Analyzing Bi$_2$Te$_2$Se by performing Angle-Resolved Photo Emission Spectroscopy

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1 Abstract

During this project ARPES measurements were performed on the new topological insulator $Bi_2Te_2Se$. The theory with regard to topological insulators is discussed as well as a theoretical description of the experimental setup that is used during the ARPES experiments. This will be followed by the results concerning these measurements as well as a conclusion. During this project the resolution for the analyser is determined to be 4.5 meV at a temperature of 17.8 K.

From the ARPES measurements one can clearly see the surface states, the valence band and what is thought to be an impurity band. The surface states intersect the Fermi level at $0.13 \pi a$ which seems to agree well with previous measurements performed on $Bi_2Te_2Se$. Also, the energy gap between the valence band and the impurity band is determined to be 350 meV.

2 Dutch Summary

In deze thesis wordt het onderzoek naar de topologische isolator $Bi_2Te_2Se$ beschreven. Topologische isolatoren zijn een nieuw en actueel onderwerp in de vaste stof fysica. Een topologische isolator is een materiaal dat aan het oppervlak geleidende toestanden of banden heeft die topologisch beschermd zijn tegen terug verstrooiing maar verder overal isolerend is. Dit maakt een topologische isolator zeer interessant voor toepassingen in bijvoorbeeld kwantum computers en spintronics.

Voor dit project zijn er zogenoemde ARPES metingen verricht aan $Bi_2Te_2Se$ waar de impuls van de elektronen in een éénkristal van dit materiaal als functie van hun bindingsenergie gemeten wordt. Hiermee is het mogelijk om de bandenstructuur te bepalen dat ons informatie verschaf over de elektronische eigenschappen van dit materiaal. De techniek die hierbij gebruikt is maakt gebruik van hoekopgeloste fotoemissie waarbij monochromatisch licht op het materiaal geschenen wordt dat de elektronen exciteert welke weer gedetecteerd worden. Deze zogenoemde fotoelektronen hebben een bepaalde bindingsenergie en impuls die gemeten en berekend worden wanneer de fotoelektronen gedetecteerd worden.

Tijdens het uitvoeren van de metingen is ook de resolutie van de gebruikte detector bepaald bij een temperatuur van 17.8 K. Uit de ARPES metingen is bepaald bij welke impuls de (geleidende) oppervlakte banden het Fermi niveau raken evenals het verschil in energie tussen de valentie band en de band die naar alle waarschijnlijkheid ontstaat vanwege onzuiverheden in het materiaal.

3 Introduction

Topological insulators are a many discussed subject among physicists today. Over the past five years new theories have risen based on spin orbit interaction that can lead to topological insulating electronic phases. In short, topological insulators are materials where the bulk has the same properties as conventional insulators whereas at the surface so called (topologically protected) gapless electronic states occur, leading to electrical conduction among the surface. In search for my project to end my Bachelor of Physics and Astronomy I knew I wanted to do an experimental project. During a small project presentation for one of the third years subjects I learned about topological insulators and the FOM Amsterdam Momentum Space microscope. It did not took me very long to decide where and what project I wanted to do. For this project I have perfomed an angle-resolved photoemission experiment on the quite unknown topological insulator $Bi_2Te_2Se$ making the group I’ve worked in the second one in the world to perform these measurements on this material. This thesis contains a well elaborated theory about topological insulators and the experimental setup that I’ve been working with. In section 4.1 you will find a theoretical discription of how topological insulators are distinguished from ordinary band insulators and how they are defined. In the sections 4.2 and 4.3 some background information with reference to the experimental setup that I’ve used can be found. Section 5 is dedicated to the properties and characteristics of the experimental setup that we used for performing
4 Theory

4.1 Topological Insulators

An ordinary band insulator has a bulk energy gap that separates the empty states in the conduction band from the occupied states in the valence band. At low temperatures, the electrons cannot be excited from the valence band into the conduction band therefore no electrical conduction is possible. Topological insulators are materials that have the same bulk properties as ordinary insulators. However, its surface (or rather edge in two dimensions) has gapless electronic states that are topologically protected that do allow electrical conduction. These edge states lead to a conducting state that has properties unlike other ordinary two-dimensional systems and therefore they may be very useful for applications such as quantum computing and spintronics.

4.1.1 Band Theory

During the 20th century the band theory of solids was developed, which describes the electronic structure of states such as the insulating, semiconducting and conducting state. The electronic states are eigenstates of the Bloch Hamiltonian $\mathcal{H}(\mathbf{k})$ where $\mathbf{k}$ is the crystal momentum which is defined in a periodic Brillouin zone where $|\mathbf{k}| < \pi/a$ is the first Brillouin zone. The eigenvalues of the Bloch Hamiltonian $E(\mathbf{k})$ define the energy bands. This all is well explained by the nearly free electron theory [1] which I will not elaborate here.

In figure 1 the band structure of an insulator and of a semiconductor are depicted. These structures are different since an insulator has a larger band gap than a semiconductor but further more they are topologically equivalent i.e. they both have a conduction band, a valence band and an energy gap. Imagine a sphere representing an insulator and a cube representing a conductor both made of clay. If one wants to deform the sphere into the cube one only need to change its shape, but does not need to punch a hole in its surface. One can imagine tuning the Bloch Hamiltonian in such a fashion as to interpolate continuously between the two states, without closing the energy gap. In fact, such states are topologically equivalent.
4.1 Topological Insulators

Figure 2: Left: The integer quantum Hall state where the electrons move in quantized circular orbits. Right: The Landau levels that may be interpreted as band structure. Schematic is reproduced from [2].

to the vacuum that also has a conduction band, a valence band and an energy gap according to Dirac’s relativistic quantum theory [2]. The insulating and semiconducting state are of the same topological order, they are topologically equivalent to the vacuum and to each other. The question is, are there electronic states with an energy gap that are not of the same topological order? There are, for example the integer quantum hall state (IQHS) and the quantum spin hall state. Since topological insulators are related to the (two-dimensional) IQHS the next section will be devoted to that. After understanding the IQHS in a two dimensional system, this theory can be expanded in order to understand three dimensional topological insulators.

4.1.2 (2D) Integer Quantum Hall State

The integer quantum hall state occurs when electrons that are confined to a two dimensional plane are placed in a strong magnetic field. The electrons on the 2D plane will move in circular orbits that are quantized, known as Landau levels with energy:

\[ \epsilon_m = \hbar \omega_c (m + \frac{1}{2}) \tag{1} \]

where \( \omega_c \) is the cyclotron frequency of the orbits, see also figure 2. If \( N \) Landau levels are filled and the rest is empty then the occupied levels and the vacant levels are separated by an energy gap just as in conventional insulators. The Landau levels may therefore be interpreted as band structure. However, for the IQHS when alongside the magnetic field also an electric field is applied the circular orbits start to drift giving rise to a Hall current that is characterized by the quantized Hall conductivity given by equation 2:

\[ \sigma_{xy} = \frac{Ne^2}{h} \tag{2} \]

The difference between the IQHS and an ordinary insulating state is a matter of topology. The insulating and semiconducting state are topologically equivalent. \( \mathcal{H}(k) \) itself is characterized by the set of \( N \) occupied Bloch wavefunctions that form a vector bundle. Different vector bundles are classified by integers and are distinguished by the Chern number:

\[ n = \frac{1}{2\pi} \int d^2k \mathcal{F} \tag{3} \]

where \( \mathcal{F} \) A is Berry’s curvature and equations (3) itself may be interpreted as the Berry’s phase, which is an integer. The Chern number \( n \) is a topological invariant since it cannot change if \( \mathcal{H}(k) \) is varied smoothly. TKNN [5] showed that \( N \) in (2) is of the same form of \( n \) in equation (3). To understand this better, consider two dimensional structures that are topologically described by their genus that counts the number of holes in a surface. A sphere has \( g = 0 \) and a doughnut or torus has \( g = 1 \). For analogy, the insulating state is
4.1 Topological Insulators

4.1.3 Edge states

I have mentioned earlier that topological insulators have edge states that are topologically protected. For analogy, consider figure 3, somewhere along the way from trivial insulator \((n=0)\) to a quantum Hall state \((n=1)\) the energy gap has to go to zero. Therefore, low energy electronic states occur that are bound to the region where the energy gap goes to zero. The cyclotron orbits of the electrons will bounce of the edge, where these low energy electronic states are, leading to skipping cyclotron orbits that propagate in only one direction along the edge. Because of the skipping motion of the cyclotron orbits a chiral edge state is formed that connects the conduction band with the valence band. These edge states are insensitive to disorder since there are no states available that provide backscattering therefore these states are topologically protected.

The Hall conductivity (equation 2) is odd under time reversal symmetry meaning that the edge states can only occur when time symmetry is broken. However, for topological insulators this is not the case i.e. time symmetry does not need to be broken. The time reversal symmetry puts a constraint on the Bloch Hamiltonian:

\[
\Theta H(k) \Theta^{-1} = H(k)
\]

where \(\Theta^{-1} = e^{iS_y \pi / \hbar}K\), \(S_y\) is the Pauli spin matrix and \(K\) is complex conjugation. For fermions \(\Theta\) has the property \(\Theta^2 = -1\) which leads to Kramers theorem and an important constraint: all eigenstates of a time reversal invariant Hamiltonian must be at least two fold degenerate. In the absence of spin orbit interaction this degeneracy is the degeneracy between spin up and spin down. However, spin orbit interaction present in topological insulators leads to the splitting up of the edge states, one for spin up and one for spin down. In the presence of edge states, Kramers theorem requires that the spin up and down bands are two fold degenerate at the time reversal invariant momenta \(k=0\) and \(k=\pm \pi a\) and therefore must cross each other. The point where the bands cross is called Kramers point. There are two possible ways for the \(k=0\) and \(k=\pi a\) points to connect. In figure 4a the bands intersect the Fermi energy twice and for figure 4b once. The difference between these two configurations is defined by the topological invariant \(Z_2\). Non-trivial \(Z_2\) invariants imply the existence of gapless surface or edge states. In two dimensions topological invariance is distinguished using one invariant which is \(\nu\), that can be either 0 or 1 meaning that the bands intersect the Fermi energy an even or an odd number of times. In the case of \(\nu = 0\) it is possible to eliminate the surface states by pushing all of the edge states out of the energy gap. If \(\nu = 1\) however, this is not possible which leads to topologically protected edge states. Now we understand what a topological invariant means we expand this to three dimensions where a time-reversal invariant band structure is characterized by four \(Z_2\) invariants.

\(^1\)Whether it is \(\pm \pi a\) or \(-\pi a\) does not matter.
4.1 Topological Insulators

4.1.4 $Z_2$ invariant in three dimensions

The four $Z_2$ invariants are denoted by $\nu_0$, $\nu_1$, $\nu_2$ and $\nu_3$ where $\nu_{1,2,3}$ rely on the translational symmetry of the lattice and are not robust in the presence of disorder. However $\nu_0$ is robust and distinguishes strong from weak topological insulators. L. Fu and C.L. Kane [3] showed that the $Z_2$ invariants can be determined from the parity eigenvalues of the occupied band eigenstates at the eight (see figure 5) time reversal invariant momenta $\Gamma_i^{\text{III}}$ in the Brillouin zone. The parity eigenvalue $\xi_{2m}(\Gamma_i)^{\text{IV}} = \pm 1$ of the $2m^{\text{th}}$ occupied energy band at $\Gamma_i$ is given by

$$\delta_i = \prod_{m=1}^{N} \xi_{2m}(\Gamma_i)$$

In two dimensions there is one $Z_2$ invariant $\nu$, which is determined by calculating the product over all $\delta_i$’s corresponding to the four time reversal invariant momenta,

$$(-1)^\nu = \prod_{i=1}^{4} \delta_i$$

whereas in three dimensions there are eight time reversal invariant points leading to four $Z_2$ invariants. $\nu_0$ can be determined by calculating the product over all eight $\Gamma$ points,

$$(-1)^{\nu_0} = \prod_{i=1}^{8} \delta_i$$

The parity eigenvalues are tabulated in band theory literature and therefore one can calculate if a material will predict to be a (strong) topological insulator. Zhang et al. [4] have followed the method proposed by Fu and Kane and stated that one has to search for insulators where the conduction band and the valence 

\[\text{II}\]
\[\text{III}\]
\[\text{IV}\]

\[\text{VI}\]
\[\text{VII}\]
\[\text{VIII}\]

\[\text{IX}\]
\[\text{X}\]
\[\text{XI}\]
\[\text{XII}\]

\[\text{XIII}\]
\[\text{XIV}\]
\[\text{XV}\]
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\[\text{XVII}\]
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\[\text{X}\]
4.1 Topological Insulators

Figure 6: Schematic showing the evolution of the $p$ orbitals of Bi and Se in $Bi_2Se_3$ at the $\Gamma$ point. The dotted line indicates the Fermi level. The stages (I), (II) and (III) represent the effect of chemical bonding, crystal-field splitting and spin-orbit coupling respectively. Since the states near the Fermi surface mainly come from $p$ orbitals, the $s$ orbitals are neglected [4].

band have opposite parity due to spin-orbit coupling effects. Such a band inversion occurs when the spin-orbit coupling is strong and will occur at the $\Gamma$ point. For clearance, consider figure 6 where the effect of chemical bonding, crystal-field splitting and spin-orbit coupling on the energy eigenvalues at the $\Gamma$ point is schematically depicted in three steps where eventually the order of the energy levels is reversed due to the spin-orbit coupling.

In stage (I) the chemical bonding is considered between the Bi and Se atoms which is within the quintupleV layer unit of Te-Bi-Se-Bi-Te. The Bi and Se $p$ orbitals are recombined with respect to their parity which results in two states for Bi and three states for Se. The chemical bonding leads to the hybridization of these five states, pushing the Bi states up and the Se states down. The states are indicated as $|P_0^{xyz}\rangle$, $|P_1^{+}\pm xyz\rangle$ and $|P_2^{\pm}\pm xyz\rangle$ in figure 6 where the + and - indicate the parity.

In stage (II) only the states that are closest to the Fermi energy are taken into account since they are of interest with respect to the state inversion. Due to the effect of crystal-field splitting, the $p_z$ orbital is split from the $p_{xy}$ orbitals into the states $|P_1^{+}z\rangle$ vs. $|P_1^{-}z\rangle$ and $|P_2^{+}z\rangle$ vs. $|P_2^{-}z\rangle$. The $p_{xy}$ orbitals do not split up since they remain degenerate. It turns out to be that after the splitting the $|P_1^{+}z\rangle$ and $|P_2^{-}z\rangle$ states are closest to the Fermi energy [4].

In stage (III) the spin-orbit coupling is taken into account. The spin-orbit coupling Hamiltonian, $\hat{H}_{so} = \lambda \mathbf{L} \cdot \mathbf{S}$ mixes the orbital and spin angular momenta $\mathbf{L}$ and $\mathbf{S}$ while preserving the total angular momentum. This leads to the repulsion between the states $|P_1^{+}z, \uparrow\rangle$ and $|P_1^{+}z, \downarrow\rangle$ (and also between states with similar configuration) pushing the $|P_1^{+}z, \uparrow\rangle$ and $|P_1^{+}z, \downarrow\rangle$ down and the $|P_2^{-}z, \uparrow\rangle$ and $|P_2^{-}z, \downarrow\rangle$ up. If the spin-orbit coupling is large enough, these states are reversed. Equation 5 is the product of all $\xi_{2m}(\Gamma_{i})$’s that are the parity eigenvalues of the occupied energy levels. In figure 6 we see that due to the reversal of the $|P_1^{+}z, \uparrow\rangle$ and $|P_2^{+}z, \uparrow\rangle$ states the parity of the level directly below the Fermi energy has changed from - to +. If the two inversed levels have opposite parity then swapping them will drive the system into the topological insulating phase according to equations 5 and 7 which determine $\nu_0$.

In figure 7 the parity values of the highest 14 bands below the Fermi energy are listed for $Sb_2Se_3$, $Sb_2Te_3$, $Bi_2Se_3$ and $Bi_2Te_3$. According to equations 5 and 7 we should be able to determine from the product of all parities if the listed materials will (probably) be topological insulators. This means that $Sb_2Se_3$ should be a trivial insulator and that the other three are strong topological insulators.

V Quintuple here means that the atomic layers form a fivefold ‘basic unit’ which repeats itself to build up the crystal.
4.2 PES and ARPES

4.2.1 Photoemission spectroscopy

Photoemission spectroscopy (PES) is based on the photoelectric effect. Electromagnetic radiation of a small wavelength - some Å - is used to excite electrons in order to be emitted from the surface of a sample. These electrons may be referred to as photoelectrons. A schematic of the photoelectric effect is depicted in figure 8. Photoelectric emission can be performed on gases and polycrystalline solids (even on liquids under particularly circumstances) however since we are dealing with topological insulators we will concentrate mainly on photoelectric emission from crystalline solids. The photoelectrons that are emitted from the surface can be detected and their kinetic energies can be measured (see section 5). For the kinetic energy, equation (8) holds:

$$E_k = h\nu - E_B - \Phi$$

Where $h\nu$ is the energy of the incoming photon, $h$ stands for Planck’s constant and $\nu$ is the frequency of the light wave, $E_B$ is the binding energy of the electron and $\Phi$ is the workfunction. The workfunction is a surface potential barrier the electron has to overcome in order to be emitted from surface. In practice $\Phi$ is the workfunction of the electron analyser rather than the workfunction of the sample being used and is determined with reference measurements such as those showed later in figure 18.

The energy of the incoming photons is known since it only depends on what source of energy is used e.g. a röntgen source or helium lamp so what one need to know is the binding energy. Calibration of the binding energy is carried out by measuring the Fermi edge of a metal, such as gold. By definition, the mid-point of the Fermi edge of a metal has a binding energy of zero.

4.2.2 Angle resolved photoemission spectroscopy

If alongside the kinetic energy also the emission angle of the photoelectrons is measured, one is performing an angle resolved photoemission spectroscopy (ARPES) experiment. When an electron is excited and being
4.3 Low-Energy Electron Diffraction

When an electron is emitted from the solid surface, the crystal momentum \( \mathbf{k} \) remains unchanged. In this picture, the electron analyser used for the ARPES experiment is included.

Transferred across the surface of the polycrystalline solid its momentum \( \mathbf{p} \) in direction parallel to the surface is conserved. Between the momenta of the photoelectron and the crystal the following relationship holds:

\[
\mathbf{p}_\parallel = \sqrt{2m \cdot E_k \cdot \sin \theta} = \hbar \mathbf{k}_\parallel
\]

The crystal momentum parallel to the surface of the solid remains unchanged meaning the internal crystal momentum equals the external crystal momentum (see also figure 9):

\[
\mathbf{k}_{\parallel, \text{int}} = \mathbf{k}_{\parallel, \text{ext}}
\]

Thus, conservation of the electron’s momentum holds only in the direction parallel to the surface of the solid. This means that for \( \mathbf{k}_\parallel \) it is the case that only \( k_x \) and \( k_y \) are conserved where:

\[
\mathbf{k}^2 = k_x^2 + k_y^2 + k_z^2
\]

and

\[
k_z = \frac{1}{\hbar} \cdot 2m \sqrt{E_k \cdot \cos^2 \theta + V_0}
\]

\( V_0 \) in equation 12 is the surface potential step felt by the electron upon crossing the surface which is generally unknown. Determining \( k_z \) is in general laborious and therefore ARPES is mainly performed on compounds that have a highly two-dimensional electronic (surface) structure such as topological insulators.

4.3 Low-Energy Electron Diffraction

In FAMoS low-energy electron diffraction (LEED) is used to determine the crystal orientation and the quality of the cleaved surface. A beam of low energy electrons impinges on the surface of the sample, that have a kinetic energy of typically 20 - 400 eV. The incoming electrons are diffracted i.e. they scatter upon the atoms in the crystal lattice so they can be considered as waves. These waves interfere with each other so they obey Bragg’s law given by:

\[
n \lambda = 2d \sin \theta
\]

where \( n \) is an integer, \( \lambda \) is the wavelength, \( d \) is the spacing between two adjacent planes and \( \theta \) is the angle between the lattice planes and the incoming electron beam. The scattered waves interfere with each other creating minima and maxima and therefore show a pattern which can be visualized using for example a phosphor screen and a CCD camera. For crystal orientation the LEED spots need to be oriented such that they have an equal distance to the edge of the screen. In this manner the \( \Gamma \) point in \( \mathbf{k} \)-space is in front
Figure 10: Photo’s of a LEED pattern recorded during measurement on Bi$_2$Te$_2$Se which has a hexagonal crystal structure. The CCD camera is positioned behind the LEED gun thus we can see the shadow of the gun in the pictures. (a-c) Different voltages were applied: 227 V, 267 V and 338 V respectively where at higher energies more maxima can be seen.

Figure 11: A schematic of a (100) face of a cubic crystal structure and the corresponding LEED pattern in k-space where the planes upon which the electrons are scattered are indicated. The spots are indexed according to the values for $h$ and $k$ (which are orthogonal to $l$), therefore only these two Miller indices are given. [7]

of the electron analyser during measurement (since the LEED camera and the electron analyser are equally aligned).

Since the electrons have low energies they do not penetrate very deep into the crystal. This means that it gives an indication of the atomic positions only near the surface which is exactly what you want for an APRES experiment. The LEED pattern thus shows a two dimensional structure of the surface. If you increase the energy of the electrons, they will have a shorter wavelength. This means that according to equation 13, the angle $\theta$ - between the planes and the electron beam - becomes smaller and the maxima will shift towards each other. In figure 10 photo’s of the LEED pattern recorded when performing a measurement on Bi$_2$Te$_2$Se which has a hexagonal crystal structure, at different energies are depicted where at higher energies more maxima are visible.

Since one sees the maxima of the diffracted waves on the screen one sees the reciprocal lattice of the crystal (see figure 11). If it is a poor cleave it means that the planes upon which the electrons are diffracted are of unequal height leading to more blurry spots instead of nice sharp ones, or even no spots can be seen at all. In this way one can determine the quality of the cleaved surface and determine if doing an ARPES measurement on the sample is meaningful.

5 An experimental setup: FAMoS

A typical experimental setup for performing (AR)PES is FAMoS$^\text{VI}$ at the Van der Waals-Zeeman Institute in Amsterdam. Figure 12 shows the most important parts of FAMoS. Ultra high vacuum$^\text{VII}$ (UHV) conditions are necessary since we want to avoid contaminants adsorbing onto the sample’s surface when performing an ARPES experiment in order to maintain the validity of equation 8, which depends on the constant potential barrier near the surface (i.e. the potential barrier should not change within the time spectrum of

$^\text{VI}$FAMoS stands for FOM Amsterdam Momentum Space microscope
$^\text{VII}$Pressures smaller than $10^{-10}$ mbar
5.1 Environmental conditions

There are several requirements that must be satisfied in order to reach sufficient experimental conditions. I will not discuss all of them, only the main important ones. To begin with, application of external magnetic fields such as the earth’s magnetic field must be avoided from the electron analyser and the main chamber. To do so, close to the sample and the analyser entrance materials that can be magnetized must be avoided. Allowed materials for sample holders and stages are titanium, copper and tantalum. All the (experimental) chambers are made of stainless steel since stainless steel does not oxidise, stain, corrode or rust as easy as ordinary steel.

A number of different pumps such as cryopumps\textsuperscript{VIII}, ion-getter pumps\textsuperscript{IX} and turbo-molecular pumps\textsuperscript{X}, are adjoined to the experimental chambers and are continuously operative to remove any unwanted gases and vapours. Also, the load lock can easily be vented for sample replacement and can afterwards be pumped down again to $10^{-8}$ mbar.

All the chambers should be free of all unwanted gases and/or other molecules in order to reach UHV. Therefore, all components that are inside the vacuum should be free of fat, oil and other contaminations of this sort. Rubbers and most plastics are not allowed. If for any reason one of the experimental chambers needs to be vented and opened up, it is most probable that after closing again some water molecules stay behind (due to air contact), condensing onto the inside walls. These cannot be removed using the pumps (while the water molecules are not gassous) therefore we cover the contaminated parts up with heating tape wrapped in aluminium foil and perform a bake-out. The heating tape is gradually set at a temperature of 140 degrees Celsius. This allows the water molecules to pass over to the gas phase, desorbing from the chamber walls so they can be removed by the pumps.

The sample is glued to a sample holder made of copper. Copper is not magnetizable and has a high thermal conductivity so as to aid sufficient cooling of the sample using the liquid helium cooled cryostat. In our case, to glue the samples use is made of silver-loaded epoxy. It is important that during measurement the electrons being emitted from the sample are replaced. Surely, we want to achieve an image of the electronic

\textsuperscript{VIII} Cryopumps trap gases by condensing them on a cold surface. Therefore they must be cooled by in our case compressed helium.

\textsuperscript{IX} An ion pump ionizes gases and applies a strong electrical potential to accelerate them into a solid electrode.

\textsuperscript{X} A molecular pump uses a high speed jet or blade to knock unwanted gaseous molecules out of the working environment.
distribution near the Fermi level and achieve an image of the band structure. If the bands become vacant due to the loss of electrons it would lead to unreliable data. Therefore it is important that the substance that is used to glue the sample to the sampleholder and the cleavage post onto the sample is conducting. A clean and flat sample surface is prepared through cleavage in the preparation chamber in vacuum. As a preparation, a cleavage post is glued onto the surface of the sample and is supposed to create enough leverage that when the cleavage post is removed\textsuperscript{XI}, it takes the top layer of the crystal with it leaving a clean, single crystalline surface behind.

5.1.1 Au reference

When performing an (ARPES) measurement, some background noise will be present and some errors may occur. This can be the consequence of thermal vibrations, an imperfect crystal lattice at the sample surface as a result of a poor cleave and/or the inhomogeneity of the detector. To correct for the inhomogeneity of the detector one needs to normalise the ARPES data using a gold spectrum. Since we know how the spectrum of gold must look like, we also know exactly where the Fermi level lies and thus where the Fermi level should be at the diagram showing the band structure of the sample. Thus as mentioned before, calibration via the Fermi-edge of a metal is necessary, for which we use gold. Therefore before cleaving, gold is evaporated on the surface of the sample holder (and the cleavage post).

5.1.2 The most important parts of FAMoS

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{famos_diagram.png}
\caption{A schematic of FAMoS showing the most important parts. The impinging photons which energy $h\nu$ are indicated by the red arrow. The sample position is indicated with a capital 'S' and the electrons that enter the analyser are indicated with a black arrow \cite{8}.}
\end{figure}

A schematic of FAMoS where the most important parts are depicted can be seen in figure 13. The preparation chamber and the main chamber are colored in white. In the preparation chamber the sample holder transfer takes place and in the main chamber the actual measurements are done. Behind the prep. chamber (on the left side) the loadlock that contains the sample holders is situated, which is not included in this schematic. When a sample holder is transferred, the prep. chamber and the main chamber are isolated from each other by a valve. This valve is protected by a shutter that is supposed to catch a sample holder if it drops down.

\textsuperscript{XI}One uses a wobble stick to gently tick off the cleavage post
5.2 The electron analyser

An important part of the FAMoS setup is the electron analyser which is in our case a hemispherical version\textsuperscript{XII}, as can be seen in figure ??\textsuperscript{XII}. How ARPES in FAMoS works is schematically depicted in figure 14. After the photoelectrons are excited from the surface they first pass through a set of lenses. These lenses assure that their velocity or rather their kinetic energy is retarded to a nominal energy called the pass energy or $E_{\text{pass}}$. This is done by varying the different potentials that are applied on the different lens elements. Also, to assure that the whole range of desired energies is measured - because the kinetic energy range is approximately 8% of the pass energy, for example at $E_{\text{pass}} = 5$ eV the window is 500 meV wide - the spectra are usually recorded in ‘swept mode’. This means that the pass energy is kept constant while the lens voltages are changed step-wise in order to ensure that the whole desired energy range is achieved.

When doing ARPES, one measures in ‘angular mode’. When the photoelectrons pass the lens elements they are radially separated by their emission angle. After passing the lens elements, the photoelectrons pass through a slit and enter the hemispherical trajectory of the electron analyser. The width of the slit can be varied which determines the resolution in energy. The more narrow the slit width the higher the resolution but also the lower the count rate.

The hemispherical trajectory consists actually of two hemispheres where the photoelectrons pass them in between. Upon the inner hemisphere a positive potential and on the outer hemisphere a negative potential is applied. In this way the energy selection takes place. Photoelectrons that have a kinetic energy which

\begin{figure}[h]
\begin{center}
\includegraphics[width=0.45\textwidth]{figure14a.png} \hspace{0.5cm} \includegraphics[width=0.45\textwidth]{figure14b.png}
\end{center}
\caption{(a) Schematical overview of how angle resolved photoemission works. The electron are being excited from the example under an angle $\theta$ where after excitation they enter the electron analyser. There they follow the hemispherical trajectory (indicated in yellow) by which they are being detected at the end [6]. (b) A schematic of the electron analyser. The photoelectrons pass the lens elements when entering the analyser. They pass through a slit and enter the hemispherical part of the analyser. At the end of this trajectory a field termination mesh separates the end of the analyser from the electron multiplying multichannel plates (MCPs). After the MCPs a phosphor screen is placed and a CCD camera [8].}
\end{figure}

\textsuperscript{XII}There are different types of electron analysers but the most common type for high resolution performance of (AR)PES is the hemispherical one
5.3 The Adam-III manipulator

The Adam-III manipulator has three translational degrees of freedom and the sample can be rotated around three axes as can be seen in figure 15a. The X and Y directions can manually be adjusted at the XYZ stage as is depicted in figure 15b, where the positions have to be verified by sight. The remaining directions (Z, polar, azimuth and tilt) are altered by using a joy stick where the positions are read with a 0.1 accuracy using the stepper motor controller.

## 5.3.1 Transferring a sample holder

New sample holders are placed and loaded in and from the loadlock. From the loadlock the sample holder must be placed into the manipulator. This goes by a number of steps. To begin with, the sample holder must be picked up from the loadlock with an extendable arm (see figures 16a-c). From there, the arm is retracted as far as the preparation chamber. By using a wobble stick (see figure 16d) the sample holder is picked up from the arm and placed into the manipulator. The sample holder is held in place by a little screw that is tightened up by using the other end of the wobble stick. Hereafter, the manipulator can be lowered into the main chamber where the actual measurement takes place.
6 Results & Discussion

In section 4 real three dimensional TI materials have been introduced such as $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_2\text{Se}_3$ where they were determined by theory to be strong topological insulators. In theory, three dimensional topological insulators are insulating in the bulk and have unusual metallic surface states that realize interesting surface transport properties. To make use of these properties it is important to search for topological insulators that show bulk insulating behaviour where the surface for the most part contributes to the total transport. Among recently discovered topological insulators, $\text{Bi}_2\text{Se}_3$ is the most attractive one because of its simple surface state structure. Nevertheless, for $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_2\text{Se}_3$ the bulk has essentially metallic properties where the surface contribution to the transport remains quite low. Thus searching for a topological insulator better suited for achieving an insulating bulk state is obviously desirable. Ren et al. [10] reported that the new three dimensional topological insulator $\text{Bi}_2\text{Te}_2\text{Se}$, that was recently confirmed to have topological protected surface states, has promising characteristics suited for better surface transport. Therefore section 6.1 contains data from Ren et al. obtained by measurements performed on $\text{Bi}_2\text{Te}_2\text{Se}$ where in section 6.3 the ARPES data obtained during this research project is discussed and in section 6.2 the resolution determination for FAMoS is discussed.

6.1 Previous research on $\text{Bi}_2\text{Te}_2\text{Se}$

Figure 17a shows the plot of a measurement of the conductivity $\sigma_{xx}$ versus the temperature T performed by Ren et al. We can see that at a low temperature the conductivity goes to a fixed value. A low resistivity (or high conductivity) indicates that a material allows the movement of electric charge. The inset shows the Arrhenius plot of the resistivity $\rho_{xx}$ where we can see that at low temperatures the resistivity saturates which implies a finite metallic conductivity at T=0.

Ren et al. observed a relatively large concentration of acceptors, of around $9 \cdot 10^{18}\text{ cm}^{-3}$ that most likely form an impurity band inside the energy gap which is probably also responsible for n-type bulk conduction at zero temperature. In figure 17b a schematic shows the surface states and band structure. The impurity band is denoted in yellow.

For the TI materials $\text{Bi}_2\text{Te}_3$ and $\text{Bi}_2\text{Se}_3$ the bulk remains to be essentially a metal while one wants to achieve a bulk-insulating state to exploit the surface transport properties. D. X. Qu et al. [11] found that for $\text{Bi}_2\text{Te}_3$ it was possible to observe a resistivity upturn at low temperature and to measure the surface quantum transport but the resistivity remained low and the surface contribution to the transport did not exceed $\sim 0.3\%$ and the same holds for $\text{Bi}_2\text{Se}_3$ [12–15]. However, Ren et al. found that for their $\text{Bi}_2\text{Te}_2\text{Se}$

\text{XIII} VRH stands for variable range hopping which is a model that describes low T conduction in disordered systems with localized states.

\text{XIV} An Arrhenius plot is designed to determine the size of an activation energy gap, in this case $\Delta$. 

Figure 16: Photo’s of the end of the arm with which a sample transfer is performed. Here an empty sample holder is used as an example. (a) The sample holder must be shifted into the sideways extendable arms using the wobble stick (which is not included here). (b) If the sample holder is in place, the wobble stick must be removed, leaving the sample holder in the arm. (c) Top view for clarity. (d) The wobble stick, which is used to pick up the the sample holder and to place the sample holder into the manipulator after which it is screwed into its position.
6.2 Resolution determination for FAMoS

In order to determine the resolution of the electron analyser, a high resolution measurement on isotropic emitting gold is performed as can be seen in figure 18a. For the determination of the resolution use is made of the full width at half maximum (FWHM) expression. This is the difference between two extreme values of the binding energy at which the intensity is equal to half of its maximum value. To determine the resolution one takes all vertical slices of the recorded spectrum and sums them up (see figure 18b). One determines the intensity at 90% and at 10% of the transition indicated in figure 18c with the green markers, where the difference between the two will give the resolution in meV. The resolution of the measurement in figure 18c has been determined to be 7.5 meV however there is still a broadening of the Fermi step present due to the finite temperature used during this experiment with a value of ∼ 4 k_B T = 6 meV. By making use of the following equation we can determine the resolution of FAMoS:

\[(\Delta E_{total})^2 = (\Delta \text{FAMoS})^2 + (\Delta E_{FD})^2\]  

where \((\Delta \text{FAMoS}) = 4.5\) meV.

6.3 ARPES measurements of Bi_2Te_2Se

In figure 19 the ARPES measurements performed on Bi_2Te_2Se are depicted. The gold reference scan recorded soon after these data was not of the highest signal to noise ratio, making the determination of the Fermi level position less accurate than is the case with data such as those shown in figure 18. Consequently, the binding energy scale in figure 19 is a good indication, but should not be seen as being as accurate as can possibly be the case. Nevertheless, there are some interesting aspects to be seen. Firstly, as is shown...
6.3 ARPES measurements of Bi$_2$Te$_2$Se

RESULTS & DISCUSSION

Figure 18: (a) Measurement of a gold spectrum at $T = 17.8$ K, with a pass energy of 2 eV, a slit width of 0.2 $\sim$ and taking 0.4 meV steps. We can see that at the Fermi level the transition is quite narrow. A more narrow transition will give a better resolution. (b) Summation of all vertical slices. (c) One vertical slice of the summed gold spectrum showing the binding energy vs the intensity. The solid lines indicate the fitting of the slopes where the green marks indicate the positions where the intensity is at 90% and 10% of the transition.

in figure 19, the topologically protected surface states displaying a linear $E_k$ dispersion relation are visible in the data, highlighted with a red solid line as a guide to the eye. This means that the global aim of the project which is to observe the Dirac quasiparticles in the new topological insulating system Bi$_2$Te$_2$Se, has been realised. Further more, the Dirac bands intersect the Fermi level at $0.13 \frac{\pi}{a}$ which is in good agreement the only known ARPES data from this compound, in the paper from Su-Yang Xu et al. [16] who found this to be $0.14 \frac{\pi}{a}$. Secondly, the top of the bulk valence band states are also visible - highlighted in figure 19a with a blue box - showing that the schematic shown in figure 17b from [10] is, in fact, a reasonable description of the real experimental solution. From previous measurements done in this group it is reasonable to assume that the band indicated with the red oval in figure 19a is the impurity band. In [10], Ren et al. state that the energy gap is approximately 300 meV large and the distance between the valence band and the impurity band is around 30 meV wide. However, the energy gap between the valence band and the upper band in figure 19a indicated with the black arrow is more than a factor 10 larger (approximately 350 meV). So either the data from Ren et al. with regard to the energy gap between the valence band and the impurity band does not agree very well with these measurements, or the assumed impurity band in figure 19a is not the impurity band but the conduction band which means that the values for the energy gap actually do agree quite well.
7 Conclusion

In the introduction it was mentioned that one of the main goals of this project was to learn how to work with the FOM Amsterdam momentum space microscope. During my project I have learned how to operate the FAMoS and how to perform an ARPES measurement. I have mounted and loaded single crystals of the topological insulator $\text{Bi}_2\text{Te}_2\text{Se}$ for ARPES and LEED experiments and done a preliminary analysis on the data achieved from the measurements. Section 5 gives a good overview of the ins and outs of the experimental setup and this, combined with my hands-on skills with the FAMoS instrument itself shows that this goal have been achieved. As for the resolution determination of FAMoS, I determined the resolution to be 7.5 meV which is a very good result. This indicates that FAMoS is still operating very well, after having been moved from the Valckenierstraat to the Science Park.

From the data achieved from measurements performed on $\text{Bi}_2\text{Te}_2\text{Se}$ one can clearly see the Dirac cone that intersects at the Fermi level at $0.13 \frac{\pi}{a}$ which agrees very well with results published by Su-Yang Xu et al. The energy gap between the valence band and what is strongly believed to be the impurity band is approximately 350 meV which is more than a factor 10 larger compared to results published by Ren et al. Thus either the data from Ren et al. does not agree with the ARPES measurements performed on $\text{Bi}_2\text{Te}_2\text{Se}$ or what is thought to be the impurity band is actually the conduction band, meaning more research is called for here. The main conclusion that can be made is that we have succeeded - as only the second group worldwide - to observe the topologically protected surface states of the new and highly promising three dimensional topological insulator $\text{Bi}_2\text{Te}_2\text{Se}$, which is a very good result.

For future research high resolution measurements performed on $\text{Bi}_2\text{Te}_2\text{Se}$ with a good gold reference would be desirable. It would be interesting to find out whether the additional, parabolic shaped band we see is actually an impurity band or is due to the occupation of the bulk conduction band. In order to do this one could measure ARPES spectra at different photon energies to examine the $k_z$ dependence. The impurity band should not show a $k_z$ dispersion and will not deform as a function of photon energy where the conduction band on the other hand should show some photon energy dependence.

Figure 19: ARPES measurements on $\text{Bi}_2\text{Te}_2\text{Se}$. (a) Measurement performed at a temperature of 20K at a pass energy of 5 eV, with a slit width of 0.3 $\mu$m and taking 3.3 meV steps. (b) The same measurement as (a) but without the indications. (c) Measurements performed on the same sample at a temperature of 34.4 K, at a pass energy of 10 eV, with the same slit width and taking 5 meV steps.
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