful in solving the interpretation problems encountered with STS measurements. Compared to very local STS measurements, the ARPES information is collected from an area of the size of the incident beam's geometric spot size (here 60 μ m × 150 μ m). The main difference, however, is that ARPES can directly image the electron structure in the entire Brillouin zone, while STS measurements only sample the electron structure near the Γ point. The ARPES results discussed in this Thesis were collected on the UARPES beamline (current name is URANOS due to a significant modernization) of the National Centre for Synchrotron Radiation Solaris in Krakow. The author, had the opportunity to get to know this beamline well during PhD by participating in the aforementioned experiment and during a 3-week intern-ship on UARPES beamline. A look at the measurement station of the beamline from that time is shown in Figure 3.8(b).

The ARPES measurements were performed at the at pressures better than $1 \cdot 10^{-8}$ Pa using horizontally polarized undulator radiation. Photoelectrons were detected with a DA30L electron energy analyzer, Scienta Omicron. The overall resolutions of the ARPES measurements is 8 meV (energy) and 0.1 deg (angular). The samples were glued with epoxy resin to a sample holder and cleaved in UHV. The measurements were carried out as soon as possible after cleaving and cooling down to 12 K.

3.4 Samples

3.4.1 Synthesis

The materials used in research are single crystals of Bi_2Se_3 and Bi_2Te_3 as well as doped with foreign elements $Bi_{1.96}Mg_{0.04}Se_3$ and $Bi_{1.98}Fe_{0.02}Se_3$, and also a series of samples with variable stoichiometry of the $Bi_{2-x}Te_{3+x}$ type.

The samples constituting the research material come from two sources. The pristine Bi_2Se_3 and Bi_2Te_3 as well as doped- Bi_2Se_3 samples were synthesized using the Bridgman method by dr I. Miotkowski at Purdue University in West Lafayette, USA. These crystals were used to investigate the influence of dopants on the electronic structure of Bi_2Se_3 as discussed in Section 4. The Bi_2Te_3 were used to investigate the possibility to influence the electronic structure through heat treatment as described in Section 6. While the $Bi_{2-x}Te_{3+x}$ series with x = 0, x = 0.0175, x = 0.0225, x = 0.035, x = 0.07, x = 0.14 synthesised at WIMiC AGH were used to investigate the influence of deviations from perfect stoichiometry on the electronic properties of samples, and are discussed in Section 5.

In the Bridgman method of synthesis used at Purdue University, the initially 5N purity elements were deoxidized in carbon boats in two-zone horizontal furnace in vacuum of 10^{-5} Pa and then purified further by multiple vacuum distillations under dynamic vacuum of 10^{-5} Pa until they reach 7N purity [18]. The introductory synthesis was performed in the same boats at 1170 K, after which material was slowly cooled under controlled Se vapor pressure. Then initially synthesized material was transferred to quartz ampoule which, after evacuation, was placed in 3-zone vertical furnace. Temperature gradient in growth zone was set on 0.5 K/cm. Ampoule velocity across the growth zone was 0.5 to 1.5 mm/h.

The series of $\text{Bi}_{2-x}\text{Te}_{3+x}$ samples with the parameter x equal to 0, 0.0173, 0.0225, 0.035, 0.07, 0.14 were synthesized by the group of prof. K. Wojciechowski at the Faculty of Materials Science and Ceramics at AGH using the Bridgman method as well. Samples with the nominal compositions of $\text{Bi}_{2-x}\text{Te}_{3+x}$ were prepared by melting high-purity Bi (shot, 99.999 %) and Te (shot, 99.999 %) in graphite-coated quartz containers with a diameter of 8 mm evacuated to a residual pressure of 10^{-7} Pa. The total mass of each sample was 5 g. The ampules for the growth of the single-crystalline samples were prepared in a special way with a very narrow region at the bottom to establish the crystallization centers. The ampules with the stoichiometric mixtures of elements were placed vertically in the muffle furnace, heated up to 923 K at the rate of 10 K/h, and kept at this temperature for 5 h followed by the mixing in a liquid state. Then the ampules were cooled down to the temperature of 600 K at a rate of 3 K/h. From the fabricated crystal, the well-shaped single crystalline samples were selected for further characterization.

As a result, easily cleavable along a-b plane and contamination free samples were obtained. The single crystalline samples used in this research are presented in Figure 3.9.



Figure 3.9: Exemplary single-crystalline samples used in research, synthesised in Purdue University. As a result of synthesis, large single crystals are obtained, which are then cut to a convenient size and thickness (1) Bi_2Se_3 , (2) Bi_2Te_3 , (3) properly cut thin and smooth piece of Bi_2Se_3 single crystal ready to be mounted on the STM holder.

3.4.2 Samples preparation for the UHV measurements

The flatness of the surface and its purity at the atomic level is essential for research. In the field of experimental physics, many methods are known to achieve the required surface cleanliness. Among them there are methods based on sample annealing leading to thermal desorption of all contamination from the surface. Electron or Ar^+ ion beam etching of surface atomic layers methods are also often used. The surface purification process is naturally facilitated for layered samples such as investigated crystals of Bi₂Se₃ and Bi₂Te₃. In such a case, the atomically clean surface can be prepared by delamination in the easily cleavable plane of the sample.



Figure 3.10: (a) sample mounted on the STM measurement support, to which a specially prepared pawn has been glued from above. In the UHV chamber, the pawn is torn off with the top layer of the material (b), which exposes a smooth and atomically clean surface ready for measurement

In a cleaving process a pawn is used glued to the upper surface of the sample mounted on the measuring holder, as shown in Figure 3.10(a). The set prepared in this way is transported to the UHV chamber. There, using a special wobble-stick, the pawn is then torn off in UHV conditions, while tearing off the upper layer of the material. In this process, a new contamination-free crystal surface can be exposed, as schematically shown in Figure 3.10(b). If the exposed layer is smooth enough to carry out the measurements, the preparation process is considered complete.

3.4.3 Basic characteristics of starting materials: pristine Bi₂Se₃ and Bi₂Te₃

The initial characteristics of the starting materials of pristine Bi_2Se_3 and Bi_2Te_3 samples included crystallographic studies using the XRD method, as well as surface tests of topography (STM), crystallographic structure (LEED) and chemical composition (AES) performed directly after cleaving in UHV.

The crystallographic structure of Bi_2Se_3 and Bi_2Te_3 was characterised by XRD technique of the powdered samples. The results are shown in Figure 3.11.



Figure 3.11: X-ray diffraction spectrum (black dots), calculated spectrum (blue solid), difference between measurement and calculation (red solid) and Bragg positions (black bars) of (a) Bi₂Se₃, (b) Bi₂Te₃ synthesised at Purdue University.

XRD measurements were carried out in a different laboratories and the author did not participated in it. However, the author conducted an analysis of the obtained spectra consisting of the background adjustment and refining the Rietveld function to Bi_2Te_3 spectrum in order to determine the size of the unit cell. The HighScorePluse environment was used to analyse the spectra. The unit cell parameters of both Bi_2Se_3 and Bi_2Te_3 samples determined by this analysis are summarized in the Table 3.1.

Table 3.1: The estimated parameters of unit cells from the XRD measurements of powdered samples of Bi_2Se_3 and Bi_2Te_3

Sample	Space group	a [Å]	c [Å]	V [Å ³]
$\operatorname{Bi}_2\operatorname{Se}_3$	R-3m (166)	4.1373(2)	28.6450(6)	424.63(3)
${\rm Bi}_{2}{\rm Te}_{3}$	R-3m (166)	4.3866(9)	30.4997(7)	508.25(5)

The obtained results are in good agreement with the literature data presented in the introductory part of the Thesis (compare Tab. 2.1).

The surface topography and crystallographic structure were characterized by STM combined with Fourier transform (FFT) and LEED methods. Prior to the STM and LEED measurements the samples were prepared by cleaving *in situ* in UHV. The exact procedure of cleavage is described in Section 3.4.2. The resulting characteristics of surface of Bi_2Se_3 and Bi_2Te_3 are presented in Figures 3.12 and 3.13 respectively.



Figure 3.12: Sutface topography and crystallographic structure of Bi₂Se₃. (a) 200×200 nm STM topography scan revealing typical atomic step between bright yellow (left) and dark yellow (right) part of the image. (b) cross-section along the profile marked in (a). (c) 100×100 nm STM topography scan on atomically flat area of the surface. (d) 10×10 nm STM scan of defect-free part of surface. The insert presents the FFT power spectrum calculated from the raw topography image. (e) LEED pattern at primary beam energy of 61 eV. STM topography images acquired in room temperature at $V_{\text{bias}} = -330$ mV, I = 200 pA

The surface prepared by cleavage is characterized by the presence of atomic steps with an atomically smooth surfaces of the order of a few square micrometers. This is a very large area in the scale of local STM scans. The atomically flat regions dominate and in fact it can be difficult to find the edge of steps, therefore the materials are a grateful object for this type of measurement. Once one manage to find the edge of the step the vast majority of them are as shown in Figure 3.12(a). The steps are in the form of a sharp setoff of about 1 nm (Fig. 3.12(b)), which is in very good agreement with the height of the single quintuple layer (QL) described in Paragraph 2.2.1. There are also very rare setoffs with a height that is a integer multiple of the QL (multiple steps). The existence of faults only between complete QLs can be understood in a simple way: inside the QL there are strong covalent-ionic bonds, while between these layers weak van der Waals interactions occur. It is therefore natural that in the splitting process the material delaminates at the boundary of the QLs, always revealing the same surface of hexagonal symmetry with selenium or tellurium termination in the case of Bi₂Se₃ (Fig. 3.12) and Bi₂Te₃ (Fig. 3.13), respectively.

STM scan performed on an atomically flat surface area is shown in Figure 3.12(c). A large number of triangular patterns are visible. These shapes are related to the large number of structural defects occurring near the tested surfaces. Considering the presence of a large number of defects, this topic will not be elaborated on here. The problem of defects and their influence on the material's properties applies to all samples tested at the Thesis and is so extensive that a separate Section has been devoted to it. A through analysis of the type and origin of defects as well the study on their impace on local and global electronic structure is provided in Section 6.

The long range surface atomic ordering was investigated using the LEED method. Figure 3.12(d)) shows LEED pattern recorded with a primary beam energy of 61 eV. The pattern shows six well-pronounced single atomic-lattice Bragg spots, which can be grouped into a hexagon. This result, collected from the global area, is confirmed by the 10×10 nm atomically resolved STM topography image shown in Figure 3.12(e). Local atomic arrangement of the examined surfaces with perfect hexagonal symmetry is clearly visible. The FFT power spectrum presented in the inset is calculated from the STM topography scan. The hexagonal symmetry of the surface is confirmed both in local and long-range atomic ordering.

The same analysis of surface structure was conducted for Bi_2Te_3 crystal, as presented in Figure 3.13. Bi_2Te_3 has similar topography features to the previously described Bi_2Se_3 . The surface reveals atomically smooth regions of a few square micrometers in size. These areas are separated by atomic steps (Figure 3.13(a)) of a height equal to the height of a single QL (Fig. 3.13(b)). As in the previous case, the dominant height of the steps results from the crystallographic structure of the crystal (Section 2.2.1).

Scans of atomically flat fragments show a large number of defects in the form of triangular patterns as shown in Figure 3.13(c). Defects occur in a comparable amount as in the case of Bi₂Se₃ and their surface imprint is very similar, which is certainly a consequence of the almost identical crystallographic structure of Bi₂Te₃ and Bi₂Se₃.



Figure 3.13: Surface topography and crystallographic structure of Bi₂Te₃. (a) 100×100 nm STM topography scan revealing typical atomic step between bright yellow (left) and dark yellow (right) part of the image. (b) cross-section along the profile marked in (a). (c) 100×100 nm STM topography scan on atomically flat area of the surface. (d) 10×10 nm STM scan of defect-free part of surface. The insert presents the FFT power spectrum calculated from the raw topography image. (e) LEED pattern at primary beam energy of 78 eV. STM topography images acquired in room temperature at $V_{\text{bias}} = -430$ mV, I = 200 pA

The global ordering was tested using the LEED method as presented in Figure 3.13(d). Whereas the local ordering with hexagonal symmetry is visible in STM atomically resolved scan (Fig. 3.13(d)) and insert containing the FFT power spectrum calculated from the corresponding STM topography. Small distorsion of the obtained hexagon is related to the thermal drift during the scan. However, the hexagonal symmetry of the surface lattice is clearly visible in both local (by STM) as well as global (by LEED) measurements.

4 Tuning the Fermi level by introducing magnetic and non-magnetic dopants of a low concentrations to Bi_2Se_3

As it was presented in introductory Section 2, the electronic structure of the real single crystalline sample of Bi₂Se₃ shows significant differences from the modelled theoretically ideal case (Paragraph 2.2.2). Due to the presence of native structural defects in Bi_2Se_3 crystals, the $E_{\rm F}$ is located deep in the BCB and the material shows n-type conductivity [55]. Therefore, the bottom of the BCB and TSS coexist at the $E_{\rm F}$ [11]. Taking full advantage of the topological properties of this material requires setting the E_F in the area of the volume band gap region, where only TSS occur, so that the realization of conductivity exclusively at the surface would be possible. One of the commonly used methods of influencing the $E_{\rm F}$ is introducing dopants in the form of foreign atoms into the crystal. These dopants are selected in such a way that they can be incorporated into the crystal lattice of the material during the synthesis of the sample, occupying the positions of the native atoms of the material. Depending on the choice of the element, the dopant atoms are then either donor or acceptor, which obviously affects the E_F of the material as a whole. Since the $E_{\rm F}$ is located in the BCB and there is a need to shift it to lower energies, a great deal of research work has been devoted to manipulating the $E_{\rm F}$ by searching for suitable p-type dopants. These efforts include volume doping with elements, such as Mn [56], Sn [11], Fe [57, 58], Ca [59, 12], Mg [60], Cr [61, 62], Pb [63], and surface adsorption with Fe [64, 65], Co [66]. Doping with magnetic materials is particularly important due to the fact that the magnetic order leads to the breaking of the time reversal symmetry, and thus, can destroy the topological order. Indeed, magnetic dopants can open the energy gap at the DP of a topological surface state [11]. This effect leads to the creation of odd multiples of Dirac fermions [65] and opens up a new branch related to magnetic topological insulators [67].

Despite the fact that the destruction of the topological electronic states by magnetic dopants of high concentration has been demonstrated [65], the question still open is whether even amounts of dopants on the level of 1% introduce such changes. In general, the main aim of this Section is to clarify better how such small concentrations of both magnetic and non – magnetic dopants in Bi_2Se_3 affect its non-trivial topology and its DC structure of topological surface states and the electronic structure in general. This includes both the location of the E_F as well as the surface and volume electronic states in relation to each other. In particular, whether the E_F shift from the conduction band to the energy gap for the volume states would be possible.

To address these questions, this Section presents a rarely seen in literature combi-

ned observations of local topography (STM), electronic structure (STS, ARPES) and magnetoresistance (which allows observing SdH quantum oscillations) for pristine Bi_2Se_3 compared to samples doped with magnesium $Bi_{1.96}Mg_{0.04}Se_3$ and iron $Bi_{1.98}Fe_{0.02}Se_3$. The results are discussed in comparison to the modelled electronic structure as obtained in the recent theoretical calculations [68, 69]. The research problems contained in this Section largely constitute the content of the article [70], which is one of the foundations of this Thesis.

4.1 Basic characteristics of doped crystals

The introduction of dopants in the form of foreign atoms of magnesium and iron into the Bi_2Se_3 structure is used to manipulate the position of E_F in this material. Contrary to most of the works found in the literature, very low concentrations of dopants were chosen: 1% Fe and 2% Mg. Following paragraphs present the basic characteristics of the doped crystals in comparison to pristine Bi_2Se_3 . This characteristics include verification of the crystallographic structure by XRD measurements as well as confirmation of the presence of dopants in the corresponding materials using X-ray Absorption Spectroscopy (XAS) and Secondary ion Mass Spectroscopy (SIMS).

4.1.1 Crystallographic structure

Crystallographic characterization of the doped crystals was performed by XRD measurements of the powdered samples. The results are presented in Figure 4.1.



Figure 4.1: X-ray diffraction spectra (black dots), calculated spectra (black solids), difference between measurement and calculation (red solids) and Bragg positions (black bars) of $Bi_{1.96}Mg_{0.04}Se_3$ (a) and $Bi_{1.98}Fe_{0.02}Se_3$ (b)

The XRD spectra of both samples are very similar. Both materials crystallize in a rhombohedral space group R-3m (166), similar to pristine Bi_2Se_3 (shown in Paragraph 3.4.3). Unit cell parameters estimated from the XRD spectra of the doped samples compared to pristine are summarized in Table 4.1. This estimation allows to state that within the limits of the measurement uncertainty, the introduced dopants in such a low concentration do not change the lattice constants of the unit cell of the Bi₂Se₃ crystal.

Table 4.1: The estimated parameters of unit cells from the XRD measurements of powdered samples

Sample	a [Å]	c [Å]	V [Å ³]	
$\operatorname{Bi}_2\operatorname{Se}_3$	4.1373(2)	28.6450(6)	424.63(3)	
$\mathrm{Bi}_{1.96}\mathrm{Mg}_{0.04}\mathrm{Se}_3$	4.1392(1)	28.6351(5)	424.88(2)	
$\mathrm{Bi}_{1.98}\mathrm{Fe}_{0.02}\mathrm{Se}_3$	4.1385(1)	28.6315(5)	424.68(2)	

4.1.2 Chemical composition

The very low concentrations of dopants present in the test samples require sophisticated methods that are sensitive enough detect it. It turned out that the AES technique available in the laboratory was not capable of detecting the tested dopants. Obviously, this technique is sensitive only to the sample surface (Paragraph 3.1.4) so it is understandable that the chances of encountering a sufficient amount of dopant atoms close to the surface are limited. Looking for an appropriate method of confirming the presence of such low concentration of dopants, we decided to perform XAS measurements on the occasion of another experiment conducted by our group on the PEEM / XAS beamline at the Solaris Synchrotron in Krakow. This task was additionally facilitated by the fact that ACMiN AGH is a co-operator of this beamline with the Jagiellonian University.



Figure 4.2: (a) X-ray absorption spectra in the near-edge structure of Bi_2Se_3 (solid line) and $Bi_{1.98}Fe_{0.02}Se_3$ (dots) collected at Se K-edge, Fe K-edge and Bi L3-edge. (b) XAS oscillations extracted from extended range of the respective spectra. Figure from [64].

XAS experiment provides information on the local atomic environment around the absorbing atom (in this case Fe), and is a powerful tool to study substitutional doping.

Figure 4.2(a) shows the results of XAS experiment performed on pristine and Fe doped Bi_2Se_3 crystals. Respective Bi L3 and Se K-edge spectra of the two samples are identical within experimental accuracy in the near edge structure. The analysis of the Fe K-edge spectrum in Figure 4.2(b) suggests that Fe ions substitute Bi sites in $Bi_{1.98}Fe_{0.02}Se_3$ crystal, as the major features in the Fe spectrum are common to those of Bi spectrum. This means that the Fe dopants are predominantly diluted impurities in the crystal, occupying Bi sites in the lattice.

As the presence of magnesium in the sample could not be confirmed in the XAS measurements due to the overlapping of the magnesium and selenium peaks, we had to use a different technique for this purpose. Secondary ion mass spectrometry (SIMS) was chosen as the appropriate method. The Figure 4.3 shows the result of SIMS preformed on a $Bi_{1.96}Mg_{0.04}Se_3$ sample ranging from 23.5 D to 26 D. The spectrum shows peaks from successive Mg isotopes, which clearly indicates the presence of this element in the sample.



Figure 4.3: Fragment of the secondary ion mass spectrometry (SIMS) spectrum. Range from 23.5 D to 26 D, visible signals from consecutive Mg isotopes.

Having direct indications from the XAS measurements that iron admixtures substitute the Bi positions in the Bi_2Se_3 crystal lattice, following the sample contractors [18] we adopt the determinations $Bi_{1.98}Fe_{0.02}Se_3$ of the sample with Fe dopants and $Bi_{1.96}Mg_{0.04}Se_3$ of the samples doped with Mg.

4.2 Surface topography of doped crystals with respect to Bi_2Se_3

The STM imaging method was used to examine the surface of the samples in terms of topographic features such as density and type of defects. Figure 4.4 shows a comparison of exemplary topography of Bi_2Se_3 , $Bi_{1.96}Mg_{0.04}Se_3$ and $Bi_{1.98}Fe_{0.02}Se_3$ samples.



Figure 4.4: 50×50 nm STM topography scans of (a) Bi₂Se₃, (b) Bi_{1.96}Mg_{0.04}Se₃, (c) Bi_{1.98}Fe_{0.02}Se₃, revealing the density of the defects on the studied surfaces (obtained at $V_{\text{bias}} = -340$ mV and I = 300 pA) and possibly the smaller features related to dopants. Based on figure in [70].

The surfaces of all tested samples are characterized by the presence of the same atomic steps and flat terraces of a large size as presented for detailed characteristics of pristine Bi_2Se_3 is in Paragraph 3.4.3. The triangle-shaped defects reported with pristine Bi_2Se_3 [22, 28] (Fig. 4.4(a)), are also found on the surfaces of the Mg-doped (Fig. 4.4(b)) and Fe-doped (Fig. 4.4(c)) samples. The STM topography images reveal randomly distributed defects, the number of which is very similar for all the samples studied. The detailed description of defects is provided in Section 6.

Comparing the topography images of pristine Bi_2Se_3 (Fig. 4.4(a)) to those of doped crystals, after more careful observation, one can notice that there are other features in the STM images of doped samples (Figs. 4.4(b) and (c)). They are also of a triangular shape, but smaller than the features related to defects. Moreover, they exist only for the doped samples and their number is larger for the sample doped with Mg compared to the sample doped with Fe, in accordance with the concentration of Mg and Fe dopants, respectively. Unfortunately, these features were noticed only in the final stage of the presented research, and the full analysis of them is not performed at the moment. However, the fact that they are present only on doped samples and the qualitative compliance of their number with the dopant concentration may indicate that they constitute a topographic imprint of the presence of dopants near the surface of the tested crystals.

4.3 Electronic structure as seen locally by STS

STS method was used to compare the surface electronic structure of the pristine Bi₂Se₃ sample to that of the samples doped with Fe and Mg. The STS measurements sample the electronic structure of the material (as shown, for example, in Fig. 2.5), where the binding energy scale is represented by the potential difference V_{bias} between the sample and the STM tip (Par. 3.1.2) under conditions of electron tunneling. The ability to change the polarization of V_{bias} makes it possible to study the electronic structure of both occupied (below E_F) and unoccupied (above E_F) states. The STS spectrum is proportional to the local density of states (LDOS) as shown in Par. 3.1.1, i.e. the summed density of states for all wave vectors in the vicinity of the Γ point of the reciprocal space, as shown in the Figures 2.3 and 2.4 presenting the calculated electronic structure and the corresponding DOS. Accordingly, at energies in the range of volume bands, the STS samples the total density of states as an overlay of the volume states with parabolic dispersion relation and a linearly dispersed surface states. Whereas for energy in the volume gap range, only surface states are sampled and the STS signal runs linearly as a function of energy. Additionally, STS offers the unique possibility to study surface electronic structure locally with lateral resolution down to almost single atoms. Here these possibilities have been fully exploited, and to avoid the influence of the defects on the LDOS, only points outside the defect area were selected for the measurements. The results are presented in Figure 4.5, where the averaged and normalized STS spectra (see Par. 3.1.2) of the investigated samples are compared.



Figure 4.5: Normalized STS spectra measured at room temperature at positions between the defects, i.e. on structurally perfect areas of the Bi_2Se_3 , $Bi_{1.96}Mg_{0.04}Se_3$ and $Bi_{1.98}Fe_{0.02}Se_3$ surfaces. The regions of the BVB, BCB and TSS are marked with the violet, orange and white background, respectively. The color gradient reflects the uncertainty of determining the boundary of the bands. The segments with a linear dispersion relation are marked with lines. Figure from [70].

In all the measured STS spectra presented in Figure 4.5 it is possible to observe the specific areas of the BVB and the BCB. The finite density of states inside the volume energy gap is due to the topological surface states (TSS). The width of the energy gap for the volume bands can be estimated at about 230 meV for all tested samples. This result is in a good agreement with the calculations presented in Paragraph 2.2.2 and ref. [22]. The range of TSS with a linear dispersion relation fulfilling the energy gap for volume states is clearly visible for all three studied samples. The minimum of the spectra signal in this range correspond to the positions of the DP at energy of -270 mV for pristine Bi_2Se_3 , -260 mV for $Bi_{1.96}Mg_{0.04}Se_3$ and -320 mV for $Bi_{1.98}Fe_{0.02}Se_3$ (below the Fermi level). The spectrum of the pristine Bi_2Se_3 indicates its n-type behaviour, as expected [25]. The spectra of the doped samples are also n-type, with a similar $E_{\rm F}$ position deep in the BCB. The edge of the BCB remains almost unaffected by doping. However, we observe some differences in the TSS region. The doping with Fe has broadened the range of linearly dispersed surface states, shifting DP further away from E_F than it is in the Bi_2Se_3 sample. The doping with Mg has had almost no effect to the surface states: the range of the linearly dispersed states was only slightly shortened with respect to the pristine Bi₂Se₃.

The presented STS data may suggest that dopants caused a change in the position of E_F relative to DP. The Mg doping shifts the DP position slightly closer to the E_F , while the Fe doping shifts it much further away from the E_F with respect to pristine Bi₂Se₃. The doping, however, does not change the nature of conductivity, as the E_F is located inside the BCB and all the tested samples show the n-type character. Within the limits of uncertainty, it can be stated that the edges of the volume bands have not been changed by doping and appear in the same positions for all samples. However, the STS technique is not precise in determining the band boundaries, because the electrons tunneling from the surface states overlap with the electrons tunneling from the volume bands. With this in mind, the designated ranges of bands should be treated suggestively, which is to be suggested by the color gradient used in Figure 4.5. Therefore, the STS spectra do not answer the question whether the observed changes concern only the the position of E_F or also shifting of the edges of the volume bands. For the purpose of resolving these fundamental issues we performed further studies of the electronic structure of the discussed samples, which will be presented in the following Paragraphs.

4.4 Electronic structure as seen globally by ARPES

The study of electronic structure is replenished by the ARPES technique, complementary to STS, which can also solve interpretation difficulties as it directly distinguishes between surface and volume states. The ARPES experiment was performed to find the relation between the local electronic structure probed by STS mostly from the near-surface atomic layers and the electronic structure probed by the electrons emerging from much deeper atomic layers (and from a larger area). The ARPES experiment was carried out at UARPES beamline at SOLARIS synchrotron in Krakow. The measurements were performed at the at pressures better than $1 \cdot 10^{-8}$ Pa using horizontally polarized undulator radiation. Photoelectrons were detected with a DA30L electron energy analyzer, Scienta Omicron. The overall resolutions of the ARPES measurements is 8 meV (energy) and 0.1 deg (angular). The samples were glued with epoxy resin to a sample holder and cleaved in UHV. The measurements were carried out as soon as possible after cleaving and cooling down to 12 K.

Figure 4.6 presents the ARPES intensity spectra measured in one selected direction in reciprocal space for: Bi_2Se_3 (a), $Bi_{1.96}Mg_{0.04}Se_3$ (b), and $Bi_{1.98}Fe_{0.02}Se_3$ (c). All the spectra reveal BCB, BVB and TSS in the form of a Dirac cone fulfilling the energy gap for volume states. The volume bands positions are not remarkably influenced by the Mg dopants with respect to the pristine Bi_2Se_3 . For pristine and Mg-doped samples, the conduction band ends at an energy of about -140 meV (below the E_F). The upper edge of the valence band appears at an energy of about -460 meV. In the case of Fe-doped sample the bottom edge of BCB appears at -170 meV, and the upper edge of BVB appears at about -490 meV. The absolute position of the edges of the BCB and BVB changes due to doping, while the distance between them (energy gap) remains unchanged. This implies the energy gap for volume states of about 320 meV, similar for all the three investigated samples.

The E_F is located in the BCB for both the pristine and the doped samples. The results allow stating that the $E_{\rm F}$ is not affected by doping at a low concentration of Mg. In the Mg-doped sample the distance between DP and $E_{\rm F}$ is 313 meV, which is exactly the position of the DP in the undoped Bi_2Se_3 sample. On the other hand, the E_F is clearly shifted towards higher energies, i.e., deeper into the BCB as a result of doping by low concentration of Fe (in the case of doping with Fe, the position of DP is changed to 373 meV with respect to E_F). The observed relative changes in the position of E_F and DP are qualitatively consistent with the analysis of the STS spectra presented in Paragraph 4.3. The results imply that the surface states with a linear dispersion relation are not gapped and E_F is clearly shifted towards higher energies, i.e., deeper into the BCB as a result of doping by low concentration of Fe. $E_{\rm F}$ is not affected by doping at a low concentration of Mg, where the distance between DP and E_F is the same (313 meV). Changing the TSS may only appear as a consequence of changing the structure of the volume bands, which is revealed in ARPES results presented in Figure 4.6 (in particular for the Fe-doped sample). Thus, the experiment clearly confirms the recently published results of the DFT calculations of the volume electronic structure of the Fe-doped Bi_2Se_3 [68, 69].



Figure 4.6: The ARPES results obtained at a photon energy of 17.5 eV for the Bi_2Se_3 samples (a), $Bi_{1.96}Mg_{0.04}Se_3$ (b), and $Bi_{1.98}Fe_{0.02}Se_3$ (c). The relative positions of the Fermi level and the Dirac point are labelled. The yellow lines represent the integrals of the ARPES intensity along the k_{\parallel} (in-plane momentum) direction. Corresponding momentum distribution curves for Bi_2Se_3 (d), $Bi_{1.96}Mg_{0.04}Se_3$ (e), and $Bi_{1.98}Fe_{0.02}Se_3$ (f) obtained from figures 6(a-c), respectively. The profiles were collected every 10 meV from the E_F to 400 meV. The TSSs are marked with the lines extrapolated to the E_F , which allowed to determine the diameters of the Fermi surfaces. Figure from [70].

More subtle changes in the electronic structure are revealed by the through analysis of the obtained ARPES spectra. Figures 4.6(d-f) present the momentum distribution curves (MDCs) obtained from the ARPES spectra shown in Figures 4.6(a-c), respectively. The TSSs are marked with the lines drawn through the centers of the fitted Lorentz functions. The lines are extrapolated to the E_F . The intersections mark the edge of the Fermi surface, which allows to determine the diameter of the Fermi surfaces as $2 \cdot k_F$ (where k_F is the Fermi wave vector; assuming circular cross section of the Fermi surface in the $k_{||}$ plane), which equals to 0.179 Å⁻¹ for the non-doped material (Figure 4.6(d)). This diameter is shortened to 0.170 Å⁻¹ by the introduction of Mg dopants (Figure 4.6(e)) and remarkably lengthened to 0.199 Å⁻¹ by doping with Fe (Table 4.2). Such significant increase of k_F in the case of the Fe-doped sample might be related to deviation from the regular circular cross section of the Fermi surface due to E_F remarkably shifted with respect to that of the pristine sample. The analysis was carried out for three photon energies: 17.5, 22.5 and 25 eV; the average values are listed in Table 4.2.

Table 4.2: Mean values of diameters of the Fermi surfaces $(2 \cdot k_F)$, Fermi velocities (v_F) and effective masses (m^*) averaged over the values obtained for diversified excitation energies, for the undoped, doped with Mg and doped with Fe samples obtained from the ARPES experiment at 12 K

Sample	$2 \cdot k_F \left[{ m \AA}^{-1} ight]$	$v_F \cdot 10^5 \ [m/s]$	$\mathbf{m^{*}} \; [\mathbf{m_{e}}]$	DP position [eV]
$\mathrm{Bi}_{2}\mathrm{Se}_{3}$	0.180	6.788	0.154	-0.313
$\mathrm{Bi}_{1.96}\mathrm{Mg}_{0.04}\mathrm{Se}_3$	0.174	6.968	0.144	-0.313
$\mathrm{Bi}_{1.98}\mathrm{Fe}_{0.02}\mathrm{Se}_3$	0.201	5.940	0.197	-0.373

The Fermi velocity (v_F) in the vicinity of the E_F was calculated from the linear part of the dispersion relation using the formula:

$$E(k) = \hbar \cdot v_{F} \cdot k \Rightarrow v_{F} = \frac{1}{\hbar} \left(\frac{dE}{dk} \right).$$
(4.1)

Finally, knowing k_F and v_F , the effective mass m^* of the charge carriers could be calculated:

$$\mathbf{m}^* = \frac{\hbar \mathbf{k}_{\mathrm{F}}}{\mathbf{v}_{\mathrm{F}}}.\tag{4.2}$$

The mean values of both the Fermi velocities and effective masses of the carriers are listed in Table 4.2.

Both in the case of v_F and m^* , there is again some systematic effect, i.e., the sample doped with Mg shows a larger v_F , whereas the sample doped with Fe shows a smaller v_F than the pristine sample. The tendency is opposite for m^* , which is smaller for the Mg-doped and larger for the Fe-doped samples. However, the Fermi level is placed in the BCB both for the pristine and doped samples despite the fact that it would be profitable to shift it to the bandgap. Therefore, this goal was not achieved by doping, however, the influence of these dopants on a number of parameters of the electronic structure of the tested topological insulators was analyzed, observing the same systematics in both STS and ARPES measurements.

4.5 Electronic structure as seen by electronic transport

The parameters obtained from the electronic structure analysis of the materials described in Paragraphs 4.3 and 4.4 have been additionally confirmed by magneto-transport measurements at very low temperatures. These measurements were conducted in parallel to this research in a laboratory adjacent to the STM laboratory. The jointly developed idea of the research, the complementarity of the methods and the compliance of the obtained results make us consider these results to be completely consistent with the content of the Thesis and should be discussed together with the results presented in this Section. For the sake of better clarity of this work, the results of magneto-transport (obtained in cooperation with dr inż. Maciej Chrobak) will now be discussed in a way that directly relates to the results obtained from STS and APRES.

The details of the electronic structure were investigated by means of magneto-transport measurements conducted in Triton dilution refrigerator (Par. 3.2) at a temperature of 200 mK, which allowed for the detection of Shubnikov-de Haas (SdH) quantum oscillations. Samples with a cuboid shape, measuring 5×5 mm at the base and approximately 0.2 mm in height, were used to measure the magnetic field dependence of the longitudinal and transverse resistivity. Prior to being put into a Triton refrigerator, each sample was cleaved using scotch tape at ambient conditions, and gold wires were attached to the corners with silver paste to create point contacts for measuring electrical conductivity.

The results of the transverse (ρ_{xy}) resistivities versus the external magnetic field for Bi_2Se_3 , $Bi_{1.96}Mg_{0.04}Se_3$ and $Bi_{1.98}Fe_{0.02}Se_3$ are shown in Figure 4.7. All samples exhibit a negative Hall resistivity, indicating that the charge carriers are electrons. These results are consistent with the n-type classification observed by STS (Paragraph 4.3) and ARPES (Paragraph 4.4), where we observed E_F located in the BCB of the samples, which also indicates electrons as charge carriers. From the low field magnetic dependence of the transverse resistivity, the carrier concentrations and their mobility were obtained and listed in Table 4.3. QHE plateau of ρ_{xy} can be discerned in the high magnetic field regime.



Figure 4.7: Transverse resistivities (ρ_{xy}) versus the external magnetic field probed at 200 mK for (a) Bi₂Se₃, (b) Bi_{1.96}Mg_{0.04}Se₃, (c) Bi_{1.98}Fe_{0.02}Se₃. Figure from [70].

Figure 4.8 shows the results of the longitudinal resistivity (ρ_{xx}) versus the external magnetic field oriented both perpendicularly and parallel to the a – b plane. For the purpose of normalization and to better show the oscillations amplitude, the results of $\rho_{xx}(B)$ are presented in the form of:

$$MR(B) = \frac{\rho_{xx}(B) - \rho_{xx}(0)}{\rho_{xx}(0)}.$$
(4.3)

The SdH quantum oscillations are visible for MR measured with the external magnetic field B oriented perpendicularly to the a - b plane of the surface of all three testes samples Bi₂Se₃, Bi_{1.96}Mg_{0.04}Se₃ and Bi_{1.98}Fe_{0.02}Se₃. These oscillations originate from 2D surface states as directly evidenced by their decay in measurements with the external magnetic field oriented in the plane of the surface (dotted lines in Fig. 4.8). For the 2D electronic states Landau levels are present only in the external magnetic field B oriented perpendicularly to the Fermi surface plane. If we tilt the sample by 90° the Landau levels of 2D surface electronic states disappear, and thus the quantum oscillations disappear, as argued in Par. 3.2. This would be different for the 3D volume states, where with any orientation of the magnetic field, there is always a component of the field perpendicular to the Fermi surface and Landau levels are present.



Figure 4.8: Megnetoresistance of Bi_2Se_3 , $Bi_{1.96}Mg_{0.04}Se_3$ and $Bi_{1.98}Fe_{0.02}Se_3$ at 200 mK. The solid lines are for B perpendicular to the a-b plane and the dashed lines are for B parallel to the a-b plane. Figure from [70].

However, since the values of ρ_{xy} and ρ_{xx} are of the same order, pure oscillations should be extracted from σ_{xx} instead of ρ_{xx} to avoid incorrect determination of the oscillation phase. The σ_{xx} conductivity is given by the formula:

$$\sigma_{\rm xx} = \frac{\rho_{\rm xx}}{\rho_{\rm xx}^2 + \rho_{\rm xy}^2}.\tag{4.4}$$

The longitudinal conductivity σ_{xx} for the tested samples is shown in Figure 4.9. However, the oscillations are very poorly visible due to the scale of dependence and the background.



Figure 4.9: Longitudinal conductivity of Bi_2Se_3 (a), $Bi_{1.96}Mg_{0.04}Se_3$ (b) and $Bi_{1.98}Fe_{0.02}Se_3$ (c) at 200 mK. Based on figure in [70].

Pure SdH oscillations were obtained from the field dependence of σ_{xx} , as the smooth background fitted using the asymmetric least square method was extracted. The resulting $\Delta \sigma_{xx}$, plotted as $\Delta \sigma_{xx} B^3$ vs. 1/B, is shown in Figure 4.10. Multiplication by B³ is an analysis procedure used to emphasize the amplitude of quantum oscillations. It does not affect in any way the values of their frequency, on which we base further analysis.



Figure 4.10: Shubnikov-de Haas oscillations plotted as $\Delta \sigma_{xx} B^3$ vs. the inverse magnetic field for Bi₂Se₃, Bi_{1.96}Mg_{0.04}Se₃ and Bi_{1.98}Fe_{0.02}Se₃ at 200 mK. Based on figure in [70].

As confirmed by the fast Fourier transform (FFT) analysis shown Figure 4.11, single frequency oscillations are observed for each sample. The frequency and amplitude of the oscillations depend on doping, and more precisely, the oscillations amplitude decreases for both dopants, whereas frequency decreases for Mg and increases for Fe doped sample with respect to the pristine sample. Since E_F is observed in the BCB, these samples would be expected to obtain quantum oscillations with two (or more) frequency components. One of these components would come from the surface states and the other from the volume states. The fact that we observe single-frequency oscillations may be due to the very high carrier mobility in these samples. As a result, the peak from the volume states has a very small amplitude and frequency similar to that of the surface states, so it is not observed. Therefore, there can be doubts whether the presented oscillations come from surface states. This is explained in Fig. 4.8, where the oscillations are visible only in measurements when the B-field is oriented perpendicular to the surface of the sample, and disappear when the B-field is oriented parallel to the surface.



Figure 4.11: Spectral intensity of SdH oscillations in magnetoresistance of Bi_2Se_3 , $Bi_{1.96}Mg_{0.04}Se_3$ and $Bi_{1.98}Fe_{0.02}Se_3$ at 200 mK. Figure from [70].

The frequency of SdH oscillations (f_{SdH}) is directly related to the cross section (A_F) of the Fermi surface in momentum space following the Onsager relation [37]:

$$f_{\rm SdH} = \left(\frac{h}{4\pi^2 e}\right) A_{\rm F},\tag{4.5}$$

where $A_F = \pi k_F^2$, k_F is the Fermi wave vector, e is the electron charge and h is the Planck constant. The Fermi wave vector is linked to the surface carrier density [71] by $n_{2D} = k_F^2/4\pi$. The oscillation frequency observed for pristine Bi₂Se₃ is 165 T. Fermi wave vector for this frequency is 0.071 Å⁻¹, so the carrier concentration is 3.98×10^{12} cm⁻². For the Mg – doped sample, the oscillations frequency is 152 T, which results in the 0.068 Å⁻¹ Fermi wave vector and the concentration equal to 3.67×10^{12} cm⁻². Fe doping results in the opposite effect of Mg doping for f_{SdH}. The obtained frequency is 230 T, which leads to the 0.084 Å⁻¹ Fermi wave vector and the carrier concentration of 5.55×10^{12} cm⁻².

Quantum oscillation analysis including oscillation frequencies and determined Fermi wave vector and two-dimensional surface carrier concentrations are listed and compared in Table 4.3.

Sample	$ \rho_{\rm xx} \ ({\rm B}=0) $	$\mathbf{n}_{\mathbf{Hall}}$	μ	$\mathbf{f}_{\mathbf{SdH}}$	k _F	n_{2D}
	$[m\Omega \cdot cm]$	$[10^{17} \text{ cm}^{-3}]$	$[\mathrm{cm}^2/\mathrm{Vs}]$	[T]	[Å ⁻¹]	$[10^{12} \text{ cm}^{-2}]$
$\mathrm{Bi}_{2}\mathrm{Se}_{3}$	0.290	2.49	8720	165	0.071	3.98
$\mathrm{Bi}_{1.96}\mathrm{Mg}_{0.04}\mathrm{Se}_3$	0.203	0.95	3245	152	0.068	3.67
$\mathrm{Bi}_{1.98}\mathrm{Fe}_{0.02}\mathrm{Se}_3$	0.059	2.05	5128	230	0.084	5.55

Table 4.3: The estimated parameters from the magnetoresistance, Hall effect and SdH oscillations obtained at 200 mK

The presented analysis of quantum oscillations can be concluded that the characteristic structures of the surface states in the form of DC observed directly in ARPES measurements and indirectly in STS measurements are confirmed by analysing the SdH quantum oscillations in the magnetotransport measurements. A single oscillation frequency was extracted from the FFT spectra of each measured sample. As the oscillation frequency changes depending on dopants, the doping affects the Fermi wave vector, which is smaller for the Mg- and larger for the Fe-doped sample with respect to the undoped Bi_2Se_3 sample. These systematics coincide qualitatively with the Fermi wave vector obtained from the ARPES analysis, which results in $k_F = 0.090 \text{ Å}^{-1}$ for Bi_2Se_3 , 0.087 Å⁻¹ for $Bi_{1.96}Mg_{0.04}Se_3$ and 0.100 Å⁻¹ for $Bi_{1.98}Fe_{0.02}Se_3$ (Paragraph 4.4, Table 4.2). Such nonperfect quantitative agreement is not surprising, having in mind that the SdH oscillations were detected at 200 mK, whereas the ARPES experiment was carried out at 12 K. Moreover, in ARPES experiments, bending of the electron bands near the surface is observed, which influences the values of $k_{\rm F}$. Analysis of the quantum oscillations reveals that doping affects the carrier concentration as well. For Mg-doped sample it decreases and for Fe-doped it increases with respect to the pristine sample.

4.6 Special role of magnetic dopants in relation to non – trivial topology in Bi_2Se_3

Magnetic dopants play a special role in the topological insulator system, because in systems with magnetic moment the time reversal symmetry, which is crucial for the formation of topological states on the surface, ceases to apply. Indeed, it has been shown that a high concentration of magnetic impurities leads to opening of the energy gap in DP, followed by the destruction of topological states [11, 65]. Such consequences, however, are not entirely obvious, as there is a whole branch of research on the so-called magnetic TIs [67]. A full description of the phenomena of magnetic TIs is beyond the scope of this Thesis, but let us discuss the most stout effect, i.e. whether the magnetic dopant significantly affected the observed electronic states of the surface. In these studies a very low concentration of dopants were chosen, contrary to most positions in literature. Therefore, the discussion of the results from the point of view of the Bi_{1.98}Fe_{0.02}Se₃ sample is justified.

The topological surface states with linear dispersion relation are clearly visible both in the STS and ARPES measurements for all three studied samples Bi₂Se₃, Bi_{1.96}Mg_{0.04}Se₃ and Bi_{1.98}Fe_{0.02}Se₃. STS measurements do not suggest the opening of the gap near the DP of the $Bi_{1.98}Fe_{0.02}Se_3$ sample, only the change of the DP position relative to the pristine sample is visible. The direct confirmation provide the ARPES spectra (Figure 4.6) presenting the TSS in the form of a DC fulfilling the energy gap for volume states. DP is clearly visible on the spectra of both pristing Bi_2Se_3 and $Bi_{1.98}Fe_{0.02}Se_3$ and no energy gap opening is observed despite the presence of dopants. In-depth analysis shows only subtle changes in the electronic structure of the doped samples with respect to pristine Bi_2Se_3 and a clear shift of the Fermi level in the Fe-doped sample. Another confirmation of the observation comes from the results of magnetotransport, where single-frequency SdH oscillations are observed for all tested samples, indicating the presence of topological states of the same nature. This leads us to the conclusion that the presence of a magnetic dopant of iron in an atomic concentration of 1% does not lead to the destruction of the topological state in the sample. The dopant, however, introduces subtle changes to the electronic structure revealed by changes in parameters such as the Fermi wave-vector, the concentration of carriers on the surface or others discussed in detail in the previous Paragraphs. Bearing in mind that the topology of electronic states can suffer destruction not due to the mere presence of a magnetic dopant itself, but due to the occurrence of a critical magnetic moment, the above considerations will now be embedded in the results of field and temperature dependencies of bulk magnetization of Bi_{1.98}Fe_{0.02}Se₃.

Field and temperature dependencies of bulk magnetization of $Bi_{1.98}Fe_{0.02}Se_3$ single crystal, obtained with a SQUID magnetometer, are shown in Figure 4.12. The magnetization at 300 K is nearly linear and negative in the function of magnetic field (Fig. 4.12(a)), which can be attributed to the low concentration of Fe in the sample and the dominant diamagnetic susceptibility of the host material, Bi_2Se_3 . At 2 K, the magnetization shows clear anisotropy, with positive values for field probed along the a-b plane. For the field probed along the c-axis positive in low field (B < 1 T) and then negative values are observed. The inflection of values from positive to negative for the c-axis can be attributed to a weak ferro- or paramagnetic component that adds to the diamagnetic linear background observed at 300 K. While the positive values along the a-b plane can be attributed to a paramagnetic contribution that is several times larger than that observed for the c-axis. The magnetization does not display any signs of saturation at high field or remanence (and hysteresis) at low field, which have been reported for crystals with higher Fe concentrations such as $Bi_{1.96}Fe_{0.04}Se_3$ [72] and $Bi_{1.84}Fe_{0.16}Se_3$ [73].



Figure 4.12: Magnetization of $Bi_{1.98}Fe_{0.02}Se_3$ single crystal at magnetic field applied along the c-axis (solid points) and within the a-b plane (open points). The diamagnetic signal of the sample holder was subtracted. (a) Field dependence at T = 2 K and 300 K (b) temperature dependence measured at 0.5 T, with the Curie–Weiss law fitted to the inplane data in the range 20–150 K (solid line). Figure from [64].

The temperature dependence of magnetization measured at 0.5 T is shown in Figure 4.12(b), and demonstrates that the magnetic anisotropy of Bi_{1.98}Fe_{0.02}Se₃ persists also at higher temperatures. The magnetization along c-axis is significantly smaller in the whole temperature range and takes negative values in temperatures above 5 K. As in the constant magnetic field the magnetization M is proportional to magnetic susceptibility χ , the Curie-Weiss law was fitted to the in-plane magnetization $\chi(T) = \chi 0 + C/(T - \Theta_{CW})$. The Curie-Weiss law is an empirical relationship that describes the temperature dependence of the magnetic susceptibility of a paramagnetic material. In the case of Bi_{1.98}Fe_{0.02}Se₃, the in-plane magnetization follows this law with $\Theta_{CW} = -9.7(5)$ K and a Curie constant, C, that corresponds to an effective paramagnetic moment per Fe ion of 2.1(1)µB.
5 Tuning the Fermi level by a non-stoichiometric composition in $Bi_{2-x}Te_{3+x}$ – type crystals

In search for a method of tuning the E_F to the preferred localization in the volume band gap, an important requirement is that the introduced modifications do not lead to simultaneous destruction of topological states at the surface. For this purpose, dopants of foreign atoms should be introduced with great care, especially magnetic ones, the small concentrations of which do not lead to the destruction of non-trivial topology, in accordance with Section 4. Another approach found in the literature is to extend the phase space of the composition to e.g. $Bi_{2-x}Sb_xTe_{3-y}Se_y$ [71, 74], indicating a series of particular combinations of (x; y) where the samples show maximally insulating behavior within their volume. Yet another approach is to grow the crystal in a non-stoichiometric fashion. The reference [71] reveals that by growing crystals from a slightly Se-rich starting composition of $Bi_2Te_{1.95}Se_{1.05}$, one can obtain crystals showing a large bulk resistivity exceeding 1 Ω cm. Recent work [75] shows that also the Te-rich starting composition results in a change in the defect density and a shift in the location of the E_F relative to the pristine Bi_2Te_3 .

This Section presents the study of the relationship between non-stoichiometric starting conditions for Bi_2Te_3 crystal growth and the properties of the obtained samples. For this purpose a series of $Bi_{2-x}Te_{3+x}$ – type samples were prepared and studied. The samples were synthesized using the Bridgman method at WIMiC faculty of the AGH University of Krakow. The proportion of Te content in the samples was selected at the stage of determining the initial amount of Te under the conditions of synthesis, so as to obtain a series of samples with the parameter x = 0, 0.0173, 0.0225, 0.035, 0.07, 0.14. The surface morphology on the atomic scale, single defects and the influence of crystal stoichiometry on local and global electronic properties were investigated. As a function of Te conductivity extracted from the observation of quantum oscillations of magnetotransport measured at sub-Kelvin temperatures. The final part of the Section presents the study of thermoelectric properties of the samples in question, obtained in cooperation with the Thermoelectric Research Laboratory at WIMiC AGH.

5.1 Initial characterization of $Bi_{2-x}Te_{3+x}$ samples

In order to be able to assume that the synthesized $Bi_{2-x}Te_{3+x}$ crystals exhibit the characteristics of a TI, it is necessary to ensure that the samples are high – quality single crystals and that the assumed Te concentrations are confirmed in its content in the samples. Therefore, the initial characterization of the crystals included XRD measurements of the crystallographic structure of the powdered samples in order to accurately determine the lattice constants of the material. Whereas the mass fraction of Te in the produced

crystals was determined using the XRF technique.

5.1.1 Crystallographic structure of samples

The phase compositions of the investigated $Bi_{2-x}Te_{3+x}$ (x = 0, x = 0.0175, x = 0.0225, x = 0.035, x = 0.07,x = 0.14) materials after synthesis were analyzed using the powder XRD technique (Fig. 5.1). Only reflections, that correspond to the Bi₂Te₃ standard pattern (ICSD #74348) were detected, suggesting the absence of the unexpected impurities and single-phase nature of the investigated materials (Figure 5.1(a)). To analyze the texturization of the sample morphology after directed crystallization, the XRD patterns for selected bulk crystals before the physical property characterization (Figure 5.1(b) were also recorded. The XRD patterns collected on the surface of $Bi_{2-x}Te_{3+x}$ investigated crystals show that only the intensities of the basal planes (001), in particular (003), (006), (0015), (0018), and (0021) can be observed, which approve the single-crystalline nature of the investigated samples. Figure 5.1(c) shows the compositional dependence of the lattice parameter for $Bi_{2-x}Te_{3+x}$ materials. The values of the lattice parameters correspond well with the previously reported values for the stochiometric Bi₂Te₃ samples [76]. The perturbation of the lattice parameter for $Bi_{2-x}Te_{3+x}$ samples with x = 0.0175 and x = 0.0225 may correspond to the change in the mechanism of



Figure 5.1: X-ray diffraction patterns of the investigated $Bi_{2-x}Te_{3+x}$ materials (a) after synthesis and (b) after directed crystallization; (c) lattice parameter of the $Bi_{2-x}Te_{3+x}$ powdered samples. During lattice parameter refinement, the LaB₆ was used as the internal standard.

the dominant point defects and transition from p- to n-type of conduction, as it was already reported in [77].

5.1.2 Synthesis conditions versus Te content in samples

Samples of the $\text{Bi}_{2-x}\text{Te}_{3+x}$ series were synthesized by the Bridgman method in conditions with the Te concentration selected in such a way as to obtain single crystals with the parameter x = 0, 0.0173, 0.0225, 0.035, 0.07, 0.14. X-ray fluorescence (XRF) measurements of the obtained crystals were carried out in ACMiN AGH to verify the stoichiometry and its slight changes caused by the increase of Te share in starting composition. In the XRF technique, the sample is bombarded with X-rays, which causes the emission of characteristic fluorescent radiation from the atoms that make up the sample. These characteristic radiations are then recorded and analyzed, allowing the chemical composition of the sample to be determined. The resulting Te mass content is presented in Figure 5.2 as a function of the parameter x assumed. The obtained results clearly indicate an upward trend in the Te mass fraction in the samples with the increase of the assumed x, as expected. The obtained values are consistent, within the measurement uncertainty, with the Te share assumed at the synthesis stage, therefore to distinguish between samples in the following discussion the convenient parameter x will be used, which can be easily converted into real stoichiometry, running one's eye over Figure 5.2.



Figure 5.2: XRF results of Te mass content as a function of the x parameter adopted in the starting composition for the synthesis of the series $Bi_{2-x}Te_{3+x}$ – type samples. The results confirm equivalence of the x-factor and the corresponding mass content of Te in the samples.

5.2 Surface defects and carrier density influenced by small changes of Te concentration

As it has already been indicated in the introductory Sections, an important role in the electronic properties of materials is played by defects, i.e. crystalline imperfections, such as losses or excesses of atoms or substitutions of some atoms for others in the crystal lattice. These defects are confirmed to behave as n-type or p-type point impurities, introducing an additional negative or positive charge to the electronic structure [75, 78]. After all, the defects are responsible for the native shift of the E_F away from the DP in stoichiometric crystals (Par. 2.2.2). That is why the number, type and distribution of defects in the the material is crucial for its electronic properties. The STM method is one of the most sensitive tools for detecting changes of the electronic structure at the surface due to the defects distributed close to the surface. In this Paragraph changes in defect density in samples observed using STM will be presented. Next, the measurements of electron transport will be discussed, detailing the measured concentration of carriers and the nature of the conductivity of individual samples. Finally, the structural (observed defects) and electronic (carrier concentration) parameters will be combined by modelling the global distribution of defects in the samples, which is crucial for the correct interpretation of the electronic structure measurements discussed later in this Section.

5.2.1 Surface morphology and defect density as seen by STM

From the point of view of STM the topographic features of the studied samples were tested. Representative 200×200 nm STM scans of all samples are presented Figure 5.3(a). The scans reveal many bright and dark spots recognized in the literature as n-type Bi for Te substitution defects (Bi_{Te}) occuring in 5th atomic layer and p-type Te vacancies (V_{Te}) in 3rd atomic layer, respectively [75]. A more detailed analysis of the individual defects including high-resolution STM scans of single defects and study of their effect on local surface properties is presented in Section 6. Here, focusing on global parameters of crystals, the presented in Fig. 5.3(a) large-scale scans enable a statistical view of changes in the surface defect density of successive samples. When the background level is limited from high and low, respectively, only V_{Te} (Fig. 5.3(b)) and Bi_{Te} (Fig. 5.3(c)) defects are isolated on individual scans.

A certain dependence of the number of defects on the stoichiometry of the samples can be observed in Figure 5.3. The bright Bi_{Te} defects in high density occur on the surface of $Bi_{2-x}Te_{3+x}$ for x = 0 (row 1), x = 0.0173 (row 2), and x = 0.0235 (row 3). At x = 0.035 (row 4) the density of bright Bi_{Te} defects is visibly smaller. After exceeding the Te content labelled with x = 0.035 the number of bright defects rapidly vanishes (rows 5, 6) preserving only single bright spots. However, the dark V_{Te} defects are observed in similar number at the surfaces of all the studied samples. The statistical analysis of the number of individual types of observed defects is presented in Figure 5.4. The volume defect density was calculated using presented in Fig. 5.3 surface images and taking into account the height of the first QL of the material equal to 0.96 nm based on the data in ref. [19]. Only the first QL was considered, because the listed defects that have been included in the calculations occur at most in the fifth atomic layer of crystals.



Figure 5.3: Surface STM topography scans of 200×200 nm of $Bi_{2-x}Te_{3+x}$ (a) and analysis of the distribution of p-type Te vacancies (b) and n-type Bi-Te antisites (c) for (1) pristine Bi_2Te_3 (x = 0), (2) x = 0.0173, (3) x = 0.0275, (4) x = 0.035, (5) x = 0.07, (6) x = 0.14.



Figure 5.4: Density of native point defects near the $Bi_{2-x}Te_{3+x}$ surface observed by STM. Column graph of the statistical analysis of the n-type Bi – Te antisite defects and p-type Te vacancies over a total area of 200×200 nm and height of a 1 QL for six crystals labelled with x parameter.

The dependence of Bi_{Te} defects density on stoichiometry is clearly visible. These substitutions only occur in samples with a lower concentration of Te than x = 0.035. At this content, a clear decrease in the substitution density is observed, which with a further increase in Te content disappears almost to 0. This effect may suggest that under the conditions of synthesis with a low concentration of Te, the formation of Bi substitutions in Te sites is energetically favorable, but under conditions of higher Te concentration, Te atoms occupy all available positions in the crystal and Bi substitutions can no longer occur. On the other hand the density of p-type Te vacancies is comparable in all investigated samples. However, a slight downward trend can be observed in the highest tested concentrations of Te (x = 0.07 and x = 0.14). The open question remains whether further increasing the concentration of Te will lead to conditions in which these defects also cannot form.

5.2.2 Carrier transport measurements

The presented changes in the density of near – surface defects in individual samples of the $Bi_{2-x}Te_{3+x}$ series have impact on the electronic properties of materials, such as the concentration of carriers or the type of conductivity of the samples. In order to verify it quantitatively, measurements of longitudinal resistivity ρ_{xx} as a function of temperature and magnetic field, as well as transverse (Hall) resistivity ρ_{xy} as a function of magnetic field were carried out as in the case of the doped samples (Par. 4.5). These measurements were performed in Triton dilution refrigerator (Par. 3.2). Samples in the shape of a classic Hall bar with height of about 100 μ m were used. Figure 5.5 presents the longitudinal resistivity ρ_{xx} measured as a function temperature. All the tested samples, except for the x content equal to 0.0173, show the characteristics of a conductor with the increasing resistivity with increasing temperature. Whereas the sample of x = 0.0173 shows a resistance 2 orders of magnitude higher than the others and shows the character typical for a semiconductor, i.e. decreasing resistance with the temperature raising.



Figure 5.5: Longitudinal resistivity ρ_{xx} as a function of temperature. The samples, except one, show the characteristics of a conductor. The sample of x = 0.0173 shows the character typical for a semiconductor.

Figure 5.6 presents the results of Hall effect measurements in tested samples. The transverse resistivity was measured over the range of 0 to 14 T of the external magnetic field at a temperature of 100 mK. The samples x = 0 and x = 0.0173 show the transverse resistance increasing as a function of the magnetic field and taking positive values, indicating the predominant contribution of holes to conductivity. Contrary to the other samples which show a different tendency: Hall resistance decreases with increasing magnetic field taking negative values and the dominant carriers are electrons.



Figure 5.6: Transverse (Hall) resistivity ρ_{xy} as a function of external magnetic field up to 14 T taken in temperature of 100 mK. The samples x = 0 and x = 0.0173 indicate semiconductor character and holes are dominant carriers, contrary to the remaining samples, where the transverse resistivity decreases with increasing magnetic field and electrons are the dominant carriers.

Basing on the Hall measurements, the concentration of surface carriers was determined for all tested samples using the formula:

$$n = \frac{1}{R_{\rm H} e},\tag{5.1}$$

where the Hall constant $R_{\rm H}$ is defined by the product of the Hall resistivity $\rho_{\rm xy}$ and the thickness of the sample d: $R_{\rm H} = \rho_{\rm xy} d$. The dependence of the carrier concentration on the parameter x determining the concentration of Te in the samples, is summarized in the Table 5.1 and plotted in the Figure 5.7.

Sample x	Carrier concentration (cm^{-3})
$\mathbf{x} = 0$	$6.94 \cdot 10^{18}$
x = 0.0173	$2.64 \cdot 10^{17}$
x = 0.225	$-6.04\cdot 10^{18}$
x = 0.035	$-6.03 \cdot 10^{18}$
x = 0.07	$-1.03 \cdot 10^{19}$
x = 0.14	$-1.76\cdot 10^{19}$

Table 5.1: Surface carrier concentrations calculated from Hall effect measurements performed at 100 mK.



Figure 5.7: Concentration of surface carriers as a function of Te content in the sample, determined on the basis of Hall resistivity measurements at temperature of 100 mK.

The results show a clear and systematic decrease in the concentration of carriers with an increase in the amount of Te. At low Te concentrations, positive carrier concentration values are observed for the samples: stoichiometric (x = 0) and x = 0.0173, which indicates hole conductivity in these samples. Then, by increasing the concentration of Te, the conductivity changes to the n-type and electrons become the majority carriers. These results suggest clear and global changes in the electronic structure of the samples, such as the position of the E_F relative to the volume bands. In samples where hole conductivity is dominant, the $E_{\rm F}$ is usually within the BVB. On the other hand, when conductivity is dominated by electrons, such as for high concentrations of Te in our samples, E_F intersects BCB. These clear changes in the nature of the conductivity of the samples are certainly related to the change in the stoichiometry of the samples, increasing the share of Te at the expense of Bi. However, it is worth noting that merely the samples with Te content marked as x = 0.0275 and x = 0.035 show similar concentrations of carriers despite the change in Te content. This suggests that a significant contribution to the concentration of carriers is made other effect as well. Namely the previously discussed changes in the concentration of defects in the samples. Note that the sample x = 0.035 was indicated as the one in which the density of Bi_{Te} defects began to decrease significantly (Par. 5.2.1). The change in defect statistics could therefore compensate for the change in stoichiometry in this particular case. Anyway, these observations indicate that both factors: the change in the stoichiometry of the samples and the related change in the density of defects determine the electronic properties of the tested samples. Therefore, before we discuss the details of the electronic structure of the tested samples, attempts will be made to model such a distribution of defects in the samples that will lead to the observed electronic properties. This model will be necessary in the further part of the Section for the correct modelling and interpretation of the electronic structure of the samples.

5.2.3 Model of defect distribution in samples

Two distinct effects of small changes in Te concentration on the physical parameters of samples have been presented in the previous Paragraphs: changes of the density of native defects in single crystals and changes of the concentration of carriers affecting the nature of conductivity. Bearing in mind the literature data clearly indicating that it is the aforementioned density of defects that has a direct implication on the concentration of carriers [78] as single defects behave as donor or acceptor point dopants depending on their type. It is therefore reasonable for a full understanding of the discussed phenomena to link the dependencies of density of defects and carrier concentration on the amount of Te in the samples. This association will mean proposing a defect distribution model in the samples that would lead to the reproduction of the measured carrier concentration values listed in Tab. 5.1.



Figure 5.8: Crystal structure of Bi_2Te_3 with highlighted individual sublattices. Figure from [19].

As a reminder, the crystallographic structure of the tested materials (fully decsribed in Par. 2.2.1) is shown in Figure 5.8. The crystallographic structure shows the ordering of alternating Bi and Te layers forming QLs with the following sublattice structure: Te(1) – Bi(1) – Te(2) – Bi(1') – Te(1'). Primed layers are equivalent to non – primed layers of the same number for reasons of symmetry. Based on STM measurements and literature data, we distinguish several types of defects occurring in the discussed crystals, which are characterized by appropriate valency [78], which is summarized in Table 5.2.

Defect	Valency	Type
Te substitution in Bi sites (Te_{Bi})	-1	n
Bi substitution in Te sites (Bi_{Te})	+1	р
Te vacancies (V_{Te})	-2	n
Bi vacancies (V_{Bi})	+3	р

The first and simplest defect density distribution model has already been presented in Figure 5.4. The spatial defect density within the first near – surface QL was estimated by

counting the defects observed on the 200×200 nm STM scans and dividing this number by the volume of the cuboid based on the STM scan size and the QL height. The adoption of only one QL is justified because the defects included in the calculations occur at most in the 5^{th} atomic layer, i.e. in the Te(1') sublattice. Then, taking into account the obtained density of defects and their valency, the resulting concentration of carriers was calculated. Unfortunately, such a simple geometrical model based only on STM observations does not lead to carrier concentrations comparable to those obtained from Hall effect measurements. However, this effect is not surprising for at least two reasons. Firstly, in STM measurements, only near-surface defects can be observed from a depth of slightly above 1 QL. There is no guarantee the defect density observed on surface is maintained in the sample volume. Secondly, STM shows only a part of all defects occurring at the surface, depending on the selected scanning parameters, such as V_{bias} . Hence, it is very possible that in addition to the defects identified in the STM scans, there are also other types of defects, invisible in terms of the measurement parameters used. Expanding the presented model, the author had to assume that there are defects in the samples that were not observed in the STM scans, namely Bi vacancies (V_{Bi}) with valency of +3 (Tab. 5.2).

On this basis, the author proposed several models of defect distribution in individual $Bi_{2-x}Te_{3+x}$ sublattices. Let us now present the one we considered the most probable, due to its high agreement of the defect density with the STM observations as well as the calculated carrier concentration with the Hall effect measurements. Figure 5.9 presents column graph of density of individual defects assumed for (Bi_{Te}) , (V_{Te}) and (V_{Bi}) in all the studied samples labelled by x parameter.



Figure 5.9: Proposed model of defects distribution in $\text{Bi}_{2-x}\text{Te}_{3+x}$. The proposed defect distribution assumes carrier concentrations consistent with STM observations and leads to carrier concentrations with values consistent with Hall Effect measurements in these samples.

Figure 5.9 shows that the global number of Bi_{Te} decreases at high Te concentrations, while V_{Te} maintains a similar density, analogous to the STM observations presented in Par. 5.2.1. On the other hand, for the compliance of the calculated carrier concentration with the measurements of the Hall effect, the V_{Bi} density increases with the increase of the Te concentration, which also seems reasonable considering the crystal synthesis under the conditions of Bi – deficient in this case. Figure 5.10 shows the assumed distribution of defects in individual sublattices of Te(1) site in Fig. 5.10(a), Te(2) site in Fig. 5.10(b) and Bi site in Fig. 5.10(c).



Figure 5.10: Atomic percentage share of defects in the atomic structure model of individual $Bi_{2-x}Te_{3+x}$ sublattices: (a) Te(1) site, (b) Te(2) site, (c) Bi site.

A look at the distribution of defects in individual atomic layers in Figure 5.10 gives a better insight into the characteristics of the proposed model in the context of $Bi_{2-x}Te_{3+x}$. The Te_{Bi} defects result from an intentionally introduced excess of Te concentration in the samples and are defined by the x parameter. All of them are assumed to locate in the Bi sublattice. Bi_{Te} and V_{Te} defects observed on STM scans occur (based on comparison with literature data) in the 5th and 3rd atomic layers, respectively. Using the sublattice notation we observe Bi_{Te} defects only in Te(1') site and V_{Te} defects only in Te(2) site. Defects were introduced into these sublattices with concentrations exactly in accordance with the STM observations (Fig. 5.4), making sure that the assumed model is consistent with the experiment. All the other defects necessary to reconcile the concentration of carriers obtained from Hall measurements were placed in other sublattices. The concentrations of defects in the sublattices were arranged so that the share of defects in individual sublattices did not exceed a few atomic percent, which reflects a realistic level of crystal defects typically observed in real materials.

All the assumptions collected above leading to the presented defect distribution model confirm its compliance with the STM observations, and reasonable distribution of defects in individual layers of the material. In addition, the carrier concentration calculated on the basis of this model is consistent to the second decimal place with the Hall effect results collected in Table 5.1. Therefore, the discussion of the nature of the conductivity and its change from p - to n - type with increasing Te concentration in the samples is applicable in the context of the discussed model. Finally, the agreement with the STM surface observations ensures that the model performs consistent combination of observations of the dependence of both: defect density and carrier concentration on the Te content in the samples. In general, the proposed model itself provides a better understanding of the properties of the $Bi_{2-x}Te_{3+x}$ material, but it was also used as a basis for DFT simulations to complete the full picture of the electronic structure discussed in the following Paragraphs.

5.3 Electronic structure of Bi_2Te_3 affected by small changes of Te concentration

5.3.1 Local surface electronic structure

The surface electronic structure of the studied samples was tested in STS measurements. The very local character of the measurement was utilized to make sure that the spectra relate only areas not affected by defects, which as we know from literature [22, 70] and Section 6, locally introduce additional states to the surface DOS. The STS spectra normalized to the total conductivity (see Par. 3.1.2) taken at areas between the defects of all studied samples are presented in Figure 5.11(a). A fixed offset has been introduced on the vertical axis between the curves to separate them and emphasize changes in the horizontal direction.

Linear TSS are visible for all tested samples and are marked with line segments in Figure 5.11(a). The parabolic nature of the spectrum below and above the TSS is due to electrons tunneling from surface states overlapped in this range with volume states, BVB and BCB, respectively. The upper edges of the BVB were determined as a starting point of linear segments by analysing the first derivative of the STS spectra. A constant threshold indicating a deviation from the linear course was used for all the spectra. The upper edges of the BVB bands are systematically shifted towards lower energies with respect to E_F with increasing Te concentration. However, STS technique is not precise in determining the band boundaries, because the electrons tunneling from the surface states overlap with the electrons tunneling from the volume bands. Interpretation problems arouse with designation the exact edges of volume bands, in particular the BCB and correct establishing of the width of energy gap for volume states.

These problems were solved by conducting DFT simulations obtained in cooperation with dr hab. inż. Bartłomiej Wiendlocha from Faculty of Physics and Applied Computer Science at AGH. The results of calculations are presented in Figure 5.11(b). These calculations were carried out using a different method than the simulations of the surface electronic structure and DOS presented in the introductory Section 2.2.2. Here, the electronic structure was simulated, considering only the volume states, without taking into account the surface states, and the starting point for the calculations was the model of defect distribution in the samples described in the previous Paragraph.

Electronic structure calculations were performed using the Korringa-Kohn-Rostoker (KKR) method. The coherent potential approximation (CPA) [79, 80, 81, 82] was used to simulate the presence of vacancies and atomic disorder. The local density approximation (LDA) in the parameterization of Perdew and Wang [83] was used to calculate the exchange-correlation potential. Our computations were limited to the spherical potential and semi-relativistic approximations; however, as earlier works showed [78, 84, 85] they are sufficient to describe the general behavior of impurities in such materials. Optimized rhombohedral crystal structure and lattice parameters from ref. [86] were used. E_F was computed using the generalized Lloyd formula [80]. The densities of states were computed on a fine mesh of 4631 points in the irreducible part of the Brillouin zone.



Figure 5.11: (a) STS spectra taken far from the defects. The spectra are separated by fixed offset for better visibility. (b) DFT calculated density of states for samples of $Bi_{2-x}Te_{3+x}$ series

In calculations, three types of defects on each of the three inequivalent crystal sublatti-

ces were taken into account, as explained with the proposed model of defects distribution in Paragraph 5.2.3: antisite Te and Bi, vacancy on Bi site, antisite Bi and Te, vacancy on both Te sites. Concentrations were adjusted to obtain the nominal carrier concentration according to the Hall measurements (Fig. 5.7). The combination of both n- and p-type defects (Tab. 5.2), which are most likely present in the studied samples, tune the position of the volume E_F as shown in Fig. 5.11(b). For the sample with x = 0, the amount of holes, delivered by Bi vacancy and Bi antisites overtakes the donor behavior of Te defects, making the whole system p-type. $E_{\rm F}$, as seen in Fig. 5.11(a), is in the valence band, BVB. When the amount of Te in samples increases, the $E_{\rm F}$ jumps over the band gap for volume states to place itself in the conduction band (BCB) for sample with x = 0.0225 (due to numerical resolution, we were not able to simulate the sample with x = 0.0173, which has about $4 \cdot 10^{-5}$ hole per primitive cell, that is one hole per 25000 cells). With increasing the Te concentration, E_F slightly moves deeper into conduction band, BCB. In calculations considering only volume of the material there are no electronic states inside the gap, and the E_F jumps over the gap, so is basically either in the of BVB or BCB. In contrast, in the STS measurements, we observe a pinning of the $E_{\rm F}$ to the surface states, as it smoothly moves from BVB to BCB. Thus, our electronic structure calculations confirm that there are not volume-related defects states, as none of the defects, expected to be present in the studied samples, form defect states in the band gap, which could explain the observed spectra. In other words, within the area of the gap for the volume states only TSS are present. Additionally, calculations show that the width of the gap for volume states remains unchanged with increasing Te content, except for the highest concentration (x = 0.14) where the gap is slightly narrowed. On this basis we were able to estimate the length TSS segment in STS spectra and consequently the edge of BCB, that are marked in Fig. 5.11(a).

Considering both the STS measurements and calculations results we can summarize that there is a clear tendency to systematically shift the edges of the volume bands and the entire TSS region towards lower energies relative to the E_F with increasing Te content in samples. The E_F as seen by STS measurements smoothly shifts from BVB in samples close to stoichiometric, through the gap for volume states where only TSS occur, to finally locate in BCB in sample with highest Te content (x = 0.14). These results clearly confirm previously discussed results of the resistivity as a function of temperature (Fig. 5.5) and Hall resistivity in function of magnetic field (Fig 5.6). Additionally in case of samples x = 0.0173 and x = 0.0225 E_F derived from STS measurements (Fig. 5.11(a)) is located very close to the edge of the BVB. That could be the confirmation of semiconducting character of sample x = 0.0173 observed in resistivity measurements in Par. 5.2.2. The change in the conductivity character from p-type (E_F located in BVB) for a stoichiometric sample to n-type (E_F located in BCB) was observed as the Te content in the samples increased. Consequently, the STS results suggest that it is possible to achieve samples in which E_F is located in the gap for volume states and pinned only to the TSS, as it is shown for samples x = 0.035 and x = 0.07.

The result presented in Figure 5.11 means a positive realization of the main objective of this Thesis formulated in Paragraph 2.3. In two samples: $Bi_{1.965}Te_{3.035}$ and $Bi_{1.93}Te_{3.07}$ the E_F was successfully located in energy gap for volume states where only TSS occur. This implies that the conductivity is realised at the surface only and the carriers are topologically protected. A further insight into the nature of electronic states of provided by magnetoresistance studies discussed in the following Paragraph.

5.3.2 Quantum oscillations of magnetoresistance in sub-Kelvin temperature

The global properties of the samples, such as the location of the E_F in relation to the volume and surface bands, have a decisive influence on the nature of the electron transport of the material. Magnetotransport measurements were performed in Triton dilution refrigerator to gain more insight into the positions of E_F determined from the STS measurements and their implications on the nature of the conductivity. Longitudinal resistivity ρ_{xx} as a function of magnetic field was measured in addition to this resistivity as a function of temperature and Hall resistivity, discussed earlier (Par. 5.2.2). These measurements allowed for the observation of SdH quantum oscillations, which is another confirmation of the high quality of the tested single crystals, and together with the previous results shows a full picture of changes in the electronic structure of crystals as a result of the discussed modifications of stoichiometry. Finally, the analysis of the SdH oscillations frequencies and the corresponding Berry phase allowed to associate certain frequencies with certain electronic bands, which provides confirmation of the electron structure studies obtained locally in the presented STS measurements.

The longitudinal resistivity (ρ_{xx}) versus the external magnetic field in range from 0 to 14 T were carried out at temperature of 100 mK. The results are shown in Figure 5.12, where the SdH quantum oscillations are visible. Analogous to the previous Section the results of $\rho_{xx}(B)$ are presented in the form of:

$$MR(B) = \frac{\rho_{xx}(B) - \rho_{xx}(0)}{\rho_{xx}(0)}.$$
 (5.2)



Figure 5.12: Magnetoresistance measured at temperature of 100 mK.

The quantum oscillations can be observed for all measured samples. Analogous to the previous Section, since ρ_{xy} and ρ_{xx} are of the same order, pure oscillations should be extracted from σ_{xx} instead of ρ_{xx} to avoid incorrect determination of the oscillation phase. The σ_{xx} conductivity is a function of presented ρ_{xx} :

$$\sigma_{\rm xx} = \frac{\rho_{\rm xx}}{\rho_{\rm xx}^2 + \rho_{\rm xy}^2}.\tag{5.3}$$

First of all the analysis of quantum oscillations is conducted on the example of a stoichiometric pristine Bi₂Te₃ sample (x = 0). The SdH pure oscillations were extracted from the field dependent conductivity by subtraction of a smooth background. The resulting $\Delta \sigma_{xx}$ plotted versus 1/B together with the FFT analysis of the oscillation frequency is shown in Figure 5.13.



Figure 5.13: Shubnikov-de Haas oscillations plotted as $\Delta \sigma_{xx}$ vs. the inverse magnetic field of pristine Bi₂Te₃ (a), FFT analysis of the frequency of the oscillation with two frequency components marked (b).

The pure SdH oscillations of the field-dependent conductivity are clearly visible directly after smooth background subtraction (Fig. 5.13(a)). Therefore, unlike in the analysis in the previous Section 4, the operation of multiplication by B^3 is not necessary here. The FFT analysis shown in Figure 5.13(b) reveals that there are two components of the oscillations shown. The frequencies 11.7 T and 27.7 T were distinguished, which are marked in Fig. 5.13(b). The following frequency peak 55.4 T is a harmonic component of the 27.7 T peak, and therefore is not significant for further analysis.

Two components of the oscillation frequency are seen, one from the surface states and the other from the volume states, as the E_F for the stoichiometric Bi₂Te₃ sample (x = 0) is located in the BVB overlapping TSS and the two components coexist on the E_F . As discussed in Section 5, where on the E_F of the Bi₂Se₃ sample, TSS and BCB coexist, yet single-frequency oscillations are observed. In Bi₂Te₃, frequency components derived from the surface and volume are visible, because 1) these states do not coincide perfectly in reciprocal space and therefore the oscillation frequencies are different, 2) the mobility of carriers of surface states is comparable to the mobility in volume states, and thus the amplitudes are also comparable. Bi₂Se₃, in turn, shows a very high mobility of carriers on the surface in relation to the volume. Therefore, the amplitudes from the surface states in the reciprocal space, the amplitudes from these two causes occur in similar frequency. Therefore, for Bi₂Se₃, a single frequency derived from surface states dominates, and in the case of Bi₂Te₃, two components of the oscillation frequency are observed.



Figure 5.14: (a) FFT filter of a bandpass 10-15 T applied to the peak of 11.7 T, (b) FFT filter of a bandpass 25-30 T applied to the peak of 27.7 T. (c) Landau Fan Diagrams.

FFT filter was applied to extract signal from the individual significant peaks. FFT filter of a bandpass 10-15 T was applied to the peak of 11.7 T (Fig. 5.15(a)). FFT filter

of a bandpass 25-30 T was applied to the peak of 27.7 T (Fig. 5.15(b)). Landau Fan Diagrams are obtained by assigning the integer value to the position of the successive σ_{xy} maxima of the SdH oscillations, and the value of N + 1/2 to the position of σ_{xy} minima as a function of B⁻¹ (Fig. 5.15(c)). Extrapolating the linear relationship to the value of B⁻¹ = 0 and determining the point of intersection with the Landau Level index, we obtain the parameter β used in the Lifshitz-Kosevich formalism. The phase factor β , which multiplied by 2π results in the Berry phase of quantum oscillations. Therefore, if the β is equal to 0.5 the Berry phase equals to π and if the β is an integer the the Berry phase equals to 0. This allows to distinguish oscillations originating from volume states with a trivial topology (parabolic dispersion) with Berry phase equal to 0 and surface states with a non-trivial topology (linear dispersion) Berry phase equals to π .

In the example of Figure 5.14(c)the prepared Landau Fan Diagrams allow to distinguish that the oscillations with a frequency of 11.7 T come from the non-trivial surface states, while the frequency of 27.7 T comes from the topologically trivial volume states. The occurrence of SdH quantum oscillations consisting of the superimposition of both of these frequencies implies that both volume (trivial) and surface (nontrivial) states occur at the E_F of the tested sample and contribute to the electronic properties of the material. In other words the E_F of pristine Bi_2Te_3 intersects one of the volume bands, as has been discussed many times in this Thesis.

All tested samples of the $Bi_{2-x}Te_{3+x}$ series were subjected to a similar analysis. The resulting FFT analysis of the frequency of the observed SdH oscilla-



Figure 5.15: Fast Fourier Transform analysis of the observed quantum oscillations revealing their frequencies for $Bi_{2-x}Te_{3+x}$ samples. Black arrows mark frequencies associated with surface states, while red arrows mark frequencies associated with volume states.

tions is shown in Figure 5.15. The FFT spectra show that in all tested samples, two frequency components can be distinguished, analogously to the example discussed earlier, with the exception of one sample. Sample x = 0.14 shows single-frequency oscillations. In

Fig/ 5.15, the peaks of the frequency components are marked with arrows for the surface (black) and volume (red) states. The observed oscillation frequencies of individual samples differ from each other, as schematically marked with dashed line in Fig. 5.15 for the frequency peaks attributed surface states. This is a consequence of different concentrations of carriers in the samples.

Without being shown here, Landau Fan Diagrams were created for all tested samples considering the significant frequencies revealed by the FFT analysis and the Berry phase of all components was determined. On this basis, individual frequencies were associated with volume or surface states, respectively, as discussed in the previous example. As a result of the discussion in our group, we propose an interpretation consisting in presenting the frequencies of individual SdH oscillations as a function of the concentration of carriers in samples, as shown in Figure 5.16. The upper axis is labelled with the parameter x of samples related to the concentration of carriers in accordance with the relationship presented in Figure 5.7.



Figure 5.16: The determined SdH oscillation frequency associated with respective bands plotted as a function of carrier concentration.

In Figure 5.16 the frequencies from the surface states are marked in black, and the frequencies from volume bands (BVB and BCB) are marked in green and red, respectively. Bearing in mind that oscillations are always measured at the E_F , we obtained relationships that delimit the individual bands mapped by the smoothly changing E_F position in individual samples. These results qualitatively confirm the STS observations, i.e. a systematic shift of the E_F as a function of carrier concentration, related in Figure 5.7 to the concentration of Te. E_F has been observed to shift from the BVB, for the lower Te content

(x = 0 and x = 0.0173) in green, through the TSS region in blue, and finally to the BCB region in red for the highest Te content (x ≥ 0.0225). A sample with a carrier concentration close to 0 (x = 0.0173) is observed to show the E_F located within both surface and volume states close to the BVB boundary, which induces the semiconductor nature of this sample discussed in the previous Paragraphs.

The presented analysis and interpretation of the magnetoresistance measurements of the tested series of samples do not show the situation that E_F would be located within the energy gap for the volume states. This would be indicated by observation of a singlefrequency oscillation whose Berry phase is equal to π and can be associated exclusively with the TSS. In our interpretation, this would mean the occurrence of a single black point in Fig. 5.16 for some concentration of carriers, most likely within the area marked in blue. Although the results suggest a smooth shift of E_F position depending on x, there is no such specific case, unlike in the discussed STS results. Despite many differences in STS and magnetoresistance measurements, such as the local and global nature of the measurements, respectively, or the temperature of 300 K and 100 mK, respectively, both methods are used to study surface states. Local studies of the thermoelectric properties of materials discussed in the next Paragraph may be helpful in understanding the observed inconsistency between observations derived from STS and SdH quantum oscillations.

5.4 Thermoelectric properties of crystals

As an element of cooperation with the group of prof. Wojciechowski, the thermoelectric properties of the synthesized series of samples were tested in the Thermoelectric Research Laboratory at WIMiC AGH. The reason is that the Seebeck coefficient is extremely sensitive to carrier concentration and can provide more insight on the electronic as seen by STS and SdH quantum oscillations.

 Bi_2Te_3 is one of the most studied thermoelectric materials. It is utilized in different thermoelectric applications such as temperature measurement devices, power generators, and energy converters. This material possesses a high Seebeck coefficient, which implies that it can produce high voltage with minimal temperature difference. Bi_2Te_3 is also durable and resistant to high temperatures, which makes it a suitable material for use in a variety of operating conditions.

One of the most important parameters that determine the energy conversion efficiency of the Bi_2Te_3 – based materials is the chemical potential of electrons, which can be well represented by the Seebeck coefficient of the material. Particularly, the position of the chemical potential is directly connected with the value of the Seebeck coefficient. Considering the acoustic phonon scattering as the dominant scattering mechanism of the charge carriers, the Seebeck coefficient can be determined as $S = \frac{k_0}{e} \left[\frac{2F_1(\mu^*)}{F_0(\mu^*)} - \mu^*\right]$, where k_0 , e, F_i , and μ^* denote the Boltzmann constant, electron charge, Fermi integrals, and reduced chemical potential, respectively [87]. If the chemical potential of electrons corresponds to the conduction band minima or valence band maxima ($\mu^* = 0$), the Seebeck coefficient S will reach $\pm 172 \ \mu V K^{-1}$. In this case, the carrier concentration will be around $5 \times 10^{18} cm^{-3}$, and the increase or decrease of the carrier concentration will cause a large change in the Seebeck coefficient value [88, 89]. Therefore, the information about the Seebeck coefficient can be extremely useful for the determination of the charge carrier concentration (chemical potential), especially in the cases of narrow bandgap nondegenerate semiconductors. In such materials, even a slight variation of the carrier concentration will lead to a significant change in the Seebeck coefficient, while the Hall measurement probably will not be so accurate.



Figure 5.17: Scanning Thermoelectric Microscope (a, b) and schematic of working principle (c) [90].

The Seebeck coefficient was measured using Scanning Thermoelectric Microscope shown in Figures 5.17(a, b)), which allows for localized measurement of the Seebeck coefficient and electrical conductivity σ on the surface of samples. Mapping of the Seebeck coefficient involves measurement of the voltage between the heated measuring electrode and reference at different points on the sample surface (Fig. 5.17(c)). The σ relies on observation of potential changes at different points when an electrical current is set through sample. The measurement was performed at the temperature of 298 K with a maximum spatial resolution of 1 μ m. In Figure 5.18(a), the Scanning Thermoelectric Microprobe map is displayed for the selected Bi_{2-x}Te_{3+x} (x = 0) sample. The Seebeck coefficient histogram was fitted using a unimodal Gauss function, and the standard deviation was used to represent the uniformity of the Seebeck coefficient (Fig. 5.18(b)).



Figure 5.18: (a) The STM map and (b) Gauss distribution of the Seebeck coefficient for $Bi_{2-x}Te_{3+x}$ (x = 0) single-crystalline sample; (c) the plot of the Seebeck coefficient and carrier concentration calculated within the single-band (dashed line) and two-band (solid line) Kane model for Bi_2Te_3 – based samples at 298 K.

To obtain the corresponding values of the carrier concentration for Bi_2Te_3 , the twoband Kane model was utilized. The calculations' specifics can be found in reference [91]. Figure 5.18(c) shows comparison plot of the Seebeck coefficient and carrier concentration calculated within the single-band (dashed line) and two-band (solid line) Kane model for Bi_2Te_3 – based samples at 298 K. Figure 5.19 shows the estimated carrier concentration maps for $Bi_{2-x}Te_{3+x}$ samples of particular interest due to the STS results suggesting that the E_F in these samples is llocatet within the volume band gap. The calculations were carried out using the Kane band model considering the effect of majority and minority carriers on electronic transport. Arrows indicate the carrier concentration obtained from Hall measurements at 300 mK.



Figure 5.19: Estimated carrier concentration maps for $\text{Bi}_{2-x}\text{Te}_{3+x}$ samples using the Kane band model considering the effect of majority and minority carriers on electronic transport. Arrows indicate the carrier concentration obtained from Hall measurements at 300 mK.

The carrier concentration maps presented in Figure 5.19 show visible inhomogeneities of carrier concentration depending on the location on the surface of the tested samples. These maps may explain some discrepancies discussed in the previous Paragraph between the local STS observations and the analysis of SdH quantum oscillations globally sampling the surface states. As shown in Figure 5.16 E_F in the tested samples, and thus the nature of conductivity strongly depends on the concentration of carriers on the surface. Therefore, it might be possible that the local STS measurements rely an area of the sample with a different concentration of carriers than the global average as seen by the SdH oscillations. As a result, the E_F as seen STS may slightly differ from the estimates based on magnetotransport. But this difference may cause that E_F was observed locally in the STS measurements in the energy gap region (Fig. 5.11), which could not be revealed globally in SdH quantum oscillations (Fig. 5.16).

Table 5.3 presents the average Seebeck coefficient (determined from the scanning thermoelectric microscope measurements) and carrier concentration (estimated using the twoband Kane model). The outcomes show little correlation with the Hall carrier concentration at 300 mK.

Table 5.3: The average value of the Seebeck coefficient and estimated carrier concentration at 300 ${\rm K}$

Sample Bi _{2-x} Te _{3+x}	Type of conduction	$\begin{array}{c} \text{Seebeck} \\ \text{coefficient} \\ \text{from Gauss} \\ \text{distribution} \\ \mu \text{VK}^{-1} \end{array}$	$egin{array}{c} { m Standard} \\ { m deviation} \\ { m of the Seebeck} \\ { m coefficient} \\ {\mu}{ m VK}^{-1} \end{array}$	Average Seebeck coefficient $\mu V K^{-1}$	Average carrier concentration cm ⁻³
x=0	р	154	46	154	5.4×10^{19}
x = 0.0175	p	2	3	14	$1.5 imes10^{18}$
x = 0.0225	n	-118	69	-95	$1.6 imes10^{18}$
x = 0.035	n	-145	9	-146	$2.0 imes 10^{18}$
x = 0.07	n	-175	14	-87	$1.0 imes 10^{18}$
x=0.14	n	-124	4	-126	$8.7 imes 10^{19}$

6 Tuning the Fermi level by native point defects

The surface topography studies carried out in this Thesis reveal the presence of numerous defects on the surface of all tested samples. These defects, which are visible as triangular patterns on STM surface scans, are a common feature of the tested materials and have been observed and described in detail in numerous surface studies of discussed TIs [28, 30, 31, 92]. The defects have a real impact on the properties of these materials, including their conductivity, as shown in detail in the previous Section. The number and distribution of these defects in the samples affect the modelled carrier concentration and must be accurately described to fully comprehend the electronic structure of the materials, as discussed in Paragraph 5.2.3. Physical properties of functional materials, e.g. conductivity, are often strongly influenced by impurities and point defects. The precise control of defects type and concentrations in semiconductors underlies the fabrication of virtually all electronic devices. Hence, defects arouse scientific interest also in the case of the discussed TIs. As it is the defects arising under typical crystal growth conditions that contribute to the native n-type doping of Bi₂Se₃ and p-type character of Bi₂Te₃, their identification and precise control may turn out to be necessary for the practical use of these materials.

The naturally occurring structural defects have significant influence on the surface electronic structure. The individual defects are recognised to behave like a charged point dopants with a charge depending on the type of the defect (ref. [78] and Tab. 5.2). No wonder than, that depending on the type and amount of structural native defects the changes of global properties like the E_F position are observed in macroscopic measurements [23, 28]. Thus, the development of a method to control the type and quantity of defects may allow the E_F to be brought to the desired position in the gap for volume bands, possibly close to the DP. For this purpose, scientific efforts have been made based on a sophisticated controlled process of single crystal growth under conditions guaranteeing a reduced number of near-surface defects [28]. Non-stoichiometric growth of single crystals [75] also shows impact on the defects density in crystals, analogous to Section 5 in this Thesis. Here, in order to influence the global number of defects, the crystal was subjected to heat treatment, which by triggering diffusion processes may lead to the creation of new defects or agglomeration of the existing defects near the surface, thus potentially affecting the surface electronic structure.

The fundamental issues addressed in this Section are:

- 1. Determination the general effect of annealing: does it lead to a change in the global number of defects and whether E_F can be shifted in this way.
- 2. Investigation whether the effects of annealing can lead to the destruction of nontrivial topology and TSS, and if so, determining the maximum safe temperature.

3. Determination of the activation temperature (energy) of defect diffusion and what are the consequences of this diffusion.

This issues are addressed by studies of thermal treatment of crystals, which include temperature-dependent investigations of the global crystal structure by means of LEED, chemical composition of the surface with AES, as well as local measurements of single defects on the surface by STM. Additional information on the impact of annealing and the resulting phenomena on the surface is provided by measurements of electron transport properties, such as magnetoresistance, including quantum oscillation analysis comparing the sample before and after annealing.

However, before the thermal treatment experiment is discussed, better insight into individual defects is needed to fully understand the discussed phenomena. For this purpose local STM and STS measurements of single defects were performed. The measurements are combined with the first principles DFT simulations obtained in cooperation with dr inż. Michał Jurczyszyn. On this basis, a detailed analysis of individual defects was carried out and specific locations in the crystal lattice where each type of defects occur were identified. Finally, STS measurements in the area of single defects at the surface revealed the local influence of each of defect on the surface electronic states.

6.1 Native point defects on surfaces of Bi_2Se_3 and Bi_2Te_3

Let us begin with the pristine materials of Bi_2Se_3 and Bi_2Te_3 . The naturally occurred intrinsic structural defects, located in the near-surface region, lead to formation of triangle-shaped patterns visible in STM measurements. The STM scans presented in the previous Sections reveal that there are several types of these shapes at the surface and, consequently, there are several types of defects. The following Paragraphs will present the results of combined STM/STS measurements and DFT calculations to distinguish between each type of defects and to carefully analyze the mechanism of their influence on surface electronic states.

6.1.1 Imprint of defects at the surface as seen by STM

The most natural method of observing and studying objects with a size of several nanometers, such as native surface defects, is STM topography scanning. As the STM reveals the perturbations in both surface topography and density of states, this method is capable to reveal the defects in first top atomic layer as well as the surface electronic imprint of the defects occurring within the subsurface layers. The topographic images of various defects occurring in the tested samples are presented in this Paragraph. These are certainly not the only defects occurring in these materials, but their observation depends on the tunneling parameters in which the STM microscope operates. The need for a quantitative comparison of materials in terms of defects forced the determination of selected parameters and their consistent use in measurements throughout the entire cycle of the presented research. This also addresses into the previously discussed Sections where not all the effects that might be expected at the surfaces were directly observed in the topography images. In turn, in Section 4, the presence of dopants has a very small effect on the surface topography of the Bi₂Se₃ samples, the images of which can only slightly suggest the presence of dopants at the surface. In turn, in Section 5, for the correct modeling of carrier concentration in Bi₂Te₃, it was necessary to introduce the assumed defects in the form of Bi vacancies. These defects have not been directly visualized in STM scans, but are most likely present in samples, as confirmed by DFT calculations. It remains an open issue to select the STM topography scanning parameters in such a way that the aforementioned effects can be visualized. With the parameters selected for these studies, the vast majority of defects that are observed are the defects described in the following Paragraphs. Therefore, the following discussion in this Section will be focused on these selected defects observed at a given tunneling parameters.

Bi₂Se₃: from Purdue University

The topography scans of Bi_2Se_3 synthesised in Purdue University are presented in Figure 6.1. In tested samples a large number of surface defects are observed, that can be divided into two types, seen as more and less intense in STM scans (Fig. 6.1(a)). The high-resolution scans focused on the selected defects reveal subtle differences of atomic arrangement of this two types of defects.



Figure 6.1: STM topography scans recorded at room temperature, $V_{\text{bias}} = -340 \text{ mV}$, I = 100 pA on Bi_2Se_3 . (a) $50 \times 50 \text{ nm}$ STM image of the Bi_2Se_3 surface, revealing the most frequent types of defects: Bi-Se substitutions in the 5th atomic layer (more intense) and 6th atomic layer (less intense). (b,c) high resolution STM topography scans depicting surface images of the defect in the 5th atomic layer (b) and in the 5th atomic layer (c)

Basing on the literature data containing both STM investigations supported by corresponding DFT calculations [28], and our DFT calculations (Paragraph 6.1.2) the discussed defects can be recognized as Bi substitutions in Se sites in crystal structure. The recognized defects occur in 5th atomic layer (Fig. 6.1(b)) or in 6th atomic layer (Fig. 6.1(c)) respectively. The exact mechanism of surface disturbance visible in the STM mode in the form of depicted patterns caused by defects located under the surface is described in Paragraph 6.1.2.

Bi₂Te₃: from Purdue University

The topography scans of Bi_2Te_3 synthesised in Purdue University are presented in Figure 6.2. Similarly to Bi_2Se_3 , a large number of more and less intense surface defects occur (Fig. 6.2(a)). The high-resolution scans of the marked individual defects is presented in Figure 6.2(b) and Figure 6.2(c). Comparing the obtained spatial atomic pattern of the defects to the literature data [75] and our DFT simulations (Paragraph 6.1.2) allows for their identification. The more intense defect (Fig. 6.2(b)) occurs as a consequence of Bi substitution in Te site in 5th atomic layer. While the less intense defect (Fig. 6.2(c)) is a consequence of Bi-Te substitution in 6th atomic layer.



Figure 6.2: STM topography scans recorded at room temperature, $V_{\text{bias}} = -440 \text{ mV}$, I = 100 pA on Bi₂Te₃. (a) 50 × 50 nm STM image of the Bi₂Te₃ surface, revealing the most frequent types of defects: Bi-Te substitutions in the 5th atomic layer (more intense) and 6th atomic layer (less intense). (b, c) high resolution STM topography scans depicting surface images of the defect in the 5th atomic layer (b) and in the 5th atomic layer (c).

Comparing the presented defect scans for the Bi_2Se_3 and Bi_2Te_3 samples, it can be seen that the corresponding substitutions in the crystals occur in the same positions of the crystal lattice, i.e. the 5th and 6th atomic layers for more and less intense defects, respectively. We note that these substitutions in the respective layers of both materials result in a very similar atomic shape distribution of the perturbation on the surface observed on STM. This is a consequence of the symmetry, as both Bi_2Se_3 and Bi_2Te_3 crystallize in the same spatial configuration with rhombohedral symmetry with similar values of lattice constants.

Bi₂Te₃: from WIMiC AGH

The topography scans of Bi_2Te_3 synthesised in WIMiC faculty of AGH University of Krakow are presented in Figure 6.3. 100×100 nm STM image of the Bi_2Te_3 surface is presented in Figure 6.3(a), revealing the most frequent types of defects. The bright triangle-shaped defects recognized as Bi-Te substitutions in the 5th and 6th atomic layers occur similarly to sample synthesised in Purdue University. This is confirmed in high resolution scan of this defect depicted in Figure 6.3(c) presenting substitution in 5th atomic layer. The defects in 6th are visible as less-intense bright defects in large scan (Fig. 6.3(a)). However, a large number of dark spots on the surface are also visible in Figure 6.3(a). Figure 6.3(b) shows a selected area of the surface focused on these dark spots, confirming their triangular-shape structure. This induces that they are undoubtedly another type of defect whose high-resolution scan is shown in Figure 6.3(d). Literature data [75] show that the presented defect shape is related to the Te vacancies (V_{Te}) occurring in the third atomic layer.



Figure 6.3: STM topography scans recorded at room temperature, $V_{bias} = -440 \text{ mV}$, I = 100 pA on Bi_2Te_3 . (a) $100 \times 100 \text{ nm}$ STM image of the Bi_2Te_3 surface, revealing the most frequent types of defects: Bi-Te substitutions in the 5th atomic layer (bright) and Te vacancies (V_{Te}) in the 3rd atomic layer (dark). (b) $50 \times 50 \text{ nm}$ STM image of dark spots revealing their triangular-shaped symmetry. High resolution STM topography scans depicting surface images of the Bi-Te defect in the 5th atomic layer (c) and V_{Te} in the 3rd atomic layer (d)

Summarising, in our samples, with the specified and given scanning parameters, we observe several types of near-surface defects. These are the Bi-Se substitutions in the 5^{th} and 6^{th} atomic layers in the case of the Bi₂Se₃ sample (from Purdue University). In Bi₂Te₃ samples made at Purdue University, analogous Bi-Te substitutions observed are also occurring in the 5^{th} and 6^{th} atomic layers. Moreover, in Bi₂Te₃ samples synthesized at AGH, apart from Bi-Te substitutions in the 5^{th} and 6^{th} atomic layers, Te vacancies in the 3^{rd} atomic layer are also revealed. The fact that the last mentioned type of defects (V_{Te}) is observed only on AGH samples indicates the possibility of formation of these vacancies must be conditioned by the details of single crystal synthesis parameters, like for example the exact rate of cooling. The synthesis parameters are summarised in Paragraph 3.4.1.

6.1.2 Imprint of defects at surface calculated by DFT

The most prominent perturbations in surface LDOS of Bi_2Se_3 are related to Bi - Sesubstitution defects in the 5th atomic layer, which is often reported in the literature [22]. The performed STM investigations of pristine Bi_2Se_3 surface confirm these observations and show numerous triangular protrusions in the topography (Fig. 6.1(a)), clearly seen for negative bias voltage. The *ab-initio* DFT calculations were performed to explain the descent of the observed defects and to confirm our methods in relation to the literature data. The most frequently appeared in Bi_2Se_3 Bi-Se substitution defect in 5th atomic layer is shown with very high resolution in Figure 6.4(a). In order to explain the origin of its peculiar shape, the partial charge density distribution calculations (for energy in range from -0.1 eV to 0.4 eV relative to the calculated Fermi level) of the surface slab were performed, taking into account the occurrence of the substitution of selenium by bismuth atom in the fifth subsurface layer (Fig. 6.4(c)). Figure 6.4(b) shows perturbation in the surface electronic gas resulting from this substitution. We observe a good agreement as to the shape of the surface disturbance between the STM image of the defect surface (Fig 6.4(a)) and the simulated distribution of the surface electron density disturbance (Fig. 6.4(b)) as a result of substituting the Bi atom for Se in the fifth layer below the surface.

Let us now discuss the very mechanism of perturbation of the surface electronic structure by imperfections located below the surface. Figure 6.4(c) shows the crystal structure of Bi₂Se₃ with the introduced substitution of selenium by bismuth atom in the fifth subsurface layer. Such structural defect induces disorder in the volume electron gas distribution, which propagates inside QL through the ionic-covalent $pp\sigma$ interaction of orbitals [30, 93] for the close-packed linear atomic chain. This disorder, reaching the surface, leads to local disturbances of surface states, creating one of the branches of the observed triangular shapes (Fig. 6.4(a, b)). Because of the three-fold symmetry axis perpendicular to (0001) plane, such five-atomic chains exist in three equivalent directions. This explains the origin of formation of the triangular shapes in the calculated surface electron density and the three-fold symmetry shapes protrusions observed in STM topography images.



Figure 6.4: Comparison between experimentally observed native defect in Bi_2Se_3 and the corresponding results of DFT calculations. (a) High resolution STM image of the most frequent defect ($V_{\text{bias}} = -0.4 \text{ V}$). (b) Simulated STM image (isosurface value of $3 \cdot 10^{-6} \text{ e/Å}^3$) for Bi_{Se} substitution at the fifth subsurface layer and (c) the cross section of the spatial charge distribution (energy window from -0.1 to 0.4 eV) in the supercell along the red line marked in (c) with an isosurface value of $4 \cdot 10^{-4} \text{ e/Å}^3$ (green boundary). From [22]

An analogous comparison of the shape of defects on the Bi_2Te_3 surface with their DFT simulations is shown in Figure 6.5. Bi-Te substitution defect in 5th atomic layer is shown with very high resolution in Figure 6.5(a) following by its DFT simulation image shown in Figure 6.5(a). The Bi-Te substitution defect in 6th atomic layer and the corresponding DFT simulation image is shown in Figure 6.5(c) and (d) respectively. In case of Bi_2Te_3 we also observe a good agreement of the shape of the surface disturbance between the STM image and the simulated distribution of the surface electron density disturbance.

Efforts that have been made to accurately distinguish between different types of defects and identify the specific locations in the crystal lattice where each type of defect occur turn out to be invaluable in the context of the correct interpretation of the electronic structure of the tested materials. On the example of Section 5, only the defect distribution model taking into account the distribution of each type of defects in specific atomic layers and the sites of the crystal lattice provided a full analysis of all the observations made and enabled their interpretation.



Figure 6.5: Comparison between experimentally observed native defect in Bi_2Te_3 and the corresponding results of DFT simulations. High resolution STM scan of the Bi-Te substitution defect in (a) 5th atomic layer, (c) 6th atomic layer ($V_{\text{bias}} = -0.4 \text{ V}$). (b, d) Simulated STM images for isosurface value of $2 \cdot 10^{-7} \text{ e/Å}^3$ for Bi_{Se} substitution at the 5th and 6th subsurface layer, respectively, for $E - E_F = -300 \text{ meV}$.

6.2 Local electronic states at the surfaces resulting from structural defects

The previous Paragraphs show the exact shape of the surface imprint of different types of defects in the subsurface layers, confirmed by the full compliance of STM measurements and DFT calculations. The global influence of defect on the electronic structure was discussed in Section 5. The defects, depending on their type play a role of either p-type or n-type point dopants, effectively adding or subtracting electrons from the system. On the scale of the entire sample, this results in global changes of key parameters for the electronic structure, such as location of E_F or carrier concentration. More subtle changes in the character of the bands are also observed as revealed by the analysis of quantum oscillations (Par. 5.3.2). These are global changes that relate to a more statistical view of the density of defects in the sample and their distribution in individual layers of the material (Par. 5.2.3). However, the possibility of imaging the local surface imprint of a defect from under the surface results from the disturbance of the local density of electronic states propagating from the defect to the surface layer as discussed in Par. 6.1.2. Therefore another question is what exactly are the local changes in the surface electron structure observed as a result of the presence of the subsurface defect.

In search of answers, the DFT calculations of the surface LDOS for both the defects area and beyond were performed. Experimental confirmation of these calculations requires the use of a technique enabling local study of objects with the size of single defects on the surface. Such a technique is undoubtedly STS, sampling LDOS with near atomic spatial resolution. STS experiment enabled to examine the local surface electronic structure of a individual defects as well as between them which corresponds perfectly with the conditions of the DFT calculations performed and provides answers to the above questions.

6.2.1 Local disturbance of electronic structure by defects as calculated by DFT

DFT calculations were performed to determine the disturbance of the surface LDOS resulting from the occurrence of near-surface defects. The results of surface LDOS calculations are presented in Figure 6.6(a) for the set of points on the Bi - Se substitution defect in 5th atomic layer as marked on surface topographic pattern simulation presented in Figure 6.6(b). At the "2" point the prominent peak for E = -0.02 eV occurs, which indicates the formation of additional surface states. The maximum value of electron density is reached at the "2" point, which qualitatively agrees with the spatial charge redistribution in defect area presented in STM scans (Fig. 6.4(a)). The map presented in Figure 6.6(b)shows the spatial distribution of the LDOS values projected on p orbital for E = -0.02 eV, calculated for the various Se atoms of the surface layer, above the 5th atomic layer defect. The p_x , p_y and p_z orbitals participate in the formation process of the triangle-shaped pattern in LDOS map, but each in a different way (bottom of Fig. 6.6(b)). The perfect accordance between the pattern in the LDOS map and the shape of triangular-shaped defects pattern observed in STM measurements (Fig. 6.4(a)) indicates that the substitution of Bi for Se in the fifth layer leads to local emergence of additional p orbitals, located at BVB.



Figure 6.6: Calculated LDOS (a) away from defects (black line) and for the different points on the topographic defect in 5th atomic layer (red lines). (b) The spatial distribution of p orbital projected LDOS value for E = -0.02 eV (upper) and relative contribution of p_{xyz} orbitals to the LDOS map (bottom). From [22]

6.2.2 Local disturbance of electronic structure by defects as measured by STS

The results of *ab-initio* calculations presented in Paragraph 6.2.1 state that in case of Bi_2Se_3 the occurring of near-surface structural defect indicate the emergence of additional surface electronic states located in BVB region. Experimental confirmation of the calculated results was obtained by the local-sampling STS technique, which enables to study the electronic structure both within the area of individual defects and beyond them. The tunneling spectroscopy curves for the Bi-Se substitution defect in Bi₂Se₃ have been already reported in literature [28, 30, 94] presenting emergence of a prominent peak in the STS spectra. Here, the object of research was to investigate both the defects on the Bi₂Se₃ surface and the influence of the dopant-modified host on the electronic states of the observed defects in the 5th and 6th atomic layer.



Figure 6.7: Normalized STS spectra measured at room temperature in positions far from the defects (black), at the 5th atomic layer defect (red) and at the 6th atomic layer defect (green) on (a) Bi_2Se_3 , (b) $Bi_{1.96}Mg_{0.04}Se_3$, (c) $Bi_{1.98}Fe_{0.02}Se_3$, respectively. From [70]

Figure 6.7 presents the STS results obtained both in the area of the 5th (red) and 6th (green) atomic layer defects and in between the defects (black) for comparison. Figure 6.7(a) presents the results for the pristine Bi_2Se_3 . Both the investigated defects introduce additional electronic states visible as local maxima in the STS spectra, which confirms earlier DFT simulations (Paragraph 6.2.1). The additional defect-induced states predicted for 5th atomic layer defect are also distinctly visible in case of defect in 6th atomic layer, although they are lower in intensity. As described in the Section 4, the electronic structure of the surface has changed due to doping, at least in the case of the Fe-doped sample. As the surface topography images of both the pristine and doped cry-

stals reveal the same structural Bi for Se substitutional defects, the another vital question is how the electronic states of defects interact with this modified electronic structure of the doped samples. The prominent peaks in STS spectra are clearly visible on Mg-doped (Fig. 6.7(b)) and Fe-doped (Fig. 6.7(c)) samples both in the area of 5th (red line) and 6th (green line) atomic layer defects.

The exact positions of the local maxima were obtained by fitting Gaussian-shaped peaks to the baseline subtracted STS spectra as shown in Figure 6.8. The centers of fitted Gaussian functions determine the energetic positions of the defect-induced states. The results for both investigated 5th and 6th atomic layer defects are summarized in Table 6.1 in comparison with the DP positions of the corresponding samples indicated in Paragraph 4.3, i.e. in positions far from defects.



Figure 6.8: Follow up to the Fig. 6.7. Normalized STS spectra measured at room temperature at the 5th atomic layer defect (red) on (a) Bi_2Se_3 , (c) $Bi_{1.96}Mg_{0.04}Se_3$, (e) $Bi_{1.98}Fe_{0.02}Se_3$ respectively. Results obtained at the 6th atomic layer defect (green) on (b) Bi_2Se_3 , (d) $Bi_{1.96}Mg_{0.04}Se_3$, (f) $Bi_{1.98}Fe_{0.02}Se_3$ respectively. Black curves correspond to STS spectra measured at positions far from the specified defects (background), the blue lines represent the spectra on individual defects after subtracting the background, and the cyanide lines show the fitted Gaussian function which allowed the determination of the energetic position of defect-induced states

	Bi_2Se_3 [V]	Bi _{1.96} Mg _{0.04} Se ₃ [V]	${\rm Bi}_{1.98}{\rm Fe}_{0.02}{\rm Se}_3~[V]$
Defect in 5 th atomic layer	-0.41	-0.39	-0.45
Defect in 6^{th} atomic layer	-0.26	-0.26	-0.32
DP far from defects (from Fig. 4.5)	-0.27	-0.26	-0.32

Table 6.1: The positions of the maxima of the additional electronic states observed at specific defects using the STS method

The states with a linear dispersion relation are not visible in the area of the defects due to the dominating defect-related electronic states. This result confirms previous simulations [22], and early STS results [30]. It is clear that the positions of the defect-induced peaks qualitatively coincide with the position of the Dirac point of the undisturbed surface structure. Figure 6.7(b) presents the results for $Bi_{1.96}Mg_{0.04}Se_3$, for which the defected areas reveal similar defect-induced states as in pristine Bi_2Se_3 . Actually, the positions of the corresponding maxima are not remarkably shifted with respect to the pristine sample, similar to the position of DP. The opposite situation occurs in the case of $Bi_{1.98}Fe_{0.02}Se_3$ (Fig. 6.7(c)). The defect-induced electronic states are shifted away from the Fermi level to lower energies coincidently with DP position. The defect-related states seem to reflect the electronic structure of the undefected surface: if the positions of the maxima related to the defect-induced states do shift, they do it facilely with changing the DP position.

6.3 Influencing electronic structure through heat treatment of crystals

Apart from the methods of influencing the position of $E_{\rm F}$ based on doping (Section 4) or changes in stoichiometry (Section 5), natively occurring defects have significant impact on the global electronic properties, as discussed in Par. 5.2.3. The defects identified in our samples as resulting from Bi_{Se} or Bi_{Te} substitutions are p-type, or relatively n-type in case of Te vacancies (observed only in Bi₂Te₃ samples synthesized at AGH), as summarized in Tab. 5.2. The investigated Bi_2Se_3 and Bi_2Te_3 crystals show the location of E_F within the volume bands mainly due to the presence of a large number of native defects. In turn, the results presented in [28] show that the intentional, sophisticated synthesis of the material almost free of defects results in the shift of the $E_{\rm F}$ to the area of the volume band gap. Also the results in Par. 5.2.3 show that the electronic structure can be influenced by changing the global number of defects in the sample, changing their location in the sample, e.g. by locating most of them near the surface, or by changing the ratio of one type of defect to another. A relatively easy method of influencing statistics of point defects is to cause them to diffuse with increased temperature. Therefore, the results presented in the following Paragraphs include both global and local (with the accuracy to single defects) surface observations as a function of sample temperature or the temperature at which the sample was annealed. The aim of these studies is to observe diffusion and determine its influence
on the number, type and distribution of near-surface defects and the influence of possible changes on the surface electronic structure of the sample.

6.3.1 Surface crystallographic structure and chemical composition as a function of temperature in global description

The initial determination of the thermal stability of the crystals and the effect of elevated temperature on the surface crystal structure was preformed by LEED measurements as a function of single crystal temperature: from RT to 700 K. The results of the LEED experiment are shown in Figure 6.9. At lower temperatures, close to RT, clear hexagonal patterns of diffraction reflections are obtained (Fig. 6.9(a, b)), indicating good, long-range atomic arrangement of the studied surface. After reaching 475 K, with a further increase in temperature (Fig. 6.9(c, d)), a gradual weakening of the intensity of the spots is observed, indicating a progressive, thermally induced increase in disorder of the surface atomic structure. In turn, exceeding 650 K led to the complete disappearance of diffraction patterns, i.e. to loss of the long-range atomic order of the Bi_2Te_3 surface (Fig. 6.9(e)). After reaching 700 K the sample was cooled down to RT, which restored the hexagonal pattern of diffraction reflections, however, of a clearly blurred character (Fig. 6.9(f)). Thus, the long-range disappearance of the atomic ordering of the surface, observed above 650 K, is not permanent and most likely it concerns only subsurface atomic layers of the tested sample. The appearance of any additional reflection spots indicating the formation of a new surface crystal structure with a different symmetry is not observed. However, some changes of the surface are certainly suggested as the LEED pattern has not returned to its original intensity after heat treatment. These changes may be local and do not lead to a change of crystallographic symmetry on the surface, or the vertical structure of the atomic layers of the surface may have changed, such as the number of atomic steps, which enhances the background of the LEED image, causing it to blur.



Figure 6.9: Selected LEED images ($E_p = 78 \text{ eV}$) of Bi_2Te_3 single crystal, recorded for temperatures a) RT, b) 375K, c) 475K, d) 575K, e) 675K and f) after cooling to RT.

Further analysis of the influence of temperature in terms of chemical composition of the surface was performed by means of the AES technique. AES peak-to-peak (AES-pp) mode (described in Par. 3.1.4) was used to continuously measure the height of the selected Auger peaks as a function of slow temperature rise. These measurements allowed to confirm the cleanliness of the surface and to study changes in chemical composition of the near-surface atomic layers of the sample due to the temperature increase. AES-pp measurements were applied to both the Bi (100.5 eV) and Te (487.5 eV) Auger peaks. The temperature of the single crystal was increased by rate of 0.3 K/min from RT to 700 K. Figure 6.10 presents AES-pp waveforms normalized to the initial (e.i. at RT) contents of the elements for Bi and Te as a function of sample temperature. The spectra reveal that after exceeding 470 K (marked with black dash) the Bi signal starts to increase with a slow decrease of Te signal. This course suggests a gradual exposure of the bismuth layers through the upper layers as the temperature increases. The 580 K marks (green dash) the temperature at which the spectra show that the surface elements contents is significantly changed, which may suggest significant changes in the properties of the sample. The marked temperatures will be referred in the later analysis.



Figure 6.10: AES-pp waveforms for Bi (100.5 eV) and Te (487.5 eV) Auger peaks as a function of temperature normalized to the initial intensity. Two characteristic temperatures are marked: 470 K where the significant increase of defects diffusion is observed in STM scans and 580 K as a starting point for observing the creation of a new phase.

6.3.2 Surface morphology as a function of temperature

The freshly cleaved sample shows large terraces with a few micrometres width as presented for the pristine material in Paragraph 3.4.3. The height of later is about 1 nm, which corresponds to height of the one QL. The STM scans reveal variable structural defects on the surface, which are characteristic for Bi_2Te_3 and discussed in details earlier. The vast majority of them corresponds to the substitution of Bi atoms for Te in the fifth $(Bi_{Te}(5))$ and sixth $(Bi_{Te}(6))$ atomic layer (Paragraph 6.1.1).

After characterising the sample in RT, the atomic-resolution STM measurements were carried out for increasingly higher sample temperatures (Fig. 6.11). At elevated temperatures, after exceeding 435 K, the diffusion of single structural defects was observed. The changes in the defect positions were observed both in between the Van der Waals space: $Bi_{Te}(5) \rightarrow Bi_{Te}(6) \rightarrow Bi_{Te}(5)$ (Fig. 6.11(c)) and in the plane of individual (both 5th and 6th) atomic layer (Fig. 6.11(d, e)) respectively. The defects' diffusion rate increased with raising the sample's temperature.



Figure 6.11: (a) and (b) the two consecutive surface topography scans carried at temperature of 480 K depicting defects' diffusion. Areas where the individual defects change their positions are marked for hopping between 5th and 6th (red squares) and within individual 6^{th} (blue squares) and 5th (green squares) atomic layers. Zooms of the areas marked in red are shown in (c) - jump from 5th to 6th atomic layer. Zooms of the areas marked in blue and green are shown in (d) and (e) for diffusion within particular atomic layer. For better view the contrast was adjusted in (c-e).

Careful analysis of positions of each of defects, seen on subsequent scans registered at elevated temperatures, allowed to distinguish the thermal stability of Bi_2Te_3 surface in atomic scale. In these temperature-dependence topographic measurements, a series of STM scans of 50×50 nm were collected for different temperatures in range of from 300 K to 570 K. Each of scans was registered during 60 s. As the substitutions of Te by Bi atoms in fifth atomic layer results in most prominent protrusion on the STM topographies, what allowed to preciously monitor the diffusion of these defects even in high temperatures, the temperature-dependent changes in defect's positions were performed only for $Bi_{Te}(5)$ defects.

Figure 6.12 presents the result of the analysis of the number of defects changing their location as a function of temperature. The insight in Figure 6.12 shows the percentage number of defects which changed their position between subsequent scans with the respect to all the observed $\text{Bi}_{\text{Te}}(5)$ within the scan area (n) versus sample temperature. The results were averaged over all registered scans in one series for particular temperature. In other words, n denotes the average percentage part of all the observed $\text{Bi}_{\text{Te}}(5)$ defects which changed their position within time of one scan. At lower temperatures no topographic changes in registered scans were observed. After exceeding 435 K, changes in the position of individual defects begin to be observed. Further increasing the temperature temperatures, showed a dynamic increase in diffusion rate. After exceeding 550 K, due to excessive mobility of defects, it was no longer possible to conduct accurate observations of changes in their positions.



Figure 6.12: Number of defects in Bi_2Te_3 changing its position (n) as a function of temperature.

Using the Arrhenius equation explaining the relation between diffusion (D(T)) and the temperature: $D(T) = D_0 \cdot \exp(-Ea/k_BT)$ one can associate the number of hops of defects with activation barrier energy for its diffusion $(E_a) : \ln(n) = c - E_a/k_BT$, where c is a constant. The results of such analysis is shown in Figure 6.12. In this approach the calculated diffusion activation energy for Bi-Te(5) defects is 0.83 eV. Similar Bi_{Te}(5) substitution analysis in Bi₂Te₃ has not been found in the literature, but the activation energy found here is comparable to the values for the diffusion of V_{Te} in Bi₂Te₃ volume [95] and Se in Bi₂Se₃ volume [96].

Although the diffusion of defects was directly observed, the collected results show that the number and type of defects on the surface before and after annealing remain the same. No visible grouping of defects, nor the formation of new defects, was observed in any of the tested surface areas.

6.4 Local results of annealing: a new phase

Figure 6.13 shows changes in the surface of the material after annealing to the temperature of 560 K and 580 K. Exceeding the temperature of 560 K led to the degradation of the surface within the first QL creating a new phase on the surface distinguished by steps of a fraction of a single QL high, not observed on the surface before heating as it was discussed in Par. 3.4.3. Fig 6.13(a) shows the beginning of the formation of a new phase covering a very small area of the surface as can be seen by analyzing the step heights in Fig. 6.13(b). As pointed out discussing the introductory analysis of the pristine materials in Paragraph 3.4.3, only full QL steps are observed prior to annealing. Further increasing the temperature resulted in more dynamic changes in the topography and after heating to 580 K a large part of the surface is covered with areas with a new phase as depicted in Figure 6.13(c and d). Observing such clear changes in the surface structure, we decided that the temperature of 580 K is the upper limit of our STM experiment. This may explain the previously discussed blurring of LEED patterns (Fig. 6.9) observed on the surface annealed and cooled to RT.



Figure 6.13: Large area scans (2 μ m × 2 μ m) revealing the atomic steps at the surface after annealing to (a) 560 K with first signs of creating the new phase on the surface with fractional step height revealed in (b), (c) 580 K with large area covered by new phase with corresponding steps height analysis in (d).

The progressive degradation of the upper atomic layer and the increase in the proportion of the thermally induced phase with the lapse of time are shown in Figure 6.14 where (a, b and c) present STM scans of the same area (thermal drift subtracted) taken one by one at 580 K. The share of the highest terrace decreases at the expense of the growing area of the new phase (cavity fragments) on the surface. However, even a very long, several-hour annealing of the sample does not result in full coverage of the surface with a new phase, but rather a partial coverage as in Fig. 6.13(c). This may suggests that the formation of the new phase may be related to the initial distribution of defects or subsurface atomic steps.



Figure 6.14: STM scans of the same area performed one by one at 580 K. Progressive disappearance of the highest terrace and the increase in the share of the new thermally produced phase are clearly visible.

6.4.1 Topography after annealing

After observing significant changes in the surface structure, the samples were cooled down to RT, and then precise measurements of topography (STM) and the local electronic structure (STS) were carried out. The STM results are presented in Figure 6.15. Figure 6.15(a) presents large scan (500 nm × 500 nm) of a surface topography clearly revealing three different regions represented as dark, middle and bright yellow areas. The differences in height of the individual fractions of surface are reviled by line profile presented in Figure 6.15(b) which corresponds to the horizontal red line marked in Figure 6.15(a). We observe the steps of a height of 1 QL between dark and bright yellow areas (also observed on the pristine-unheated surfaces) indicating that the regions present exactly the same atomic surface terminating individual QL. The other step between bright and middle yellow in Figure 6.15(a) is of a height of approx. 0.6 nm constituting a fraction of height of single QL. Such fractional steps are not observed on the unheated surfaces. This result suggest simply that one of the layers inside the QL has been exposed as a result of annealing.

Figure 6.15(c) presents scan of the interface of the normal and thermally induced phases corresponding to the green-marked area in Figure 6.15(a). In the lower part of the Figure 6.15(c), the undisturbed surface with characteristic triangular defects is visible. The upper part, on the other hand, shows the area clearly changed as a result of annealing dotted with triangular cavities.

Figure 6.15(d) presents high resolution scan of the fraction of surface exposed after annealing with exact location marked in blue in Figure 6.15(a). Non-uniform nature of this surface is clearly observed resulting in dark and bright fractions on the scan. Scan presented in Figure 6.15(e) corresponds to the area marked in yellow in Figure 6.15(a). This scan presents a typical topography of Bi_2Te_3 rich in characteristic structural defects of threefold symmetry widely described in Paragraph 6.1.1. The fraction of surface presented in dark and bright yellow in Figure 6.15(a) represent the atomic layers terminating individual QL, which indicate that these surfaces are identical due to crystal symmetry. This surface seems to be unchanged by annealing up to discussed temperature, which one can confirm by comparison of Figure 6.2 (before annealing) and Figure 6.15(e) (after annealing).



Figure 6.15: STM scans of the sample surface after heating to 580 K taken in RT. (a) depicts three regions on the surface represented as dark, middle and bright yellow areas. The line profile presented in (b) corresponds to the horizontal red line marked in (a). Steps of a height of 1 QL and a fraction of a QL are clearly visible. (c) presents the interface of the normal and thermally induced phase (green marked area). (d) shows topography of a new phase in high resolution (blue marked area). (e) presents surface topography of the thermally unchanged region (yellow marked area).

The surface topography of atomic layer terminating QL of Bi_2Te_3 before heating (Fig. 6.2) and after annealing to 580 K (Fig. 6.15(e)) is very similar in terms of kind and number of defects. The visible differences are the small dark spots revealed on the annealed surface (Fig. 6.15(e)), which are not observed before annealing (Fig. 6.2). These dark spots show poor adhesion to the surface and significant mobility. Therefore, we equate them as surface contamination caused by heating. In our system, it is not possible to eliminate these contaminants since during the radiational annealing of the sample, the entire sample holder heat up, which is the suspected source of these contaminants.

6.4.2 Local electronic structure after annealing

Local electronic structure of the samples' surface was tested by means of STS measurements. The local nature of the measurement of this technique, combined with the high resolution of STM scans, enabled to compare the electronic structure of the distinguished areas of the surface. Combined results of STM topography scan and corresponding STS spectra taken on surfaces terminating QL are presented in Figure 6.16. Fig. 6.16(a) shows an exemplary topography of the area unchanged due to the annealing. STS measurements were carried out away from visible defects, which was schematically marked. Figures 6.16(b) and (c) present STS spectra taken on surface before and after annealing to 580 K respectively. The spectra present relationship with a minimum at about 0 V (Fermi level) and a linear segment representing surface states forming DC with a linear dispersion relation typical for TI. The E_F is located close to the BVB edge, as expected for pristine Bi_2Te_3 . We do not observe significant differences between the spectra before and after annealing, which suggests that in areas where the topography has not been affected by annealing, the electronic structure also retains its features.



Figure 6.16: Combined results of STM topography scans and local electronic structure probe by STS taken on thermally not-modified regions. (a) STM topography scan of a surface terminating QL, (b) STS spectrum of pristine Bi₂Te₃ before annealing, (c) STS spectrum after annealing to 580 K.



Figure 6.17: Combined results of STM topography scans and local electronic structure of a thermally modified region after annealing to 580 K. (a) STM topography scan of the new phase on annealed surface, (b, c) STS spectra taken at point b and c respectively.

Turning to the area of thermally induced phase, the topography of which is shown in Fig. 6.17(a), STS measurements carried out in this region in darker spots corresponding to cavities (Fig. 6.17b)) shows the presence of a clear linear dispersion, shifted by 0.25 eV towards lower energies in relation to unheated or not affected by thermal treatment Bi_2Te_3 surface (Fig. 6.16). As a result the E_F in this case is located is at an energy above the states of a linear dispersion, i.e. in the BCB region. However, the brighter fractions of topography, although also showing a shift from the spectra of the original sample, correspond to the parabolic nature of the STS spectra, and the linear segment is not observed at all. The new thermally induced phase appears to introduce an E_F shift relative to the starting material of about 250 meV and the dual nature of its electronic structure: fractions where the linearly dispersed states are preserved and other fractions where these states no longer exist.

In reference [97] the results of molecular beam epitaxy (MBE) deposition of Bi_2 bilayers on the Bi_2Te_3 surface is discussed. The STS studies presented there show that the spectrum shifts rigidly to lower energy and DP position is moved from -210 meV to -290meV below the E_F . These observations are very similar to ours and might constitute a clue for determining the new phase on the surface.

One can speculate whether the shifting effect persists only locally near the surface where the atomic arrangements changes after annealing or the effect refers to the whole sample. This question is answered by Fig. 6.16 showing that the electronic structure as probed by STS is exactly the same before and after annealing for this part of the sample which does not show any atomic rearrangements after annealing if observed by STM. It can therefore be concluded that the new phase formed as a result of annealing only introduces a localized change in the electronic structure, while the material base remains unchanged. This confirms the topological protection of surface states discussed in the introductory Paragraphs 1.2.4 and 2.1. These states show resistance even in conditions when large areas of the surface are covered with a new phase with a clearly different electronic structure. A deeper insight into the nature of the changes that occur as a result of heat treatment is provided by the global measurements of electron transport discussed in the next Paragraph.

6.5 Electronic structure as seen by electron transport

The preceding Paragraphs demonstrate that annealing of Bi_2Te_3 leads to noticeable changes of its surface in both local atomic arrangement (as seen through STM) and local electronic structure (as seen through STS). Specifically, a new phase appears on the surface, and in its region conductivity seems to change from p-type (of pristine Bi_2Te_3) to n-type, accompanied by partial loss of linear dispersion. To confirm our interpretation of these effects, electron transport measurements at sub-Kelvin temperatures were performed, which provide more insight on changes in electronic structure due to heat treatment. Electron transport measurements were made on samples in the shape of a classic Hall bar in a Triton dilution refrigerator.

Three specifically prepared samples were selected for electron transport measurements. The pristine Bi₂Te₃ sample was tested as a reference, and in addition, samples after annealing to 560 K and 580 K were measured, in which significant changes were observed as shown in previous Paragraphs. Transport measurements were carried out on exactly the same crystals prepared and imaged in STM, the results of which were discussed earlier in this Section. The results of longitudal resitivity ρ_{xx} versus temperature measurements preformed during samples cooling are shown in Figure 6.18. All samples reveal metallic behaviour. At temperatures below 30 K, all measured samples show saturation of resistivity, implying the finite residual resistivity.



Figure 6.18: Temperature dependence of zero field longitudinal resistivity for Bi_2Te_3 single crystals: unheated, annealed at 560K and annealed at 580K.

The similar nature of the conductivity of the samples both before and after annealing suggests that thermal treatment did not significantly affect global parameters such as location of E_F with respect to volume bands. However, during annealing the distribution of defects changes, which was shown in detail in Paragraph 6.3.2, where diffusion of single defects was directly observed on STM scans. Ultimately, no significant change in the density of defects on the surface was observed, but their global (also in the volume) distribution affects the transport properties. Changes in the residual resistance value depending on the annealing temperature may result from the fact that annealing changes the number of defects in the volume of samples and causes stress relaxation in the crystals, as a systematically lower resistivity is observed at higher annealing temperatures.

The magnetic field dependence of longitudinal resistivity ρ_{xx} and transverse resistivity ρ_{xy} measured at 200 mK for all tested samples are shown in Figure 6.19.



Figure 6.19: Magnetic field dependence measured at 200 mK of (a) longitudinal resistivity ρ_{xx} , (b) transverse resistivity ρ_{xy} for Bi₂Te₃ single crystals: unheated, annealed at 560 K and annealed at 580 K.

The positive slope of the ρ_{xx} curves indicates that holes are the dominant carriers in all tested samples, suggesting that the E_F is located within the BVB. One may see some inconsistency with the STS results presented in Pragraph 6.4.2, which indicated a change in the conductivity of the sample from p-type to n-type in the areas covered with the new phase, i.e. after annealing to 580 K. However, the effect of changing conductivity to n-type where electrons are dominant carriers was observed only on these areas of the surface with clearly changed atomic arrangements as a result of annealing. Surface areas not affected by these changes show an electronic structure identical to that before annealing, as seen by STS. It was there explained that the conductivity change from p-type to n-type occurs only locally on areas covered with the new phase, and most likely only at the surface, as suggested by the results of magnetoresistance. We can assume that these changes of conductivity type seen by STS observed on thermally changed fragments of surface do not propagate into the crystal volume and therefore constitute a very small quantitative contribution to the total conductivity probed in magnetoresistance. It is possible that in global measurements of electron transport, the surface effect observed by STS is immeasurably small, and thus holes are the measured charge carriers in all our samples.

Shubnikov-de Haas quantum oscillations constitute important probe to analyze the shape and sizes of the Fermi surface as well as the topological surface states of materials. The procedure for extracting pure SdH oscillations has already been presented in the previous Sections. The oscillations are discerned from $\sigma_{xx} = \frac{\rho_{xx}}{\rho_{xx}^2 + \rho_{xy}^2}$, which is a function of ρ_{xx} shown in Fig. 6.19(a). The pure SdH oscillations were extracted from the field dependent conductivity σ_{xx} by subtraction of polynomial background and are plotted as

 $\Delta \sigma_{xy}$ against the inverse field B⁻¹, as shown in Figure 6.20 for three investigated samples: pristine Bi₂Te₃, after annealing to 560 K and after annealing to 580 K.



Figure 6.20: SdH oscillations in σ_{xx} after subtracting the smooth background for Bi₂Te₃ (a) unheated, (b) annealed at 560 K and (c) annealed at 580 K.

Analogously to the previous Sections, FFT analysis of the detected oscillations was performed in order to determine their characteristic frequencies. The results are presented in Figure 6.21.



Figure 6.21: The fast Fourier transform analysis of SdH oscillations for Bi_2Te_3 (a) unheated, (b) annealed at 560 K and (c) annealed at 580 K.

For all the tested samples we observe oscillations with one dominant frequency. A dominant peak is observed at 21.6 T, 22.3 T and 24 T for unheated, annealed at 560 K and annealed at 580 K samples, respectively. This frequency is attributed to the surface electronic states with the linear dispersion relation, in accordance with the data published in the literature [98, 99]. The second, more diffuse frequency peak, also observed for all tested samples, is associated with volume states. Its occurrence suggests that the Fermi level in all samples is located in volume states, most likely in BVB as suggested by previously discussed results. More interesting from the point of view of these studies is the main peak, concerning surface states. Its frequency is directly related to the extreme crosssection of the Fermi surface A_F by the Onsager relation already cited in previous Sections: $f_{SdH} = \left(\frac{h}{4\pi^2 e}\right) A_F$. This relation enables to calculate the Fermi wave vector $k_F = \sqrt{\frac{A_F}{\pi}}$ and consequently the surface carrier density: $n_{2D} = \frac{k_F^2}{4\pi}$. The calculated parameters for all three tested samples are summarised in Table 6.2.

Table 6.2: Parameters obtained from Hall effect measurements and FFT analysis of SdH oscillations.

Calculated parameter	Unheated	Annealed at 560 K	Annealed at 580 ${\rm K}$
$n_{Hall} \ [10^{19} \ cm^{-3}]$	1.01	1.24	1.77
f_{SdH} [T]	21.6	22.1	24
$k_{\rm F}$ [Å ⁻¹]	0.0256	0.0259	0.027
$\rm n_{2D}~[10^{11}~cm^{-2}]$	5.22	5.34	5.8

As the annealing temperature of the samples increases, so do the carrier concentration values (both n_{Hall} and n_{2D}), and Fermi wave-vector. This trend qualitatively suggests that the position of the E_F in the samples is likely changing. However, all the samples show p-type conductivity, meaning that the E_F is still located within the BVB.

In general, lower frequencies of f_{SdH} correspond to lower carrier concentrations n_{2D} and Fermi radii k_F . Comparing the results obtained here for the unheated Bi₂Te₃ sample from Purdue University to the pristine Bi₂Te₃ from WIMiC AGH discussed in Section 5 and pristine Bi₂Se₃ from Purdue University discussed in Section 4, we can notice some relations with respect to obtained parameters. The stoichiometric sample Bi₂Te₃ (WIMiC) showed an oscillation frequency SdH of 11.7 T, which is lower than the obtained 21.6 T for the pristine Bi₂Te₃ (Purdue University). This is due to differences in the retail parameters of the synthesis of the samples, as stated in Par. 3.4.1. The sample from Purdue University shows a higher frequency of oscillations and thus a higher concentration of 2D carriers. Whereas the Bi₂Se₃ sample from Purdue University discussed in Section 4 showed the oscillation frequency of 165 T, which is significantly higher than both discussed above. This outcome is not surprising, as it is well-documented in the literature that Bi₂Se₃ typically exhibits a much higher carrier concentration (on the order of $4 \cdot 10^{12}$ cm⁻²) than Bi₂Te₃ (on the order of $5 \cdot 10^{11}$ cm⁻²).

The Berry phase of quantum oscillations was also checked as one of the criteria of the existence of the surface electronic states of non-trivial topology by analysing the Landau level fan diagram shown in Figure 6.22. The Landau level fan diagram was constructed in the same way as it is described in the previous Sections i.e. by assigning the integer value to the position of the successive σ_{xy} maxima of the SdH oscillations, and the value of N + 1/2 to the position of σ_{xy} minima. The linear function was fitted to assigned

values and extrapolated to the y-axis as shown in Figure 6.22. The intercept of the fitted function is the phase factor β , which multiplied by 2π results in the Berry phase of quantum oscillations. Therefore, if the β is equal to 0.5, the Berry phase equals to π .



Figure 6.22: Landau level fan diagram for SdH oscillations in Bi₂Te₃ measured at 200 mK.

For the creation of Landau fan diagrams, only frequency dominant peaks were analyzed equal to 21.6 T, 22.3 T and 24 T for unheated, annealed at 560 K and annealed at 580 K samples, respectively. The obtained values of β are equal to 0.49 ± 0.03 for unheated, 0.39 ± 0.07 for annealed at 560 K and 0.52 ± 0.03 0.52 ± 0.03 for annealed at 580 K sample, respectively. The obtained values are close to 0.5, i.e. the Berry phase of the measured oscillations is equal to π , which proves that the oscillations originate from the massless Dirac fermions occupying the topologically non-trivial surface states. Annealing does not destroy these states, which is a great proof of their topological robustness to lattice imperfections and even the distinct surface phase presented in this Section. The line fitted to the data of the sample annealed at 580 K has a slightly steeper slope than the others, suggesting that β tends to 0, and so the Berry phase, with further increasing of the annealing temperature. This result suggests that further increasing the temperature could therefore lead to the destruction of the non-trivial topology of the material.

6.6 Attempts to identify a new phase

The results regarding the crystallographic structure, chemical composition and electronic structure of the new phase observed on the Bi_2Te_3 surface, formed by annealing to a temperature of at least 560 K, were presented in the previous Paragraphs. Despite a numerous details regarding the new phase were gathered from images of the surface topography or the local and global electronic structure, they are insufficient to determine the accurate interpretation of the new phase.

An important clue seems to be the height of the edges of the areas covered with the discussed phase, which is about 60% of the height of a single QL of Bi_2Te_3 . This suggests that, as a result of annealing, a part of the QL disintegrated and one of the intermediate layers was exposed. Additionally, the AES results show an increase in the proportion of Bi at the expense of Te close to the surface as the annealing temperature increases. This could indicate that at an elevated temperature Te, which is the top layer of the material, tends to desorb thus revealing the initially covered Bi layer. Further insight is provided by the local electronic structure observed through STS. The E_F in the area of the new phase is found to be shifted from the BVB by 250 meV towards higher energies to locate within the BCB. This is similar to effect observed in Section 5 caused by over-stoichiometric amount of Te at the expense of Bi in the tested samples.

In order to propose the identification of the observed new phase on the surface of Bi_2Te_3 and to explain its peculiar electronic structure, DFT calculations were performed (in cooperation with dr inż. Michał Jurczyszyn). Basing on our STM observations, STS measurements, and their confirmation derived from SdH quantum oscillations, several different surface termination variants, that might result from annealing, were proposed to be simulated. Calculations assumed a number of atomic configurations/arrangements and different surface termination variants of Bi₂Te₃ surface. The band structure and surface density of states (DOS) were calculated and the results are shown in Figure 6.23. The left panel (Figure 6.23(a, c, e)) shows the band structure of the pristine Bi_2Te_3 (a), Bi-bilayer on top of Bi_2Te_3 (c), and Te-adlayer on top of Bi_2Te_3 (e). The band structures shown correspond to the projection of band structure of the entire slab onto a selected atom in the upper layer. The color intensity of the individual bands of the band structures corresponds to the contribution of electrons from that atom to the band structure of the entire slab. In the right panel, surface DOS is shown for the corresponding variants on the left. Red line corresponds to the projection of density of states of the entire slab onto a selected atom in the upper layer, whereas the grey background represents projections on the whole first QL completed with the Bi-bilater and Te-adlayer in (b) and (d), respectively.

Based on Figures 6.16 and 6.17, it can be concluded that the situation where there is a clear contribution to tunneling from electronic states with linear dispersion and a shifted E_F to the valence band is best reflected in the DFT calculations related to the Bi-bilayer on top of Bi₂Te₃, as shown in Figure 6.23(c) and (d). However, there is some disagreement between Figure 6.17(b) and (c), which show the local electronic structure detected by STS from the part of the sample surface that is clearly influenced by annealing, and the results of the DFT calculations shown in Figure 6.23(c) and (d). STS results show that annealing changes the volume electronic structure from p-type to n-type, i.e., the E_F of the sample after annealing is located at the bottom of the BCB instead of the BVB before annealing. However, this is not surprising since the formation of the Bi-bilayer causes Bi-deficiency



Figure 6.23: DTF calculations of electronic structure and surface density of states (DOS) for pristine Bi_2Te_3 (a, b), Bi-bilyer on top of Bi_2Te_3 (c, d), Teadlayer on top of Bi_2Te_3 (e, f). The band structures shown correspond to the projection of band structure of the entire slab onto a selected atom in the upper layer. The color intensity of the individual bands of the band structures corresponds to the contribution of electrons from that atom to the band structure of the entire slab. In the DOS results, the red line corresponds to the projection of the density of states per atom in the first layer, while the gray background is the projection to the first QL with the additional adlayer taken into account.

underneath, resulting in the "switching" of the E_F from BVB to BCB. Interestingly, the same result was obtained in Section 5 as the samples with over-stoichiometric Te content were tested. This also leads to Bi-deficiency, which can be seen by looking at the number of Te_{Bi} substitutions and Bi vacancies V_{Bi} in samples with over-stoichiometric Te contents (Par. 5.2.3). As a result, E_F was observed to be shifted from BVB to BCB in this case as well. This effect, however, is not observed in the calculations in Fig. 6.23, because the simulated design slab cannot take into account defects or small Bi-deficiencies, unlike the calculations in Par. 5.3.1 carried out by a different method and for other purposes. Summarising, the calculated density of states shown in Figure 6.23(d) assumes stoichiometric Bi₂Te₃ covered with a bilayer of Bi, while in a real sample under the Bi bilayer there is probably a Bi deficiency, which could not be taken into account when simulating DOS of the surface.

Topographic structures with a height of a fraction of single QL, very similar to our results presented in Par. 6.4.1 were previously observed in STM scans on both Bi₂Te₃ and Bi₂Se₃ and described in the literature. In the references [100, 101], the monocrystalline Bi₂Se₃ and Bi₂Te₃ were ion sputtered and/or annealed to 623 K and 573 K respectively. In both cases, the authors observe characteristic areas on the surface with steps of a height of about 0.6 QL. However, the electronic structure was simulated only for Bi₂Te₃. Particularly the variants Bi₂Te₃ with a TeBi bilayer on top, and Bi₂Te₃ with a Bi₂ bilayer on top were simulated. In both cases, changes in the band structure relative to pristine Bi₂Te₃ were observed, in particular for the Bi₂ bilayer variant, authors observe that the BVB edge is shifted towards lower energies with respect to E_F.

7 Conclusions

This Thesis was aimed to explore various methods of controlling the position of the Fermi level in topological insulators Bi_2Se_3 and Bi_2Te_3 , with respect to topologically protected surface states of a unique electronic properties. Through a systematic investigation of doping with foreign elements, changing stoichiometry, and manipulation of native defects in the materials, the effects of these modifications on the surface topography and electronic structure parameters were studied using a range of experimental techniques. The results obtained from this research provide insights into the ability to tune the electronic properties of topological insulators, which could be essential for realizing their full potential in future technologies. In this concluding Section, we summarize the main findings of this Thesis and discuss their implications for the future development of TIs.

The samples investigated in this Thesis were obtained from two sources: Purdue University and WIMiC AGH. All samples are of high quality single crystals, as indicated globally by XRD and observation of SdH quantum oscillations in electronic transport measurements, which are an indicator of the highest quality crystals. STM and LEED as strictly surface-sensitive techniques also confirm both local and long-range perfect arrangement of atoms on the surfaces. Tested materials crystallize in a rhombohedral lattice with hexagonal symmetry on the surface, forming characteristic quintuple layers (QL) reproduced in the crystal, which consist of five atomic layers arranged alternately in the crystal.

Starting with pristine materials, electronic structure measurements performed both locally (STS) and globally (ARPES, electron transport) show n-type conductivity of Bi₂Se₃ and and p-type conductivity of Bi₂Te₃, as expected basing on literature data. The native doping results from defects occurring in the materials. When simulating (using DFT) an atomically ideal single crystal, the E_F is very close to the DP. However, in real crystals, defects act as point dopants, leading to an unintentional shift of the E_F away from the DP. Consequently, the E_F is located within the volume bands, resulting in unwanted volume conductivity that masks the topologically protected surface states. This makes it crucial to control the position of the E_F with respect to the DP in order to take full advantage of the unique electronic properties of TIs and became the main focus of this Thesis.

The first method discussed for manipulating the position of E_F is the introduction of foreign atoms as dopants into Bi₂Se₃. In this study, Mg and Fe dopants were chosen, with low concentrations in the samples in contrast to many literature reports. Great care was taken with adjusting the concentration of magnetic Fe dopants, as it is well-known that these dopants in high concentration can destroy the nontrivial topology of the system. According to our XAS observations, both discussed dopants are located in the crystal lattice of Bi_2Se_3 by substituting Bi atoms. Therefore, the following designations for the doped samples can be adopted: $Bi_{1.94}Mg_{0.04}Se_3$ and $Bi_{1.98}Fe_{0.02}Se_3$. The dopants do not significantly change the topography of the samples, but STM scans may suggest their presence close to the surface, through the revealed defect-like patterns, whose exact atomic configuration slightly distinguishes them from known defects. The introduced dopants slightly modify the BVB and BCB as observed by ARPES, shifting their position relative to E_F . However, the energy gap for volume states remains unchanged. The surface states are also modified by dopants. Fe clearly shifts the DP with respect to E_F , while both dopants modify the DC by changing values of Fermi wave-vector k_F , and consequently Fermi velocity v_F and effective mass m^{*} of carriers.

Summarising, we investigated the electronic structure with a rarely seen in the literature set of different methods, obtaining very convergent observations that can be concluded that the non-trivial topology in Bi_2Se_3 is resistant to the introduction of both magnetic and non-magnetic dopants with a concentration of about 1%. As confirmed by STS and ARPES measurements, where TSS with a linear dispersion relationship are clearly visible. Furthermore, the analysis of quantum oscillations clearly indicates the occurrence of oscillations with a single, well-defined frequency, which allows us to conclude that the topology of all Bi_2Se_3 , $Bi_{1.94}Mg_{0.04}Se_3$ and $Bi_{1.98}Fe_{0.02}Se_3$ is the same. This frequency is different for individual samples, which implies changes in DC parameters by dopants qualitatively consistent with the STS and ARPES observations.

Another method used to manipulate the position of the E_F was the controlled change of the stoichiometry of Bi_2Te_3 by synthesis under conditions of Te over-stoichiometry, resulting in a series of single crystals defined by the parameter x, denoted as $Bi_{2-x}Te_{3+x}$.

The STM studies show that the density of near-surface p-type defects, which are formed as a result of Bi substitutions at Te sites, depends on the stoichiometry of the crystals. These defects occur in large numbers in the stoichiometric samples of Bi₂Te₃ and with a small overstoichiometry of Te. When the Te concentration in the samples is high and all available Te sites are occupied, Bi-Te substitutions cannot occur and the associated defects disappear in surface topography images. On the other hand, the density of n-type defects (Te vacancies) is comparable in all studied crystals. However, at high Te concentrations, a downward trend in the density of these defects is observed, which may suggest that for even higher Te contents than those tested here, these vacancies may not be formed. Thus, at high Te concentrations, we would have a trend indicating a global reduction in the number of defects, which is consistent with the literature data. Since we observe Te vacancies only on the surface of samples synthesized at WIMiC AGH, we are inclined to postulate that they are formed as a result of detailed crystal synthesis parameters, such as the exact cooling rate. The electronic structure of a series of $\text{Bi}_{2-x}\text{Te}_{3+x}$ samples was investigated using STS and electron transport measurements. In STS measurements, a clear shift of the upper edge of the BVB with respect to E_{F} is observed. As the parameter x increases, the E_{F} is systematically shifted towards the maximum of BVB, then smoothly through the energy gap for volume states, and ultimately into the BCB. This shift is due to the change in the Te/Bi ratio, which affects the band structure and the position of the E_{F} . Electron transport measurements also show a clear dependence of the electrical conductivity on the Te/Bi ratio, in particular, a change in the nature of the conductivity of the sample from p-type for stoichiometric Bi₂Te₃ and slightly over-stoichiometric Te to n-type for strongly overstoichiometric Te is observed. A sample with the characteristics of a semiconductor with a very low concentration of carriers and a decreasing resistance as a function of temperature was also observed. This behavior is typical for material with E_F located in the energy gap.

The observed changes in the electronic structure and transport properties with the change of the Te/Bi ratio can be attributed to the formation of Bi-Te substitutions and Te vacancies, as well as modifications of the band structure due to changes in the crystal. These conclusions are justified by the results of the DFT simulation of the electronic structure of the tested series of samples, for which the correct model of the distribution of defects in the crystal turned out to be crucial for simulating the correct carrier concentration values. The simulation results also confirm the change in the position of the $E_{\rm F}$ in relation to the electronic structure and the change in the nature of the material from the p-type for x close to 0 to the n-type for larger x. Simulations also solved an important STS interpretation problem, namely that they showed that the width of the energy gap in the samples remains unchanged depending on the parameter x, and only in the most over-stoichiometric sample (x=0.14) it becomes slightly narrower. This made it possible to determine the range of the STS spectra of states with a linear dispersion relation to $E_{\rm F}$ and to conclude that in the tested series there are samples with the parameter x=0.035and x=0.07, in which E_F is located in the volume gap, where only TSS with a linear dispersion relation occur. This means, based directly on STS data and indirectly on Hall effect measurements and DFT calculations, that the main goal of this Thesis has been achieved with a positive result.

Additional information is provided by the analysis of SdH quantum oscillations observed in all samples of the tested series. In all cases, two oscillation frequencies are distinguished, one of which is related to the TSS and the other to the volume states that coexist on the E_F . However, unlike STS, this is a global result (from the surface of the entire sample) and, as discussed in Paragraph 5.3.2, strongly depends on the concentration of carriers. We do know, however, that this surface carrier concentration fluctuates, as has been imaged with the Scanning Thermoelectric Microscope. It is therefore possible that the STS measurements were carried out in a place with a slightly different concentration of carriers and, as a result, the E_F was measured in the volume gap. Nevertheless, qualitatively, the analysis of quantum oscillations is fully consistent with the results discussed earlier and shows a smooth shift of E_F as a function of x going from BVB to BCB.

Defect manipulation was chosen as the last but not least significant method of influencing the location of the $E_{\rm F}$. Their crucial importance for the concentration of carriers and the nature of conductivity has already been outlined. It shows that the electronic structure can be influenced by changing the global number of defects in the sample, changing their location in the sample, e.g. by locating most of them near the surface, or by changing the ratio of one defect to another or even introducing new defects in the crystal structure. All these paths are related to diffusion processes, which in this approach we decided to enhance by thermal treatment of Bi_2Te_3 . Indeed, the diffusion of defects was found to be thermally activated, meaning that an increase in temperature provided the necessary energy for the diffusion process to occur. Specifically, Bi-Te antisite defects were observed to have a calculated diffusion activation energy of 0.83 eV. The diffusion of these defects occurred through a change in position within a given atomic layer, as well as possible jumps between layers, which were directly observed through STM scans. However, even with elevated temperature and thermal activation, there was no significant change in the statistics of defects near the surface. This means that there was no type of defect agglomeration, increase or decrease in the number of defects, or formation of new types of defects observed after heat treatment.

The studies have shown that Bi_2Te_3 can be safely annealed up to 560 K, at which point irreversible surface changes begin to occur. By these changes, we mean the formation of a new phase covering fragments of the surface, with a height that is a fraction of the QL of the original material. This phase shows hexagonal symmetry of the surface, which is confirmed by the STM and LEED observations, but the transverse configuration of the atoms is clearly disturbed compared to the original Bi_2Te_3 . The new phase is covered with regular cavities with a height of about 300 pm. Interestingly, the areas that changed the atomic configuration after annealing show a very unusual electronic structure. The STS spectra observed in these regions show an E_F shift of about 250 meV towards higher energies, specifically to the BCB region, inducing that the conductivity in these regions is n-type. Moreover, a linear TSS dispersion relationship can be observed only in the defect region. On hills, the relationship is parabolic throughout the measured range. It is also interesting to note that the new phase appears to be inhomogeneously distributed on the surface, forming small fragments rather than covering the entire surface uniformly. This suggests that the formation of the new phase may be related to the initial distribution of defects or subsurface atomic steps. Nevertheless, the areas that are not covered with the new phase do not show changes in terms of the configuration of surface atoms, the density and type of defects, etc., and the electronic structure, which is no different from pristine Bi_2Te_3 . Thus, we have obtained a great proof of the topological protection of surface states, which remain undisturbed even when a significant part of the surface is covered with a separate phase showing different electron properties. This is also confirmed by electron transport measurements, which show that the dominant charge carriers both before and after heat treatment are holes, and therefore the E_F is located in the BVB. The effect observed in the areas of the new phase is therefore only superficial and does not propagate to the volume of the crystal. Simulations of the electronic structure for different variants of the adlayer on the Bi_2Te_3 surface seem to confirm the literature data, and the observed new phase is most likely the Bi bilayer, as also suggested by the AES-pp measurements, showing an increase in the share of Bi with annealing.

Finally, the studies presented in this Thesis have provided valuable insights into the methods of controlling the position of the E_F in TIs of Bi₂Se₃ and Bi₂Te₃. By exploring various approaches it has successfully demonstrated the ability to tune the electronic properties of these materials. The findings offer promising prospects for the future development of TIs, as they provide a deeper understanding of their unique electronic structure and pave the way for harnessing their full potential in advanced technologies. The ability to control and engineer the position of the E_F opens up possibilities for exploiting the surface states and realizing novel functionalities, such as robust quantum transport and topologically protected devices. These studies contribute to the growing field of topological materials and provide a foundation for further research and technological applications in the future.

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