

Magnetic Order in Three-Dimensional Topological Insulators



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Abstract

Topological insulators, a type of quantum material, are of intense interest to researchers due to their ability to house time reversal symmetry protected, gapless, linearly dispersed surface states, offering dissipationless conductivity. Through the introduction of magnetic dopants or proximity coupling which induces long-range ferromagnetic order, time reversal symmetry can be broken, introducing a band gap in the surface state. This has led to the experimental observation of exotic quantum effects such as the quantum anomalous Hall (QAH) effect which does not require an externally applied magnetic field in order to be realised and is the anomalous counter part to the quantum Hall (QH) effect. However, the QAH effect has only previously been observed in magnetic topological insulators (MTI) at sub mK temperatures, limiting the application potential of these extremely promising materials.

This thesis presents an investigation into the structural and magnetic properties of 3D MTI thin films grown by molecular beam epitaxy (MBE) using reflection high energy electron diffraction (RHEED), X-ray reflectometry (XRR), X-ray diffraction (XRD), vibrating sample magnetometry (VSM), X-ray absorption spectroscopy (XAS), X-ray magnetic circular dichroism (XMCD) and polarised neutron reflectometry (PNR). The element specific magnetometry of XMCD and magnetic depth profiling capabilities of PNR allows for an in-depth investigation of the different magnetic coupling scenarios which occur in magnetically doped samples as well as magnetic enhancements caused by proximity coupling and interface effects in MTI heterostructures.

Firstly, an investigation of single-layered TI thin films and the effects of using different magnetic dopants in the form of the transition metal Cr and the rare earth Dy ions is presented. Using Cr as a dopant in Sb_2Te_3 is shown to produce samples of a high structural quality with long-range ferromagnetic order which persists up to a $T_C \approx 120$ K. XRD, XAS and

XMCD measurements demonstrate that Cr substitutionally replaces Sb during growth. PNR measurements demonstrate an equal distribution of Cr throughout the sample with no surface enhancement. XMCD measurements demonstrate that the long-range ferromagnetic order is caused by a carrier-mediated coupling mechanism where the exchange interaction is mediated by polarised Te valence holes, leading to the formation of Cr $3d$ impurity bands near the Fermi level, which is detrimental to the observation of the QAH effect.

Using a Dy dopant with Bi_2Te_3 leads once again to a sample of high structural quality. VSM and XMCD measurements demonstrate that there is no long-range ferromagnetic order induced. PNR measurements combined with Muon spin relaxation measurements show that the Dy dopant leads to a system which displays short-range ferromagnetic order within patches of the material where a large internal magnetic field can be induced at moderate applied fields. Unlike in the case of Cr-doped Sb_2Te_3 , the exchange interaction in the sample is not mediated by the conduction band, as demonstrated by XMCD. In an attempt to enhance the magnetic properties of an MTI system, two transition metal dopants Cr and V are used to codope Sb_2Te_3 . This leads to the formation of Cr_2Te_3 within the sample which is caused by the V acting as a surfactant which prevents the Cr from substitutionally replacing Sb within the MTI structure as demonstrated by XRD, XAS and XMCD measurements.

The previous studies conducted on the single layer MTI samples are then used to inform the fabrication of MTI heterostructures in an attempt to investigate proximity coupling and interface effects in multilayer structures. Growing a ferromagnetic Co layer on top of $\text{Cr:Sb}_2\text{Te}_3$ demonstrates the strength of the long-range ferromagnetic order, where Co is unable to polarise the Cr moments contained within the MTI to a significant degree, as demonstrated by Arrott plots which show that the single layer $\text{Cr:Sb}_2\text{Te}_3$ with a T_C of 86.7 K is only minimally enhanced to 92.7 K after the deposition of ferromagnetic Co.

Producing high quality heterostructures consisting of multiple bilayers of $\text{Cr:Sb}_2\text{Te}_3/\text{Dy:Bi}_2\text{Te}_3$ with well defined interfaces leads to the enhancement of the magnetic properties of the $\text{Dy:Bi}_2\text{Te}_3$ layers, where XMCD measurements show that they demonstrate ferromagnetic behaviour up

to a temperature of 17 K as determined by Arrott plots. XMCD measurements demonstrate that despite single layer Cr:Sb₂Te₃ and Dy:Bi₂Te₃ having an easy axis of magnetisation perpendicular to one another, the average Cr and Dy moments contained within the structure are parallel out-of-plane, demonstrating that the dopants magnetically couple.

This research demonstrates the possibility of enhancing MTI systems through the use of magnetic heterostructures. It also shows how XMCD and PNR are powerful techniques for gaining insight into the magnetic properties of such systems in order to understand how these materials can be both utilised and enhanced to further the field of MTIs in the pursuit of a QAH effect realised in a device friendly scenario.

To my dearest Elizabeth,
for allowing me to share every adventure
with you.

“Who is the more foolish? The fool or the fool who follows him?”
- Obi Wan Kenobi, A long time ago in a galaxy far, far away...

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Chapter 1

Introduction

In 1965, Gordon Moore wrote an essay in which he predicted that the number of transistors and other electronic components existing on a microprocessor chip, the heart of computing technology, would double every year [17]. Moore’s ‘law’, which was later revised in 1975 to a more realistic doubling every two years, has come to define the advancement of computing technology for over 50 years [18]. In the early 2020s, it is predicted that the continued scaling-down of the transistor will be no longer possible with the electron behaviour of silicon being governed by quantum uncertainties at the 2-3 nm limit, leading to the end of the rate of technological advancement defined by Moore’s ‘law’ [19]. To continue to advance the power of microprocessors despite these issues, it is important to consider the use of new quantum computational devices or spintronic materials, which can not only be scaled down to much smaller levels, but can also reduce the amount of heat generated by their components.

In 2016, the Nobel Prize in Physics was awarded to David Thouless, Duncan Haldane and Michael Kosterlitz for theoretical discoveries of topological phase transitions and topological phases of matter. One of these new topological phases of matter is the topological insulator (TI), an experimentally realised quantum material which is of intense interest to the condensed matter physics community as it houses topo-

logically protected, conducting and dissipationless surface states. These topological surface states (TSS) consist of separated spin-up and spin-down electron channels with spin momentum locking properties that are protected from backscatter events by time reversal symmetry (TRS). TIs are therefore the perfect material for use in the creation of spintronic or dissipationless transport devices required by modern advancements in technology.

By inducing long-range ferromagnetic order in the TI through the use of magnetic doping or proximity coupling, TRS can be broken and the usually gapless TSS can be made to have a gap a few meV in size, the so-called magnetic topological insulator (MTI). This has lead to the experimental observation of exotic quantum phenomena such as the quantum anomalous Hall (QAH) effect, a quantised version of the anomalous Hall (AH) effect, which has only a single spin quantised Hall conductance channel unlike the quantum Hall (QH) effect which demonstrates two. This can be realised without the need for the application of high magnetic fields. Achieving long-range ferromagnetic order in TIs at temperatures suitable for device applications has so far not been possible, with the demonstration of the QAH effect only being possible at extremely low temperatures, motivating the need for fundamental studies on MTI systems in an attempt to explore new avenues of enabling TI/MTI applications.

1.1 Background

This section discusses the theoretical background required to understand the key concepts used throughout this thesis. First, the band structure of a TI and how this leads to its fundamental properties is discussed. The following section is a discussion of the realisation of the MTI. Subsequently, an explanation of the QAH effect is given. Finally, the relevant magnetic exchange interactions which lead to the observed magnetic properties for the types of systems looked at in this research are then

discussed.

1.1.1 Topological Insulators

Topological insulators (TIs) are a class of theoretically predicted and experimentally realised quantum material with a unique electronic structure when compared to an insulator or semiconductor. Even though the TI is a band insulator, there exists a metallic surface state which has novel properties, the existence of which can be explained by consideration of a simplified model. In a TI the bulk band structure is the same as that of an insulator, however the valence band and conduction band have inverted parity, i.e. the conduction band is below the valence band as demonstrated by Fig. 1.1 [20]. This band inversion occurs due to the heavy elements that typically make up TI materials demonstrating strong spin-orbit coupling (SOC) [21]. SOC occurs when an internal magnetic field is generated by the electrons motion around a nucleus interacting with its spin [21]. This results in the electron energy levels being shifted due to Zeeman splitting [21].

The band structure of a conventional insulator and a TI are topologically distinct, i.e., one of these band structures cannot be transformed smoothly into the other without closing the energy gap between the conduction and the valence band [22]. If we consider what happens to the band structure at the surfaces of a TI, i.e., at the boundary where the inverted TI band structure meets the conventional insulator band structure of vacuum, only states of identical character can join and this gives rise to two metallic states located at the surface of the TI [20]. It is important to note that this simplified model, which is sufficient to motivate the research carried out in this thesis, has limitations because it is derived from atomic states and not bands [20]. A more in depth look at how topologically protected surface states exist for a TI is given in ref. [20].

TIs are therefore bulk insulators with surfaces that support localised metallic

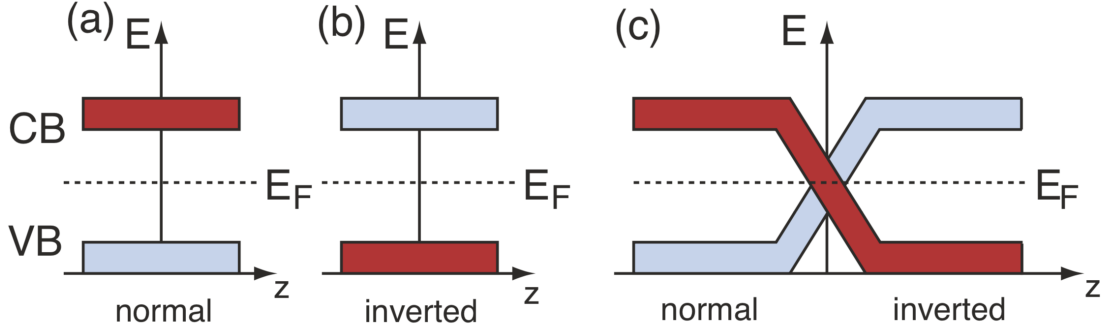


Figure 1.1: Simplified band diagram in order to demonstrate the origins of the TSS. The Fermi level is denoted by E_F . (a) The band diagram for a normal insulator, the conduction band (CB) is above the valence band (VB) in energy. (b) The band diagram for a TI system demonstrating strong SOC such that the VB is higher in energy than the CB leading to an inverted band diagram. (c) When the TI system is placed next to a normal insulator, such as vacuum, the bands of the normal insulator and SOC system connect at the surface (where $z = 0$) such that a metallic surface state is realised. Figure taken from ref. [1].

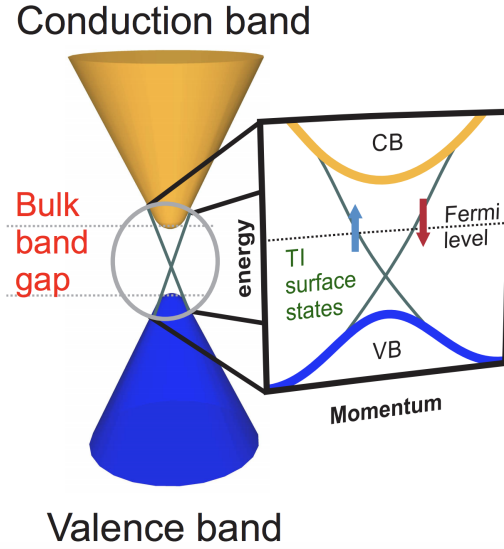


Figure 1.2: The band structure of a TI demonstrating the bulk conduction band and bulk valence band with bulk band gap. A closer inspection of the bulk band gap reveals the spin-polarised (as demonstrated by the spin-up [blue] and spin-down [red] arrows) linearly dispersed surface states that bridge the bulk bands. Figure taken from ref. [2].

states which bridge the bulk insulating band gap. The surface state consists of two separated spin momentum locked channels which are either spin-up or spin-down. These topological surface states (TSS) are not a property of the surface but instead are required by the topology of the bulk band structure, their very existence is a bulk property of the material which makes them far more robust than surface states found to be present in semiconductor systems [20]. In reality, materials that are topological insulators are actually small gap semiconductors with band gaps of ~ 300 meV [20]. TIs exist in both two-dimensional (2D) and three-dimensional (3D) forms and in both cases TSS of a TI demonstrate properties which are unlike any known one-dimensional (1D) or 2D electronic system [22].

1.1.1.1 2D Topological Insulators

The 2D TI was experimentally realised in CdTe/HgTe/CdTe quantum wells and was shown to demonstrate the quantum spin Hall (QSH) effect as shown by Fig. 1.3 [23]. This essentially means that a 2D TI has edge states of counter-propagating spin polarised conduction edge channels [23]. These channels are time reversal symmetry protected [24]. When an electron in one of these QSH channels reaches an impurity in the crystal structure, it is reflected, just like a photon from a surface. Due to quantum mechanical considerations, these reflection paths interfere with one another and all of the possible reflected paths from an electron in a QSH state destructively interfere [3]. Backscatter events which can be caused by weak disorders or impurities within a crystal structure are therefore not possible giving rise to dissipationless transport within these channels [25]. This makes TIs of intense interest as their robust spin momentum locking surface states make them the perfect candidates for many device applications such as low-power dissipation electronics, spintronics and quantum computation [22].

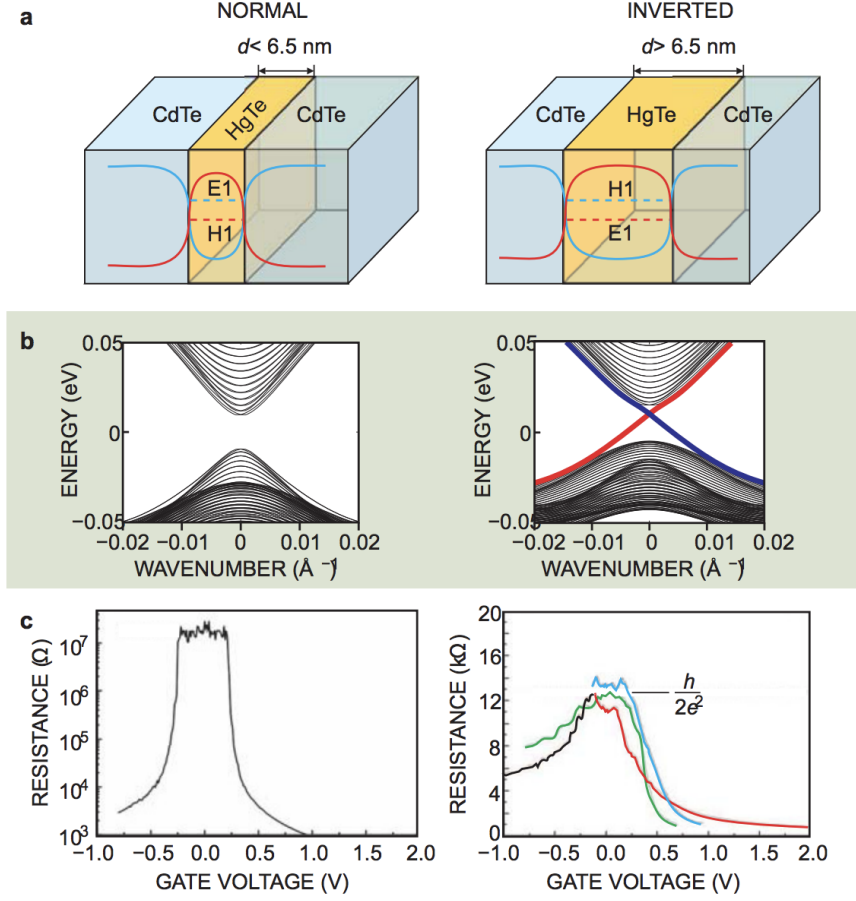


Figure 1.3: The first experimental verification of the 2D TI using CdTe/HgTe/CdTe quantum wells. (a) Diagram to demonstrate the CdTe/HgTe/CdTe structure. The blue and red curve represent the potential-energy well experienced by the electrons in the conduction band and the barrier for holes in the valence band. For a HgTe layer thinner than 6.5 nm the energy of the lowest energy conduction subband (E1) is higher than that of the highest valence band (H1). When the HgTe thickness is larger than this, the VB and CB become inverted and the system is topologically non-trivial. (b) Model of the band structure for each case. In the topologically non-trivial case, edge states are formed. (c) Resistance against gate voltage (and in turn Fermi level) measurements for each case. A rather large resistance is seen for the topologically trivial case, whereas a quantised resistance is observed for the topologically non-trivial case due to the perfect conduction of the edge states present. It should also be noted that there are two conduction channels for the topologically non-trivial case and the quantised resistance is halved. This resistance value remains the same for HgTe thicknesses above 6.5 nm as indicated by the red (0.5 μm) and blue (1.0 μm) lines. Figure taken from ref. [3].

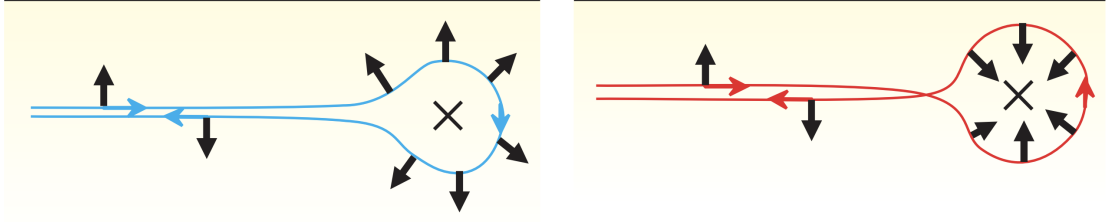


Figure 1.4: Diagram to demonstrate the path of a spin-polarised electron from the QSH edge state when it backscatters from a non-magnetic impurity. The backscatter event for both the spin-up (blue) and spin-down (red) polarisations is opposing which causes the backscatter events to cancel out. This means that the QSH edge states are time reversal symmetry protected from backscatter events. Figure taken from ref. [3].

1.1.1.2 3D Topological Insulators

3D TI systems have metallic surface states which are easily accessible as they exist at bare surfaces. Surface states of systems such as Bi_2Te_3 have been shown to be detectable at room temperature with techniques such as angularly resolved photoelectron spectroscopy (ARPES) [26]. They have linearly dispersed Dirac cone surface states which support massless Dirac fermions and have similar spin-momentum locking properties to their 2D counterparts which are also TRS protected [26]. The direction of electron motion along the surface of a 3D TI is determined by the spin direction in the same way as it is for a 2D TI's edge state [27]. The spin direction varies continuously as a function of propagation direction resulting in a planar metal where spin direction is locked to the direction of propagation [27]. The 3D TI systems that have been dealt with during the research demonstrated here, Bi_2Te_3 and Sb_2Te_3 , are renowned for having TSS consisting of a single Dirac cone at the Γ point of the Brillouin zone where $(k_x, k_y, k_z) = (0, 0, 0)$ [4].

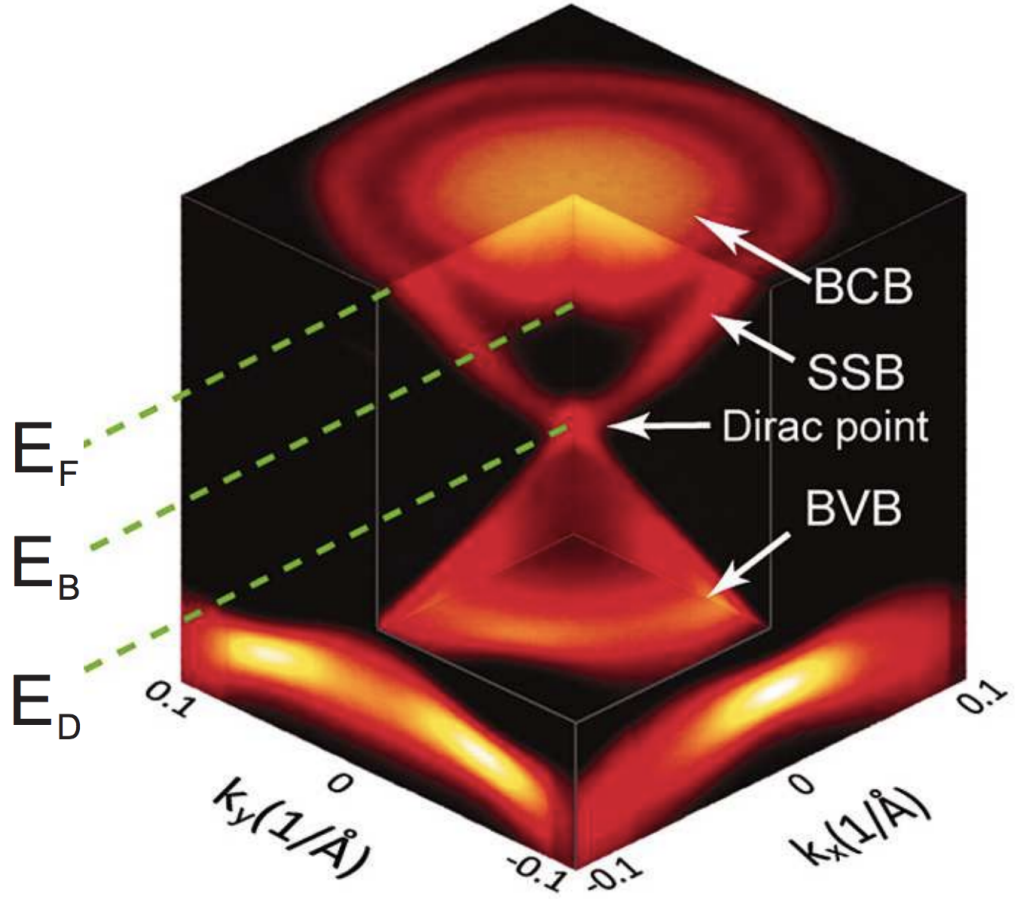


Figure 1.5: ARPES measurements of Bi₂Se₃ demonstrating the electronic band structure of the 3D TI system. The bulk conduction band (BCB) and bulk valence band (BVB) can clearly be identified at the highest and lowest energies. The surface state band (SSB) which takes the shape of a Dirac (linearly dispersed) cone bridges the BCB and BVB and is seen to close at the Dirac point (E_D). The Fermi energy (E_F) and bottom of the BCB (E_B) are also shown. Figure from ref. [4]. Reprinted with permission from AAAS.

1.1.2 Magnetic Topological Insulators

Although TRS protects the TSS of a TI from non-magnetic impurities, the introduction of magnetism within the TI system causes TRS to be broken and induces a band gap in the usually closed TSS. Unlike the impurities discussed in 1.1.1, magnetic impurities are spin scattering defects which cause the TSS electrons to no longer completely destructively interfere when they are reflected from them.

In the case of doping a 3D TI with magnetic impurities, when the exchange coupling between magnetic ions is strong enough, long-range ferromagnetic order is induced in the system causing the linearly dispersed Dirac cone surface state to develop a gap of a few meV at the Dirac point [28]. Upon opening, the linear Dirac cone becomes parabolic and the TSS can be transformed to a massive Dirac fermion state [4]. It has been theorised that this TSS will lead to the formation of a number of exotic quantum phenomena such as the QAH effect [28], TSS magnetoelectric effects [29] and image magnetic monopoles [30]. Magnetic doping of the TI system $(\text{Bi,Sb})_2(\text{Se,Te})_3$ with both Cr and V has lead to the experimental observation of the QAH effect [31,32].

1.1.3 Quantum Anomalous Hall Effect

The QAH effect, as the name suggests, is the quantised version of the AH effect much in the same way that the QH effect is the quantised version of the Hall effect [33]. In 1881, two years after reporting that applying a magnetic field to a current carrying conductor causes a Lorentz force which presses electrons to one side of the conductor (Hall effect), Edwin H. Hall stated that this pressing effect was ten times larger in ferromagnetic iron than in a non-magnetic conductor [34]. This AH effect can only theoretically be explained by concepts of topology and geometry only recently formulated [35].

The quantised version of the AH effect is closely related to the QH effect which was

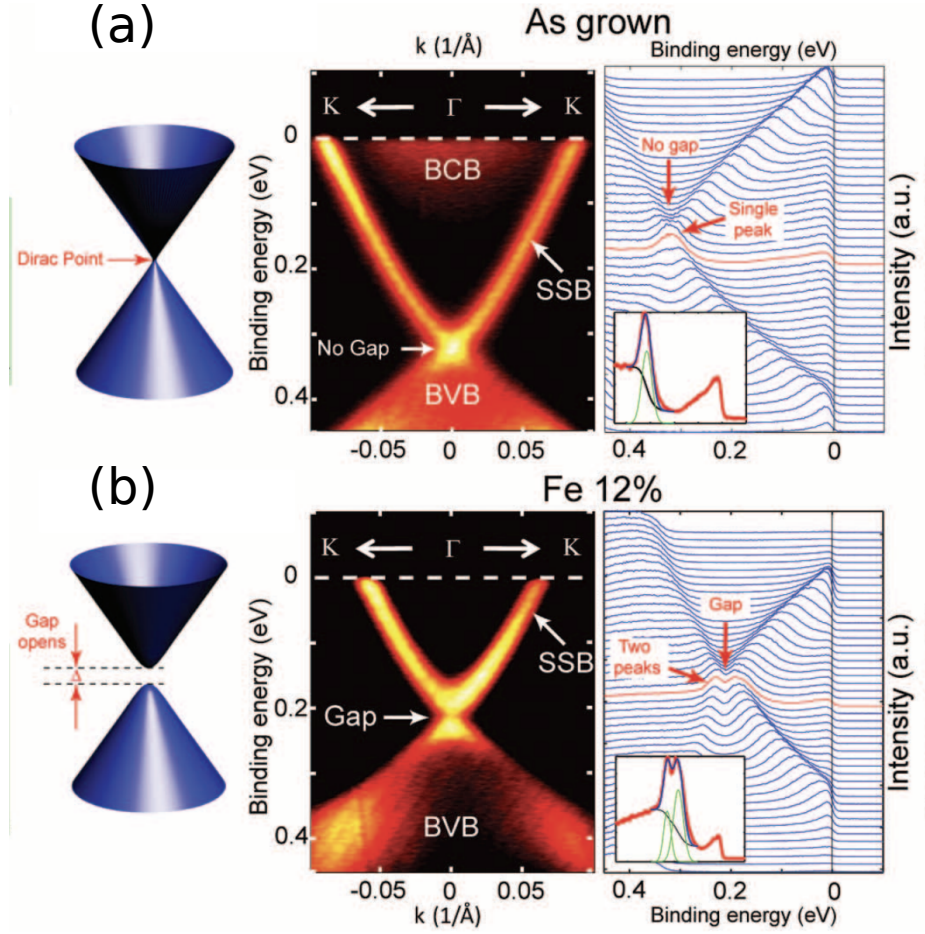


Figure 1.6: ARPES measurement of as-grown Bi_2Se_3 (a) and Fe-doped Bi_2Se_3 (b) electronic band structure. When doped with Fe, the originally closed TSS is seen to be gapped. Note also that the prior linearly dispersed Dirac cone also becomes parabolic either side of the gap. This causes the usually massless Dirac state to become massive. Figure from ref. [4]. Reprinted with permission from AAAS.

experimentally demonstrated in a two-dimensional electron gas (2DEG), formed at the interface of a metal-oxide-semiconductor field effect transistor (MOSFET) [36]. The major significance of a system demonstrating the QH state is that the Hall conductance (the ratio of electrical current to voltage perpendicular to the current flow) will be quantised in units of fundamental constants when the material is at low temperatures [27].

When electrons are constrained to move in a 2D plane at low temperatures and a strong perpendicular magnetic field is applied, the Lorentz force acting on the electrons causes them to move in circular cyclotron orbits with frequencies dependent upon the strength of the applied field, the charge of the electron and their mass [37]. The electrons occupy orbits with quantised energy as defined by the quantum mechanical harmonic oscillator [38]. At the bulk of the material these Landau levels act similarly to the band structure of an insulator where energy levels are separated by band gaps so electrons occupy localised orbitals and cannot move freely [27]. However, at the boundary of the material the circular path of the electrons becomes interrupted resulting in unidirectional skipping orbits at the edges of the material [27]. The magnetic field constrains the electrons to only travel in one direction so backscatter events are not possible leading to metallic edge states which support dissipationless quantised transport [27].

The QH state's properties much like a TI can be explained more directly through the use of the concept topology. If we consider that the QH state is topologically non-trivial in its bulk (in the same way that the TI was as discussed in 1.1.1) then at the boundary between the non-trivial topology and conventional topology of vacuum there must be a formation of an edge state in the same way as the TSS was formed for a TI, but in this case only in one direction. The QH state is the simplest topologically ordered state; the existence of the edge states of the QH state are directly related the topology of the system [27]. Despite the QH state demonstrating dissipation-

less transport and having metrological applications in the defining of fundamental constants these systems are limited by the need for a strong magnetic field.

The QAH state exhibits the same quantised conductance as the QH state but does not require the application of an externally applied magnetic field making it far more suitable for such applications. Another way of visualising the QAH effect is to consider the QSH effect which was discussed in section 1.1.1.1. The QSH effect is the quantised version of the spin Hall (SH) effect, where a system with SOC can cause electrons with different spin directions to experience different forces which cause each spin direction to move in different motions [39–41]. In this system there is no net charge current as each channel cancels out but there is a net spin current which does not require TRS breaking to be observed. The QSH effect describes electrons with opposite spin carrying opposite quantised Hall conductance [6]. Essentially, the QSH effect in its simplest form can be considered to be two QAH states with opposing spin components where the Hall conductance from each spin state cancels out. This is evident from Fig. 1.8. To realise the QAH, one of the spin components has to be removed so that the Hall conductance becomes non-vanishing.

The criteria required for realising the QAH effect state are a band inversion caused by strong SOC and long-range ferromagnetic order that breaks TRS [28]. This makes magnetically doped TIs the perfect candidates for its observation, as the broken TRS leads to massive Dirac fermions. The Fermi level of the magnetic topological insulator must also be tuned to be in the induced band gap i.e. the material must remain an insulator [28]. The first experimental observation of the QAH effect was realised in HgTe/CdTe doped with spin polarised Mn impurities which still required the application of an external magnetic field due to the paramagnetic nature of Mn [42].

The QAH effect was experimentally realised in the transition metal doped 3D topological insulator $\text{Cr}_{0.15}(\text{Bi}_{0.1}\text{Sb}_{0.9})_{0.185}\text{Te}_3$ where a plateau in the Hall resistance as

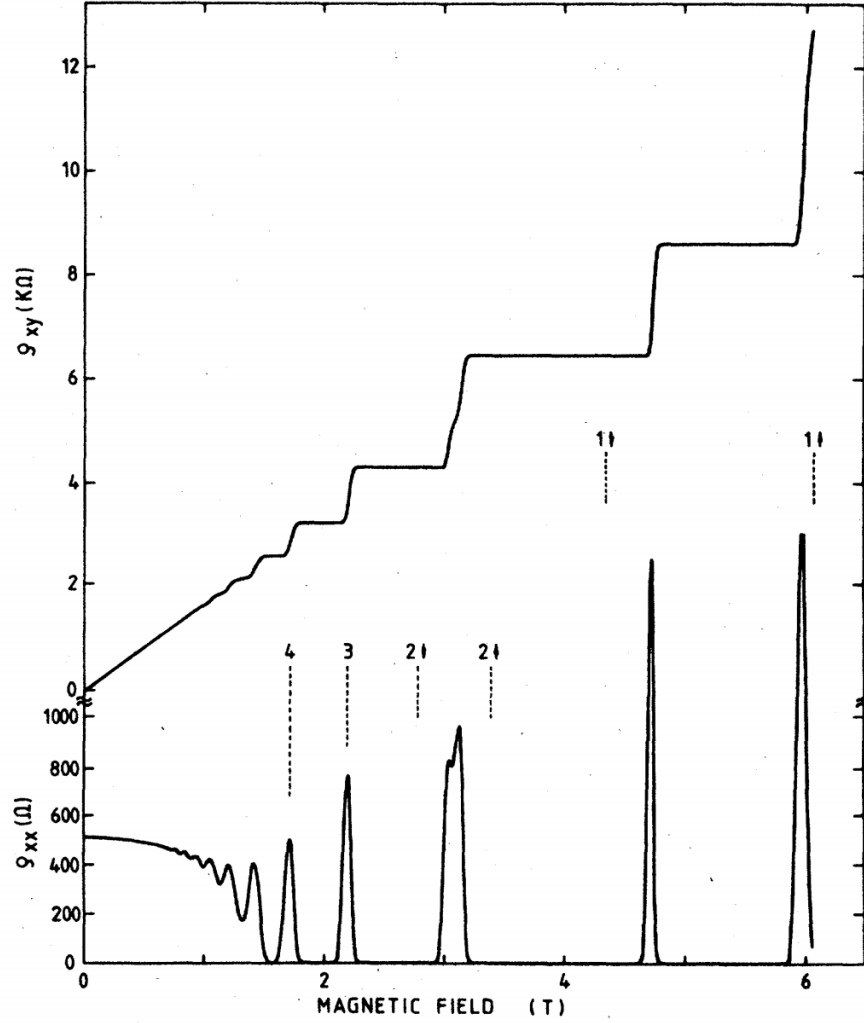


Figure 1.7: The hallmark of the QH effect, the Hall resistance ρ_{xy} and longitudinal resistivity ρ_{xx} as a function of applied magnetic field measured for a GaAs/Al_xGa_{1-x}As heterostructure at a temperature of 8 mK. The Hall resistance demonstrates steplike increases with plateaus in the magnetic field region where the longitudinal resistance vanishes. The width of the longitudinal resistance peaks indicate the number of extended states. Reprinted from ref. [5] with permission from the APS.

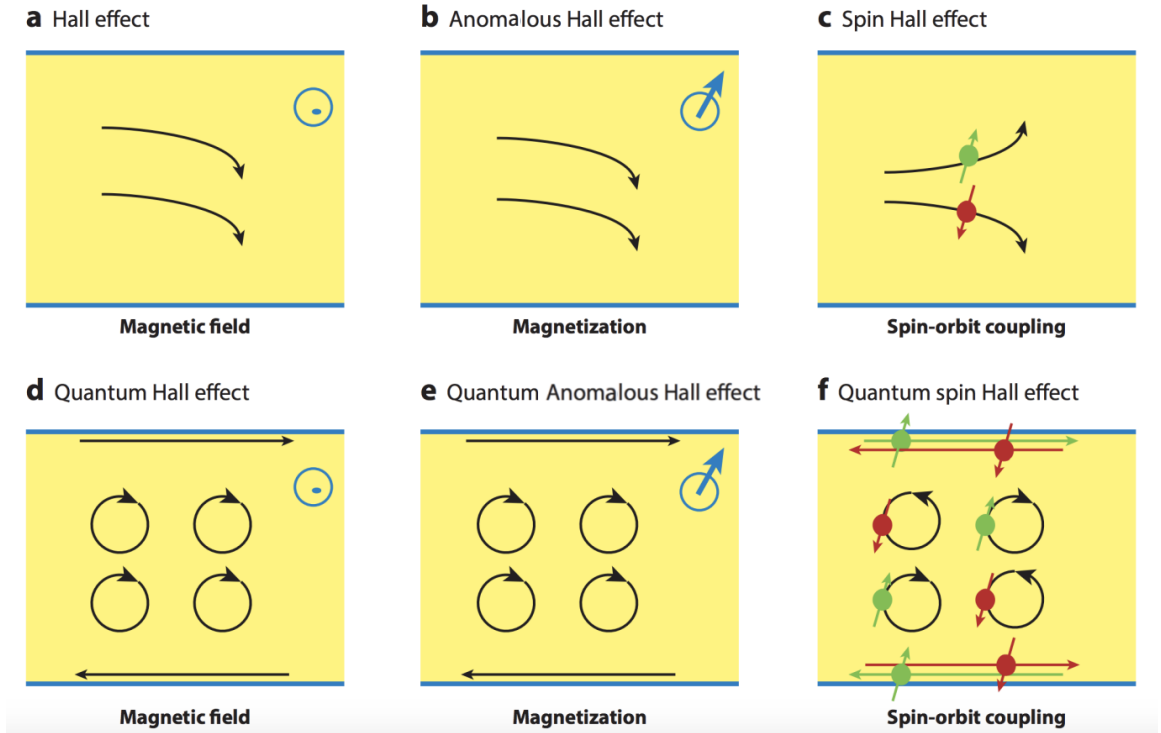


Figure 1.8: Schematic representation of each Hall effect. The dot-like symbol found in the top right corner of diagram (a) and (d) is used to represent that an applied magnetic field is required. In diagram (b) and (e) an arrow symbol in the top right corner is used to demonstrate that an internal magnetic field is needed. It is important to note that the QAH effect (e) is closely related to both the QH effect (d) where the applied magnetic field is replaced by an internal magnetisation and QSH effect (f) where only one of the two spin-polarised channels is the QAH effect. Figure taken from ref. [6].

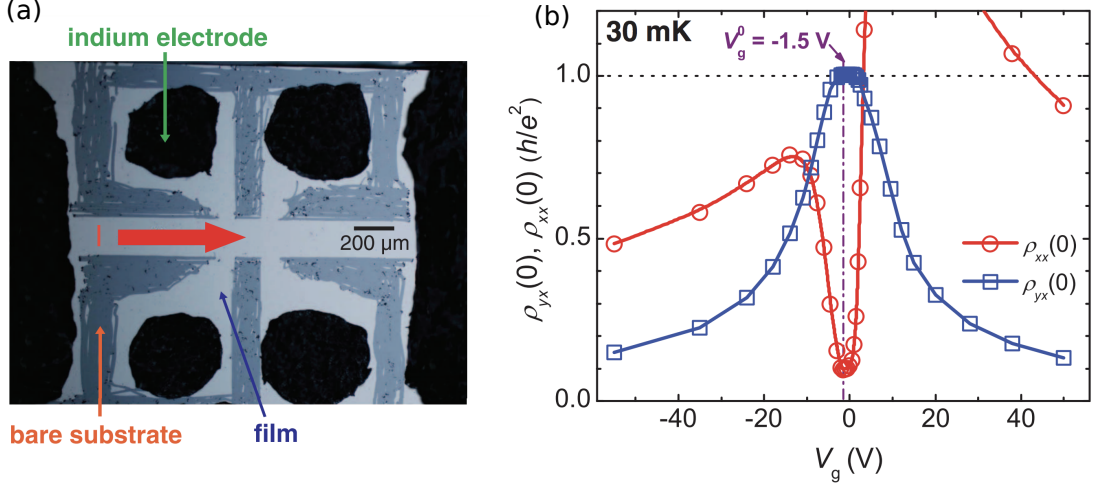


Figure 1.9: Experimental realisation of the QAH effect in $\text{Cr}_{0.15}(\text{Bi}_{0.1}\text{Sb}_{0.9})_{0.185}\text{Te}_3$. (a) Image of the Hall bar made from the $\text{Cr}_{0.15}(\text{Bi}_{0.1}\text{Sb}_{0.9})_{0.185}\text{Te}_3$ used to observe the QAH effect. The Hall bar was achieved by scraping away the material to reveal the SrTiO_3 substrate below. Indium electrodes were used with the red arrow indicating the measured current flow direction. (b) Gate voltage (V_g) dependence of $\rho_{yx}(0)$ and $\rho_{xx}(0)$ at zero field. The QAH effect is realised at 30 mK in zero field as the Hall resistance exhibits a distinct plateau with the expected quantised value of h/e^2 when $V_g = -1.5$ V. ρ_{yx} at the same time demonstrates a sharp dip down to $0.098 h/e^2$ indicating the expected drop in longitudinal resistance. Figure from ref. [7], reprinted with permission from AAAS.

a function of gating voltage was observed at very low temperatures (30 mK) without the need for an applied magnetic field [7]. These findings clearly demonstrate the possibility of being able to observe the QAH effect in similarly magnetically doped TI systems.

1.1.4 Magnetic Exchange Interactions

When doping TIs with magnetic dopants in an attempt to induce long-range ferromagnetic order, it is important to consider the different types of magnetic interactions which allow the magnetic moments to communicate with one another. The concepts and examples given here to explain each exchange interaction are taken from ref. [43].

The exchange interaction originates from how the energy of a system can be

reduced when considering the electrostatic interactions of electrons. If we consider a simple atomic system with only two electrons in close proximity, when attempting to construct the Hamiltonian, the wavefunction for the joint state can be written as a product of the single electron states. In order to obey exchange symmetry and taking into account that we are dealing with fermions, the overall wavefunction must be antisymmetric and therefore can consist of either a symmetric spatial state with an antisymmetric singlet state or an antisymmetric spatial state with a symmetric triplet state. The effective Hamiltonian for the system will therefore consist of a constant term and a term which depends on spin. Considering that in a system consisting of many atoms and electrons, this same interaction will apply between all neighbouring atoms (consistent with the nearest neighbour Heisenberg model) and the Hamiltonian can be written:

$$\hat{\mathcal{H}} = -2 \sum_{i>j} J_{ij} S_i \cdot S_j \quad (1.1)$$

where $S_i \cdot S_j$ and J_{ij} represent both the coupling and the exchange integral between the i^{th} and j^{th} spin, respectively. In the simplified two electron model, for a singlet state, $S_1 \cdot S_2 = -3/4$ and for a triplet state $S_1 \cdot S_2 = 1/4$. When the Hamiltonian is expressed in this form, the $i > j$ avoids ‘double counting’ and a factor of two is required. The exchange integral is dependent upon the type of interaction taking place within the system which is in turn dependent upon the positioning of electrons within the materials structure.

1.1.4.1 Direct Exchange

Direct exchange occurs when the electrons of neighbouring magnetic atoms interact directly without the need for an intermediary. This is usually caused by the direct overlap of neighbouring magnetic orbitals, however, it is usually the case that there is insufficient direct overlap and direct exchange is not an important mechanism partic-

ularly in the case of the magnetically doped systems discussed here. For example, the $4f$ electrons of rare earths are very strongly localised and with little probability density extending further than a tenth of the interatomic spacing. For transition metals the $3d$ orbitals extend further from the nucleus but the role of conduction electrons also needs to be taken into account.

1.1.4.2 Superexchange

Superexchange is an indirect exchange interaction between non-neighbouring magnetic ions mediated by a non-magnetic ion which is placed between them. The exchange integral for this type of system consists of two parts. The first is a potential exchange term which represents the electron repulsion, favouring a ferromagnetic ground state. This term is small when ions are well separated. The second term is a kinetic energy exchange term.

This type of exchange interaction typically occurs in ionic solids including oxides and fluorides. In the case of MnO the kinetic energy exchange term dominates the exchange integral leading to antiferromagnetic behaviour. By considering the simplified scenario of two Mn transition metal ions separated by an O ion, where the magnetic moment on each Mn occurs due to a single unpaired electron in a d orbital, with the O having two p electrons in its outermost occupied states, it can be demonstrated that antiferromagnetic coupling reduces the overall energy of the system.

Superexchange can also be ferromagnetic, for example in the case of having two magnetic ions, one with an occupied orbital and one with an unoccupied orbital on either side of a non-magnetic ion then it can be energetically favourable for an electron to move to the unoccupied orbital if, when it arrives, its spin is aligned with the other electrons due to Hund's rule coupling. However, this is a weaker interaction which is less common than antiferromagnetic superexchange.

1.1.4.3 Ruderman-Kittel-Kasuya-Yosida Interaction

The RKKY interaction occurs for metals where there is an indirect exchange interaction between magnetic ions mediated by conduction electrons. This occurs because the localised magnetic moment spin-polarises the conduction electrons which then in turn couples to a neighbouring localised magnetic moment. The exchange integral has an oscillatory dependence on the distance between magnetic moments and is long range. Depending on the separation of the magnetic ions it can lead to ferromagnetic or antiferromagnetic behaviour.

1.1.4.4 Double Exchange Interaction

The double or Zener type exchange interaction occurs for systems where there is more than one valency for the same ion leading to ferromagnetic behaviour. This type of exchange interaction usually occurs for oxide systems, for example in magnetite Fe_3O_4 which contains an equal mixture of Fe^{2+} and Fe^{3+} ions on octahedral sites and another set of Fe^{3+} ions which occupy tetrahedral sites. The double exchange interaction ferromagnetically aligns the Fe^{2+} and Fe^{3+} ions on the octahedral sites while the Fe^{3+} ions on the tetragonal sites, which don't take part in the double exchange are coupled to the octahedral Fe^{3+} ions by an antiferromagnetic superexchange mediated by oxygen. This means that the Fe^{3+} magnetic moments cancel out, leaving a net moment which can be attributed to the ferromagnetic Fe^{2+} ions.

1.2 Outline of Thesis

The research presented in this thesis was conducted in an effort to investigate both the structural and magnetic properties of magnetically doped topological insulators in an effort to understand the physical processes behind different material properties caused by the use of particular dopants. These findings could then be used to inform

a decision about how to improve the chances of producing an MTI sample capable of being able to observe the QAH effect at higher temperatures. The research was conducted using a range of lab based, synchrotron and neutron source techniques. All of the samples used throughout these studies were grown by the author using molecular beam epitaxy (MBE). Both X-ray magnetic circular dichroism (XMCD) and polarised neutron reflectometry (PNR) techniques were used in order to determine the element specific magnetic properties as well as to retrieve an in-plane magnetic depth profile of samples in order to inform on the magnetic coupling scenarios present.

Chapter 2 discusses the experimental techniques used to both produce and study samples. Chapter 3 collects together the studies of single layer MTI samples which were produced by using both transition metal and rare earth dopants as well as exploring the scenario of codoping a TI with two different transition metals. A study of the basic structural and magnetic properties of Cr-doped as well as Cr and V-doped Sb_2Te_3 and Dy-doped Bi_2Te_3 are performed, culminating in XMCD and PNR measurements which are used to gain an insight in the chemical properties, as well as the magnetic coupling mechanism present in the samples. These findings lead us to the research presented in Chapter 4, where in an effort to enhance the magnetic properties of the single layer MTI systems already discussed, MTI heterostructures are grown. A Co overlayer is deposited on top of Cr-doped Sb_2Te_3 and heterostructures consisting of multiple Cr: Sb_2Te_3 /Dy: Bi_2Te_3 bilayers are fabricated and studied using both XMCD and PNR in the hopes of demonstrating and understanding the enhancement of the magnetic properties of the MTIs contained within. Finally, Chapter 5 summarises the findings of the research presented in previous chapters giving an indication of where further research in the field of MTIs is required.

Chapter 2

Experimental Methods

This chapter discusses the various experimental methods used throughout the different studies conducted in this thesis, the basic principles behind how they operate and also how they were specifically utilised in this research. Firstly MBE, the technique used to fabricate the samples is discussed including the basic principles behind growth and the configuration for the specific system used to produce samples. The various basic techniques used to check the structural characteristics of samples are then discussed. Magnetometry techniques are used to check the magnetic characteristics of samples. Synchrotron based techniques which give an indication of chemical composition and element specific magnetometry are then looked at. Neutron based techniques in the form of polarised neutron reflectometry are also examined. In the final section, the properties of the 3D TI systems Bi_2Te_3 and Sb_2Te_3 are examined in order to lay the foundations for the investigations discussed in later chapters.

2.1 Molecular Beam Epitaxy

MBE is the growth technique of choice when it comes to producing high quality thin films down to atomic or molecular dimensions with exceedingly low impurity levels [44]. Originally developed as a technique for growing single crystal films of

semiconductor materials [45], MBE is an ultra high vacuum (UHV) based evaporation method where elemental or compound constituents are heated to cause mass transfer from an evaporator to a substrate maintained at elevated temperatures [44]. When the molecular beam constituents reach the heated substrate they form an ordered overlayer and are deposited epitaxially [44]. It is important therefore to consider careful selection of substrates. MBE can be differentiated from other vacuum deposition techniques via its superior control of beam fluxes and growth conditions which allow for slower precise growth rates [46]. This precise control of material flux can also be used for controlled doping of materials. MBE has been instrumental in the study of TI systems, allowing for the realisation of the first experimentally realised 2D TI system HgTe/CdTe [23] as well as the first experimentally observed QAH state in the transition metal doped 3D TI Cr-doped $(\text{Bi,Sb})_2\text{Te}_3$ [7].

An MBE system requires the use of turbomolecular pumps as well as a cryoshroud cooled with liquid nitrogen in order to reach the UHV pressures of below 1×10^{-9} Torr used to ensure the limitation of impurities that can contaminate films during the slow growth process, where deposition rates can be much lower than 1 monolayer/s [46]. This guarantees not only the chemical purity of samples but also maintains crystalline order. The UHV vacuum also allows for the use of in-situ characterisation tools such as reflection high energy diffraction (RHEED) (see section 2.2.1), residual gas analysers (RGA) and scanning tunnelling microscopy (STM) which allow for the real time observation of sample characteristics during growth.

The MBE system used throughout the research conducted in this thesis was the chalcogenide MBE situated in the Research Complex at Harwell (RCaH), Oxfordshire. This MBE is composed of three chambers, a load lock where samples are loaded/unloaded into/from the MBE system, an interface chamber and a growth chamber where samples are fabricated, as demonstrated by Fig. 2.1. A quarter segment of a 2-inch substrate is inserted into 2-inch diameter Riber style holders (Fig.

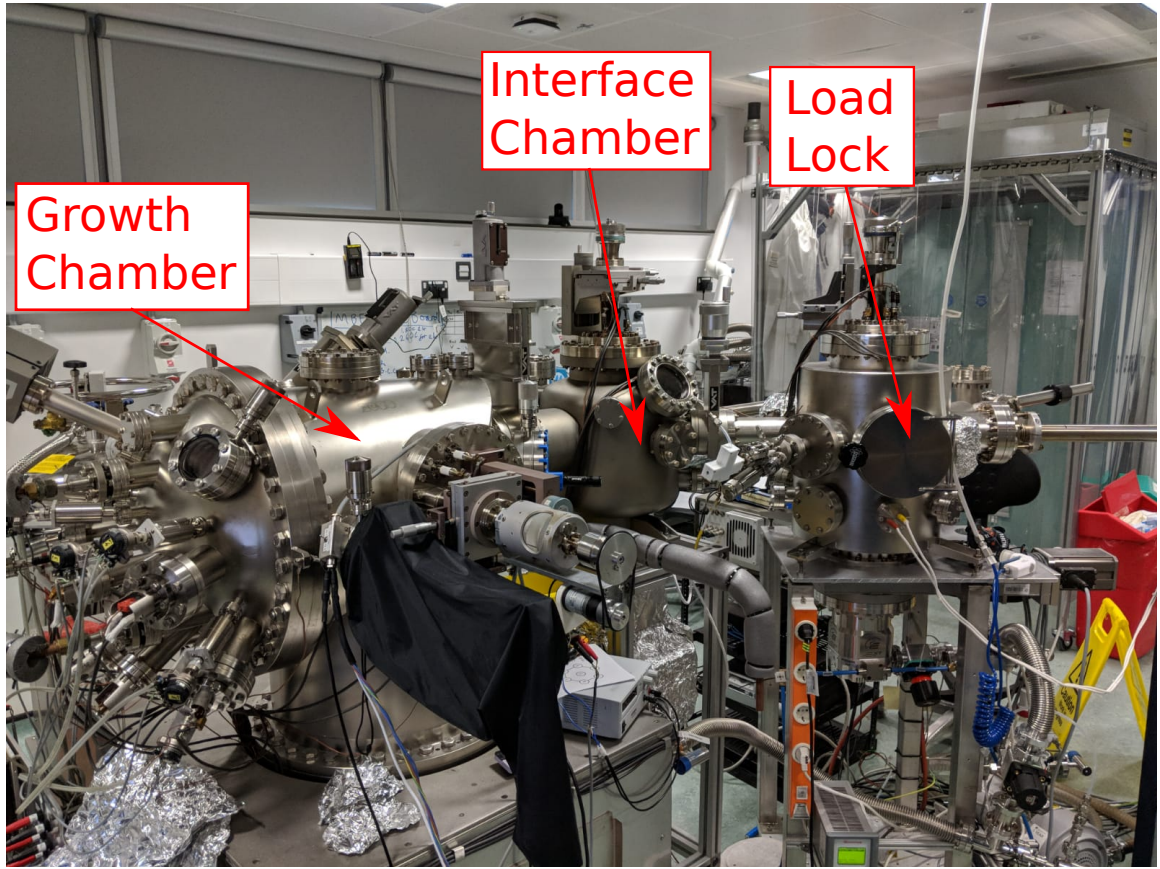


Figure 2.1: Photograph of the Oxford chalcogenide MBE system used to grow samples in pursuit of the research demonstrated in this thesis. The load lock, interface chamber and growth chamber are indicated.

2.3) before being loaded into the load lock which can hold up to four sample holders. The load lock can then be pumped initially using a scroll pump to get to a pressure of 1×10^{-3} Torr and then finally using an Edwards nEXT 400D turbomolecular pump in order to reach UHV. The load lock is then baked using a 1 kW lamp at a temperature of 140°C for typically 8 hours where a vacuum of 1×10^{-9} Torr is reached.

The substrates can then be transferred through to the growth chamber via the interface chamber. The interface chamber has an ion pump which allows a base pressure of 1×10^{-11} Torr to be reached. It serves as both a sample storage area, allowing for a further 4 samples to be housed and also further isolates the growth chamber from the load lock in order to protect its vacuum. The growth chamber is

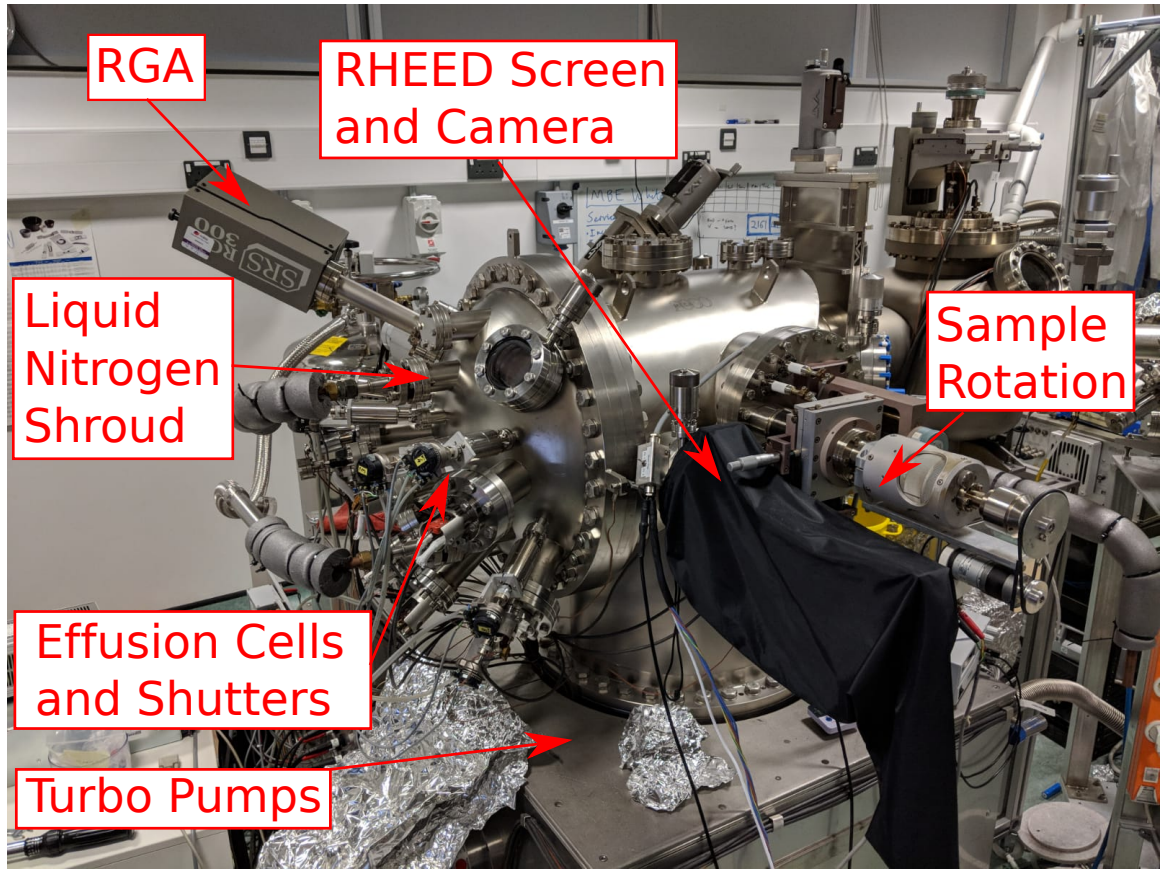


Figure 2.2: Photograph of the growth chamber of the chalcogenide MBE. The various key components are labelled. The RHEED gun is found on the opposite side of the chamber to the RHEED screen and camera. The turbomolecular pumps and ion pump are contained underneath the chamber in the metal box.

pumped with a Leybold magnetic levitation turbomolecular pump which is backed by a smaller Pfeiffer mechanical turbo pump. Both turbomolecular pumps are in turn backed by a low vacuum scroll pump. The growth chamber also features a Gamma Vacuum ion pump and is fitted with a cryoshroud which can be filled with liquid nitrogen. The cryoshroud is used to remove the kinetic energy of free gas molecules, trapping them at the walls of the chamber. All of these systems are in place to ensure that UHV is maintained even with the high vapour pressures produced by the elemental sources. The UHV also maintains the thermal stability of low temperature and high temperature cells even when being operated at the same time.

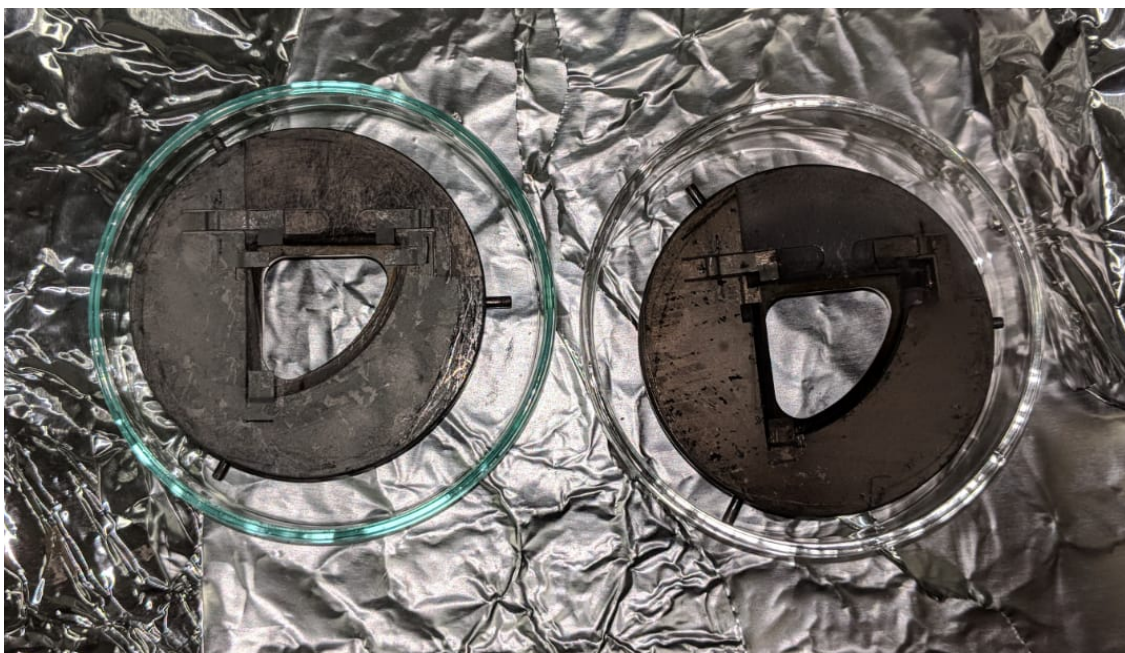


Figure 2.3: Photograph of Riber style sample holders used to house and transport 1/4 2-inch sized samples while in the MBE system.

When a new cell or elemental source is first loaded into the chamber, it must be outgassed. This process involves the continuous heating of the cell in order to remove significant quantities of water, hydrogen and hydrocarbons which when released into the chamber cause pressure increases. During growth their presence increases the occurrence of impurities within grown films. A titanium sublimation pump is also present in the growth chamber and is used to pump away the hydrogen produced by the outgassing process. A residual gas analyser (RGA) can also be fitted to the growth chamber which utilises mass spectrometry to determine the molecular gas present within the chamber. This is shown in Fig. 2.2. This is used to observe the outgassing process; when the unwanted molecular gases are no longer detectable by the RGA (down to a detection limit of 1×10^{-13} Torr), the cell has been successfully outgassed.

The growth chamber is fitted with eight Knudsen style effusion cells (Fig. 2.4)

which have been reconfigured a number of times during the studies detailed here in order to produce various systems. The relevant configurations for the sources during the conducted research were the base elements of the chalcogenide TIs Bi, Sb, Te, transition metal dopants Cr, V and rare earth dopant Dy. Each of the effusion cells consisted of a specially selected material crucible in order to ensure the elemental sources held within do not undergo a reaction with their container. These crucibles are then surrounded by a heater filament which is monitored by a proportional-integral-differential (PID) feedback system consisting of a thermocouple in thermal equilibrium with the crucible connected to a Eurotherm electronic temperature controller. The Eurotherm is used to control the current through the effusion cell filament which in turn resistively heats the crucible. The electronic temperature controller allows for stable and precise control of the ramping rates of temperatures which is necessary to ensure the cells are protected from heat damage. To reduce heat loss to surroundings and to isolate each cell from radiative heating, heat shielding surrounds each cell.

During the growth process, the elemental source contained within the crucible is heated until it sublimates or evaporates, depending on the element in question. The effusion cell is aligned in the chamber such that the collimated molecular beam of gas is directed towards the substrate holder. The use of shutters just beyond the mouth of the effusion cell allows for the blocking of this molecular beam to ensure no material is deposited on the substrate until the intended growth temperature of the cell is reached. The substrate holder can also be rotated out of the way of the incoming beam during set up of the effusion cells. A beam flux monitor (BFM) is also fitted to the back of the rotating substrate holder which allows for the monitoring of the molecular flux arriving at the substrate position before and after growth. This allows for fine tuning of the ratio between elemental sources which defines the chemical composition of the material being grown. The ratio of these fluxes are also important

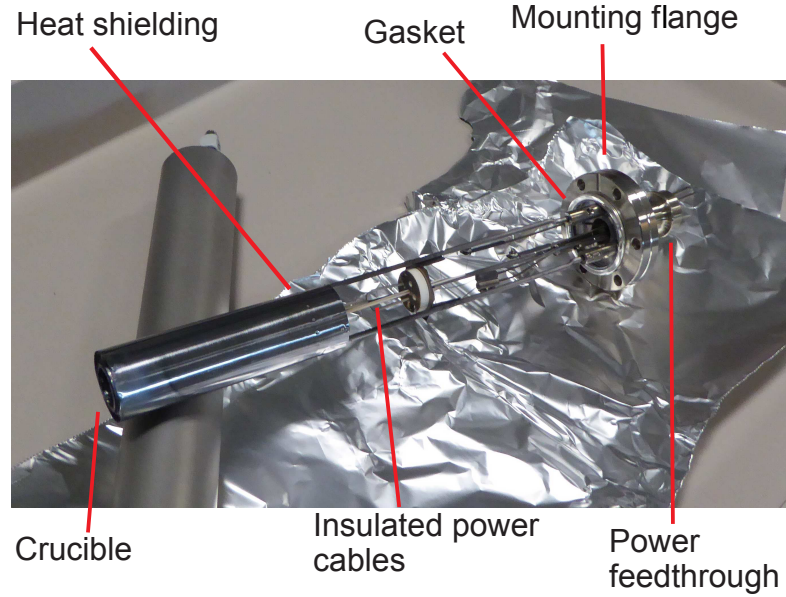


Figure 2.4: Picture to demonstrate the key parts of the Knudsen effusion cell used throughout the pursuit of this research. Figure taken from ref. [8]

to control doping concentrations and also give an indication of the growth rate of the sample. Ultimately, the BFM allows for a great degree of reproducibility when it comes to sample production.

The substrate holder allows for the sample to be heated, via the use of a resistive heating Ta wire, to a maximum temperature of 800°C . This increased temperature ensures that the deposited material has sufficient thermal energy in order to reorganise itself to form a complete monolayer of atoms before the growth of the next layer commences. This layer-by-layer growth is known as the Frank van der Merwe growth mechanism. In the case of all samples grown in pursuit of this research, this was the sought after growth type which requires good matching of lattice constants between the substrate and intended sample growth in order to limit epitaxial strain. Care must be taken to ensure that the sample is not at too high a temperature during growth as this can cause undesired evaporation of material from the substrate. A detailed discussion of the growth method used to grow films is given in section 2.4.

In the case of growing magnetically doped TI samples, the doping concentration x of a sample is represented by using the convention $A_xB_{2-x}C_3$, where A is the dopant and $B = \text{Bi or Sb}$ and $C = \text{Te}$.

2.2 Structural Characterisation Techniques

After samples have been produced it is important to ascertain their structural properties allowing for an optimisation of growth recipes. This section discusses the lab/synchrotron based techniques used to qualitatively and quantitatively investigate the samples crystal structure, surface quality and chemical composition. Reflection high energy electron diffraction (RHEED) allows for the *in-situ* observation of the surface quality of the growing sample. X-ray reflectometry (XRR) and X-ray diffraction (XRD) can be used to investigate the surface roughness, total thickness and crystal structure of the samples. Atomic force microscopy (AFM) is used to observe the topography and surface morphology of the samples. Finally X-ray absorption spectroscopy (XAS) is a synchrotron based technique used to analyse the chemical properties of the constituent elements which make up the sample.

2.2.1 Reflection High Energy Electron Diffraction

The growth mechanism behind fabricated samples is monitored *in-situ* by the use of a RHEED system contained within the growth chamber. RHEED is a technique which is used to study the structure of surfaces during growth giving information about roughness, crystal quality and orientation. It works using the principle of electron diffraction by utilising electrons with energies of typically 8 to 30 keV [47] where the electron wavelength is the same order of magnitude as the lattice constants of the sample. The set-up consists of an electron gun, where a cathode thermally emits electrons and a phosphor screen, where the electrons arrive after being diffracted

from the sample as demonstrated by Fig. 2.5. The electron beam produced by the cathode is accelerated by a high voltage and can be steered and focused via the use of a magnetic lens. The electrons arrive at the sample at grazing incidence and are then diffracted by the surface crystal structure onto the phosphor screen where the diffraction pattern can be observed.

The use of small grazing angles means that RHEED is surface sensitive, only probing the first few monolayers of the sample. The 2D surface of the growing film can be considered as a series of reciprocal lattice rods in reciprocal space which intersect with an Ewald sphere with the radius of the incident electron wave vector, where constructive interference occurs. The high energy of the electrons used in this process means that the Ewald sphere's diameter is larger than the spacing between each of the lattice rods [44]. Lattice vibrations and crystal imperfections cause the lattice rods to have a finite thickness [44]. This means that the RHEED pattern produced on the phosphor screen is 2D streaks rather than the points expected for a perfect 2D atomic lattice.

This technique provides a qualitative method of discerning the way the surface is growing. A high quality epitaxial film which has grown via the Frank van der Merwe mechanism will lead to thin streaks on the phosphor screen. The Volmer-Weber growth mechanism [47] causes 3D island formation, where the deposited material is not entirely covering the surface of the substrate but is in patches. This can be observed using RHEED as the 3D nature of the surface causes the RHEED streaks to break up into spots [48]. If the sample growth consists of many randomly oriented crystalline parts and is polycrystalline then the streaks become concentric circles as the film appears isotropic [48]. In the case of an amorphous growth where all structure is entirely lost then no pattern is observed on the phosphor screen [48].

RHEED can also be used to investigate the crystal symmetry group of the film which is growing. By taking into account the rotation of the film relative to the

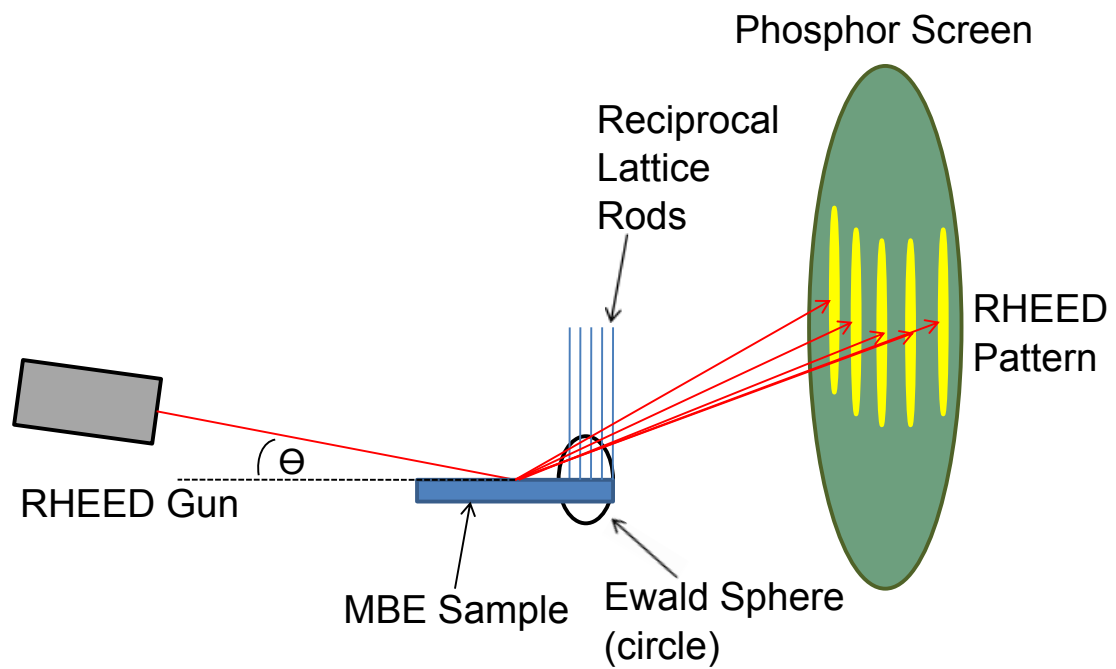


Figure 2.5: RHEED set-up in MBE growth chamber. Electrons hit the sample surface at small incident angles and are diffracted. The Ewald sphere has a radius of the wave vector of the incident electrons. When the lattice rods of the 2D surface in reciprocal space coincide with the surface of the Ewald sphere, the Bragg condition is fulfilled. This occurs a number of times across the 2D surface of the sample leading to the streak-like RHEED pattern on the phosphor screen.

electron beam allows for the observation of different crystallographic directions. By making a note of the different RHEED patterns at certain sample orientations one is able to build up an idea of the orientation of the film relative to the substrate and discern if the film growing has the expected crystal symmetry group.

2.2.2 X-Ray Reflectometry

X-ray reflectivity (XRR) is an interference based technique that provides an insight into the structural properties of grown films such as film thickness, layer structure, interfacial mixing and roughness. Snell's law defines the behaviour of a ray of light when it enters a transparent medium. This is dependent on the refractive index of the transparent medium which is affected by the frequency of the incoming light. In the case of X-rays these frequencies are much higher than visible light and the refractive index becomes slightly smaller than unity [49]. When an X-ray is incident on a flat, sharp interface at glancing angles, total internal reflection can occur if the angle is below a certain critical angle, dependent upon the density of the interface [49]. At angles just beyond the critical angle, X-rays continue to be reflected from the interfaces with a decreasing intensity with increasing angle.

The behaviour of an X-ray reflected from a sharp, flat interface for different angles, is given by the Fresnel equations [49] in a similar manner to optical reflections. In reality however, the interfaces X-rays are reflected from are rarely sharper than the length scale of an Å and are not ideally flat. Deviations from the ideal sharp, flat interface which define the Fresnel equations can be modelled to give structural parameters of grown films. The Fresnel equations in the X-ray region when calculated for the reflection from a homogeneous slab of finite thickness with smooth surface demonstrate oscillations known as Kiessig fringes which occur due to the interference of waves reflected from the top and bottom interfaces of a film [50]. The period of these oscillations is directly related to the inverse of the total film thickness z_{tot} by

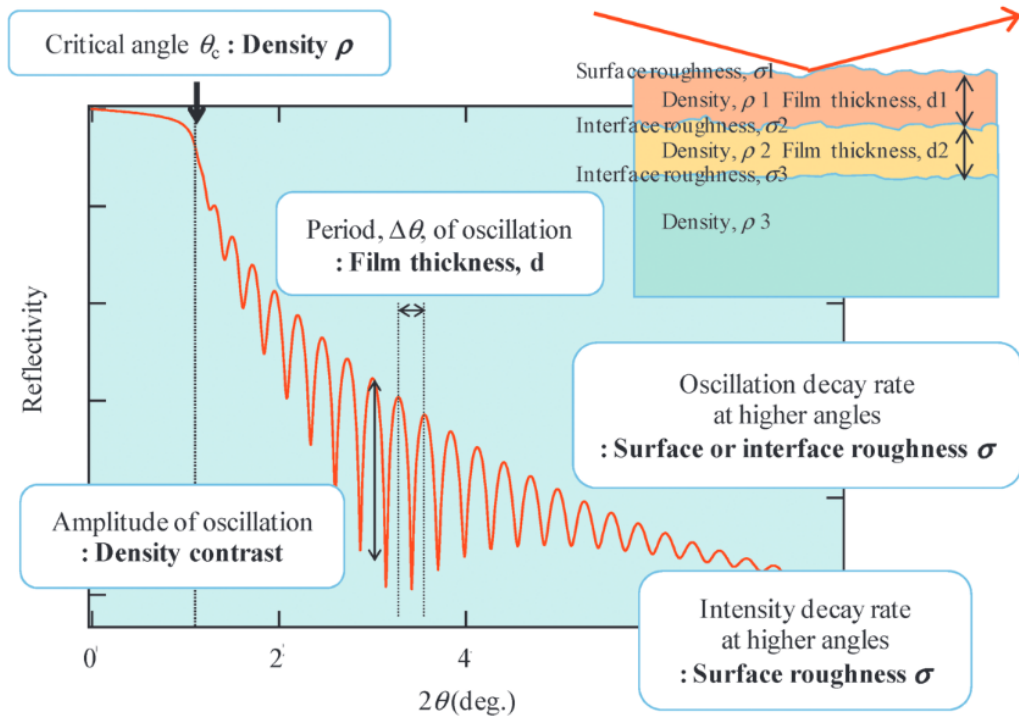


Figure 2.6: The main features of an XRR measurement along with the sample properties indicated by them. Figure taken from ref. [9].

the equation:

$$z_{tot} = \frac{2\pi}{\Delta q} \quad (2.1)$$

where q denotes the momentum transfer vector of the reflected X-rays. In the case of multilayer systems, there is an interference of the electrons reflected from the different interfaces of each layer leading to phase shifts which generates a beating pattern in the Kiessig fringes.

XRR measurements were carried out using a Bruker D8 diffractometer at Diamond Light Source which uses the Bragg-Brentano geometry shown in Fig. 2.7. The set-up utilises a moving source and detector with stationary sample. Cu-K $_{\alpha 1}$ X-rays at 45 keV and 200 mA are produced using a rotating Cu anode operating at a generator setting of 40 keV and 40 mA. XRR measurements were modelled using the package GenX using an iterative regression technique to fit a simulated reflectivity curve to an experimentally measured one [60]. For the XRR data measured for all samples, the critical angle, quality of Kiessig fringes and their frequency was used as an indication of sample density, surface quality and to calculate total film thickness.

2.2.3 X-Ray Diffraction

For X-ray diffraction (XRD) a monochromatic X-ray beam is directed towards the surface of the sample, but at larger incidence angles than those used in reflectivity. It is used to characterise the structure of samples, crystal phases and can be used to calculate lattice constants. The crystal lattice of the sample acts as a diffraction grating, causing diffracted X-rays from certain atomic planes to constructively interfere at certain incidence angles. The Bragg equation details the condition for the constructive interference of X-rays with wavelength λ incident on a crystalline material with interplanar separation d , at an angle θ between the X-ray beam and scattering

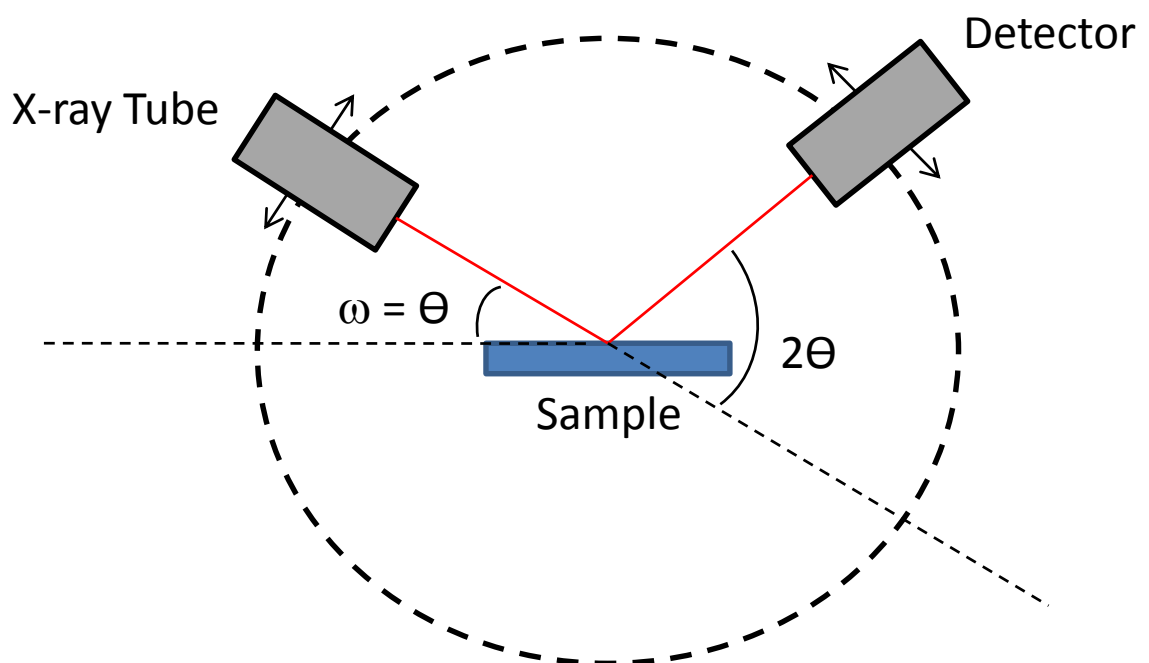


Figure 2.7: Bragg-Brentano geometry of Bruker D8 diffractometer used for X-ray studies. The sample remains stationary while the X-ray source and detector move symmetrically around the sample.

planes:

$$n\lambda = 2d \sin \theta \quad (2.2)$$

n is the order of the diffraction. All XRD measurements were performed in an out-of-plane diffraction geometry using the same experimental equipment and set-up as described in section 2.2.2. Symmetric $2\theta - \omega$ or coupled scans were used to identify $(00l)$ peaks allowing for the determination of the crystal phase of the grown film by comparing the measured data to well known crystal structures recorded on the Inorganic Crystal Structure Database (ICSD).

The chalcogenide TI materials investigated throughout the course of this research belong to the rhombohedral symmetry group, $R\bar{3}m$. The d -spacings calculated using Equation (2.2) are related to the lattice parameters $|a| = |b|$ and c for this symmetry group by the equation:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (2.3)$$

where h, k and l are the Miller indices of the considered reflection. In the out-of-plane diffraction geometry Equation (2.3) becomes:

$$\frac{1}{d^2} = \frac{l^2}{c^2} \quad (2.4)$$

The c -axis lattice parameter can therefore be calculated using the equation:

$$c = \frac{n\lambda}{2 \sin \theta} l \quad (2.5)$$

It is important to note that throughout these studies there are several different conventions used to indicate the Miller indices of Bragg peaks for example, $(h, k, l) = (hkl) = (h \ k \ l)$. In order to highlight the index in double figures, the following

conventions are used: $(hk.l) = (hkl)$.

2.2.4 Atomic Force Microscopy

Atomic force microscopy (AFM) is used to directly map the surface topology of grown samples. It does this by utilising a cantilever with a sharp tip which is resonated at a certain frequency and then scanned over the sample surface. The measurements performed in this research were done in contact mode where the tip is in direct contact with the sample. As the tip approaches the surface of the sample, the force of the tip interacting with the surface interrupts the usual frequency of resonance which is picked up by a laser interferometer set-up. In this way the tip can be used to measure the forces between the probe and surface as a function of their separation. AFM scans were acquired by using a Veeco Multimode V AFM at Diamond Light Source and were analysed using the software Gwyddion [51]. These scans are used to understand the surface morphology of samples giving an indication of growth modes.

2.2.5 X-Ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is a synchrotron based technique which allows for element specific probing of the chemical make up of samples. It can be used to study site occupation and atomic valences. X-ray photons of a particular energy when incident on a sample are absorbed depending on the atomic make-up which in turn defines the energy transitions available within the sample. By selecting a particular energy range of X-ray photons, regions of maximum absorption can be seen where there are core-level transitions occurring in the absorbing atom species. The energy ranges where absorption takes place are unique to each element and are known as the absorption edges.

Core-level transitions take place when a core electron is excited from its ground state to a higher energy state. The ground state is then left with a vacancy or hole

which is eventually filled by a valence electron which transitions from a higher to a lower energy. This energy jump causes a photon or Auger electron to be released from the atomic species which is then detected through measurement. The shape of the absorption spectrum measured can then be used to indicate the valence of the ion contained within the sample.

In the research presented here XAS was conducted at the same time as XMCD measurements at a number of synchrotron beamlines (see section 2.3.2) in order to ascertain the chemical structure of samples. XAS was detected by either measuring fluorescence or luminescence from the sample or substrate via the use of a photodiode or by measuring sample drain current (see section 2.3.2.2). For the $3d$ transition metal and $4f$ rare earth dopants looked at in the studies presented here the $L_{2,3}$ edge and $M_{4,5}$ edge are of particular interest. The $L_{2,3}$ edge corresponds to the transition from the spin split $2p_{\frac{1}{2}, \frac{3}{2}}$ core states to the $3d$ valence states and the $M_{4,5}$ edge corresponds to the transition from the $3d_{\frac{3}{2}, \frac{5}{2}}$ core levels to the empty $4f$ state.

2.3 Magnetic Characterisation Techniques

2.3.1 SQUID Vibrating Sample Magnetometry

Magnetometry was used throughout this work to measure the magnetisation of samples as a function of both applied field and temperature. This was achieved through use of a vibrating sample magnetometer (VSM) where the sample is oscillated within a set of superconducting pick-up coils where, through electromagnetic induction (EMF), a current is induced. This current is proportional to the strength of the magnetic moment of the sample. These currents can be small so a very sensitive current measuring device known as superconducting quantum interference device (SQUID) is utilised. The pick-up coils are connected in a superconducting circuit to an inductor placed next to the SQUID such that when a current is generated in the coil, it generates a

magnetic field in the inductor which is detected via the SQUID.

A SQUID consists of a superconducting loop with two parallel superconductor-insulator-superconductor or Josephson junctions. For a SQUID to be used as a magnetometer, a constant bias current is applied to it which is slightly larger than the initial maximum current that can pass through the SQUID before it turns from superconducting to resistive. This is called the critical current. Under these conditions, when an external field is applied to the SQUID the critical current oscillates between a minimum and maximum value. There is therefore a periodic relationship between the voltage measured across the SQUID and the applied magnetic flux, where one period is a quantised value of magnetic flux known as the flux quantum. By measuring the voltage across the SQUID, which is proportional to the current induced in the pick-up coils, the magnetic moment of the sample can be deduced. It is important to note that the VSM measures the average magnetic moment of the whole sample.

SQUID VSM measurements were performed using two identical Quantum Design MPMS 3 SQUID-VSM systems situated at both Diamond Light Source and ISIS Neutron and Muon Source. These systems are capable of applying a maximum magnetic field of 7 T along the axis of vibration and are able to cool samples to a temperature of 1.5 K via the use of cryogenics. For measurements, samples were mounted to quartz rods with GE varnish. The rods with samples attached were then moved through the pick-up coils. The quartz rod provides a linear diamagnetic background that has to be subtracted before proper analysis.

Magnetisation was measured in electromagnetic units (emu) which in the case of samples doped with only a single species of magnetic ion was converted into Bohr magnetons per ion, (μ_B/ion). The calculation of the magnetic moment M was carried out by using the equation:

$$M[\mu_B/\text{ion}] = M[\text{emu}] \frac{m_{rel}d}{N_A \mu_B \rho V} \quad (2.6)$$

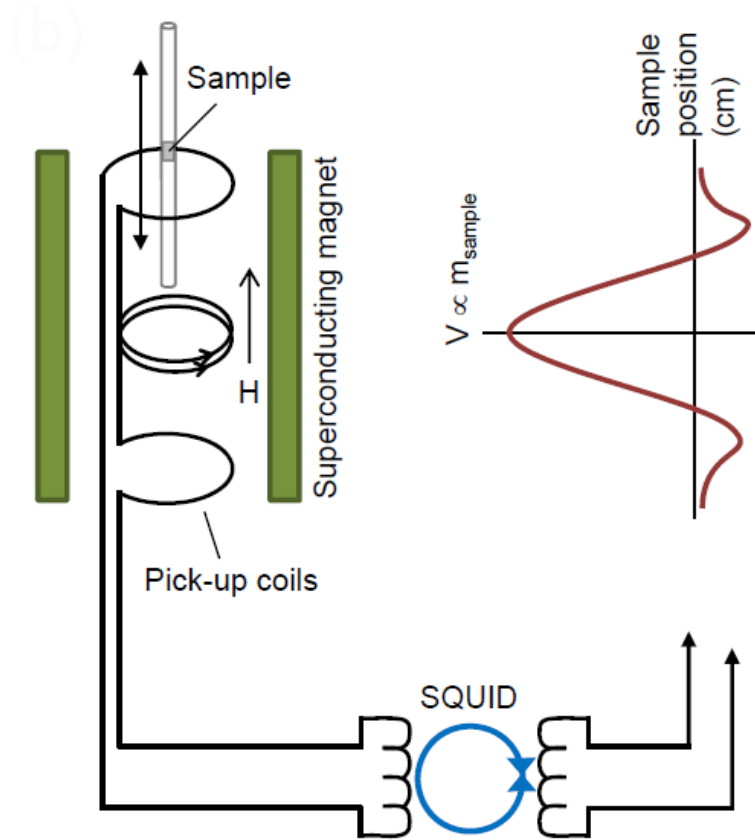


Figure 2.8: Schematic of VSM electronic setup. The magnetic sample is passed through the pick-up coils inducing a current which is then passed through an inductor. The current, which is proportional to the magnetic moment of the sample is measured by observing the voltage across a SQUID in close proximity to the inductors generated magnetic field. Figure taken from ref. [10].

where m_{rel} is the relative molecular mass of the thin film sample, d is doping concentration in atomic percentage, N_A is Avagadro's constant, μ_B is the Bohr magneton in emu, ρ is the thin film density and V is the volume of the film. The volume of the film was calculated by multiplying the film thickness as measured by XRR with the cross sectional area A of the film, which is calculated using the equation:

$$A = \frac{m}{\rho_{sub}t_{sub}} \quad (2.7)$$

where m is the total mass of the sample (thin film and substrate), ρ_{sub} is the density of the substrate and t_{sub} is its thickness.

Magnetisation as a function of temperature measurements (MvT) were used in order to observe the ferromagnetic transition temperature of samples T_C by taking the first derivative of the data with respect to magnetisation and identifying the minimum. Magnetisation as a function of applied magnetic field measurements (MvH), also referred to as hysteresis loops, were performed in order to determine the saturation field of samples and were used as a means to identify ferromagnetism through determination of coercive fields. Hysteresis loops were performed with the applied magnetic field in both in-plane and out-of-plane with reference to the plane of the grown film to identify magnetic anisotropies.

2.3.2 X-Ray Magnetic Circular Dichroism

X-ray magnetic circular dichroism (XMCD) is a synchrotron based technique which allows for the study of element specific magnetic properties of a sample. Based off of the process of XAS (see section 2.2.5) it can be used for the calculation of spin and orbital moment contributions, total moment and through the use of Arrott-Noakes theorem can be used to determine an accurate value of the T_C of each of the magnetic elements contained within the sample. During XAS, if the incident X-rays have been

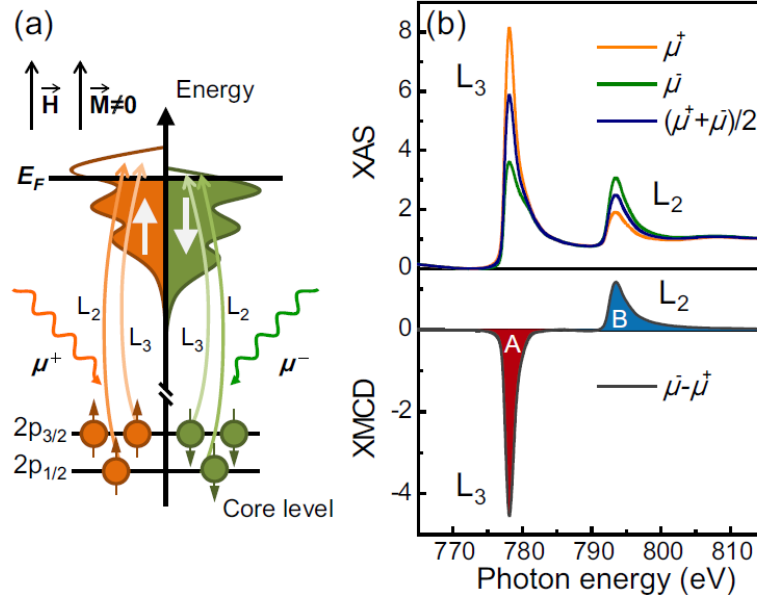


Figure 2.9: (a) Diagram demonstrating the energy level transitions for a 3d metal undergoing an absorption process for different helicities of the light. Depending on the helicity of the circularly polarised light, electrons of each spin have differing probabilities of being excited from the spin split 2p levels into the unoccupied 3d level. The L_3 spectra is generated by the transition from the $2p_{3/2}$ energy level and the L_2 is generated by the transition from the $2p_{1/2}$ level. For a magnetic material, there are differing densities of unoccupied states for each electron spin. (b) XAS and XMCD spectra generated for the 3d metal. The difference in the XAS spectra generated by sweeping the energy across the $L_{2,3}$ absorption edges for each helicity of the light gives the dichroism which indicates the selection rules of the absorption of the polarised photons. Figure taken from ref. [11].

either left or right circularly polarised, there is a different transition probability for spin-up and spin-down electrons being excited into the unoccupied valence states. This probability depends on both the helicity of the polarised light and the magnetic state of the sample.

XMCD is used to probe the difference in the density of empty states with different spin moments as shown in Fig. 2.9(a). The XMCD can be calculated by taking two XAS measurements with different circular polarisations or opposing magnetisations of the sample. This gives absorption coefficients with left μ^- and right μ^+ helicities of circularly polarised light as a function of photon energy. The XMCD is then

calculated using the equation:

$$XMCD(E) = \mu^-(E) - \mu^+(E) \quad (2.8)$$

Figure 2.3.2(b) shows an example of the XAS and XMCD spectra generated for Co at the $L_{2,3}$ edge. The intensity of the XMCD effect is the result of the dot product of the magnetisation vector of the sample and the polarisation vector of the incoming X-rays. If the magnetisation and X-ray beam direction are perpendicular to one another then the resultant dot product is zero and there will be no XMCD observed.

In the research demonstrated here, atomic multiplet calculations have been carried out by collaborator Prof. Gerrit van der Laan to determine the total moment of the element from the XMCD spectra. Atomic multiplet theory takes into account information such as valence state, crystal field and spin orbit interaction to calculate the XMCD spectrum for a given atomic coordination. This calculated spectra can then be compared to the experimental data in order to determine parameters such as the total moment, site occupation and crystal field splitting [52, 53].

2.3.2.1 Arrott Plots

XMCD can also be used to accurately determine the T_C of magnetic elements contained within the sample. This is done by observing the intensity of the XMCD as a function of field for a number of fixed temperatures. When attempting to practically find a value for the T_C of a material, it needs to be in a single domain state. In order to ensure this, a magnetic field has to be applied which in turn effects the measured value of the T_C . The T_C can also be determined through the use of hysteresis loops measured at different temperatures, however it can be difficult to observe the closure of the hysteresis loop for materials with small coercive fields. The most reliable way to experimentally determine the T_C for a ferromagnet is given by the Arrott-Noakes criterion [54]. The Arrott-Noakes equation minimizes the effects of multiple magnetic

domains and magnetic anisotropy within a material:

$$\left(\frac{H}{M}\right)^{1/\gamma} = \frac{T - T_C}{T_1} + \left(\frac{M}{M_1}\right)^{1/\beta} \quad (2.9)$$

where M is magnetisation, H is the applied field, T is the temperature and T_1 and M_1 are material dependent parameters. In mean field theory $\beta = 0.5$ and $\gamma = 1$ and Equation (2.9) simplifies to:

$$M^2 = A \frac{H}{M} + B(T - T_C) \quad (2.10)$$

where $A = M_1^2$ and $B = -(M_1)^2/T_1$. An Arrott plot consists of a set of isotherms for M^2 versus H/M . In the case of a conventional second-order ferromagnetic transition, the isotherm should be a positively sloped straight line in the high field region where possible domain and stray field effects are negligible, however disorder in the system can lead to a bending towards the lower field region [55, 56].

Equation (2.10) demonstrates that the value for the T_C is equal to the temperature for which the isotherm passes through the origin. This is found by fitting the high field region of each isotherm with parallel straight lines which have the same gradient. The intercept value is then taken from these fitted lines and plotted against temperature in order to find the T_C of the sample. Practically speaking M is obtained by using the maximum intensity from a background corrected XMCD. For determining the T_C of rare earth elements the maximum intensity of the M_5 edge is used and for transition metals the L_3 edge is used.

2.3.2.2 XMCD Setup

XMCD measurements were taken at beamline I10, BLADE at Diamond Light Source, Harwell, Oxfordshire, UK, beamline ID32 [57] at the European Synchrotron Radiation Facility (ESRF), Grenoble, France and beamline 29 BOREAS at ALBA, Barcelona,

Spain. All of these beamlines utilise soft X-rays with a maximum energy of 1.5 keV. The X-rays are produced via the use of a synchrotron particle accelerator where electrons are accelerated close to the speed of light before being directed into travelling around a storage ring at a constant velocity. The storage ring uses the magnetic field from a number of quadrupole and sextupole magnets in order to focus and steer the electrons as they travel. When the electrons reach a curved section of the storage ring, they are accelerated and produce high intensity X-rays of a particular wavelength.

X-rays can also be realised via the use of an insertion device which produces an electron beam on straight sections of the ring. An array of magnets is used to achieve a periodic field that causes the electron beam to oscillate with a constant period, producing X-rays. Constructive interference of the emitted light can also be used to produce a beam of much higher intensity than that achieved through the use of storage ring curvature. The X-rays are then directed towards the beamlines out of the storage ring and passed through a monochromator which selects the energy band of the light needed by the beamline, focussing mirrors and diagnostics before reaching the experiment chamber.

As discussed earlier, when the X-rays eventually reach the sample they are absorbed. This absorption process can be measured via total electron yield (TEY), fluorescence yield (FY) or luminescence yield (LY). In the case of TEY, an electrical contact is made to the sample surface via the use of conducting paste which allows the photoelectrons generated through the absorption process to be measured. TEY is a surface sensitive technique as electrons can only escape the surface up to a certain distance of 5 nm. FY uses a photodiode placed away from the sample to detect Auger electrons (see section 2.2.5) which allows for measurements that probe much deeper (200 nm) into the sample than TEY.

In LY measurements, the incident X-rays pass through the sample and are absorbed by the substrate and through a recombination process of trapped excitons,

visible light is emitted through the back of the substrate. This visible light carries information about the entirety of the sample with it allowing for detection of XAS and XMCD via the use of a photodiode. In the case of samples used for LY measurements, the substrate is Al_2O_3 which has a strong enough optical emission line for a suitably intense signal to reach the photodiode.

2.3.3 Polarised Neutron Reflectometry

Polarised neutron reflectometry (PNR) is able to discern the magnetisation of samples as a function of depth. In the case of multilayer samples, it is able to distinguish the difference in magnetisations for different layers. Neutrons, when reflected from a sample surface, behave in much the same way as X-rays (described in section 2.2.2), and therefore their reflectivity as a function of incident angle can be explained by the use of a Fresnel equation which shows that the neutron is totally internally reflected until some critical angle where the reflectivity begins to reduce. Constructive and destructive interference of neutron waves scattered by different interfaces contained within a sample will also lead to the formation of Kiessig fringes in neutron reflectivity curves [58].

Neutrons interact with matter in two ways, there is a strong interaction where the Neutron interacts with nuclei and a magnetic interaction, where they interact with magnetic moment. This is because neutrons themselves also carry a magnetic moment. Unlike X-rays which interact with the electron shells orbiting nuclei, neutrons interact with the nuclei themselves. Neutrons can be polarised into their spin-up and spin-down states. In a PNR experiment, a magnetic field is applied in the plane of the sample as demonstrated by Fig. 2.10. The Neutrons are polarised parallel to this magnetic field (spin-up) or antiparallel (spin-down). For Neutrons directed at a sample at grazing incidences, there is an effective interaction potential made up of both a nuclear and magnetic component described by the equation:

$$V = \frac{2\pi\hbar^2}{m}Nb^{\text{nuc}} - \vec{\mu} \cdot \vec{B} \quad (2.11)$$

where m represents neutron mass, $\vec{\mu}$ denotes magnetic moment, N is atomic density, b^{nuc} is coherent nuclear scattering length and $\vec{B}$ represents the magnetic induction. This potential can be used to calculate the neutron reflectivity of the sample by solving the Schrödinger equation [58]. It is important to note that for a sample made up of multiple magnetic layers, there is a different interaction potential for each layer. Equation (2.11) can be separated into two terms, a term which results from the interaction of the neutron with the nucleus and the second which is from the interaction with the magnetisation of the sample layers:

$$V = \frac{2\pi\hbar^2}{m} \cdot (Nb^{\text{nuc}} \pm Nb^{\text{mag}}) \quad (2.12)$$

The properties of the sample can now be discussed in terms of scattering length densities (SLD) where the Nb^{nuc} term is representative of the nuclear SLD and the Nb^{mag} term demonstrates the magnetic SLD. The nuclear SLD is dependent upon the species of atoms making up the structure of the sample. The magnetic potential is dependent upon the orientation of the magnetic induction in the layer with respect to the magnetic moment of the neutrons and is not sensitive to a perpendicular magnetisation component [59].

The potential is different depending on whether the neutron interacting with the layer is spin-up, leading to a positive magnetic SLD term or spin-down, producing a negative one and the total SLD is either increased or reduced respectively. This essentially means that for samples where the layers have no magnetisation, the reflectivity curve generated for both spin-up and spin-down neutrons is exactly the same. However a magnetisation of the layer results in a difference in the reflectivity curves generated by the two spins of the neutrons. The difference between these two signals

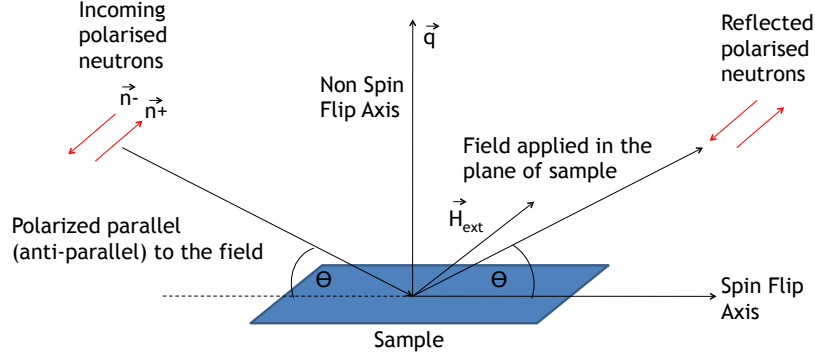


Figure 2.10: Diagram showing the PNR measurement geometries. A magnetic field is applied in the plane of the sample. Neutrons which are spin polarised parallel and antiparallel to the direction of the applied field are incident on the sample at angle θ . The neutrons are then reflected from the sample. The neutrons are not sensitive to an out-of-plane magnetisation in this set-up. In-plane sample magnetisations perpendicular to the applied field cause the neutrons spin to flip whereas magnetisations parallel to it do not.

is the spin asymmetry which indicates many of the magnetic properties of the sample.

PNR is an ideal technique for gaining information about magnetic structures because the nuclear SLD and magnetic SLD are the same order of magnitude [59]. It is also able to discern the in-plane orientation of magnetisation of layers whether it be collinear with the externally applied magnetic field or perpendicular to it. Perpendicular in-plane magnetisations lead to spin-flip events where the incoming spin-up (down) neutron has its spin reversed to spin-down (up) after interacting with the magnetic layer. This means that PNR can be exploited to measure magnetic structures consisting of antiferromagnetically coupled layers and it can also discern the type of antiferromagnetic coupling.

The PNR studies presented in this thesis were carried out at both Offspec and PolRef situated at the ISIS Neutron and Muon Source (ISIS), Harwell, Oxfordshire. ISIS produces its neutrons through the process of spallation leading to the production of neutron pulses. A heavy metal tungsten target is bombarded by highly energetic protons accelerated by a synchrotron. Highly energetic protons hit the target and

produce neutrons through spallation processes. These released neutrons have high energies and velocities and are then slowed down by hydrogenous moderators surrounding the target which cause collisions between neutrons and hydrogen nuclei with large scattering cross-sections. The temperature of the moderator determines the spectral distributions of the neutrons which are then used for different types of experiments.

Both instruments were used in their time-of-flight reflectometer configurations. The incident angle of the neutrons is fixed and the pulse contains a range of neutron energies/wavelengths. The reflectivity signal for each wavelength of the available spectrum is then measured, where each wavelength corresponds to a different scattering wave vector magnitude Q .

Reflectivity curves generated by PNR experiments were analysed using GenX where a simulated neutron reflectivity curve is optimised to the experimental data using a differential evolution algorithm [60]. The optimisation of fits is achieved by adjusting certain sample parameters such as roughnesses, thicknesses and magnetic moment magnitudes. This process gives an indication of the samples layer thicknesses and inhomogeneities, interfacial roughnesses and interdiffusion, layer density, doping concentration, layer magnetisation and orientation, nuclear SLD and magnetic SLD.

2.4 Growth of Thin Film Topological Insulators

Before discussing the magnetically doped systems which are the main topic of this study it is important to first consider the growth processes and characteristic properties of the un-doped TI systems Sb_2Te_3 and Bi_2Te_3 . A more in depth study of the fabrication of these systems can be found in refs. [9, 61]. These studies formed the basis for the approach taken with the growth and characterisation of samples produced for the purposes of the research demonstrated in this thesis so it is important

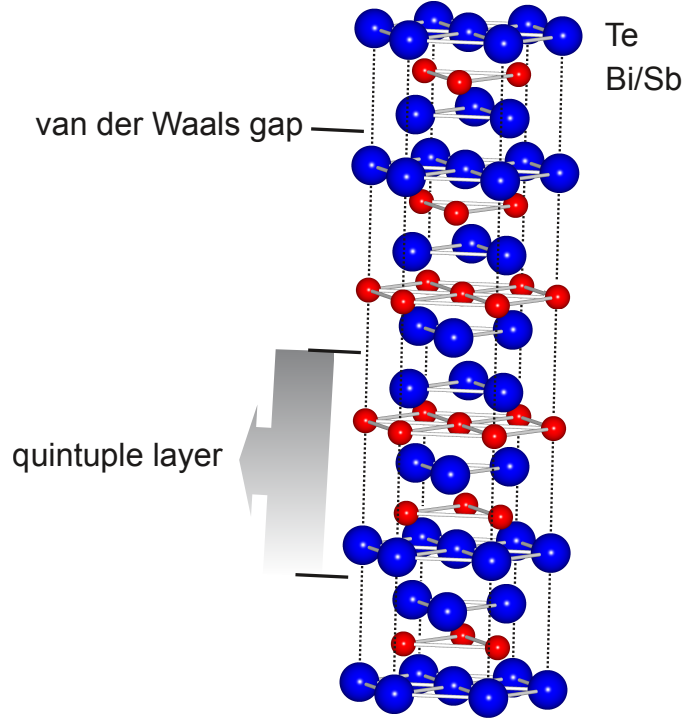


Figure 2.11: Crystal structure of both Bi_2Te_3 and Sb_2Te_3 . Single Te and Bi/Sb layers are arranged into quintuple layers with a van der Waals gap between each. The crystallographic cell has rhombohedral symmetry with space group $R\bar{3}m$. The atoms display hexagonal close packing. Figure adapted from ref. [12].

to summarise the relevant findings here.

2.4.1 Antimony Telluride and Bismuth Telluride

Antimony and bismuth chalcogenides, Bi_2Te_3 and Sb_2Te_3 are tetradymites, based on the stacking of quintuple layer building blocks, where each layer consists of one kind of atom. This gives a crystallographic cell of rhombohedral symmetry, space group $R\bar{3}m$ where atoms are hexagonal close packed [62].

The crystal structure parameterisation for Sb_2Te_3 is $a = 4.264 \text{ \AA}$, $c = 30.458 \text{ \AA}$ [63] and for Bi_2Te_3 it is $a = 4.395 \text{ \AA}$, $c = 30.440 \text{ \AA}$ [64]. Despite being TIs, both materials are narrow band-gap semiconductors and are relatively poor insulators. Sb_2Te_3 is strongly p -type, with high carrier concentrations and has yet to be successfully made

n -type through doping. Bi_2Te_3 is also naturally p -type although it can be doped to display either n -type or p -type behaviour.

As discussed in section 1, both Sb_2Te_3 and Bi_2Te_3 are the most simplest of 3D TI systems with surface states consisting of only one Dirac cone. These surface states have been both theorised using first-principle electronic structure calculations and observed experimentally using angle resolved photoemission spectroscopy (ARPES) [26,65,66]. The simplicity of the single Dirac cone surface states makes these systems favourable when it comes to studying the physics of TIs.

These systems have also been successfully doped with a number of magnetic ions such as Fe [67], Mn [68], Dy [61], V [69] and Cr [70] making them ideal for use in the study of magnetic order in TIs. This has lead to the experimental observation of the QAH state in both Cr-doped and V-doped antimony bismuth chalcogenide systems [7,71].

2.4.2 Selection of Substrate

When attempting to achieve heteroepitaxy, a type of epitaxy where a single crystal layer is grown on a substrate of different material with compatible crystal structure, it is important to consider the in-plane lattice parameter of the intended film growth and substrate. If these parameters differ too much then this can result in the formation of unwanted defects and strain in the grown sample. There should be as close a match as possible between the two in order to ensure a good quality of growth.

The growth of both Bi_2Te_3 and Sb_2Te_3 however, is mediated through the mechanism of van der Waals epitaxy, where heteroepitaxial growth can be ensured even when using substrates with a large in-plane lattice parameter mismatch [72]. In van der Waals epitaxy, growth proceeds between the substrate and incident material via a weak van der Waals interaction rather than via dangling bonds present on the substrate. It is possible to promote this growth mechanism through the passivation of

these dangling bonds. Films grown via this growth mechanism have their own in-plane lattice constants with crystallographic axis still being aligned to those of the substrate.

The substrate of choice for the growth of films studied in this thesis was *c*-plane (0001) sapphire Al_2O_3 . Sapphire has an in-plane lattice parameter $a = 4.785 \text{ \AA}$ leading to a mismatch of 8.9% and 12.2% when compared with the in-plane lattice parameters of Bi_2Te_3 and Sb_2Te_3 , respectively. Its wide use in the semiconductor industry means it is a readily available, low cost substrate which is easy to prepare. It is also insulating at room temperature so is suitable for electronic measurements. Sapphire substrates were received from Crystec in quarter pieces of a 2-inch wafer. Before being loaded into the MBE chamber the substrates are cleaned with standard solvent cleaning procedure in order to remove any capping layer or dirt and were then baked in the load lock at a temperature of 140°C in order to ensure water desorption.

2.4.3 Two-temperature Step Growth Technique

The substrate temperature is found to be largely responsible for the growth mechanisms of chalcogenide based TI systems. In the case of Sb_2Te_3 and Bi_2Te_3 when depositing material at room temperature, films are found to be amorphous or polycrystalline with large amounts of Te due to poor surface mobility. A 2D growth regime can be found by increasing the substrate temperature to $150\text{-}300^\circ\text{C}$ however, the surface of the films demonstrates poor crystallinity. Increasing the substrate temperature beyond this regime results in a growth of overall higher crystalline quality, but with the formation of 3D defect structures. Increasing the substrate temperature even further results in evaporation of the deposited material from the surface of the substrate.

To prevent there being a trade off between crystallinity and defects when growing the chalcogenide TIs at a fixed temperature, a two-temperature step growth technique

was established [73]. This process was originally developed to grow high quality Bi_2Te_3 films grown on *c*-plane sapphire, however it has been shown that this technique can also be used to produce high quality Sb_2Te_3 films grown on the same substrate [9].

The two-temperature step growth technique involves initially depositing a low temperature nucleation layer on the substrate which ensures that the substrate surface is fully covered. This nucleation layer is then annealed at a higher substrate temperature in order to increase the mobility of the species in the nucleation layer which ensures the filling of lattice defects to improve the crystalline quality of the film. The anneal is done in a Te-rich environment as lattice defects often occur as a result of Te which evaporates from the surface at high substrate temperatures. This process essentially ensures that there is a very high quality chalcogenide TI layer present on the surface of the substrate which the rest of the growth can use as a basis. Once the anneal process is complete the chalcogenide TI layer is continued at the same substrate temperature as the anneal was performed at. It has been shown through the use of surface sensitive and bulk sensitive analytical techniques that the two-temperature step growth technique produces chalcogenide TI samples with a higher crystalline quality which contain larger atomically flat terraced domains with lower defect densities [1].

After being baked in the load lock overnight, the substrate is moved into the growth chamber and is first heated via the use of the Ta wire heater to a temperature of 450°C after being pointed away from the effusion cells within the chamber. This is to ensure that once the material in the effusion cells is released into the chamber background during the flux calibration process, material does not settle on the substrate. This step also helps to outgas the substrate further.

The effusion cells are then heated to the temperature at which the correct flux value for each element is achieved as measured by the BFM. In the case of both chalcogenide TI systems grown throughout the studies presented here, a flux ratio of

1:10 (Bi,Sb):Te was used. The increased flux of Te reduces lattice defects caused by Te deficiencies as well as allowing the material to grow with the correct phase. The Bi/Sb flux is usually set to $\sim 4 \times 10^{-8}$ Torr. The growth of the sample is mediated by the Bi/Sb deposition rate, any Te not incorporated into the crystal structure is found to evaporate into the chamber at growth temperatures.

The RHEED system is then used to observe the surface of the substrate to ensure that it is clean for growth. This is done by using an electron energy of 30 keV. The RHEED system has to be blanked during the growth of the chalcogenide TI systems as the high energy electrons damage the surface of the sample if incident upon it for large periods of time. Once this is done, the substrate temperature can be set to the nucleation layer sample temperature and the growth can commence. For both Sb_2Te_3 and Bi_2Te_3 the optimum substrate temperatures which are found to ensure the highest crystalline quality samples are 200°C for the initial low temperature nucleation growth and 250°C for the anneal stage and overgrowth. The anneal process is always carried out for 30 minutes. The overgrowth deposition time can then be tuned depending on the sample thickness required.

2.4.4 Growth of Bismuth Telluride

At various stages of the growth of Bi_2Te_3 films, RHEED measurements were carried out using 30 keV incident electrons. The surface of the grown sample consistently demonstrated a RHEED pattern of well defined streaks indicative of its 2D nature. When comparing the RHEED pattern before and after the anneal of the nucleation layer, the streaks were found to become visibly sharper and demonstrate higher orders. This demonstrates the improved in-plane crystal order gained via the use of the two temperature step growth technique.

There are 2 different streaked RHEED patterns found to be 30° apart, along the $[10\bar{1}0]$ and $[11\bar{2}0]$ azimuths of the sapphire substrate as demonstrated in Fig. 2.12.

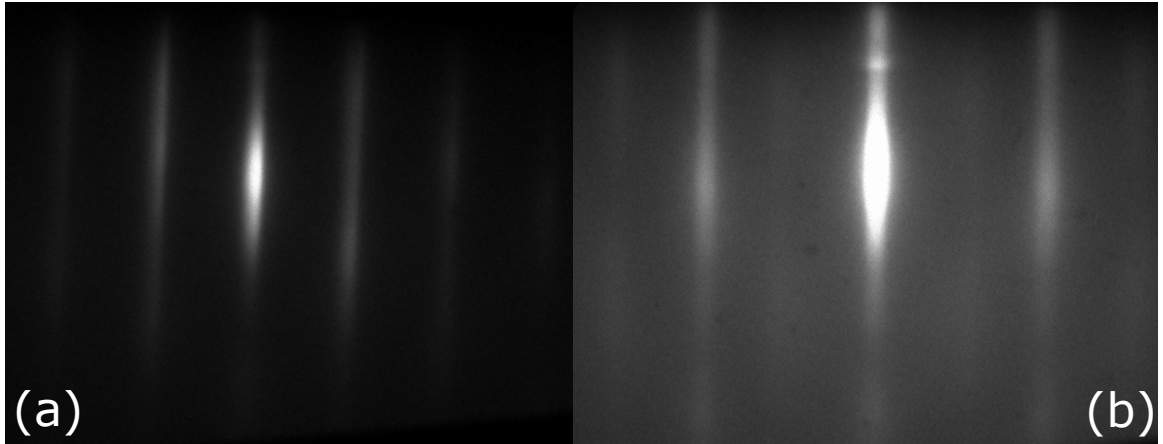


Figure 2.12: RHEED measurement conducted on MBE grown Bi_2Te_3 after a deposition time of 60 minutes on top of a 5 nm nucleation layer. (a) The RHEED pattern captured along the $[10\bar{1}0]$ azimuth of the c -plane sapphire substrate. (b) The RHEED pattern captured along the $[11\bar{2}0]$ azimuth. These patterns were found to be 30° apart when the sample was rotated. Each pattern repeated six times before the sample underwent a full rotation indicating twin domains. The RHEED measurements are indicative of the $R\bar{3}m$ space group of Bi_2Te_3 . The streak-like diffraction pattern demonstrates a film with 2D nature which is expected for a growth of high crystalline quality.

Each RHEED pattern is found to repeat six times during a full sample rotation demonstrating that there are twin domains. The twin domains are rotated around the $[001]$ axis by 180° [74]. Taking the twinning into account the sample demonstrates the 3-fold symmetry of the $R\bar{3}m$ space group. The ratio between the fringe spacings taken 30° apart is found to be consistent with the value $\sqrt{3}$ for the expected space group.

It has previously been demonstrated that the surface of Bi_2Te_3 grown using the two temperature step technique on sapphire consists of a number of triangular domains approximately a micrometer in size which are aligned with one another or rotated by 60° due to twinning [73]. These triangles are atomically smooth terraces with a concentric step structure and are consistent with the expected 3-fold symmetry of the crystal structure of Bi_2Te_3 . This type of growth mode has been attributed to the growth front becoming pinned during island growth and the occurrence of dislocations

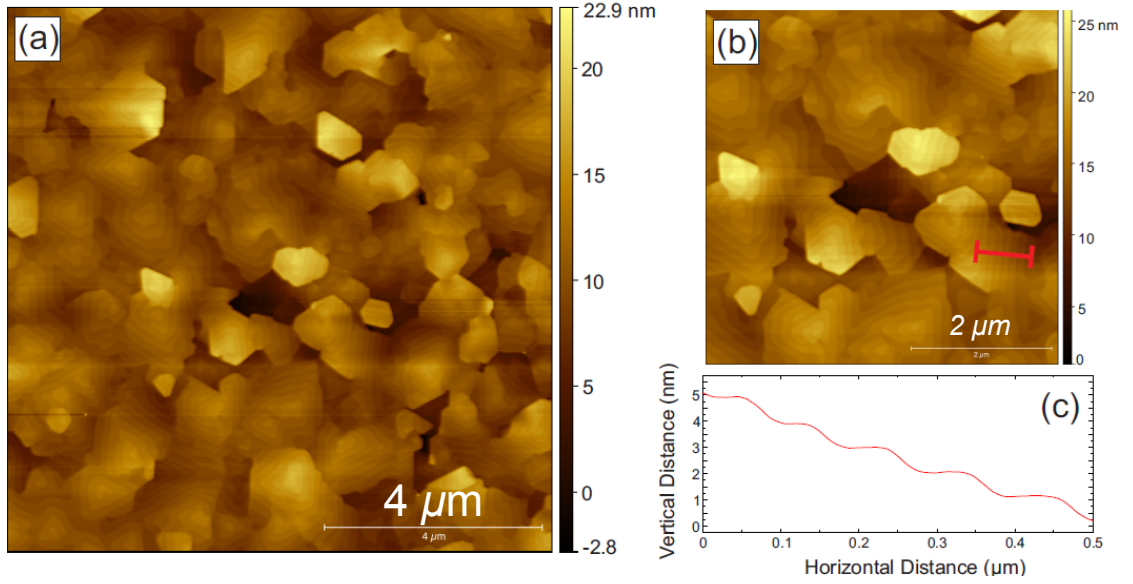


Figure 2.13: AFM measurements conducted by collaborator Dr. Liam Collins-McIntyre on MBE grown Bi_2Te_3 grown on a sapphire substrate. (a) Scan ($10 \times 10 \mu\text{m}^2$) of area of film surface demonstrating an overall smooth surface with triangular shaped terraces which have spiral-like properties. (b) Scan ($5 \times 5 \mu\text{m}^2$) showing the terraces in greater detail. The red line indicates where a line scan has been carried out of the AFM image. (c) The line scan of AFM image (b) demonstrates that each terrace is atomically flat with a step height of 1 nm indicative of the quintuple layer of Bi_2Te_3 . Figure taken from ref. [9].

at interfaces [75–77]. These same large triangular terraces with spiral-like growth have been observed in Bi_2Te_3 in samples grown using the Oxford chalcogenide MBE as demonstrated by Fig. 2.13(a) and (b). The AFM measurements, carried out by collaborator Dr. Liam Collins-McIntyre, demonstrate that each terrace is the same height as a quintuple layer of Bi_2Te_3 as shown by Fig. 2.13(c).

XRR measurements of Bi_2Te_3 films grown using the Oxford chalcogenide MBE can be used to determine the thickness of grown samples as well as give an indication of the roughness of the sample surface through the appearance of Kiessig fringes. Figure 2.14(a) demonstrates XRR measurements taken for a sample with a nucleation layer deposited for 10 minutes which has a thickness of 5 nm. After the 30 minute anneal at 250°C , an overgrowth layer is deposited for 120 minutes using the same typical Bi and

Te cell fluxes. The Kiessig fringes in Fig. 2.14(b) demonstrate that there is a uniform and finite film thickness with smooth interfaces throughout. The periodicity of the Kiessig fringes can be used to calculate the total thickness of the film as discussed in section 2.2.2. In this case the film is calculated to be 77 nm thick.

XRD measurements (Fig. 2.14(a)) of the same film are used to indicate the phase and crystal structure of typical Bi_2Te_3 films grown. The data was taken after the diffractometer was aligned to the sapphire (006) peak. The XRD spectrum is shown to be consistent with Bi_2Te_3 (00 l) diffraction peaks demonstrating that the film is indeed aligned along the c -axis with the expected crystal structure being devoid of unwanted phases or distortions. These peaks can be used to calculate the out-of-plane lattice constant of the grown film. In the case shown here $c = (30.43 \pm 0.01)$ Å which is in agreement with the expected lattice constant for Bi_2Te_3 film indicating little imposed epitaxial strain.

2.4.5 Growth of Antimony Telluride

RHEED measurements for grown Sb_2Te_3 films indicate the same sharp streaks which are improved during the annealing of the nucleation layer demonstrating that this system has a smooth 2D surface and also benefits from the two temperature step growth technique. The final RHEED images taken for these samples as shown by Fig. 2.15 indicate some slight signs of 3D growth as demonstrated by the spot-like features at the top of the images. This is likely due to the sample holder clip. There are 2 different RHEED patterns separated by a 30° rotation of the sample with the ratio between the two different spacings found to be $\sqrt{3}$. Once again, each RHEED pattern is observed to repeat six times with twin domains when the sample is rotated a full 360° demonstrating the $R\bar{3}m$ space group of the material.

XRR measurements are shown for a typical Sb_2Te_3 film grown during this research. For this sample the nucleation layer was deposited for 20 minutes corresponding to

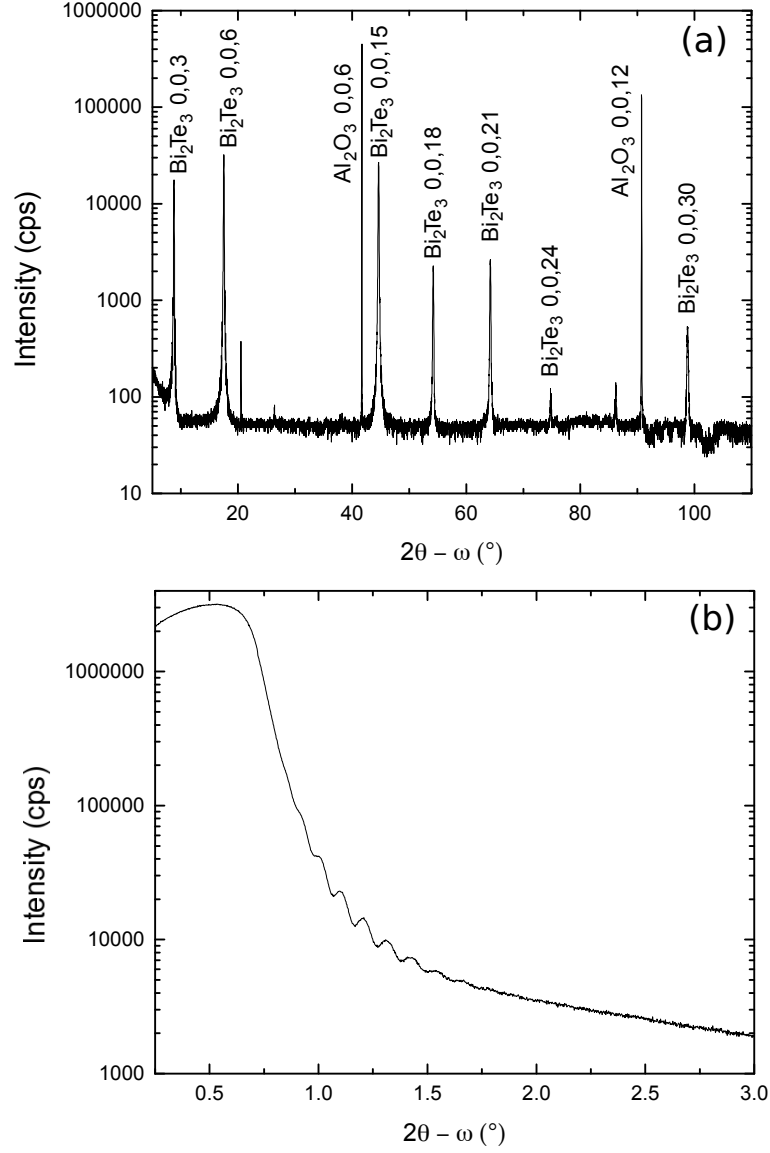


Figure 2.14: Structural X-ray measurements of Bi_2Te_3 film grown for 120 minutes deposition time after a 5 nm nucleation layer. (a) XRD measurements demonstrate the $(00l)$ peak positions which are consistent with the location of reference peaks (ICSD 158366). These peaks can be used to calculate the c -axis lattice parameter. (b) XRR measurements demonstrate Kiessig fringes which indicate a smooth sample surface. The spacing of these fringes is used to calculate the total thickness of the sample.

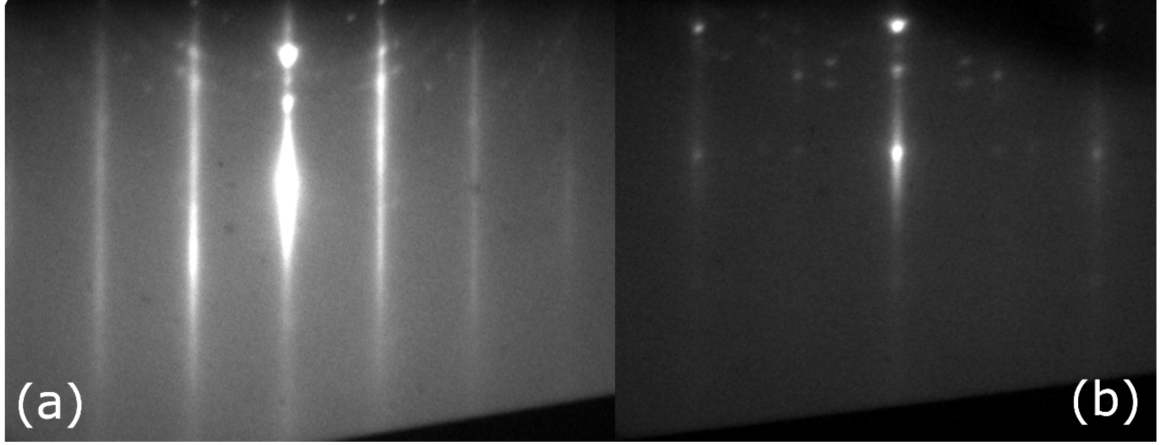


Figure 2.15: RHEED measurement conducted on MBE grown Sb_2Te_3 along the (a) $[10\bar{1}0]$ azimuth of the c -plane sapphire substrate and (b) $[11\bar{2}0]$ azimuth. These RHEED measurements were once again taken 30° apart. The RHEED images show a strong streak-like diffraction pattern demonstrating a film with smooth interfaces. The appearance of small spots and the onset of rings towards the top of the images likely comes from the sample holder clip and not the film itself. Each RHEED image repeated six times with twin domains in a full sample rotation indicating the $R\bar{3}m$ symmetry group of Sb_2Te_3 .

a thickness of once again ~ 5 nm. The overgrowth was then carried out after a 30 minute anneal for 120 minutes. The Kiessig fringes once again demonstrate the films smooth interfaces and their periodicity is used to calculate a total film thickness of 55.5 nm.

XRD measurements for the same film, carried out in the same manner as for Bi_2Te_3 once again demonstrate the well ordered structure of the thin film sample which is devoid of parasitic phases with only the $(00l)$ peaks being present. The c -axis lattice parameter is calculated to be $c = (30.41 \pm 0.01)$ Å which when compared to Bi_2Te_3 suggests there a slightly greater degree of epitaxial strain likely due to the larger mismatch in in-plane lattice constant between the sapphire and Sb_2Te_3 . Nevertheless this strain is rather small demonstrating that high quality Sb_2Te_3 films can be successfully grown on sapphire.

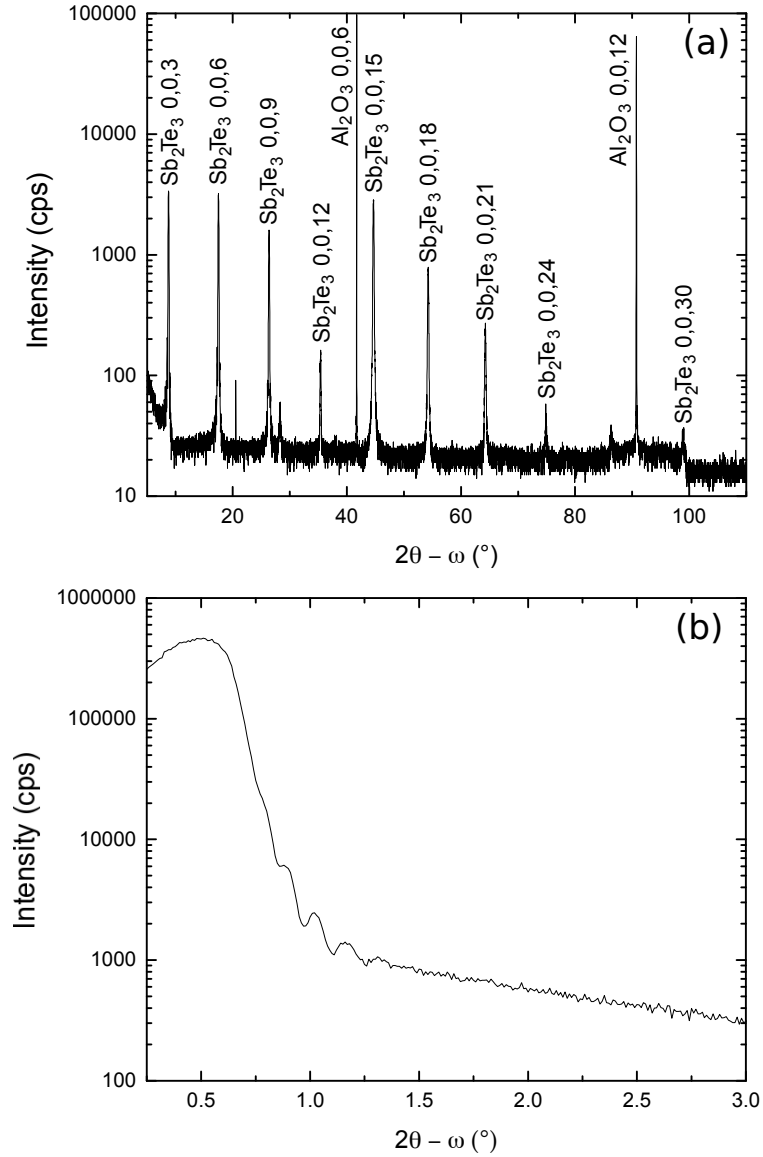


Figure 2.16: Structural X-ray measurements of Sb_2Te_3 film grown for 120 minutes deposition time after a 5 nm nucleation layer. (a) XRD measurements demonstrate the $(00l)$ peak positions which are consistent with the location of reference peaks (ICSD 2084). These peaks can be used to calculate the c -axis lattice parameter. (b) XRR measurements demonstrate Kiessig fringes which indicate a smooth sample surface. The spacing of these fringes is used to calculate the total thickness of the sample.

Chapter 3

Magnetic Topological Insulator Thin Films

3.1 Transition Metal Doped Sb_2Te_3

The introduction of magnetic dopants into 3D TI systems has lead to the experimental observation of the QAH state through the breaking of TRS. The introduction of long range ferromagnetic order in the TI causes the normally gapless linearly dispersed Dirac cone surface states to form a band gap at the Dirac point. A ferromagnetic ground state has previously been achieved in bulk samples of $(\text{Bi,Sb})_2(\text{Se,Te})_3$ doped with the transition metals Fe and Mn however, these dopants also cause the normally insulating materials to become conducting preventing the realisation of the QAH state [78–81]. Cr doping of these TI systems is predicted to lead to a ferromagnetically ordered insulating ground state [28, 82]. As discussed previously the QAH state has been experimentally observed in Cr-doped $(\text{Bi,Sb})_2\text{Te}_3$ [7]. Long range ferromagnetic order has also been observed in *n*-type Cr-doped Bi_2Se_3 [83, 84]. The Cr *d* bands are found to have a strong hybridization with the Se *p* bands located above and below the Fermi level such that the mixing of electrons between the two bands is increased and

does not contribute to the free-carrier concentration [85, 86]. It has been proposed that Cr doping of Sb_2Te_3 may lead to a long range ferromagnetic order caused by the Van Vleck mechanism where the exchange interaction is mediated by local valence electrons [28], however in the case of V-doped $(\text{Bi,Sb})_2\text{Te}_3$ a more complex coupling mechanism has been observed [87]. It is clear from these results that the $3d$ states of the transition metal impurities provide additional mechanisms for ferromagnetic coupling and play an important role in MTIs, however a more in-depth study is needed to understand the magnetic state of the material class in greater detail.

This section details the structural and magnetic study of transition metal Cr-doped Sb_2Te_3 thin films grown by MBE. The films were grown, studied with RHEED, XRR, XRD and SQUID VSM in collaboration with Dr. Liam Collins-McIntyre. The PNR measurements were conducted by Dr. Nina-Juliane Steinke and were analysed by the author. XAS and XMCD measurements were conducted in collaboration with Dr. Adriana Figueroa and Prof. Gerrit van der Laan and were analysed by the author. Atomic multiplet calculations were carried out for comparison with the XAS and XMCD experimental results by Prof. Gerrit van der Laan. The results featured in this section are also discussed in the publications ref. [12, 13].

3.1.1 Thin Film Growth

A number of different $\text{Cr:Sb}_2\text{Te}_3$ samples with varied Cr concentrations were prepared on c -plane Al_2O_3 (001) using the two temperature growth method as described in section 2.4.3 using the Oxford chalcogenide MBE system. Both the Sb and Te cells were set to the temperatures that produced the same flux values as discussed in section 2.4.5 as measured by the BFM. A flux ratio of 1:10 (Sb:Te) was once again used in order to ensure Te deficiencies did not occur in the crystal structure of the grown $\text{Cr:Sb}_2\text{Te}_3$. The Cr flux was measured as an indication of doping level of the $\text{Cr:Sb}_2\text{Te}_3$ samples. It has previously been demonstrated in the case of $\text{Cr:Bi}_2\text{Se}_3$ that the Cr

dopant substitutionally replaces the Bi sites contained within the crystal structure of Bi_2Se_3 [85]. It was assumed that this would be the case also for Sb_2Te_3 . This means that a good indication of the doping concentration for samples during growth is the ratio of fluxes between Cr and Sb. This assumption is not perfect because not all Cr and Sb incident on the sample during growth will reach the substrate and take part in the growth process, however it still allows for a certain degree of reproducibility certainly in the case of differentiating sample growths between low, middling and high doping concentrations. For example, the lowest doping concentration Cr: Sb_2Te_3 sample had a Cr cell BFM measurement of 7×10^{-10} Torr and the highest had a BFM measurement of 5×10^{-9} Torr compared to the fixed Sb flux of 4×10^{-8} Torr for each sample.

During each sample growth, after being moved into the growth chamber the substrate was initially outgassed at 450°C while a RHEED measurement was taken to ensure the Al_2O_3 was ready for growth. The substrate temperature was then reduced to 200°C and an undoped Sb_2Te_3 layer of approximately 5 nm was deposited and annealed for 30 minutes at the elevated temperature of 250°C . It has been found that an initial undoped layer helps to ensure that a doped overgrowth layer maintains a high quality of crystal structure for these thin film samples as indicated by RHEED measurements. Thinner, better defined RHEED streaks indicative of high quality 2D growth are found for samples with undoped nucleation layers. After the anneal, the doped film is then deposited at this elevated substrate temperature by opening the Cr, Sb and Te cells at the same time. In the case of samples discussed in this study, the deposition time for this overgrowth layer was 120 minutes.

Rutherford backscattering spectrometry (RBS) was carried out by collaborators at the IBM Almaden Research Center, San Jose, in order to accurately determine the Cr concentration of grown samples. A discussion of the RBS technique can be found in ref. [88]. The $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ samples used throughout the studies shown in

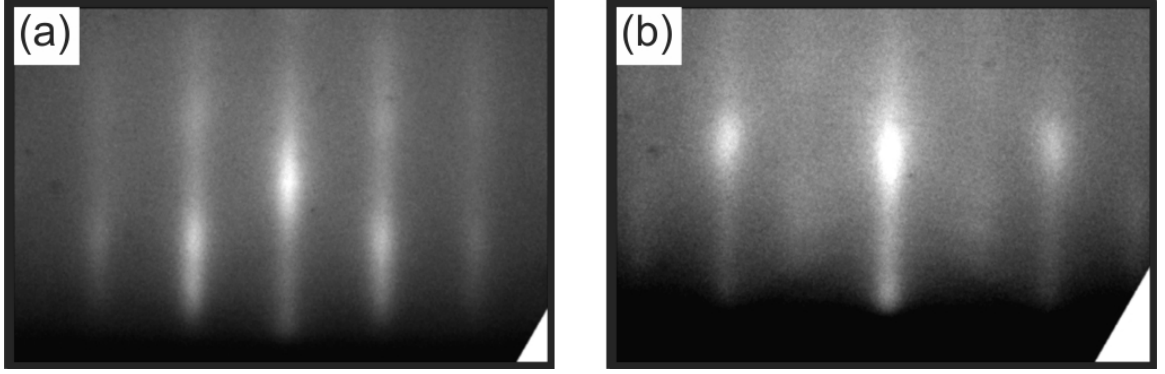


Figure 3.1: RHEED measurement conducted on $\text{Cr}_{0.42}\text{Sb}_{1.58}\text{Te}_3$ sample along the (a) $[10\bar{1}0]$ and (b) $[11\bar{2}0]$ azimuth of the c -plane sapphire substrate. The two RHEED patterns are separated by a 30° sample rotation and each repeat six times with twin domains when the sample is rotated a full 360° demonstrating the $R\bar{3}m$ symmetry group of the sample. Compared to undoped Sb_2Te_3 the RHEED images demonstrate more diffuse streaks of a rougher 2D surface. Figure adapted from ref. [13].

this thesis were $x = 0.15, 0.26$ and 0.42 .

3.1.2 Structural Characterisation

3.1.2.1 Reflection High Energy Electron Diffraction

RHEED measurements were taken at various stages throughout the growth of the Cr-doped samples. Figure 3.1 shows the RHEED images taken for the $x = 0.42$ $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ sample surface at the end of the growth. The RHEED measurements indicate a smooth 2D-like surface as demonstrated by the streaked pattern. The $R\bar{3}m$ structure of Sb_2Te_3 is maintained even at these high doping concentrations as demonstrated by each of the RHEED images repeating six times with twin domains throughout a full sample rotation. Two different RHEED images are found along the $[10\bar{1}0]$ and $[11\bar{2}0]$ azimuths of the c -plane sapphire substrate, separated by a 30° rotation which is once again the same as undoped Sb_2Te_3 .

3.1.2.2 Atomic Force Microscopy

AFM measurements shown in Fig. 3.2 of the surface morphology of the $\text{Cr:Sb}_2\text{Te}_3$ samples demonstrate that like undoped Bi_2Te_3 (as discussed in section 2.4.4) the surface is smooth with triangular like terraces which grow like spirals. This is to be expected, as Bi_2Te_3 and Sb_2Te_3 share the same crystal symmetry group of $R\bar{3}m$ and also have similar lattice constants. Figure 3.2(b) demonstrates that when a line profile is taken across one of these spirals, each terrace is approximately 1 nm in height, the size of a single quintuple layer of Sb_2Te_3 . These terraces however, appear to be more irregular than those observed for Bi_2Te_3 , in agreement with the diffuse RHEED streaks observed for these sample. This is likely due to the doping process. The smaller radii Cr is likely to substitutionally replace the larger Sb ions within the crystal structure. For the AFM measurements, the very localised areas which are probed will have a non-uniform distribution of Cr dopants affecting the quality of the terraces. Note that this does not necessarily mean that the doping of Cr is non-uniform throughout the entire structure or that clustering of the Cr is occurring.

3.1.2.3 X-Ray Reflectometry

XRR measurements were carried out for the $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ in the same manner as described in section 2.2.2. The data was then fitted in GenX to determine structural information for each sample. Figure 3.3 shows the XRR measurements for the $x = 0.15, 0.26$ and 0.42 $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ samples complete with the model that was used to fit each data set. The Cr concentration for each fit was fixed at the value measured by RBS. The same three layer model was found to produce the best fit in each case. The first layer, takes into account the Sb_2Te_3 nucleation layer which is grown first. The overgrowth layer of $\text{Cr:Sb}_2\text{Te}_3$ is then split into two layers, a majority Cr-doped Sb_2Te_3 layer (with the Cr concentration fixed at the RBS measured value) and a thinner Cr-doped Sb_2Te_3 top layer which is used to take into account a possible

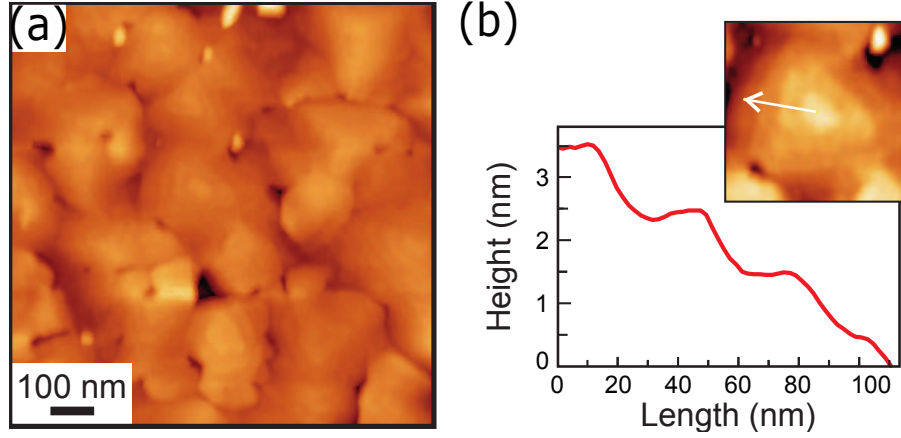


Figure 3.2: AFM measurements of the $\text{Cr}_{0.42}\text{Sb}_{1.58}\text{Te}_3$ sample. (a) 100 nm size scan across the surface of the sample demonstrating the expected three-fold triangular growth features of this materials symmetry group. (b) Line scan across one of the triangle-like terraces inset with the position of the line scan indicated by the inset AFM image. The profile demonstrates the quintuple layer terraces of the sample. The terracing is rougher when compared to an undoped TI likely due to the inhomogeneous nature of the doping process in localised areas. Figure adapted from ref. [13].

different doping concentration or reduced filling factor which may occur due to Te evaporation at the samples surface.

Table 3.1 demonstrates key parameters from the XRR fits including layer thicknesses and the roughnesses for the interfaces and surface. Slight variations in Cr concentration and filling factors at different layers of the samples result in only very minute changes in the SLD for the incident X-rays, therefore it is hard for XRR to discern the individual layer thicknesses as long as the total film thickness remains the same for these types of samples. The XRR data gives a good indication of the total thickness of each of the films with a larger error in the individual layer thicknesses due to the lack of contrast in SLD. This means that the contrast is not great enough for the X-rays to accurately measure the interfacial roughnesses between each of the layers. The interfacial roughness values given in table 3.1 are the best fitting root mean square values.

The XRR fits demonstrate a clear trend towards smoother film surfaces at higher

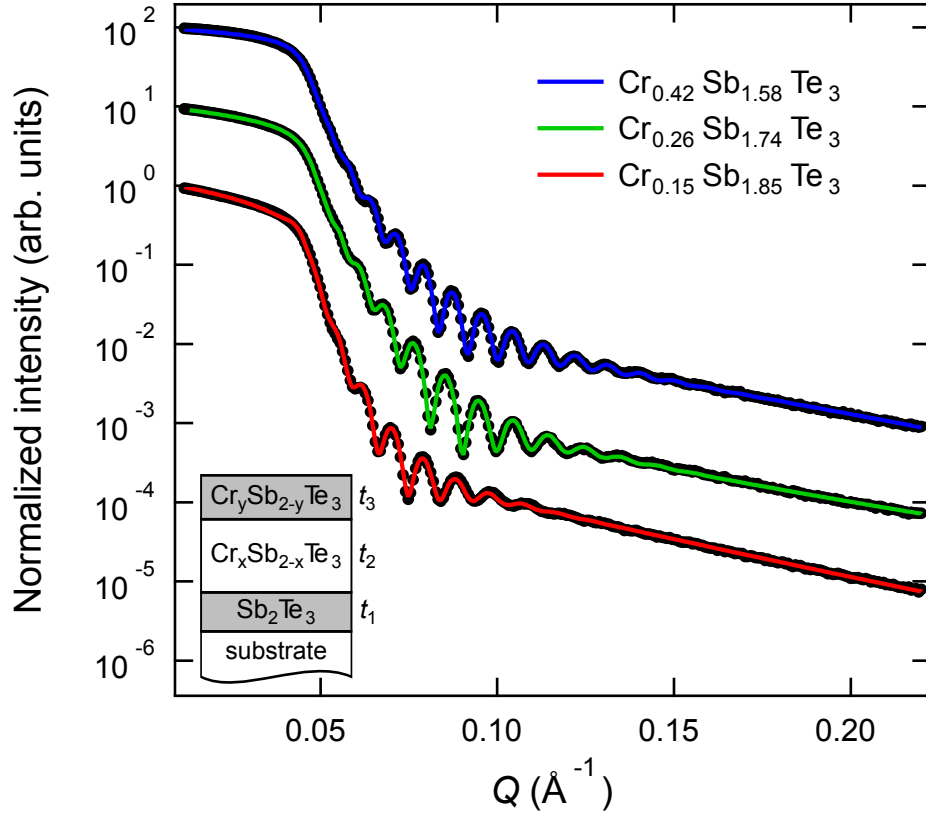


Figure 3.3: XRR measurements for the $x = 0.15, 0.26$ and 0.42 $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ samples with the maximum intensity of each data set being normalised and then offset by a factor of 10. Each data set has a fit generated for it using the three layer model shown in the inset of the figure which takes into account the nucleation layer and possible changes in doping concentration and Te deficiencies at the sample surface. Figure adapted from ref. [13].

Table 3.1: Fitted parameters to simulated model of XRR measurement depicted in Fig. 3.3. A representation of the film structure used in the model is shown as inset to Fig. 3.3. Errors are computed based on 95% confidence bands of the relevant fit parameter. The given concentrations are from RBS results according to the nominal stoichiometry $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$.

x_{Cr}	Layer thickness (Å)			Roughness (Å)	
	t_1 (Sb_2Te_3)	t_2 ($\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$)	t_3 ($\text{Cr}_y\text{Sb}_{2-y}\text{Te}_3$)	<i>Interfacial</i>	<i>Surface</i>
0.15	5.0 ± 1.2	600.550 ± 0.001	37.575 ± 0.001	18.96 ± 0.01	75.0 ± 1.0
0.26	5.47 ± 0.6	557.47 ± 0.2	31.06 ± 2.1	13.73 ± 1.0	50.00 ± 1
0.42	8.537 ± 0.001	603.19 ± 0.01	8.261 ± 0.004	13.33 ± 0.01	24.65 ± 0.01

doping concentrations. This can also be seen in Fig. 3.3 by the increase in the order of Kiessig fringe oscillations for the $x = 0.42$ sample. This surface roughness reduction may come from the formation of smaller islands during the growth of higher doping concentration samples. The introduction of the Cr dopant is likely to disrupt the normal growth mode of Sb_2Te_3 . This is supported by the smaller triangular formations of $\text{Cr:Sb}_2\text{Te}_3$ shown by Fig. 3.2 when compared to Bi_2Te_3 . From the perspective of the incident X-rays, the surfaces of the higher doped film with smaller island formations will appear smoother.

3.1.2.4 X-Ray Diffraction

XRD measurements taken in an out-of-plane geometry for each sample give an indication of the crystal quality and phase of each of the grown films. Figure 3.4 shows the positioning of the $(001\bar{5})$, (0018) and (0021) Cr-doped Sb_2Te_3 peaks of each film in comparison to the Al_2O_3 (006) peak and corresponding undoped Sb_2Te_3 peaks.

Each film is well ordered with clear $(00l)$ peaks being observed with the absence of extra peaks which could be attributed to other phases. The c -axis of the film is normal to the plane of each substrate as is to be expected for good ordered growth. The film peaks shift to higher angles for Cr-doped Sb_2Te_3 films when compared to undoped Sb_2Te_3 . This shift increases as a function of the doping concentration. This is consistent with a decreasing c -axis lattice parameter for higher doped samples.

When the Cr dopant is introduced into the crystal structure of the Sb_2Te_3 , the dopant can either insert itself into the van der Waals gap between each of the quintuple layers or it can substitutionally replace the Sb ions. In the case of Cr ions being inserted into the van der Waals gap, the c -axis lattice parameter for the film would be expected to increase as extra atoms are inserted into the structure. If we consider the ionic radius of the constituent atoms within the Sb_2Te_3 structure we can see that for sixfold coordinated Sb^{3+} and Te^{2-} , the ionic radii are 76 and 103 pm respectively [89].

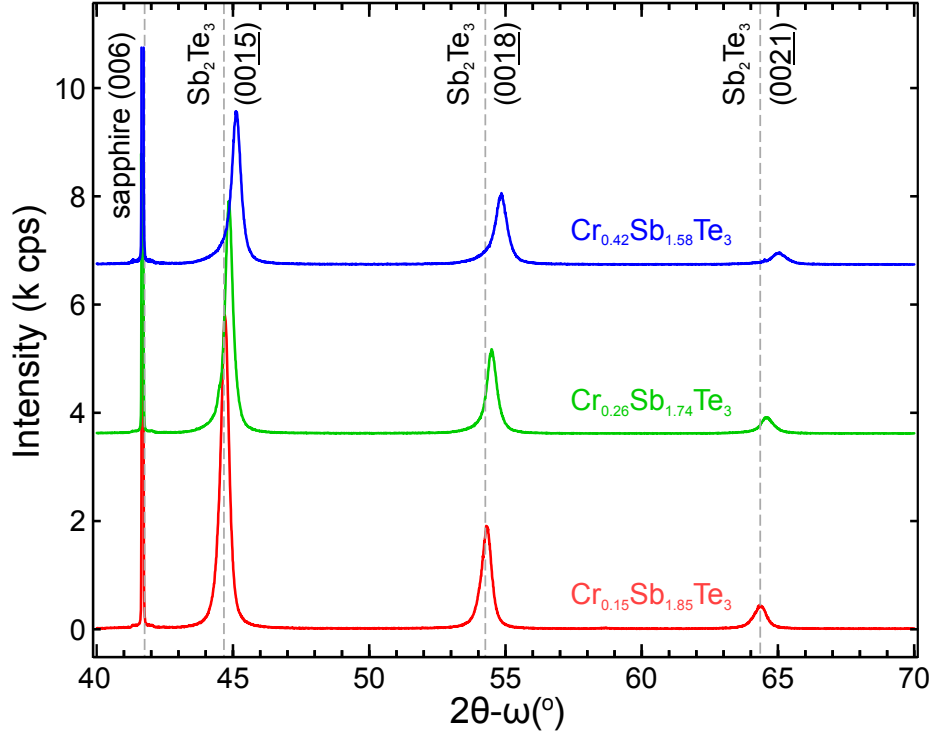


Figure 3.4: XRD measurements for the $x = 0.15, 0.26$ and 0.42 $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ thin film samples measured in an out-of-plane geometry. Before the measurement was taken, the sample was aligned to the Al_2O_3 substrate peak in order to maximise the intensity of the thin film peaks measured. The dashed lines are the positions of the undoped Sb_2Te_3 (00 l) peaks (ICSD 2084). The XRD measurements for each film are shifted in intensity for clarity. Figure adapted from ref. [13].

There are a number of different valencies Cr can have depending on how it dopes into the crystal structure. Cr^{2+} high spin, Cr^{2+} low spin, Cr^{3+} , Cr^{4+} and Cr^{5+} have ionic radii 80, 73, 61.5, 55 and 49 pm, respectively. For a substitutional doping scenario Cr is likely to have 2+ low spin character as this atomic radius value closely matches that of Sb. Evidence for this valency will also be discussed in section 3.1.3.2. Therefore a shrinking c -axis lattice parameter would be consistent with a substitutional doping scenario as the Cr-Te bond length would be shorter than that of Sb-Te. This scenario is observed for Cr-doped Bi_2Se_3 [10] where a c -axis lattice parameter reduction was observed for higher Cr doping concentrations.

The c -axis lattice parameters for the $x = 0.15$, 0.26 and 0.42 samples were calculated from the XRD data as being 30.395 Å, 30.308 Å and 30.127 Å, respectively. These values are consistent with the Cr is substitutionally replacing the Sb ions within the crystal structure of Cr-doped Sb_2Te_3 . It is also likely that there are no Cr ions present in the van der Waals gaps as the c -axis lattice parameter decrease can be approximated as being linear with doping concentration. This method can also be used to approximate Cr doping concentrations via observing the shift in $(00l)$ peaks.

3.1.3 Magnetic Characterisation

3.1.3.1 Magnetometry

The magnetisation of the thin films was observed as a function of temperature using a SQUID VSM. A magnetic field of 2 mT was applied out-of-plane to the sample throughout the measurements. Figure 3.5 shows the MvT measurements for each doping concentration of sample. As discussed in section 2.3.1, the magnetisation which was measured in emu was converted into μ_B/Cr by measuring the volume of the film and by using the doping concentration of each sample as measured by RBS. The MvT measurements are then differentiated with respect to temperature where a clear minimum can be seen for each sample. The temperature at which this minimum

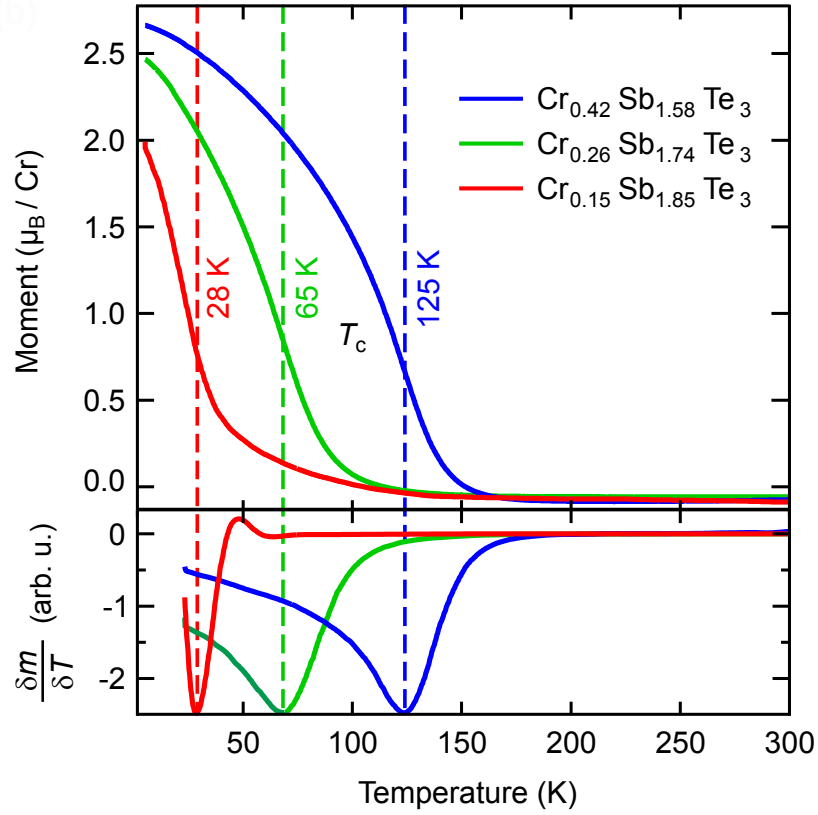


Figure 3.5: Magnetisation versus temperature measurements for the $x = 0.15, 0.26$ and 0.42 $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ samples. Measurements were carried out in a magnetic field of 2 mT applied out-of-plane to the samples surface. The bottom plot shows the first derivative of the MvT measurements with respect to temperature. The minimum of the first derivative plots gives the ferromagnetic transition temperature of each sample and is indicated. Figure adapted from ref. [13].

occurs is the ferromagnetic transition temperature (T_C) of the sample.

The set of measurements for each sample demonstrate a clear ferromagnetic to paramagnetic transition as the temperature is increased. The samples with doping concentrations $x = 0.15, 0.26$ and 0.42 each have a $T_C = 28$ K, 65 K and 125 K, respectively. This demonstrates that not only does the T_C of each sample vary strongly with the doping concentration, but the higher the doping concentration, the higher the samples T_C . The T_C is observed to increase approximately linearly with doping concentration and therefore this can also be used to indicate the Cr doping concen-

tration of films. It has been found that increasing the Cr concentration further than the highest doping concentration shown here can result in the formation of Cr_2Te_3 phases in samples. Seeing as Cr_2Te_3 has an expected T_C of approximately 180 K, this can lead to the erroneous conclusion that the T_C increases further than 125 K when in reality this is likely the T_C of the Cr_2Te_3 being observed. These measurements also demonstrate that for different doping concentration films the saturation magnetisation is likely to be different with the value increasing for increasing doping concentrations of films.

The SQUID VSM was also used to measure hysteresis loops for the $x = 0.42$ $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ sample at various temperatures both in an in-plane and out-of-plane to the sample surface applied magnetic field. Figure 3.6 shows the out-of-plane hysteresis loop measured at 5 K along with the in-plane hysteresis loops measured between 5 K and 200 K. Each hysteresis loop was measured by ramping the field from a maximum of 5 T to -5 T and then back to 5 T again. The diamagnetic response from the Al_2O_3 substrate has been subtracted by fitting a straight line to the high field region of the hysteresis loop where the sample was fully saturated. The magnetisation has once again been converted into μ_B/Cr from emu by taking into account the film volume and Cr doping concentrations.

It is clear from these hysteresis loops that there is a clear magnetic anisotropy in these samples with an easy axis out-of-plane where the samples are much easier to magnetise. The out-of-plane hysteresis loop demonstrates soft ferromagnetic behaviour at 5 K. An open loop can be clearly seen for both in-plane and out-of-plane hysteresis loops up to a temperature of 150 K where the loop is seen to close confirming the transition from ferromagnetism to paramagnetism at high temperatures as confirmed by the MvT measurements. At the lowest measurement temperature of 5 K, the saturation field for the sample is 200 mT out-of-plane and approximately 2 T in-plane. The magnetic coercivity is 6 mT both out-of-plane and in-plane. The

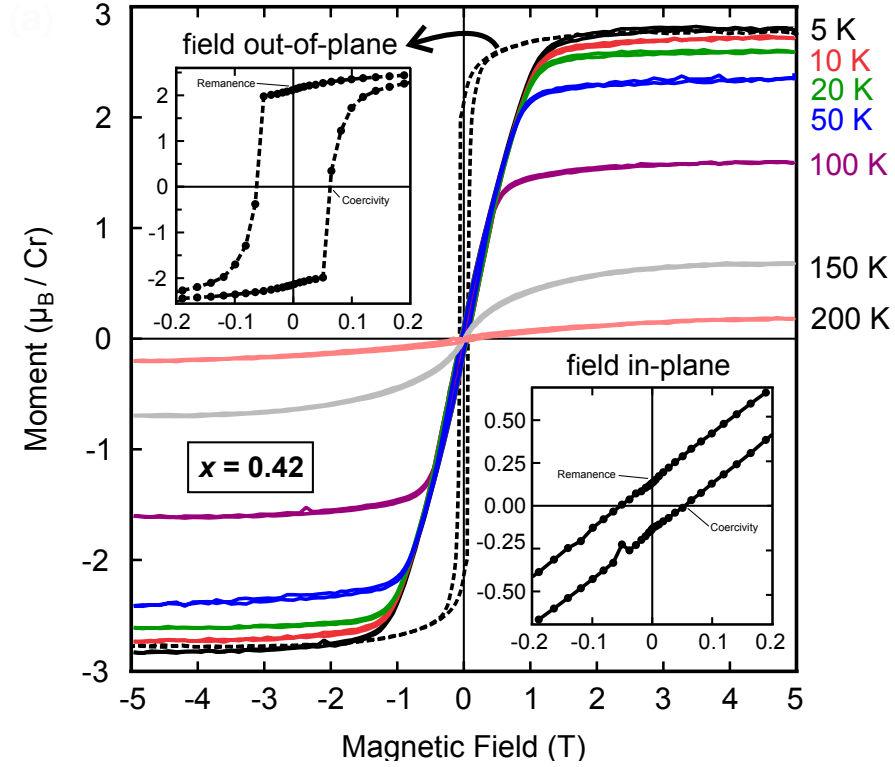


Figure 3.6: Magnetisation of $\text{Cr}_{0.42}\text{Sb}_{1.58}\text{Te}_3$ as a function of applied magnetic field. The broken black line shows the hysteresis loop taken with an applied magnetic field out-of-plane to the samples surface at a temperature of 5 K. The top left inset shows this same hysteresis loop with a smaller range of fields to highlight the open shape of the loop and coercivity value. The solid colour lines demonstrate the hysteresis loops measured for an in-plane applied field at various temperatures. The bottom right inset shows the in-plane hysteresis loop taken at 5 K for a similar smaller field range to once again show the loop is open. Figure adapted from ref. [13].

saturation remanence is approximately $(2 \pm 0.2) \mu_B/\text{Cr}$ out-of-plane and $0.13 \mu_B/\text{Cr}$ in-plane.

The saturation moment is found to be $(2.8 \pm 0.2) \mu_B/\text{Cr}$ at 5 K with the stated uncertainty being dominated by a statistical error in the determination of the area of the film. This error also takes into account the uncertainty in the measured Cr doping concentration of each sample from RBS. This is less than the expected magnetic moment for Cr calculated using Hund's rule where the Cr should have a value $3 \mu_B/\text{Cr}$. This was also found to be the case for Cr-doped Bi_2Se_3 where it was found that there was a hybridization between Cr d and Se p orbitals increasing the sharing of electrons within the chemical composition, reducing the oxidation state of the Cr dopant [10]. It is likely that there is also the same hybridization between Cr d and Te p orbitals in Cr-doped Sb_2Te_3 leading to a similar effect.

3.1.3.2 X-ray Absorption Spectroscopy and X-Ray Magnetic Circular Dichroism

XAS and XMCD measurements were carried out at beamline ID32. These measurements were performed on a $\text{Cr}_{0.32}\text{Sb}_{1.68}\text{Te}_3$ sample where the doping concentration was calculated from the shift in the c -axis lattice parameter ($c = 30.238 \text{ \AA}$) and from SQUID VSM MvT measurements where the first derivative of the temperature dependent magnetisation gave a $T_C = 72 \text{ K}$. In order to ensure that there was no oxide layer at the surface of the sample, as has been previously observed for Cr-doped TIs [10], it was cleaved in UHV. This was achieved by glueing the sample film side down with silver paste to the copper sample holder and then glueing a cleaving post to the back of the substrate. Once loaded into the chamber, the cleaving post was then knocked off with a sample transfer stick inside the chamber, taking the substrate with it and leaving the thin film behind. It is assumed that the film will cleave at the interface between it and the substrate or at one of the van der Waals gaps of

the structure. This cleaving process ensures a pristine Cr-doped Sb_2Te_3 layer can be investigated.

XAS and XMCD measurements were carried out at normal incidence to the sample surface with respect to the incoming X-rays and applied magnetic field. Before the measurements were carried out, the sample was magnetised with an applied magnetic field of 1 T. This magnetic field was then withdrawn to ensure that the XMCD measurements were recorded at remanence. The XMCD signals were calculated by taking the difference between XAS spectra recorded using X-rays with helicity vectors both antiparallel and parallel to the applied magnetic field. The consistency of the XMCD signal was also checked by reversing the initially applied magnetic field. Each spectrum was measured using TEY where it is important to note that the TEY measurements probe only 3 to 5 nm deep into the film giving a surface sensitive measurement [11].

Figure 3.7(a) demonstrates the Cr $L_{2,3}$ XAS and XMCD spectra measured by TEY for the cleaved $\text{Cr}_{0.32}\text{Sb}_{1.68}\text{Te}_3$ sample at a temperature of 10 K. The XAS for the Cr L_3 peak demonstrates a double peak structure where the second peak is found at ~ 0.5 eV higher energy than the first. The first peak is more dichroic than the second with a larger difference in absorption for the different helicities of light as shown by the XMCD spectrum. Compared to the Cr XAS spectrum recorded for Cr-doped Bi_2Se_3 , this second peak is much lower in intensity [10, 90]. The method used to cleave the film has successfully prevented the presence of oxidation at the surface as there is no peak at 1.5 eV higher energy which can be seen in both the Cr_2O_3 reference and the XAS data for the Cr-doped Bi_2Se_3 sample shown in ref. [10].

The line shape of the XMCD spectrum for the $L_{2,3}$ edge is also very similar to that of Cr-doped Bi_2Se_3 demonstrating a small shoulder at ~ 0.6 eV lower energy than the first L_3 peak. The XMCD L_3 peak is negative and there is a sharp negative peak at 584.6 eV which corresponds to the start of the L_2 peak. The overall intensity

of the L_2 XMCD edge is positive and therefore opposite to the L_3 peaks as is to be expected for a system with spin split $2p$ energy levels due to spin orbit coupling [52]. The Cr $L_{2,3}$ edge largely coincides with the Te $M_{4,5}$ edges leading to a strong sloping background witnessed in the XAS measurements. The Te M_5 peak is negative and is found at 573.4 eV as highlighted in Fig. 3.7(a). This peak was also observed to become positive for a negative applied initial magnetic field and changes sign for an opposing X-ray helicity order.

Density functional theory calculations show that for Cr substitutionally doped into Sb_2Te_3 , the Cr ions are trivalent with $3+$ character due to a weak hybridization between the Cr d and Te p states [91]. The XAS measurements for the Cr $L_{2,3}$ edge give us an indication of the valency of the Cr present within the Cr-doped Sb_2Te_3 . As discussed previously, the Cr can dope both interstitially into the van der Waals gap or substitutionally by replacing the Sb sites. If the Cr dopes interstitially it does not form a strong bond and therefore it would likely lose its electrons to the conduction band behaving as a donor.

Figure 3.7(b) demonstrates a calculated Cr XAS and XMCD spectra using atomic multiplet theory [52, 53]. This calculated spectrum using an octahedral crystal field is in good agreement with the experimental data only by having a strong divalent Cr^{2+} character rather than being largely trivalent Cr^{3+} . Similar to the case of Cr-doped Bi_2Se_3 this divalent character originates from the hybridisation between the Cr d and Te p bands located just below and above the Fermi level respectively. This hybridisation corresponds to a substitutional doping scenario as discussed previously in section 3.1.2.4.

The hybridisation of these bands indicates the type of exchange coupling mechanism within the crystal structure. It is important to note that the Cr-Te bond in this case is not ionic and has covalent character. This is due to the initial Sb-Te bonds covalent character and the fact that the Sb and Cr substitution is isoelectronic and

does not provide any more electrons. This leads to a weak charge carrier dependence for the Cr concentration even though it is a dopant.

Figure 3.8 shows the XAS and XMCD spectra for the Sb $M_{4,5}$ absorption edge in an applied magnetic field of 8 T at 5 K. This absorption edge corresponds to electrons from the $3d$ energy level being excited to the $5p$. The sharp peaks of the Sb M_4 and M_5 edges can be seen at ~ 527.0 eV and 536.3 eV respectively. Both these peaks are dichroic in an applied field of 8 T demonstrating that there is an induced magnetic moment on the Sb sites within the crystal structure of Cr:Sb₂Te₃. This dichroism is very weak and cannot be observed at lower applied fields. The Sb M_5 XMCD is positive having an opposing sign to the Cr L_3 and Te M_5 XMCD edges. The sloping background seen in the XAS can once again be attributed to the presence of the Te $M_{4,5}$ edge.

These XAS and XMCD results provide us with evidence for the type of exchange interaction taking part in the Cr-doped Sb₂Te₃ which creates the long range ferromagnetic order in the system. The Cr $L_{2,3}$ edge corresponds to the $2p$ to $3d$ transition whereas the Sb $M_{4,5}$ edge corresponds to the $3d$ to $5p$ transition. Figure 3.7 and Fig. 3.8 demonstrate that the XMCD's shown inverse signs when compared to one another, the L_3 edge of Cr being negative and the M_5 edge of Sb being positive. Despite this because of their transitions, the magnetic moment determined for each XMCD data set has the same sign. This is due to the orbital quantum numbers which change sign depending on the initial and final states of the transition [11]. This means that the Sb $5p$ and Cr $3d$ moments are coupled parallel to one another [92]. These measurements show that both Sb and Cr have a similar field dependence and that the moments couple together.

The Te M_5 edge which is negative is clearly visible in the XMCD data shown in Fig. 3.7 at 574.3 eV demonstrating that a magnetic moment also resides on the Te site within the crystal structure. This absorption edge also corresponds to a $3d$

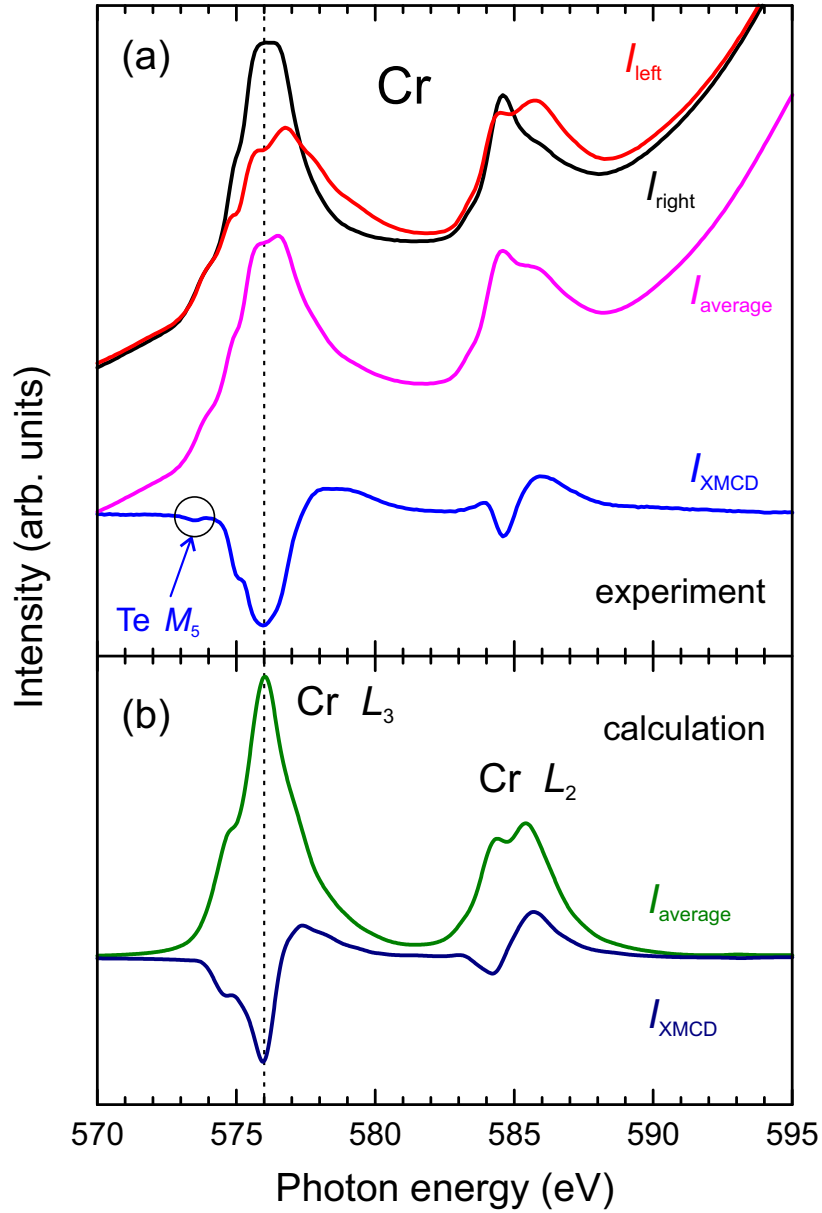


Figure 3.7: XAS and XMCD measurements of the $\text{Cr}_{0.32}\text{Sb}_{1.68}\text{Te}_3$ sample at the Cr $L_{2,3}$ absorption edge. The measurement was taken at a temperature of 10 K using TEY with the sample at normal incidence to the incoming X-rays. An initial field of 1 T was applied parallel to the direction of the beam before being removed in order for the XMCD measurement to be taken at remanence. (a) The experimental XAS generated for the left and right circularly polarised X-rays and average XAS. The difference between the left and right circularly polarised XAS is the XMCD. This energy range also includes the Te $M_{4,5}$ absorption edge and a small negative peak can be seen corresponding to the Te M_5 edge at 573.4 eV. (b) Atomic multiplet calculations for the Cr $L_{2,3}$. The average XAS and XMCD spectra closely matches the line shape of the experimental data for a hybridized Cr ground state with 70% d^4 (Cr^{2+}) and 30% d^3 (Cr^{3+}) character. Figure adapted from ref. [12].

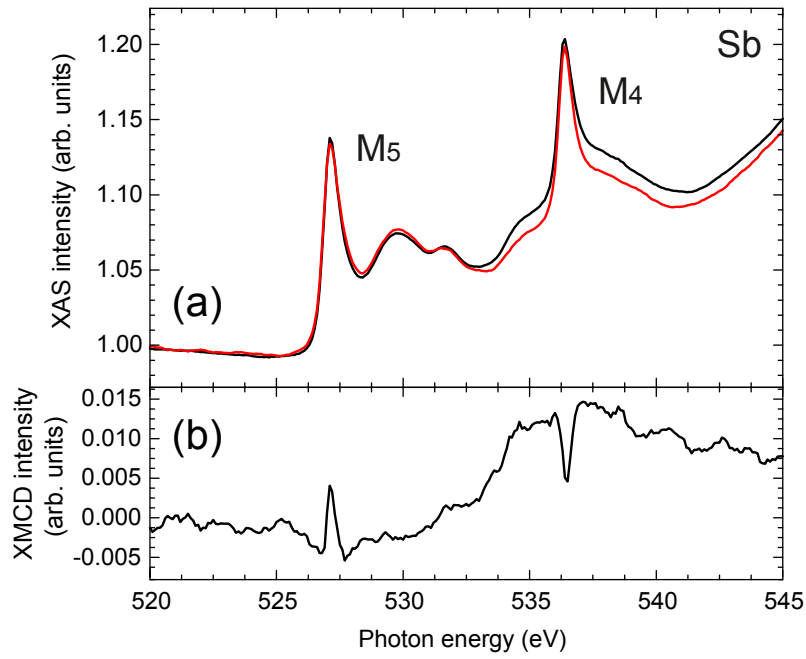


Figure 3.8: XAS and XMCD spectra for the Sb $M_{4,5}$ absorption edges recorded at 3 K in an applied field of 8 T. (a) The XAS spectrum for left (black) and right (red) circularly polarised X-rays. (b) The difference between the XAS signals producing the XMCD. There is a clear dichroism demonstrating the induced magnetic moment on the Sb sites. Figure adapted from ref. [12].

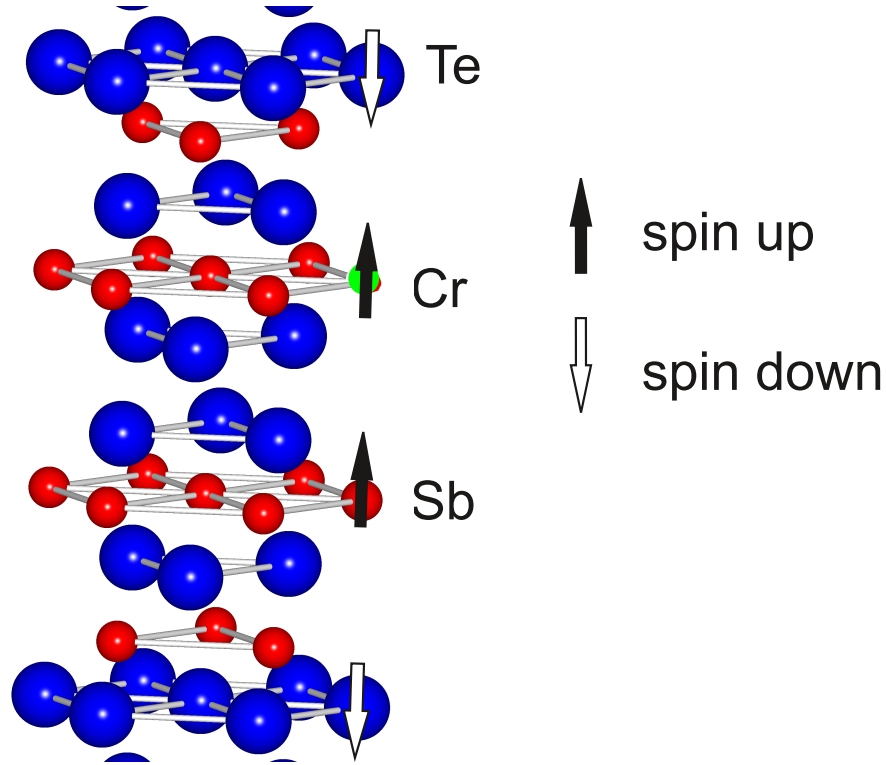


Figure 3.9: Model demonstrating the crystal structure of Cr-doped Sb_2Te_3 . The quintuple layers consisting of both Te and Sb layers separated by van der Waals gaps is highlighted. The Cr dopant which substitutionally replaces one of the Sb sites is shown to be surrounded by six Te atoms. The orientations of the magnetic moments of each species of atom are indicated using arrows with Cr and Sb magnetic moments being aligned parallel and Te moments being aligned antiparallel. Figure adapted from ref. [12].

to 5p transition and since it is negative like the Cr L_3 edge, the Te 5p and Cr 3d magnetic moments must be aligned antiparallel. An indication of the arrangement of the magnetic moments within the Cr-doped Sb_2Te_3 crystal structure can be found in Fig. 3.9.

The way the magnetic moments behave for each species of atom within the Cr-doped Sb_2Te_3 crystal structure is consistent with a carrier mediated coupling mechanism. The Cr ions present within the structure ferromagnetically couple via an exchange which is mediated by spin polarised Te valence holes. The magnetic moments induced at the Te and Sb sites therefore couple antiparallel and parallel with

the Cr as confirmed by the XMCD results shown here. This coupling mechanism has also been observed in the traditional dilute magnetic semiconductor Mn doped GaAs where the Mn substitutionally replaces Ga sites and As mediates the exchange between the Mn ions [93, 94]. This type of ferromagnetic superexchange mechanism is also consistent with the ferromagnetic transition temperature being proportional to the doping concentration as the more Cr ions present in the structure, the easier it is for the interaction to overcome thermal excitations.

The XMCD data provides no evidence for the onset of ferromagnetism to be tied to the Van Vleck model for Cr-doped Sb_2Te_3 . It has been demonstrated that for V-doped Sb_2Te_3 [95], the measured V $L_{2,3}$ XAS spectrum shifts by 0.6 eV when the sample is cooled from room temperature down to 10 K. At 10 K the sample becomes ferromagnetic and the energy shift is attributed to the Van Vleck model of ferromagnetism. There is no energy shift witnessed for the Cr-doped Sb_2Te_3 when cooling the sample to its ferromagnetic transition temperature.

These results are also in agreement with those published for Cr-doped $(\text{Bi,Sb})_2\text{Te}_3$ where the magnetic moment of Te also favours an anti-parallel coupling with the Cr dopant and the long range ferromagnetic order is found to be mediated by the hybridisation of the $5p$ states of Te and Sb and the $3d$ states of Cr [96]. It is also found that substituting Bi for Sb within the structure leads to the suppression of the ferromagnetic transition temperature as the $6p$ Bi states are well separated energetically from the Cr states leading to a much weaker hybridisation [96].

They also agree with spin-polarised first principle calculations where the exchange mechanisms of transition metal doped Sb_2Te_3 were investigated [97]. The calculations show that there are two different exchange mechanisms contributing to the long range ferromagnetic order, one being the double-exchange interaction mediated by Te and the other being the indirect exchange coupling via free carriers. An exchange is found between Cr magnetic moments located within the same quintuple layer but on

different Sb layers. The Te atom between each Sb layer mediates this exchange and is of double-exchange type. There is also an exchange between the Cr ions found on the same layer as one another where the interaction is mediated indirectly by free carrier *sp* states [98]. The magnitude for the different types of exchange coupling is the same for both adjacent atomic layers and in-plane interactions. The calculations show that the Cr *3d* impurity exhibits a high density of states near the Fermi level with the overall magnitude and sign of the exchange constants being strongly dependent on the filling of the *d* states. The simultaneous presence of the ferromagnetic superexchange and Zener-type double exchange interaction has also been demonstrated in V-doped $(\text{Bi,Sb})_2\text{Te}_3$ where the results are consistent with the findings shown here [87].

3.1.3.3 Polarised Neutron Reflectometry

PNR measurements were performed on the $x = 0.42$ and 0.26 $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ samples using the PolRef beamline. The samples were measured in time of flight mode at several fixed angles and the wavelength of neutrons was taken into account at the detector. A magnetic field of 0.65 T was applied in the plane of each sample using a bipolar electromagnet, with the direction also being collinear to the neutron spin. Measurements were carried out at both 300 K and 5 K above and below the T_C of the samples, respectively. A reflectivity curve was measured for each neutron spin eigenstate without the use of polarisation analysis.

The reflectivity data was then fitted using an optical transfer matrix approach [99] and a differential evolution fitting algorithm by utilising the GenX package [60] in order to extract a structural and magnetic depth profile of each of the samples. A number of different models were constructed in order to investigate whether a number of different situations for the samples compositions fit the reflectivity and asymmetry data sets. The samples were split into several Cr-doped Sb_2Te_3 layers with each layer being able to have a unique layer thickness, density, roughness, Cr concentration

and Cr magnetic moment. This was to allow for the possibility that the Cr dopant is spread inhomogeneously through the depth of the sample. Figure 3.10 shows the reflectivity data and spin asymmetries for both the $x = 0.42$ and $x = 0.26$ $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ samples along with the best fits to the data. The reflectivity data is normalised to the maximum reflectivity and spin asymmetry is calculated as the normalised difference between the reflectivity data sets associated with each neutron spin.

The spin asymmetries for both samples shown in Fig. 3.10 demonstrate splitting indicative of the magnetisation of the thin film samples. The amplitude of this splitting increases for the higher doping concentration sample. The splitting has a relatively low amplitude and the samples demonstrate rather dilute magnetism, similar to a dilute magnetic semiconductor. This has also previously been observed for Cr-doped Bi_2Se_3 thin films [83].

The best fitting model for the $x = 0.42$ sample was of a similar construction to the one discussed in section 3.1.2.3 and shown in the inset of Fig. 3.3 where there were three separate layers. The first layer consists of undoped Sb_2Te_3 , the second of Cr-doped Sb_2Te_3 with a doping concentration equal to that of the RBS measurements and a third much thinner Cr-doped Sb_2Te_3 layer with the same doping concentration, but a different Cr magnetic moment. The majority of the sample is made up of the second layer. For the $x = 0.26$ sample, the best fit occurred for a two layer model consisting of the undoped Sb_2Te_3 first layer and second Cr-doped layer.

The roughness of the interface between the substrate and the undoped buffer layer were found to be below the measurable limit for both of the samples. The interface between the buffer and doped layers is found to have a roughness of ~ 3 nm. The $x = 0.42$ sample also has a roughness of ~ 3 nm at the interface between the main doped layer and top layer of the sample. In both cases the surface of the samples have a roughness of ~ 2 nm.

In both cases the initial undoped Sb_2Te_3 layer corresponds to the buffer layer that

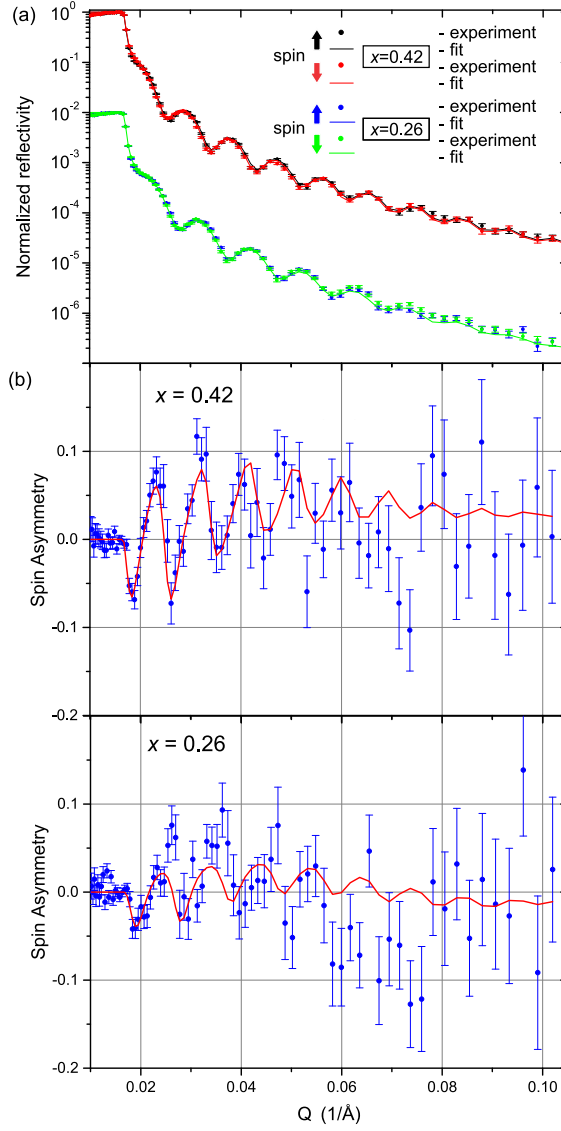


Figure 3.10: PNR data for the $x = 0.42$ and $x = 0.26$ $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ samples at 5 K in an in plane applied magnetic field of 0.65 T, parallel to the polarisation of the neutrons. (a) The reflectivity curve generated by spin up and spin down neutrons for each of the samples which have been offset by 100 for the purposes of clarity. The experimental data sets are demonstrated by points with associated error bars and the fits for each of the data sets are represented by a continuous line. (b) The spin asymmetry as a function of wave vector transfer for each of the samples with the experimental data once again being shown as points with associated error bars (blue) while a solid line (red) is used to represent the fit calculation for the best model. Figure adapted from ref. [13].

was grown initially during the growth procedure. In the case of the $x = 0.26$ and $x = 0.42$ sample the thickness of the buffer layer was (6.5 ± 0.2) nm and (3.9 ± 0.5) nm respectively. Since both buffer layers were grown identically it seems reasonable that the greater doping concentration of Cr causes the dopant to diffuse into the buffer layer to a greater degree making the undoped layer smaller in that case. Figure 3.11 demonstrates the magnetic and structural SLD for the $x = 0.42$ sample. The SLD for the buffer layer is seen to be low. The magnetisation of the buffer layer was allowed to vary in each model however, in both cases the undoped layer has no magnetic moment.

The majority of each sample is seen to consist of $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ with a thickness of (59 ± 2) nm and (54 ± 1) nm respectively for the $x = 0.42$ and $x = 0.26$ samples. The density of each of these layers was allowed to vary in order to allow for changes that can be attributed to the substitutional doping of the Sb for Cr ions. The densities are found to remain within 6% of their nominal values consistent with this doping scenario [63]. The Cr doping concentrations for these layers were fixed the values given by RBS measurements. For both samples, the best fitting models suggest a uniform magnetisation throughout the samples with gradual transitions between the buffer layer and doped layer as demonstrated by Fig. 3.11. For the $x = 0.26$ sample a gradual decay in the magnetisation is seen towards the sample surface. The top layer of the $x = 0.42$ sample is 4.3 nm thick and is found to have a reduced SLD compared to the rest of the film. The best fitting model occurs when the top layer Cr doping concentration is also fixed at $x = 0.42$. The magnetic moment of the layer was allowed to vary and no magnetisation was favoured demonstrating the same decay in magnetisation at the surface of the sample.

This decay in magnetisation demonstrates that there is no surface enhanced magnetisation for either sample within the detection limit of around 5 Å. These results show no evidence of near-surface modification to the polarization which may occur

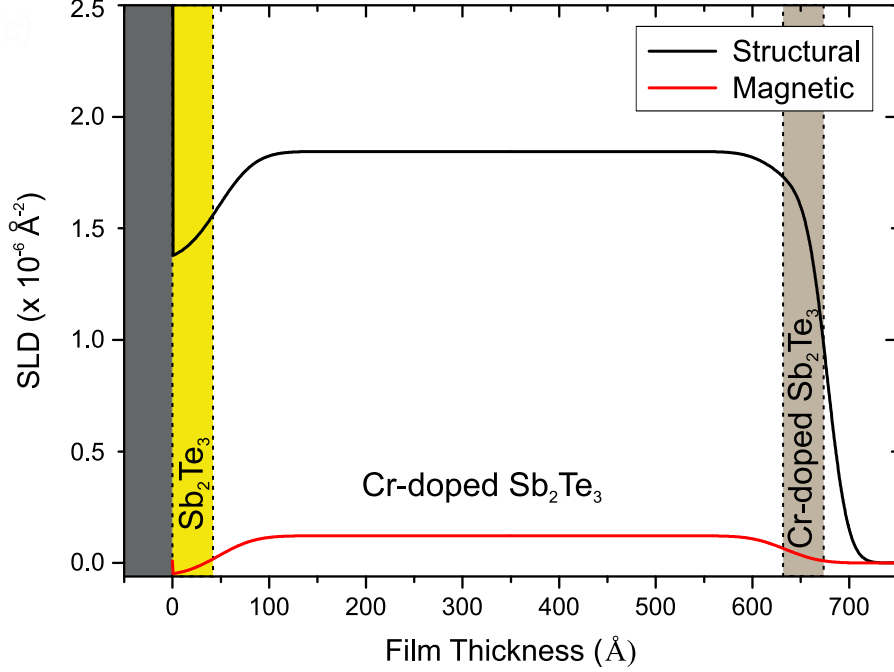


Figure 3.11: Model for the structural and magnetic SLD at 5 K for the $x = 0.42$ $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ sample. The layered system consists of Al_2O_3 substrate, undoped Sb_2Te_3 buffer layer, a majority Cr-doped layer and a thinner Cr-doped surface layer with no magnetisation. Figure adapted from ref. [13].

due to the surface states of the MTI. For each sample the magnetic moment was found to be $\sim 1.5 \mu_B/\text{Cr}$ in agreement with the SQUID VSM data at a field of 0.65 T and temperature of 5 K as demonstrated in section 3.1.3.1.

3.1.4 Conclusion

It is clear from the results presented above that $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ thin films of a high crystalline quality have been successfully fabricated by the use of molecular beam epitaxy. These films demonstrate long range ferromagnetic order up to a temperature of 125 K for the highest doping concentration where $x = 0.42$ as shown by SQUID VSM measurements. The ferromagnetic transition temperature of the samples increase with doping concentration. The saturation moment for the Cr contained within the highest doped sample is $(2.8 \pm 0.2) \mu_B/\text{Cr}$. The easy axis of magnetisation is found

to be out-of-plane for the films. Both XRD and XAS measurements provide evidence for a substitutional doping mechanism where the Sb sites are replaced by Cr when doping takes place.

XMCD measurements provide an indication of the exchange interaction taking place within the structure. The XMCD results demonstrate that Sb and Te magnetic moments contained within the crystal structure couple parallel and antiparallel with the Cr dopant magnetic moments. This demonstrates a carrier mediated coupling mechanism where the exchange is mediated by polarised Te valence holes. The long range ferromagnetic order is therefore mediated by the hybridisation of the $5p$ states of Te and Sb and the $3d$ states of Cr. These measurements are in agreement with previously published spin-polarised first principle calculations which show that there is the simultaneous presence of two exchange interactions of equal magnitude, the previously mentioned ferromagnetic superexchange and double exchange interaction. It is important to note that these exchange interactions point to the existence of Cr $3d$ impurity bands which exist near the Fermi level.

PNR measurements and the accompanying best fit models demonstrate that the samples are homogeneously doped with Cr and exhibit no near-surface enhancements of the magnetisation. The in-plane magnetic moment of the Cr measured by PNR is found to be consistent with that measured by SQUID VSM. The spin asymmetry from the PNR measurements show low amplitude oscillations reminiscent of a magnetically dilute semiconductor.

When concluding whether these Cr-doped systems are suitable for the observation and utilisation of the QAH effect for technological purposes there are a number of considerations to be taken into account. These samples do demonstrate a high temperature long range ferromagnetic state which at the highest doping concentrations persists up to 125 K. As previously discussed a robust long range ferromagnetic order is required in order to observe the QAH state. However, muon measurements of these

samples which have been carried out by collaborator Dr. Nina-Juliane Steinke demonstrate that the ferromagnetic ordering of the sample is very disordered. The muon measurements, which are used to measure the magnetic disorder within the system as a function of temperature show that instead of a sharp disorder being localised at the T_C of the sample, the disorder is broad and persists over a range of temperatures for all doping concentrations of Cr. This would make it difficult to observe a robust QAH state in these samples.

Transport and ARPES measurements carried out by collaborators Prof. Crispin Barnes and Prof. Yulin Chen, respectively, also confirm the existence of the previously discussed Cr $3d$ impurity bands which are inherently tied to the exchange interaction which mediates the magnetisation of the samples. In these measurements it has been demonstrated that increasing the doping concentration of the Cr increases the strength of the impurity bands. It has been previously demonstrated for both V-doped and Cr-doped $(\text{Sb,Bi})_2\text{Te}_3$ that in order to observe the QAH state these dissipative conduction channels have to be frozen out with low temperatures (below 100 mK) [7, 71]. Lower doping concentrations can limit these impurity bands but in the case of transition metal dopants, this leads to lower ferromagnetic transition temperatures and lower magnetic moments. The size of the magnetic moment is directly linked to the size of bandgap which opens in the TSS and a larger bandgap leads to a more robust QAH state. The drawbacks of the Cr: Sb_2Te_3 system serve as a motivation to explore other types of magnetic dopant which could solve these issues in order to realise a QAH effect that can be experimentally realised at more accessible temperatures for device applications.

3.2 Rare Earth Doped Bi_2Te_3

As demonstrated in the previous section, long range ferromagnetic order has been achieved in TIs traditionally through the implementation of transition metal dopants such as Cr [83, 84], Mn [4, 81, 100] and V [7, 71]. The QAH effect has been realised in both Cr-doped and V-doped $(\text{Bi,Sb})_2\text{Te}_3$ systems but has only been observed at milli-Kelvin temperatures even with samples where the ferromagnetic transition temperature has been observed to be in the order of 15 K [7] and 30 K [71]. This is due to the deterioration of electronic transport properties caused by the presence of non-topological impurity bands near the Fermi surface which leads to bulk conduction [87, 101]. Low temperatures are therefore required to both enhance the magnetic properties of the dopants and suppress dissipative transport channels. Lower doping concentrations tend to reduce the chances of the formation of these impurity bands and higher magnetic moments are required to open up a sizeable Dirac gap [4]. It is therefore favourable to use reduced doping concentration dopants with much higher effective magnetic moments. $4f$ rare earth dopants with high-moment ions such as Ho, Gd and Dy with $m_{\text{eff}} \approx 10.65 \mu_{\text{B}}$ are therefore favourable alternatives to transition metal doping.

The TI Bi_2Te_3 has successfully been doped with Gd, Ho and Dy up to large doping concentrations of $x = 0.6$, 0.42 and 0.7 respectively for each dopant without the loss of crystalline quality [61, 102, 103]. The Gd^{3+} ions are found to substitute isoelectronically onto Bi sites, preventing the introduction of additional charge carriers and have a large effective moment of $\sim 7 \mu_{\text{B}}/\text{Gd}$ close to the maximum free ion value of $7.94 \mu_{\text{B}}$ which is independent of doping concentration [102]. Despite this however, no long-range ferromagnetic order was observed and the films remained paramagnetic down to 2 K [102]. Similar paramagnetic behaviour down to low temperature has also been observed in both Ho and Dy-doped Bi_2Te_3 due to the well shielded nature of $4f$ shells [61, 103]. For Ho doping an effective moment of $\sim 5 \mu_{\text{B}}/\text{Ho}$ is observed and

ARPES results demonstrate the TSS remains intact consistent with the materials paramagnetic behaviour [102].

ARPES measurements of higher concentration Dy dopants however, have indicated sizeable gaps in the TSS up to room temperature despite their paramagnetic behaviour [104]. This is similar to the transition metal doped TI system Mn:Bi₂Te₃ where TSS gaps persist up to temperatures well above the ferromagnetic transition temperature of the films implying that the magnetic properties of the film do not play a role in the formation of the gap [105, 106]. The microscopic nature of the Dy dopant is clearly complex requiring further investigation.

This section details the structural and magnetic studies of rare earth Dy-doped Bi₂Te₃ thin films grown by MBE. The films were grown, studied with RHEED, XRR, XRD and SQUID VSM by the author. The PNR measurements were conducted in collaboration with Dr. Nina-Juliane Steinke and were analysed by the author. XAS and XMCD measurements were conducted in collaboration with Dr. Adriana Figueroa and Prof. Gerrit van der Laan and were analysed by the author. The results discussed in this section lead to the publication ref. [14].

3.2.1 Thin Film Growth

For the purposes of this study, several Dy-doped Bi₂Te₃ samples were grown on Al₂O₃ (0001) using the two step temperature growth procedure outlined in section 2.4.3. Bi₂Te₃ was initially deposited for 10 minutes at a substrate temperature of 250°C using the same fluxes as measured by the BFM outlined in section 2.4.4. This seed layer was then annealed at 300°C for 30 minutes and then the main growth layer of Dy:Bi₂Te₃ was deposited for 120 minutes at this same substrate temperature. For main growth layer of Dy:Bi₂Te₃, the Bi₂Te₃ was doped with a consistent flux of Dy which was varied for each sample in order to vary the doping concentration of the Dy:Bi₂Te₃. All three material cells were opened at the same time to perform

this growth. The relevant samples for this study were grown with the Dy cell held at a temperature of 850°C and 870°C corresponding to flux values of 3×10^{-9} Torr and 5×10^{-9} Torr respectively. In order to ensure that the samples did not oxidise when exposed to air, after the growth of the main layer, the temperature of the substrate was reduced to 100°C and a pure Te layer was deposited for 60 minutes. The Dy concentration values quoted throughout this section were determined using PNR measurements.

3.2.2 Structural Characterisation

3.2.2.1 Reflection High Energy Electron Diffraction

During the sample growth the quality of the surface of the thin films were investigated via the use of the in-situ RHEED system. Figure 3.12 demonstrates a typical RHEED pattern received from both of the Dy:Bi₂Te₃ samples grown during this investigation along both the $[11\bar{2}0]$ and $[10\bar{1}0]$ azimuth of the *c*-plane sapphire substrate before the deposition of the Te cap. The Dy:Bi₂Te₃ samples demonstrate the same streak-like patterns separated by a 30° rotation with each pattern repeating six times with twin domains during a full rotation of the sample. This indicates both the maintained smooth 2D-like nature of the surface and the $R\bar{3}m$ symmetry group of the samples even with the Dy dopant being introduced. After the deposition of the Te the RHEED pattern became concentric circles indicative of isotropic randomly oriented crystalline Te.

3.2.2.2 X-Ray Reflectometry

XRR measurements of the Dy-doped Bi₂Te₃ samples were conducted in order to provide an indication of the structure and thickness of the samples. Figure 2.6 shows the XRR measurements conducted for the two different doping concentrations of Dy:Bi₂Te₃. The Kiessig fringes characteristic of these types of thin films are not dis-

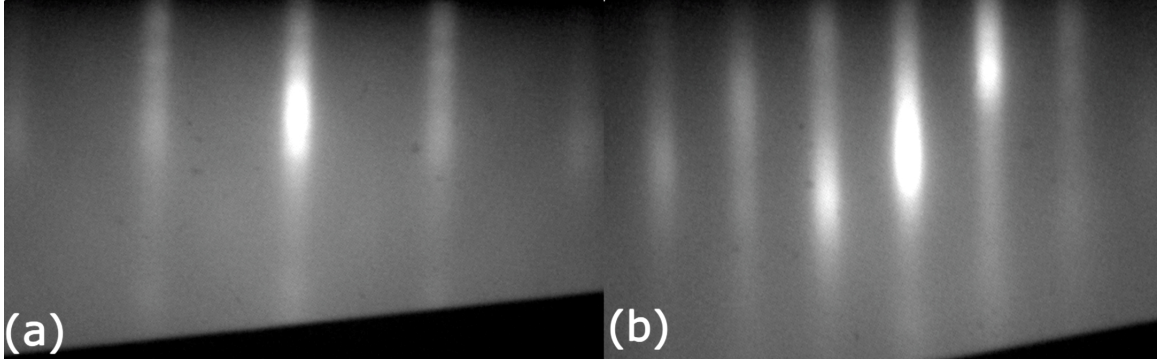


Figure 3.12: RHEED measurement conducted on $\text{Dy}_{0.62}\text{Bi}_{1.38}\text{Te}_3$ sample along the (a) $[11\bar{2}0]$ and (b) $[10\bar{1}0]$ azimuth of the c -plane sapphire substrate. Each RHEED pattern is repeated six times with twin domains during a full 360° rotation of the sample and is separated by a 30° rotation. The introduction of the rare earth dopant does not effect the $R\bar{3}m$ symmetry group of the sample or the quality of the 2D-like surface of the undoped sample.

cernible for either sample. This is due to the presence of the Te cap which dominates the thin film sample in thickness. The isotropic nature of the Te cap and its thickness in comparison to the MTI decrease the intensity of Kiessig fringes which would occur due to the $\text{Dy}:\text{Bi}_2\text{Te}_3$ thin film. It is important to note that the Bragg peak characteristic of the quintuple layer structure of the $\text{Dy}:\text{Bi}_2\text{Te}_3$ can still be found at $\sim 8.5^\circ$ for both films. This indicates the Te cap and rare earth dopant have not disrupted the structure of the MTI.

3.2.2.3 X-Ray Diffraction

In order to further investigate the structure of the Te capped Dy-doped Bi_2Te_3 samples, XRD measurements were performed in out-of-plane geometry after aligning the diffraction equipment to the Al_2O_3 (006) peak of each sample. Figure 3.14 demonstrates the measurements for each doping concentration of sample. The $(00l)$ peaks of the $\text{Dy}:\text{Bi}_3\text{Te}_3$ are labelled by comparison to data taken from the ICSD (158366) for undoped Bi_2Te_3 . Other peaks in the XMCD spectrum reflect the different crystallographic orientations of Te present within the cap which are also labelled by

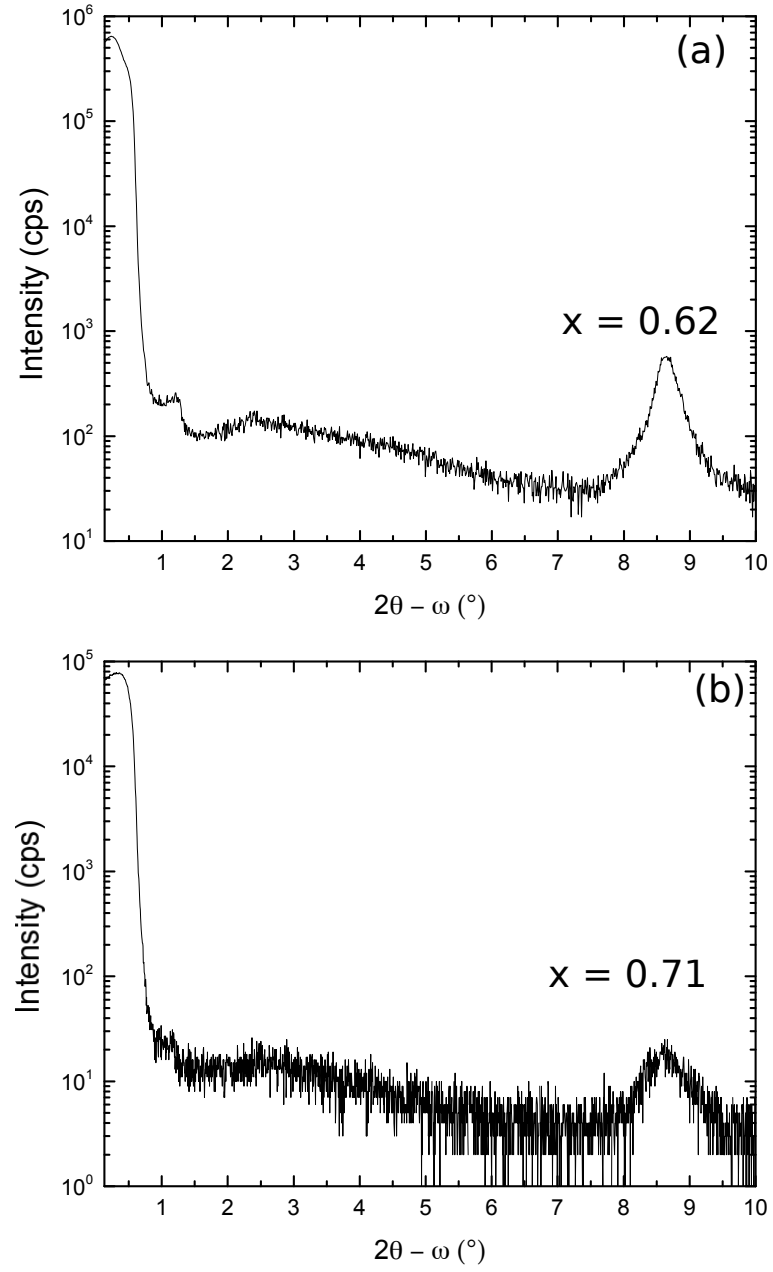


Figure 3.13: XRR measurements of the (a) $\text{Dy}_{0.62}\text{Bi}_{1.38}\text{Te}_3$ and (b) $\text{Dy}_{0.71}\text{Bi}_{1.29}\text{Te}_3$ samples.

comparison to Te XRD data taken from the ICSD (96502). This is consistent with the RHEED measurements which show the surface of the sample is isotropic after the deposition of the Te cap.

The XRD measurements demonstrate that the rare earth doped films are free from secondary phases and grow entirely *c*-axis oriented. The structure remains rhombohedral even though the binary compound Dy_2Te_3 , one of the possible unwanted secondary phases which could form at high Dy concentrations, is orthorhombic in structure making phase segregation likely for samples with high Dy content [61]. Phase segregation has previously been observed in a number of MTI systems at doping concentrations much lower than this [13, 107].

How the Dy ions arrange themselves when doping into the Bi_2Te_3 structure is once again indicated by the shifting of the $(00l)$ peaks of the $\text{Dy}:\text{Bi}_2\text{Te}_3$. The positioning of these peaks can be used to calculate the *c*-axis lattice parameter for each $\text{Dy}:\text{Bi}_2\text{Te}_3$ film. The ionic radii for sixfold coordinated Bi^{3+} and Te^{2-} which make up the Bi_2Te_3 structure are 117 pm and 103 pm respectively [89]. The likely valence for the Dy dopant is Dy^{3+} which has an ionic radius of 105 pm [61]. If the doping scenario was purely substitutional a reduction in the *c*-axis lattice parameter is to be expected, and the $(00l)$ peaks would be shifted to the lower angles. The calculated *c*-axis lattice parameters from the XRD data shown in Fig. 3.14 are both (30.7 ± 0.1) Å which is larger than the expected *c*-axis lattice parameter of 30.4 for an undoped Bi_2Te_3 sample grown in the same chamber. It is likely therefore that a fraction of the Dy dopant also dopes interstitially in the van der Waals gap leading to an overall increase in the MTI films *c*-axis.

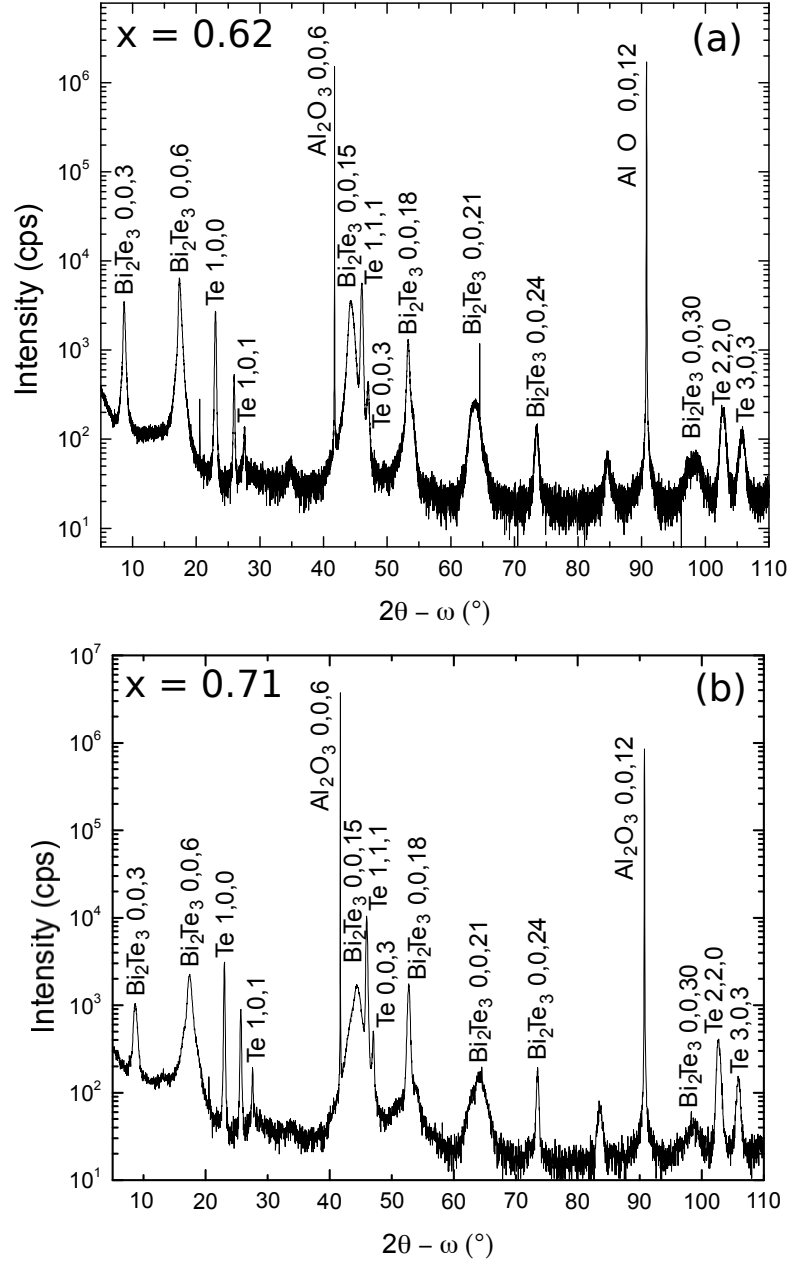


Figure 3.14: XRD measurements for (a) $\text{Dy}_{0.62}\text{Bi}_{1.38}\text{Te}_3$ and (b) $\text{Dy}_{0.71}\text{Bi}_{1.29}\text{Te}_3$ films capped with Te. The (00 l) crystallographic reflections for the Dy-doped Bi_2Te_3 indicate that the films demonstrate the rhombohedral crystal structure of Bi_2Te_3 . The peaks characteristic of the isotropic Te cap are also indicated.

3.2.3 Magnetic Characterisation

3.2.3.1 Magnetometry

Figure 3.15 shows the magnetisation of the two Dy-doped Bi_2Te_3 samples as a function of temperature as measured by SQUID VSM with the sample in-plane in an applied magnetic field of 20 mT. Taking the first derivative of this data with respect to temperature demonstrates that there is no ferromagnetic transition down to a temperature of 1.8 K and 5 K for the $x = 0.71$ and $x = 0.62$ samples and the samples remain paramagnetic as there is no minimum to be found. The inset of Fig. 3.15(a) demonstrates the inverse of the magnetisation of the samples, which is proportional to the inverse of the magnetic susceptibility. No deviation from linear behaviour is found for either sample and they remain paramagnetic.

The magnetisation was observed as a function of field as demonstrated by the hysteresis loops of Fig. 3.16 which were also taken with both samples oriented such that the applied magnetic field was in the plane of the sample. For the $x = 0.62$ and $x = 0.71$ samples the hysteresis loops were taken at a temperature of 5 K and 1.8 K respectively. The diamagnetic response from the Al_2O_3 substrate was subtracted by fitting a straight line to the high field region of the loops. For both MvH and MvT measurements, the moment which was measured in emu was converted into μ_B/Dy by taking into account the Dy: Bi_2Te_3 film thickness and doping concentration taken from PNR measurements as well as the area of the piece of sample used during the measurement.

Both samples demonstrate saturation at a field of approximately 3 T. For the $x = 0.71$ sample the magnetic moment of the Dy ions contained within the MTI is $(4.4 \pm 0.2) \mu_B/\text{Dy}$ at a temperature of 1.8 K. For the $x = 0.62$ this value is $(3.4 \pm 0.3) \mu_B/\text{Dy}$ at a temperature of 5 K. The uncertainties given here reflect the uncertainty which comes determining the volume of the film. It is important to note that for

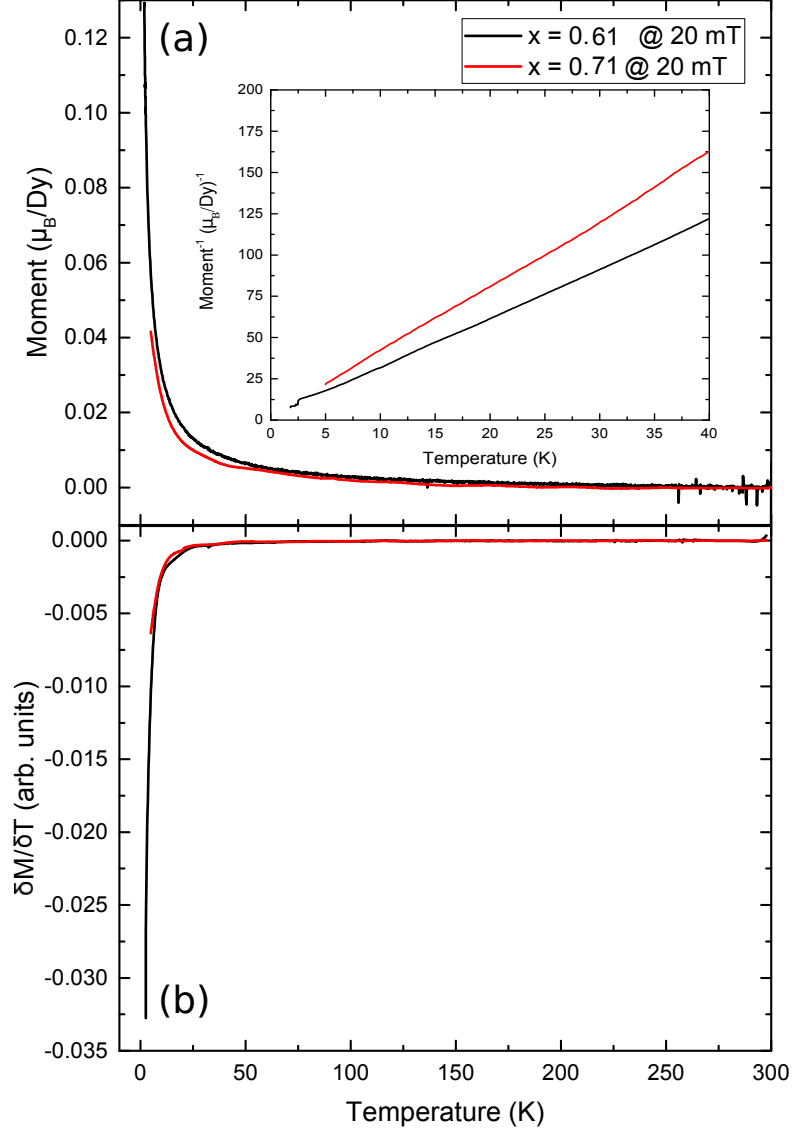


Figure 3.15: (a) Magnetisation versus temperature plot for the two different doping concentrations of Dy-doped Bi_2Te_3 samples with the applied magnetic field of 20 mT parallel to the plane of the sample. The inset shows the inverse of the magnetisation of each sample where no deviation from linear behaviour is found. (b) First order derivative of the MvT data. No minimum can be found indicating there is no ferromagnetic transition temperature for either sample down to 1.8 K and 5 K for the $x = 0.71$ and $x = 0.62$ indicating that the samples remain paramagnetic even at low temperature.

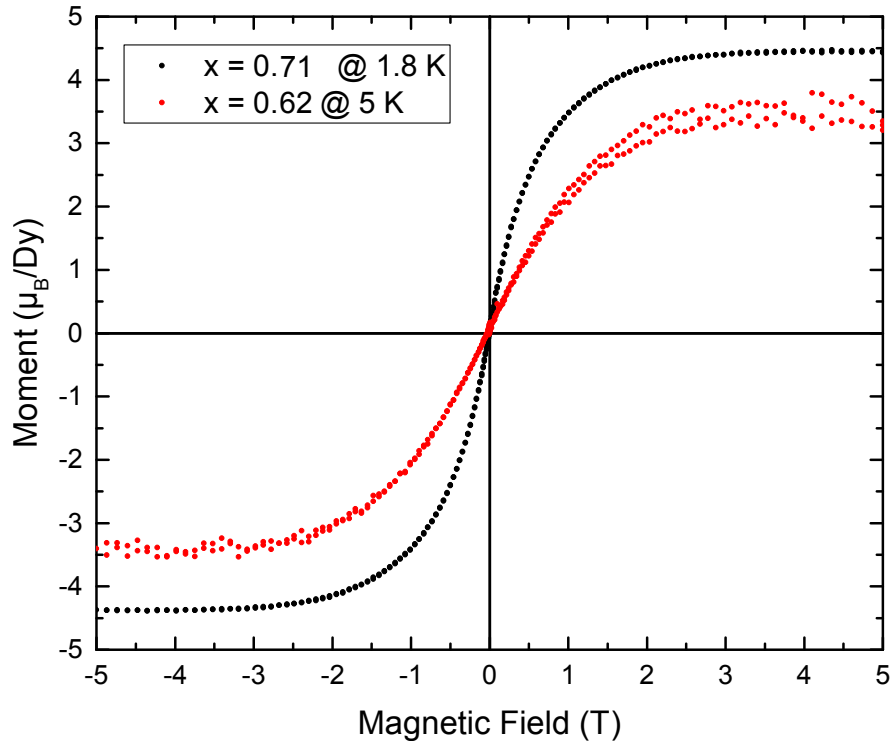


Figure 3.16: Magnetisation versus field measurements for the two different doping concentrations of Dy-doped Bi_2Te_3 samples. The measurements were carried out with the samples oriented with the sample plane parallel to the applied magnetic field. Both samples saturate at an applied magnetic field of approximately 3 T. Neither hysteresis loop demonstrates an opening once again indicating the paramagnetic behaviour of the MTI samples.

Dy-doped Bi_2Te_3 it has previously been observed that lower doping concentration samples lead to higher saturation magnetic moments at identical temperatures [61]. The reasonably high magnetic moment for the $x = 0.62$ sample at 5 K seems to suggest that it is likely these samples also follow this trend. The values for the effective magnetic moment of Dy contained within the MTI are far below the free ion value of $10.64 \mu_{\text{B}}/\text{Dy}$. It has previously been suggested that these lower values arise from an onset of antiferromagnetic ordering of the Dy ions which has been observed in a number of different systems [84, 108–110]. The degree of antiferromagnetic ordering is suggested to increase with higher Dy doping concentrations [61].

There is no opening in either of the hysteresis loops, further demonstrating the paramagnetic behaviour of the MTI films with an absence of long-range ferromagnetic order. The paramagnetic behaviour of the Dy-doped Bi_2Te_3 samples is in agreement with previous measurements performed on this materials class [61].

3.2.3.2 X-Ray Absorption Spectroscopy and X-Ray Magnetic Circular Dichroism

XAS and XMCD measurements were performed at beamline ID32 on the $\text{Dy}_{0.62}\text{Bi}_{1.38}\text{Te}_3$ sample in order to probe the element specific magnetic properties of the sample. The sample was glued face down (Te cap first) onto a copper sample holder and cleaved in a UHV chamber before being transferred into the chamber where the XAS and XMCD measurements were performed. This was to ensure a pristine unoxidised surface of the Dy-doped Bi_2Te_3 could be used for TEY based measurements which probe to a sample depth of only 3 to 5 nm. The sample was oriented 30° from grazing incidence in order to ensure that the magnetic field, parallel to the X-ray beam, was applied in the plane of the sample.

Figure 3.17 shows the XAS and XMCD measurements performed at the Dy M_5 absorption edge at a temperature of 4 K in an applied field of 2 T. The averaged XAS

measurement shown by the black line in Fig. 3.17 demonstrates the characteristic spectrum of Dy which consists of the relative contributions of the three fundamental left circular I_L (lower photon energy peak), right circular I_R (higher photon energy peak) and linear I_Z (central photon energy peak) polarisations along the incoming X-ray beam which are separated by ~ 2 eV. The Dy M_5 absorption edge is the result of electric-dipole transitions from the $3d$ core level into empty $4f$ states. It is important to note that the $4f$ electrons in Dy are not directly involved in chemical bonding and also screen the $3d$ hole. This leads to the XAS spectrum being relatively insensitive to chemical changes such as the formation of alloys, oxidation and compounds.

The XMCD signal is determined by subtracting the XAS spectra taken with the X-ray helicity vector and applied field parallel and anti-parallel. There is no discernible XMCD signal found in remanence at 4 K. This once again demonstrates the paramagnetic behaviour of the Dy ions present in the MTI. Figure 3.17 shows the Dy M_5 XMCD, which appears in an applied in-plane field of 2 T, is composed of the I_L and I_R contributions with the integrated intensity for I_R being largely negative in comparison to the small positive I_L resulting in an overall negative XMCD. It is important to note that due to its localized nature and well shielded shell, the XMCD signal at the Dy M_5 edge is directly proportional to the $4f$ magnetic moment allowing for a direct calculation of the effective magnetic moment by comparing the peak asymmetry of the experimental data to the expected asymmetry for Dy Hund's rule ground state [111, 112].

The peak asymmetry is given by the equation $A = (I_{-1} - I_{+1}) / (\frac{2}{3} I_{ISO})$, essentially subtracting the intensities of the Dy M_5 spectra measured in both negative and positive helicities and dividing the result by $2/3$ of the isotropic spectrum intensity $(I_L + I_R + I_Z)$. Performing this calculation results in a value of $A_{Exp} = -0.3776$ which is compared to $A_{theory} = -1.217$. This means that the XMCD shown in Fig. 3.17 corresponds to an effective moment which is 31% of $10.65 \mu_B/\text{Dy}$, a value of 3.3

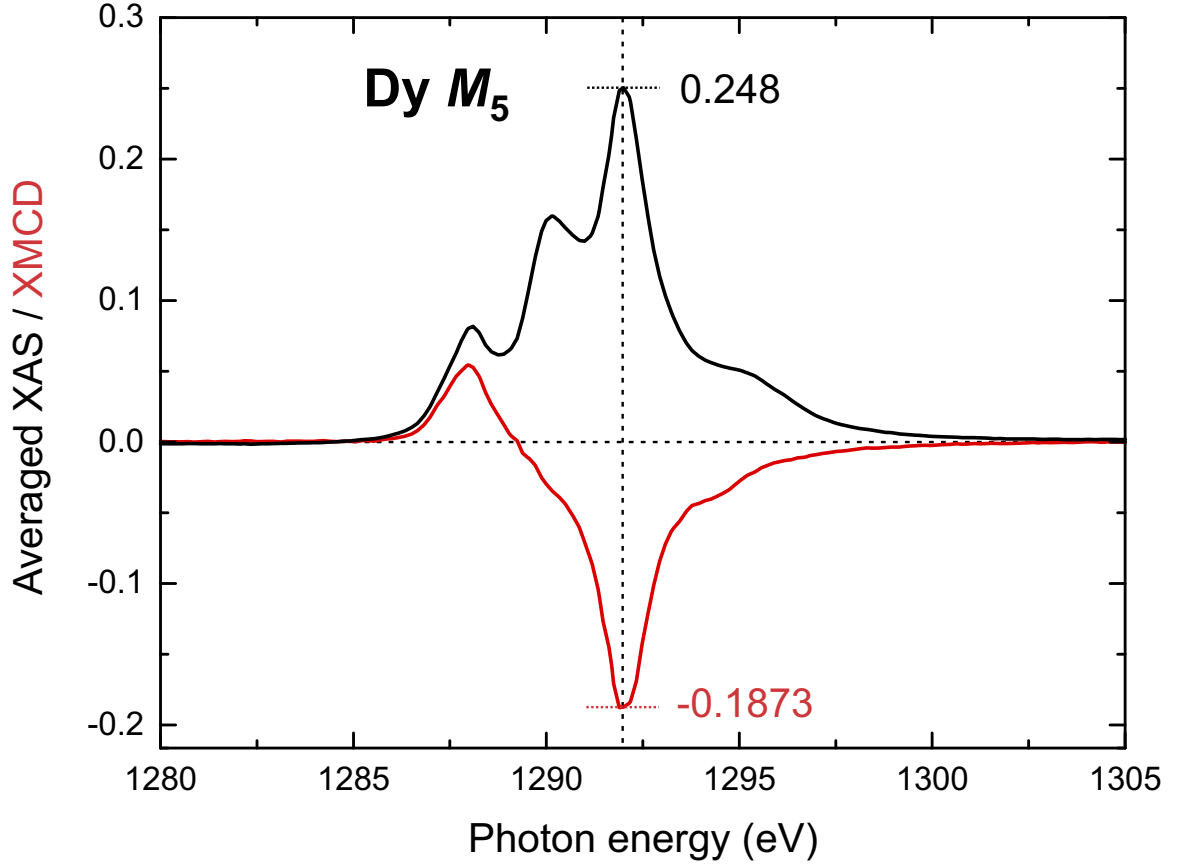


Figure 3.17: XAS and XMCD measurements performed on the $\text{Dy}_{0.62}\text{Bi}_{1.38}\text{Te}_3$ sample at the Dy M_5 absorption edge in an in-plane applied field of 2 T at a temperature of 4 K. The black spectrum demonstrates the averaged XAS for both positive and negative helicities of X-ray and the red spectrum demonstrates the XMCD calculated by taking the normalised difference of the two helicities. Reprinted from ref. [14] with permission from the APS.

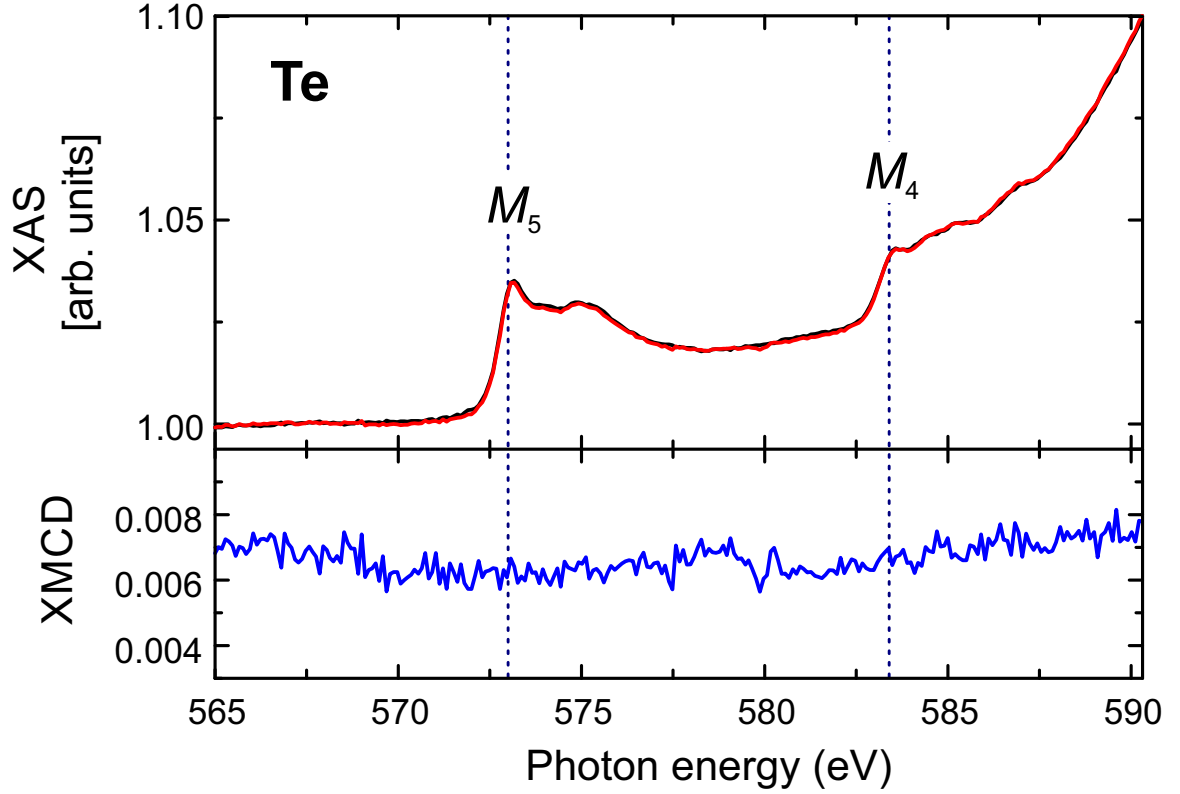


Figure 3.18: XAS and XMCD measurements performed on the $\text{Dy}_{0.62}\text{Bi}_{1.38}\text{Te}_3$ sample at the Te $M_{4,5}$ absorption edge in an in-plane applied field of 8 T at a temperature of 4 K. The black and red spectrum at the top of the plot demonstrates the XAS for both positive and negative helicities of X-ray respectively. The blue spectrum at the bottom of the plot demonstrates that there is no discernible XMCD signal. Reprinted from ref. [14] with permission from the APS.

μ_{B}/Dy . This reduction corresponds to a fraction of the Dy contained within the MTI sample being non-magnetic or antiferromagnetic and is consistent with magnetometry measurements.

XAS and XMCD measurements were also performed at the Te $M_{4,5}$ absorption edge as demonstrated by Fig. 3.18. At 4 K and in an in-plane applied magnetic field of 8 T, no XMCD is observed. This is in clear contrast to previously investigated transition metal-doped ferromagnetic TIs where such measurements have shown a measurable polarisation on the anion site, confirming a conduction-band-mediated magnetic response in those systems that is absent in the Dy-doped case [12, 15, 96].

3.2.3.3 Polarised Neutron Reflectometry

PNR measurements allow for the investigation of the structural and magnetic depth profiles of the two sample with different Dy concentrations. They were conducted without polarisation analysis at the PolRef beamline. The measurements were carried out at room temperature and low temperatures of 5 K for the $x = 0.62$ and 3 K for $x = 0.71$ in an in-plane applied magnetic field of 0.02 T and 0.7 T. The neutron spin polarisation was parallel to the applied field. Reflectivity curves were acquired for both spin-up and spin-down neutron polarisations. The measurements configuration means the reflectivities are sensitive to the structural depth profile of each sample as well as the magnetic component parallel to the applied field with the neutron sensing the total magnetic induction as a function of depth. The reflectivity curves and calculated asymmetry were fitted using the GenX package [60] which is based on an optical transfer matrix approach and a differential evolution fitting algorithm [99].

The high temperature PNR measurements give an estimate of the concentration of Dy contained within the structure as the Dy which replaces the Bi ions in Bi_2Te_3 in the substitutional doping scenario has a much higher bound coherent nuclear scattering length ($b_c^{\text{Dy}} = 16.9$ fm and $b_c^{\text{Bi}} = 8.5$ fm). In the estimation of the Dy doping concentrations the assumption is made that the accumulation of Dy in the van der Waals gap does not measurably alter the number of atoms present per unit volume as the increased number of atoms in the gap is offset by the expansion of the lattice.

Figure 3.19 shows the reflectivity curves generated for the $x = 0.62$ sample at 5 K and $x = 0.71$ sample at 3 K with incident spin-up and spin-down neutrons in an applied field of 0.7 T. There is a clear spin splitting demonstrated by both samples indicating a magnetic response for moderate applied fields and low temperatures. For a typical paramagnet away from any phase transitions, even in a high applied magnetic field the total internal field is too weak to be detected by neutron reflectometry. The calculated spin asymmetries from the two reflectivity channels for each sample are

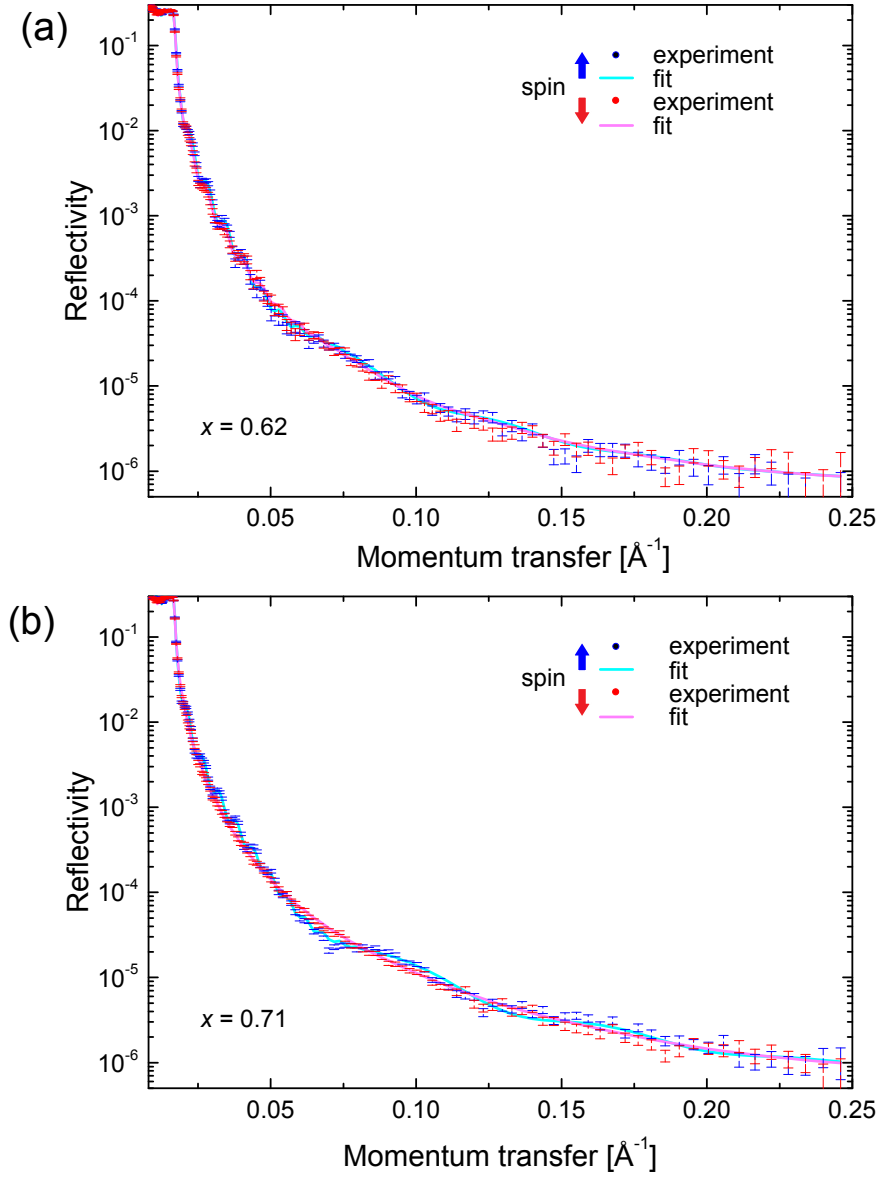


Figure 3.19: (a) PNR data and fit of the $x = 0.61$ sample at 5 K under and in-plane applied field of 0.7 T, spin-up blue and spin down red. (b) PNR data and fit of the $x = 0.71$ sample at 3 K under an in-plane applied field of 0.7 T. Reprinted from ref. [14] with permission from the APS.

shown in Fig. 3.20. Sizeable oscillations with a maximum amplitude of 0.15 for the $x = 0.62$ and 0.2 for the $x = 0.71$ are present. The oscillations are higher in amplitude than those seen for ferromagnetic transition metal doped topological insulators [83].

The best fit for the data was achieved with a model where each sample consists of a seed layer of Bi_2Te_3 , a single layer of uniform Dy-doped Bi_2Te_3 and a thick Te cap. For the $x = 0.62$ and $x = 0.71$ Dy: Bi_2Te_3 sample the Te caps were 133 and 190 nm with roughnesses of 11 and 12 nm, respectively. The seed Bi_2Te_3 layers of the $x = 0.62$ and $x = 0.71$ samples are 7.5 and 12 nm with negligible roughnesses. The Dy: Bi_2Te_3 layers of the $x = 0.62$ and $x = 0.71$ samples are 84 nm with a roughness of 3 nm and 93 nm with 2 nm roughness. Figure 3.21 shows both the structural and magnetic SLD for each sample. The magnetic SLD is uniform across the entire Dy-doped Bi_2Te_3 layer demonstrating that the doping is uniform across the entire MTI. The structural and magnetic uniformity of the Dy-doped layer is likely due to the protective Te cap.

The effective magnetic moment measured along the quantisation axis of the neutron is $1.7 \mu_B$ per Dy atom for the $x = 0.62$ sample and $2.8 \mu_B$ per Dy atom. It is important to note that the increase in the magnetic response for $x = 0.71$ sample results from the lower measurement temperature as a higher doping concentration has been shown to lead to a lower effective moment [61]. The measurements clearly show that there is a large effective magnetisation of more than 1/4 of the full Dy moment which can be induced in the Dy atoms, even though the TI itself does not order ferromagnetically at these temperatures.

3.2.4 Conclusion

It is clear from the measurements presented above that despite the lack of a ferromagnetic transition temperature the Dy-doped Bi_2Te_3 samples investigated during this study demonstrate a large internal magnetic field at moderate applied fields and

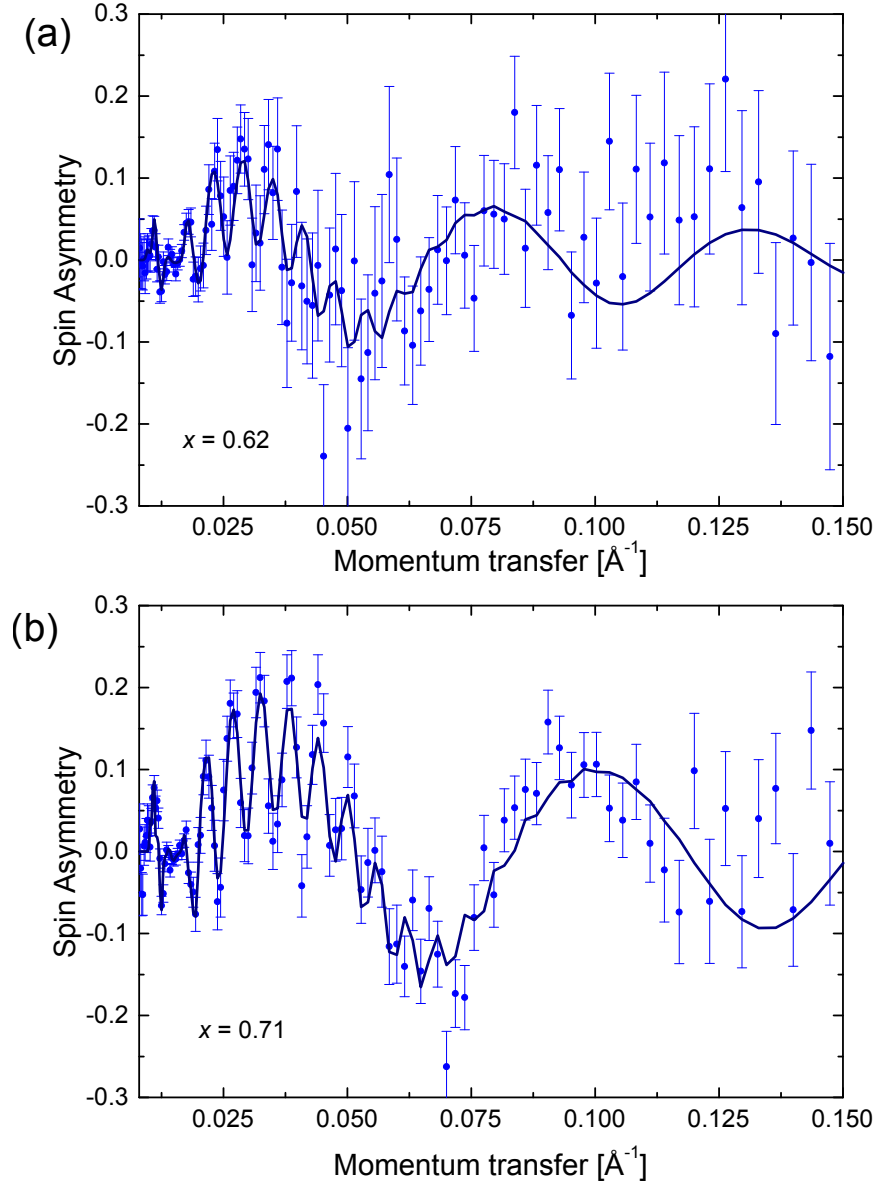


Figure 3.20: (a) Corresponding spin asymmetry and fit for the $x = 0.62$ sample in an applied in-plane field of 0.7 T at 5 K. The spin asymmetry is calculated by taking the normalised difference between the two spin-dependent reflectivities. (b) Corresponding spin asymmetry and fit for the $x = 0.71$ sample in the same in-plane applied field but at a temperature of 3 K. Reprinted from ref. [14] with permission from the APS.

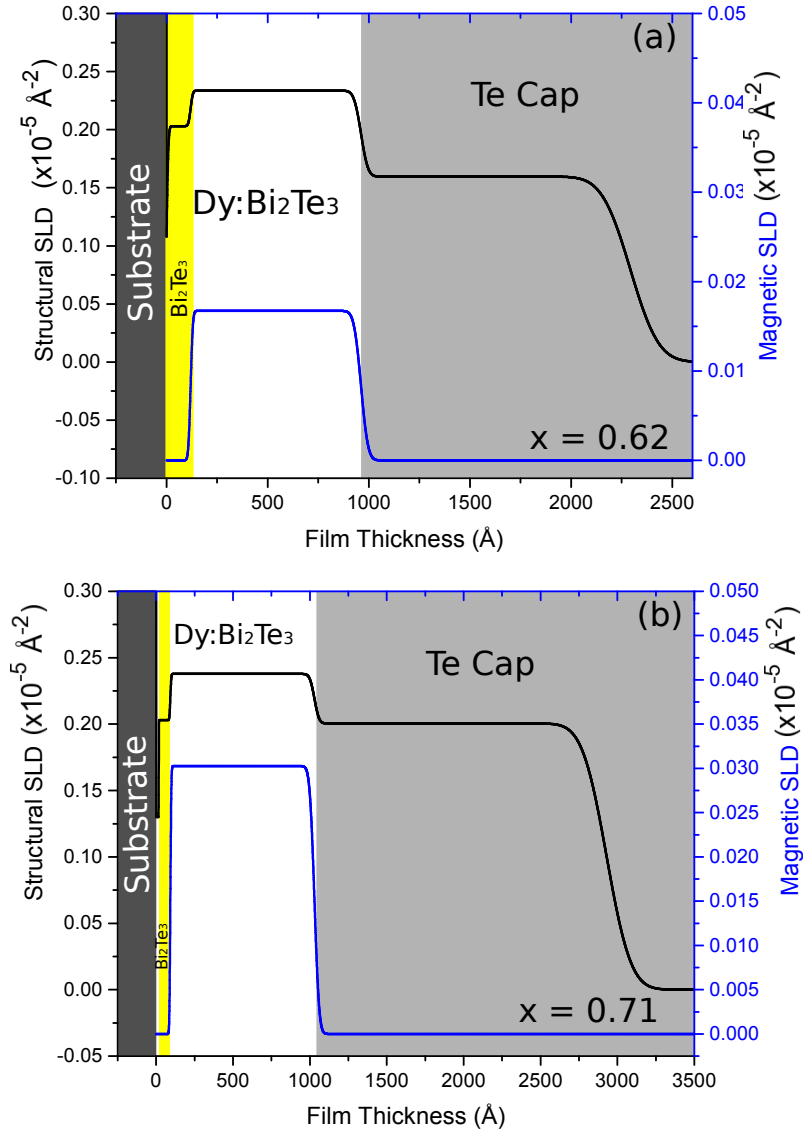


Figure 3.21: Structural and magnetic SLD for both the (a) $\text{Dy}_{0.62}\text{Bi}_{1.38}\text{Te}_3$ and (b) $\text{Dy}_{0.71}\text{Bi}_{1.29}\text{Te}_3$ samples at 3 K and 5 K respectively in an applied field of 0.7 T. Structurally each sample consists of a seed Bi_2Te_3 layer, uniform Dy-doped Bi_2Te_3 layer and Te cap.

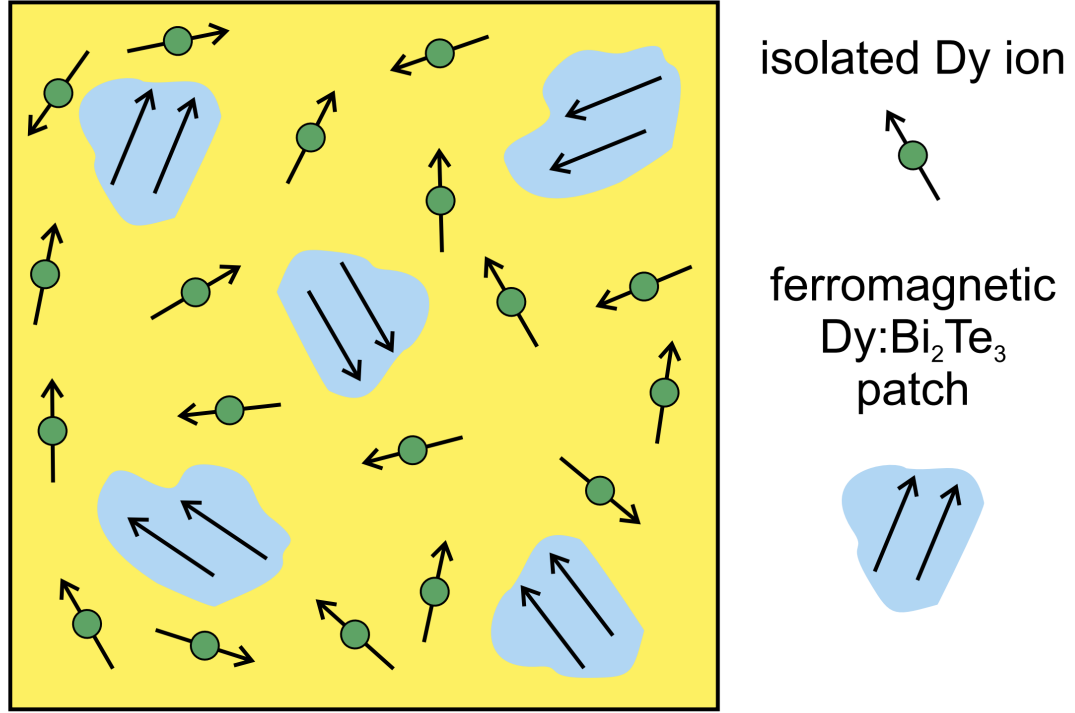


Figure 3.22: Cartoon of the magnetically ordered island model. The green circles represent individual Dy ions with their associated spin, and the larger blue areas represent magnetically ordered Dy patches. Reprinted from ref. [14] with permission from the APS.

low temperatures. Transverse, longitudinal and zero-field muon-spin rotation measurements carried out by collaborator Prof. Tom Lancaster reveal a complex picture of the behaviour of the Dy ions within the Dy-doped Bi_2Te_3 film. The behaviour of the magnetic fields in the paramagnetic region can be attributed to the stray fields emanating from magnetically ordered islands within the $\text{Dy:Bi}_2\text{Te}_3$. These ordered islands form due to patches of ferromagnetically ordered $\text{Dy:Bi}_2\text{Te}_3$ in amongst isolated Dy ions as demonstrated by Fig. 3.22.

Although the muon measurements allow for the dynamic measurement of the spins within the film, it is important to note that the PNR measurements discussed above demonstrate a static measurement where the extracted moments correspond to a net

increase in the alignment of the Dy moments with the applied magnetic field and not to a slowing of fluctuations of the moments.

ARPES and resonant photoemission measurements were carried out on the samples by collaborator Dr. Zaher Salman. These measurements provide evidence for possible dopant-induced charge carriers which according to the XMCD results demonstrated do not contribute to the magnetic ordering as there is no measurable Te XMCD even at high magnetic fields. It is important to note that these samples are highly doped and a lower doping concentration may eliminate these impurity bands. Samples with a third of the doping concentrations used for this investigation demonstrated a sizable band gap [61].

The rare-earth element Dy is clearly an intriguing dopant for use in 3D TI systems. The structure remains consistent even at the high doping concentrations presented in this study without the formation of ferromagnetic impurity phases. The measurements presented here show that the samples are not fully paramagnetic and are on the verge of becoming ferromagnetic. PNR measurements clearly demonstrate that a large effective magnetisation can be induced, demonstrating the possibility of exploiting its properties in heterostructure systems which will be explored in Chapter 4. The layered crystal structure of TI systems such as Bi_2Te_3 and Sb_2Te_3 should allow for the growth of van der Waal heterostructures. Unlike transition metal doped TI systems, the electronic and magnetic properties of Dy-doped Bi_2Te_3 is not intertwined allowing for independent control of these parameters for QAH effect applications.

3.3 Codoping Sb_2Te_3 with Transition Metals

As mentioned previously, transition metal doped TI systems such as Cr and V-doped $(\text{Bi,Sb})_2(\text{SeTe})_3$ epitaxial thin films have been used to realise the QAH effect at extremely low temperatures (~ 100 mK) [32, 71, 113, 114]. Doping Sb_2Te_3

with V has been reported to lead to a more stable ferromagnetic long range order than using Cr, while also retaining the high magnetic transition temperatures [115]. The mechanism behind the induced ferromagnetic order in both of these systems is still not completely understood, with different theories presented by various research groups [12, 28, 87, 91, 95–97, 116, 117]. It is possible therefore to explore the possibility of codoping the Sb_2Te_3 TI system with both Cr and V dopants in order to take advantage of the superior properties of each respective dopant in order to optimise the formed band gap which is proportional to the out-of-plane magnetic moment. Codoping has previously been utilised by using high-moment rare-earth elements which are alloyed with high-coercivity transition metals in order to obtain high-performance permanent magnets. In the case of MTIs, the higher magnetic moment of Cr can be combined with the larger coercivity found in V-doped systems. In dilute magnetic semiconductor systems (which behave similarly to the systems previously discussed), codoping is predicted to lead to enhanced magnetic properties due to the interplay between spin polarised magnetic defects [118]. Previously codoped bulk crystals of $\text{Sb}_{1.98-x}\text{V}_{0.02}\text{Cr}_x\text{Te}_3$ ($0 < x < 0.022$) have demonstrated an increased remanent magnetisation while transition temperature were within ~ 20 K of only Cr-doped crystals [119].

The layered structure of the chalcogenide TI systems has made the controlled substitutional doping of these systems difficult. Thermoelectric applications of these types of systems have demonstrated the deterioration of the material when in contact with metal electrical contacts [120]. Diffusion and reaction of metals contained within these materials occur at moderate temperatures, even down to room temperature [121]. The resulting inhomogeneities result in a variation of structural and magnetic properties effecting measured parameters such as carrier concentration, magnetic transition temperatures, saturation magnetisations and magnetic anisotropies. Understanding and controlling the complex defect chemistry and formation of sec-

ondary phases is a great challenge in thin films where grain boundaries are present. It has previously been demonstrated that resultant magnetic disorder such as strongly pinned domains does not affect the precisely quantised QAH effect [122]. It is important to study the structural and chemical properties of the doping scenario which determine the electronic and magnetic properties of the system through the use of synchrotron based spectroscopies and XMCD which allows for the analysis of the individual contributions of dopants in a codoping scenario.

This section details the structural and magnetic studies of the codoped system (V,Cr):Sb₂Te₃. The films were grown, studied with RHEED, XRR, XRD and SQUID VSM by the author. XAS and XMCD measurements were conducted in collaboration with Dr. Adriana Figueroa and Prof. Gerrit van der Laan and were analysed by the author. The results discussed in this section resulted in the publication ref. [15].

3.3.1 Thin Film Growth

The thin film samples used during this investigation were once again grown via the use of an MBE system. The films were deposited on *c*-plane Al₂O₃ (0001) substrates using once again the two step temperature deposition technique. The growth chamber was kept at a base pressure of 1×10^{-10} Torr throughout the growth. An initial ~ 5 nm seed layer of Sb₂Te₃ was first deposited at a substrate temperature of 200°C with a Te:Sb ratio of 10:1 as measured by a BFM. This layer was then annealed in a Te background at a substrate temperature of 250°C for 30 minutes. A codoped layer was then grown on top by depositing all materials at the same time at the heightened substrate temperature. The Cr doping concentration was fixed for each sample by keeping the measured Cr, Sb and Te flux consistent for each sample. The V flux was varied between 10% and 40% of the Cr flux. For the measurements carried out in this investigation a sample with a V:Cr flux ratio of 1:5 was used. For comparison, a pure Cr:Sb₂Te₃ sample was grown with the same doping concentration.

3.3.2 Structural Characterisation

3.3.2.1 Reflection High Energy Electron Diffraction

RHEED measurements were carried out *in-situ* during the growth of both the codoped and monodoped samples in order to observe their surface morphology. The monodoped Cr:Sb₂Te₃ sample demonstrated the same RHEED pattern discussed in section 3.1.2.1 and demonstrated in Fig. 3.1 indicating the $R\bar{3}m$ symmetry group of the sample. Figure 3.23 shows the RHEED measurement taken along the $[11\bar{2}0]$ azimuth of the *c*-plane Al₂O₃ substrate for the codoped (V,Cr):Sb₂Te₃ sample at the end of the growth. The codoped sample demonstrates the same $R\bar{3}m$ symmetry group with the RHEED pattern repeating six times with twin domains during a full rotation of the sample. However, there is a dot-like appearance to the RHEED streaks demonstrating that the surface has a 3D like structure. This is likely due to the V which XAS measurements indicate may sit at the surface of the sample. It could also be due to the formation of Cr₂Te₃ phases within the thin film as demonstrated by XRD measurements. The formation of the phase may effect the usual layer by layer growth mechanism of the Cr:Sb₂Te₃ causing the formation of islands at the surface.

3.3.2.2 X-Ray Reflectometry

XRR measurements were conducted in order to give an indication of the film thickness and roughness of the samples. The measurements for both the monodoped and codoped sample are presented in Fig. 3.24. Both samples demonstrate Kiessig fringes indicating a high quality thin film sample with well defined interfaces. These fringes can be used to calculate the thickness of each of the samples; the Cr:Sb₂Te₃ sample has a thickness of 60 nm and the (V,Cr):Sb₂Te₃ sample has a thickness of 30 nm.

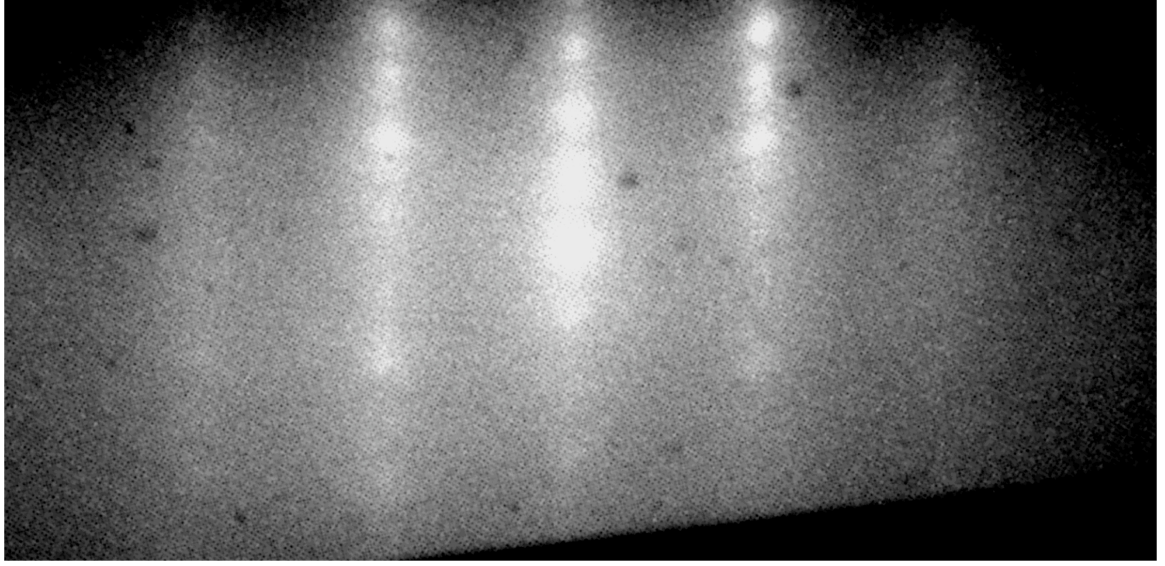


Figure 3.23: RHEED measurement taken at the $[11\bar{2}0]$ azimuth of the c -plane Al_2O_3 substrate. This pattern repeats six times with twin domains during the full rotation of the substrate indicating the sample demonstrates the $R\bar{3}m$ symmetry group. The pattern is dot like instead of streak like indicating that the sample has a 3D surface.

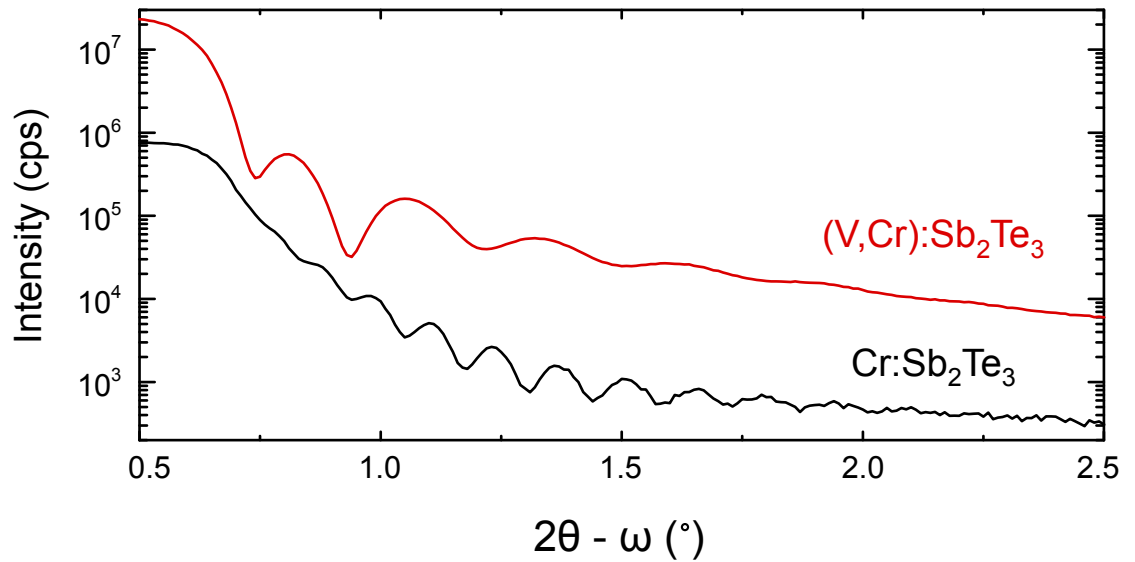


Figure 3.24: XRR measurement of the codoped $(\text{V,Cr})\text{:Sb}_2\text{Te}_3$ sample (red line) and corresponding monodoped $\text{Cr:Sb}_2\text{Te}_3$ sample (black line). The Kiessig fringes are clearly visible indicating both films are of a high structural quality. Reprinted from ref. [15] with permission from the APS.

3.3.2.3 X-Ray Diffraction

XRD measurements carried out in an out-of-plane geometry were also conducted for both the codoped and monodoped thin film samples in order to determine the crystalline phases and crystal quality of the films. Figure 3.25 presents the XRD data for the investigated films. The Al_2O_3 (0001) substrate and undoped Sb_2Te_3 peak positions are labelled using data taken from the ICSD (2084). The $\text{Cr}:\text{Sb}_2\text{Te}_3$ sample is well ordered with the c -axis lattice parallel to the surface normal. The expected reduction in the c -axis lattice parameter indicating the substitutional doping mechanism of the Cr onto the Sb sites is demonstrated by the shift of the peak positions to higher angles than those of undoped Sb_2Te_3 . The codoped $(\text{V},\text{Cr}):\text{Sb}_2\text{Te}_3$ sample does not show this same reduction and the peaks remain in the same positions as the undoped Sb_2Te_3 . It is likely that the Cr in this sample does not substitutionally replace Sb. The presence of a Cr_2Te_3 phase is also demonstrated by comparison to ICSD data (15038). The Cr_2Te_3 phase peaks appear as the (112) and (224) peaks demonstrating that the phase does not occur parallel to the surface normal.

There is no indication of V-Te compounds such as VTe (ICSD 52509) or V_3Te_4 (ICSD 52510) or metallic V (ICSD 241937) being present as indicated by the polycrystalline peak positions taken from the ICSD which do not match the experimental peaks.

3.3.2.4 X-Ray Absorption Spectroscopy

XAS measurements were performed at beamline I10, in order to compare the chemical composition of both the monodoped and codoped sample. The samples were held in an UHV sample environment which allows for a base temperature of ~ 2.5 K where a 14 T magnet could be used to apply a magnetic field to the samples. The samples were cleaved within the UHV chamber by glueing the sample face down with silver paste and then cleaving the substrate from the back of the sample using a cleaving

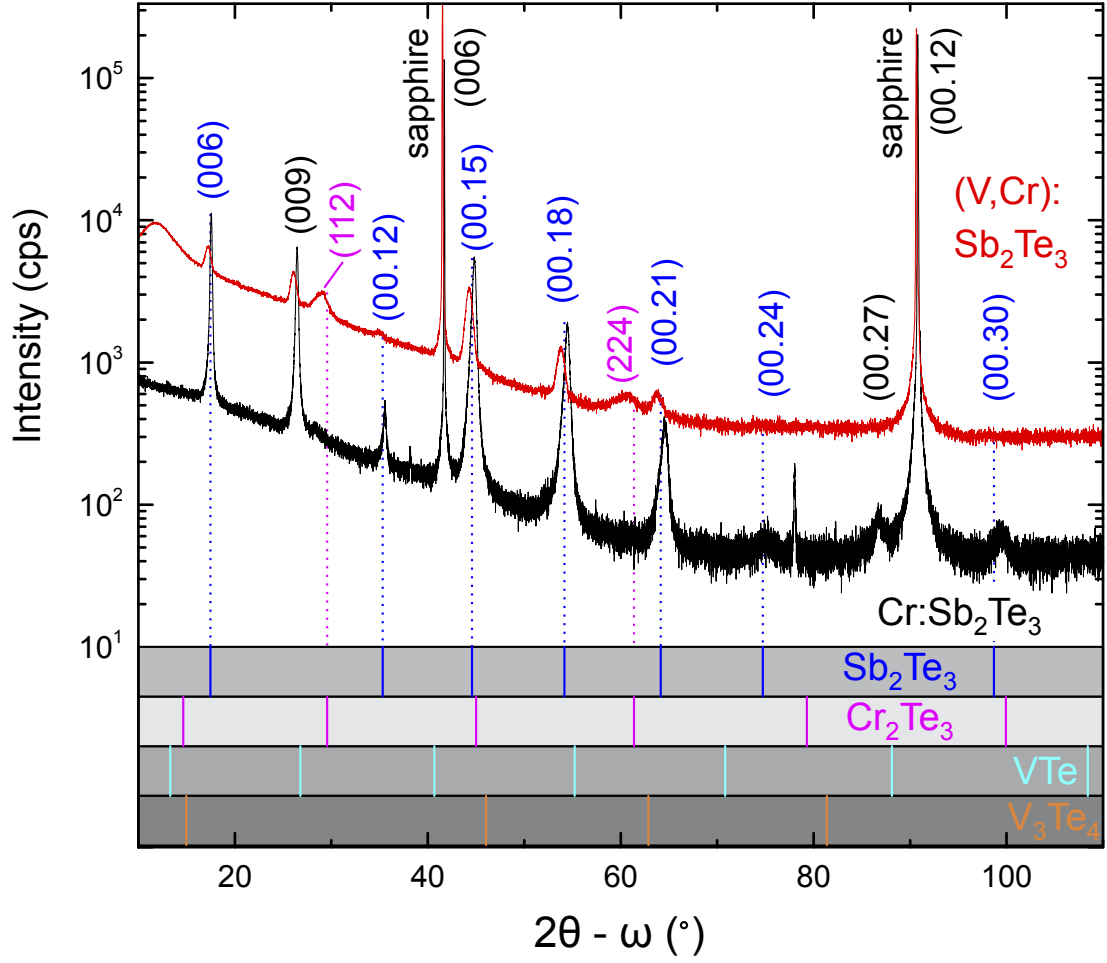


Figure 3.25: XRD measurement in out-of-plane geometry for the codoped and monodoped (V,Cr):Sb₂Te₃ (red spectrum) and Cr:Sb₂Te₃ (black spectrum) samples. The Cr:Sb₂Te₃ sample shows a well ordered single phase film with *c*-axis lattice parallel to the surface normal. The (V,Cr):Sb₂Te₃ sample demonstrates the formation of a Cr₂Te₃ phase which does not occur parallel to the surface normal. Reprinted from ref. [15] with permission from the APS.

post. This was to ensure a pristine surface free from a surface oxide was measured. In the case of the (V,Cr):Sb₂Te₃ sample, the sample surface before cleaving was also investigated. The measurements were performed with the sample oriented 30° from grazing incidence with respect to the X-ray beam.

Figure 3.26 demonstrates the XAS measurements performed at the Cr $L_{2,3}$ edges of both the Cr:Sb₂Te₃ sample and codoped (V,Cr):Sb₂Te₃ sample after cleaving at a temperature of 10 K with no applied field. The measurements were performed using TEY and so are surface sensitive. There are two XAS spectra for each sample representing the measurement performed with both left and right helicity of X-ray. The sample was magnetised in a field of 7 T and then the field removed. The line shape of the Cr edge for each sample is clearly different, indicating that the Cr is incorporated differently in each of the samples in agreement with the XRD measurements.

The chemical properties of the V contained within the (V,Cr):Sb₂Te₃ sample were also investigated using XAS. Figure 3.27 demonstrates the XAS measurements performed at the V $L_{2,3}$ absorption edges for both the grown surface of the sample and the cleaved sample with the sample being oriented at 30° grazing incidence to the incoming X-ray beam. At a temperature of 300 K for the as grown surface, the XAS measurement performed in TEY demonstrates a large V signal corresponding to oxidised V at the surface of the film. The XAS measurement for the cleaved piece of the sample, which is indicative of a lower-lying layer of the film, demonstrates a very weak signal for unoxidised V, even at a temperature of 3 K where the signal to noise ratio should be reduced. This measurement was also performed in TEY mode so is surface sensitive. This provides evidence that the V is mostly found at the top of the sample and is not distributed evenly throughout the layers of the sample.

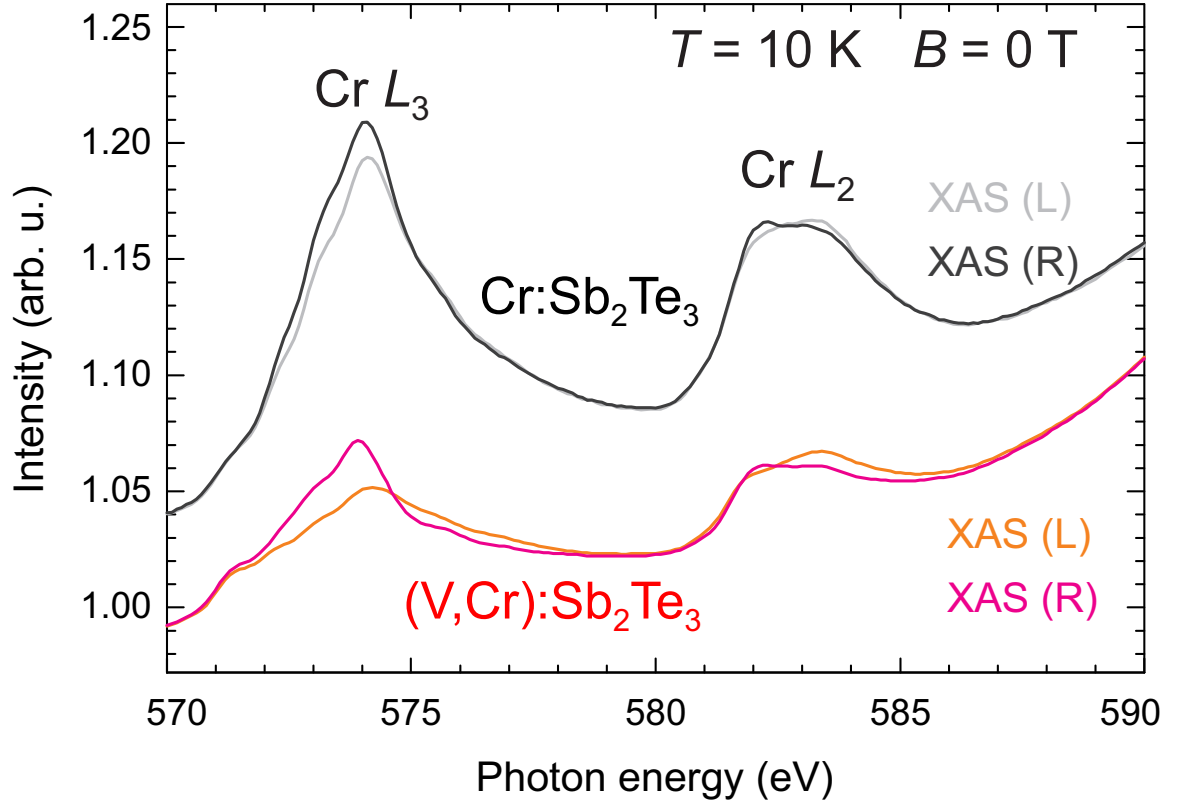


Figure 3.26: XAS measurements performed at the Cr $L_{2,3}$ absorption edge for both the monodoped and codoped samples in TEY. The measurements were performed for different X-ray helicities at a temperature of 10 K without the application of a magnetic field. The $\text{Cr:Sb}_2\text{Te}_3$ XAS spectra is shown in black (right helicity) and grey (left helicity) and the $(\text{V,Cr}):Sb_2Te_3$ XAS spectra is shown in magenta (right helicity) and orange (left helicity). The line shape of the Cr XAS spectrum is different for each sample indicating that the Cr is incorporated differently for each sample. Reprinted from ref. [15] with permission from the APS.

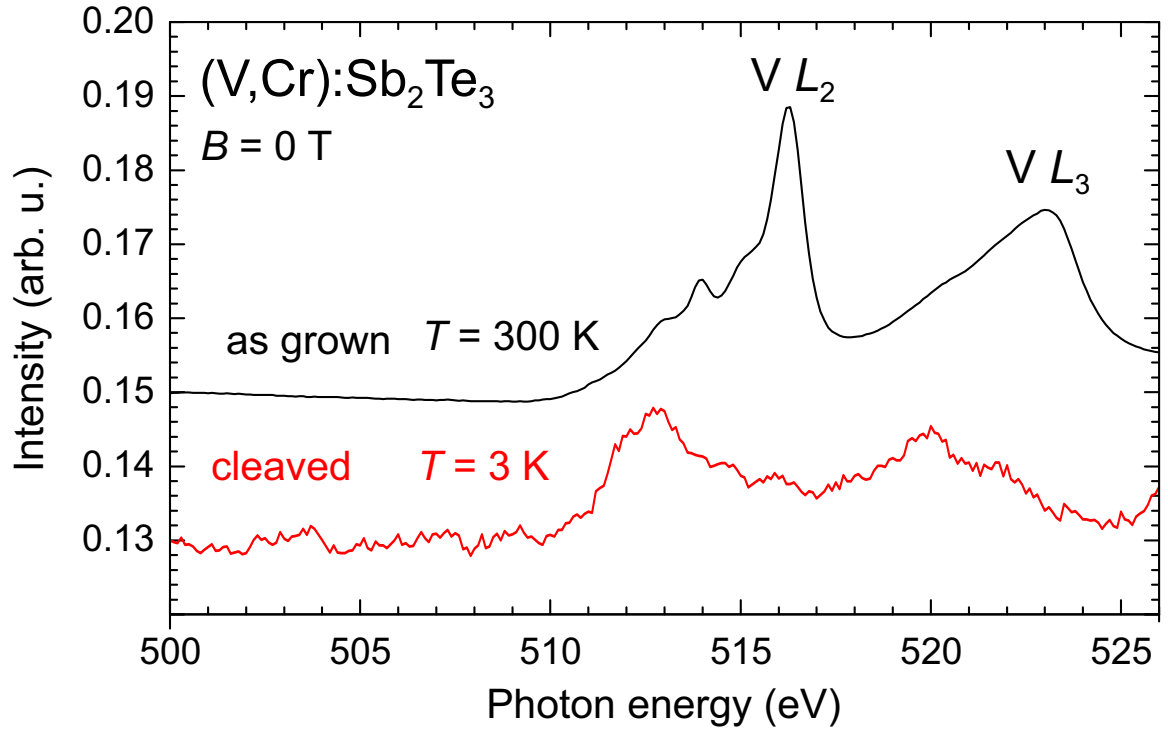


Figure 3.27: XAS measurements performed at the V $L_{2,3}$ absorption edges of the V,Cr:Sb₂Te₃ samples as grown surface (black) and cleaved surface (red) in TEY mode. The as grown surface measured at a temperature of 300 K indicates the presence of V oxide at the surface of the sample. After cleaving, there is a very weak unoxidised V signal found even at a temperature of 3 K where the signal to noise ratio is reduced. Reprinted from ref. [15] with permission from the APS.

3.3.3 Magnetic Characterisation

3.3.3.1 Magnetometry

Magnetometry measurements were performed with a SQUID VSM in order to compare the bulk magnetic properties of both the monodoped Cr:Sb₂Te₃ and codoped Cr:Sb₂Te₃ samples. Figure 3.28 demonstrates the measurement of magnetisation as a function of temperature in an applied magnetic field of 2 mT in the plane of the samples surface. The ferromagnetic transition temperatures for each sample are found by taking the first order derivative of this curve with respect to temperature. the Cr-doped Sb₂Te₃ sample demonstrates a $T_C = 72$ K while the T_C of the codoped sample measured here (V:Cr ratio 1:5) has a value of 148 K.

The Cr:Sb₂Te₃ sample also demonstrates a higher magnetic moment than the codoped sample. The increased T_C of the codoped sample can be attributed to the presence of the Cr₂Te₃ phase which was demonstrated by XRD measurements. Cr₂Te₃ is ferromagnetic with a stoichiometry-dependent transition temperature between 180 and 340 K [123]. For the measurements presented in Fig. 3.28 the originally measured magnetisation in emu was converted into μ_B/Cr ion by taking into account the Cr doping concentration (estimated by XRD shift for the Cr:Sb₂Te₃ sample) and volume of the sample, even in the case of the codoped sample. XMCD measurements indicate that the V contained within the sample does not contribute to the bulk ferromagnetic properties of the sample.

3.3.3.2 X-Ray Magnetic Circular Dichroism

XMCD measurements were also carried out at the BLADE I10 beamline using the same set up as for the XAS measurements. The XMCD is obtained by subtracting XAS spectra measured with the X-ray helicity vector antiparallel and parallel to the applied magnetic field measured in TEY. The Cr XMCD signal generated for

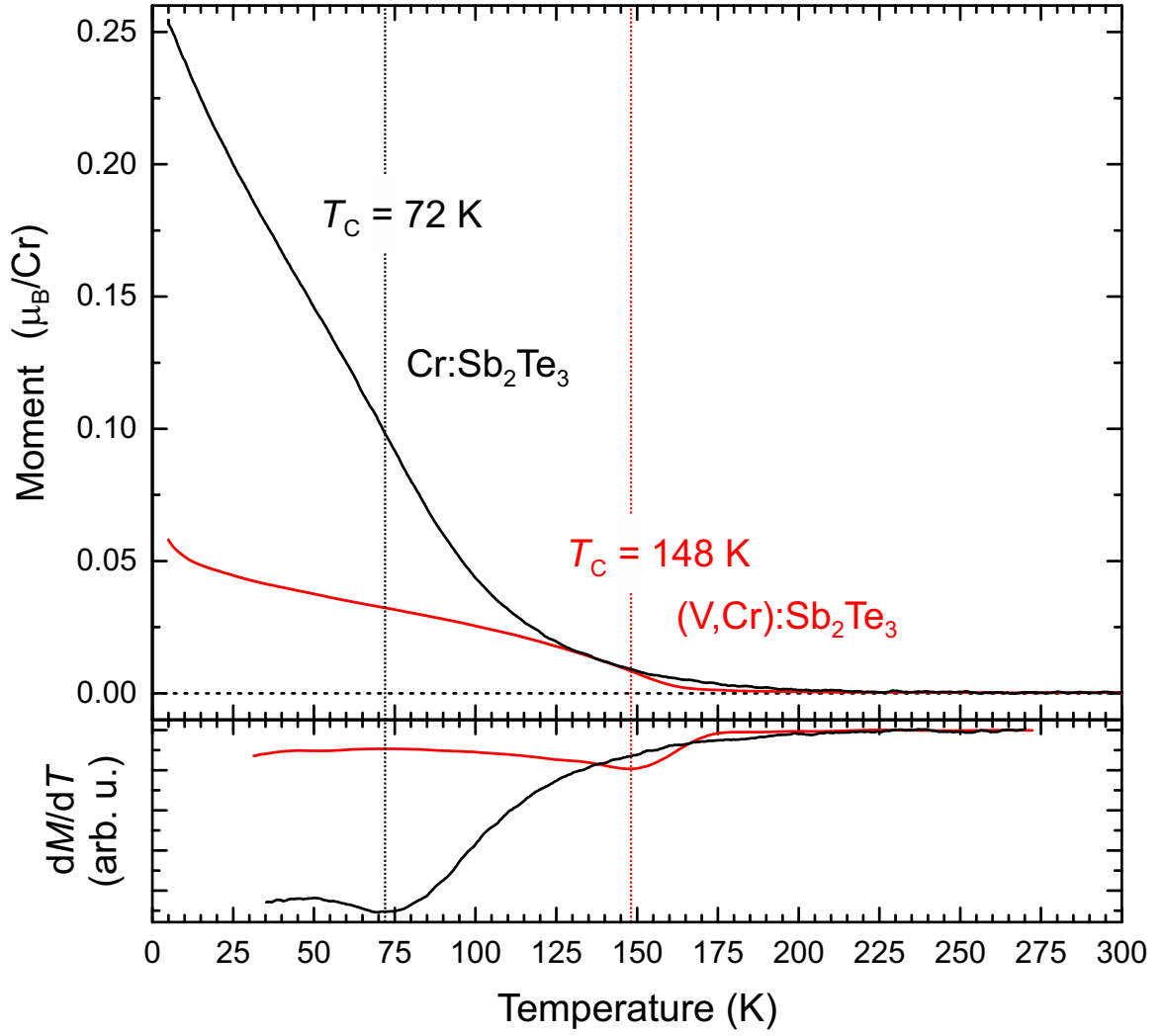


Figure 3.28: Magnetisation versus temperature measurements for both the $\text{Cr:Sb}_2\text{Te}_3$ (black) sample and $\text{V,Cr:Sb}_2\text{Te}_3$ (red) sample in an in-plane applied field of 2 mT. The bottom of the plot demonstrates the first derivative of each M vs T curve with respect to temperature. The minimum of these curves indicate a T_C of 72 K for the single doped and 148 K for the codoped sample. Reprinted from ref. [15] with permission from the APS.

the Cr-doped Sb_2Te_3 sample at a temperature of 10 K in remanence is identical to the spectrum shown in 3.7 as is to be expected. In agreement with the SQUID measurements shown in Fig. 3.28, the XMCD signal from the codoped sample is weaker under these same conditions. Figure 3.29(a) and (b) shows the XAS spectra for the different helicities of X-ray and calculated Cr XMCD signal produced for the codoped (V,Cr): Sb_2Te_3 sample in a 5 T field at a temperature of 3 K. The magnetic field was applied parallel to the X-ray beam. These are compared to the atomic multiplet theory calculated average Cr XAS spectra and XMCD spectra shown in Fig. 3.29(b) and (c).

The calculations were once again performed by collaborator Prof. Gerrit van der Laan in order to determine the valence state of the Cr dopant in order to determine their environment [11]. The calculated spectra shown here corresponds to the local ground state of Cr in Cr_2Te_3 . For a more in depth discussion of how these calculations were performed see ref. [15]. The comparison with the experimental spectra of (V,Cr): Sb_2Te_3 suggests that the dominant contribution is due to Cr_2Te_3 however there are other contributions present. This is in agreement with the XRD measurements which show the significant presence of the Cr_2Te_3 phase in this sample as well at the bulk magnetic measurements of the sample which demonstrate a T_C outside of the expected range of Cr_2Te_3 demonstrating a more complex magnetic coupling scenario.

As demonstrated by Fig. 3.27, the V XAS signal at the $L_{2,3}$ edge was too noisy to obtain an XMCD signal. The intensity of the Cr XMCD at the L_3 edge for each of the samples was measured at a number of different temperatures in order to observe the element-specific transition temperature for Cr, defined as the temperature at which the XMCD signal disappears completely. Figure 3.30 shows the data for both the single doped and codoped sample. This data was then compared to the bulk temperature dependent magnetisation measurements, which contains the contributions

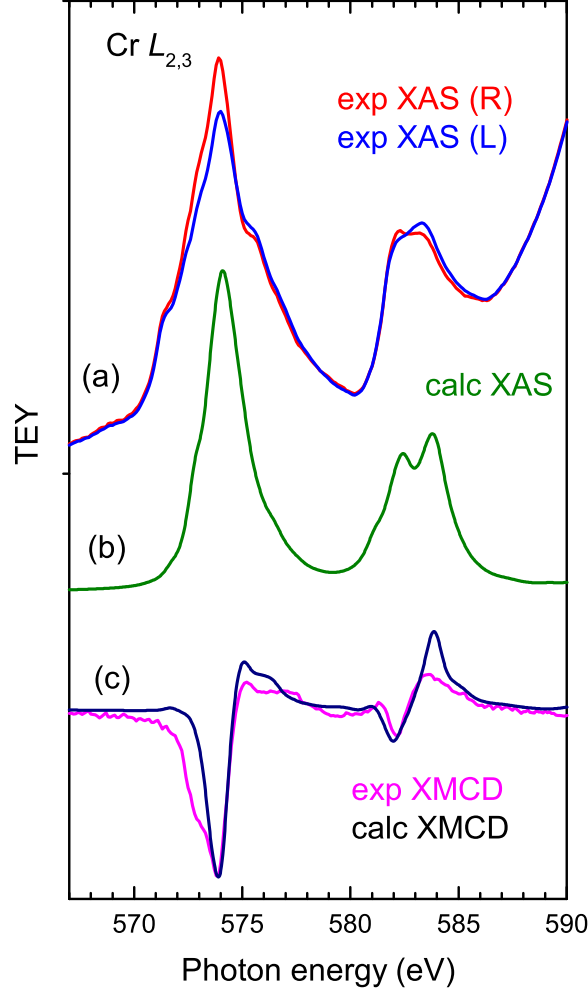


Figure 3.29: XAS and XMCD measurements performed on the codoped (V,Cr):Sb₂Te₃ sample at the Cr $L_{2,3}$ absorption edge at a temperature of 3 K in an applied field of 5 T with the sample 30° from grazing incidence of the incident X-ray beam. (a) The experimental XAS measurements for both helicities of X-ray. (b) The average XAS spectrum corresponding to the local ground state of Cr in Cr₂Te₃ calculated using atomic multiplet theory. (c) The experimentally measured Cr XMCD (magenta) compared to the calculated XMCD for Cr in Cr₂Te₃ (dark blue), once again using atomic multiplet theory. There is good agreement between the experimental and calculated spectra however, there are other contributions present in the experimental data not corresponding to Cr₂Te₃. Reprinted from ref. [15] with permission from the APS.

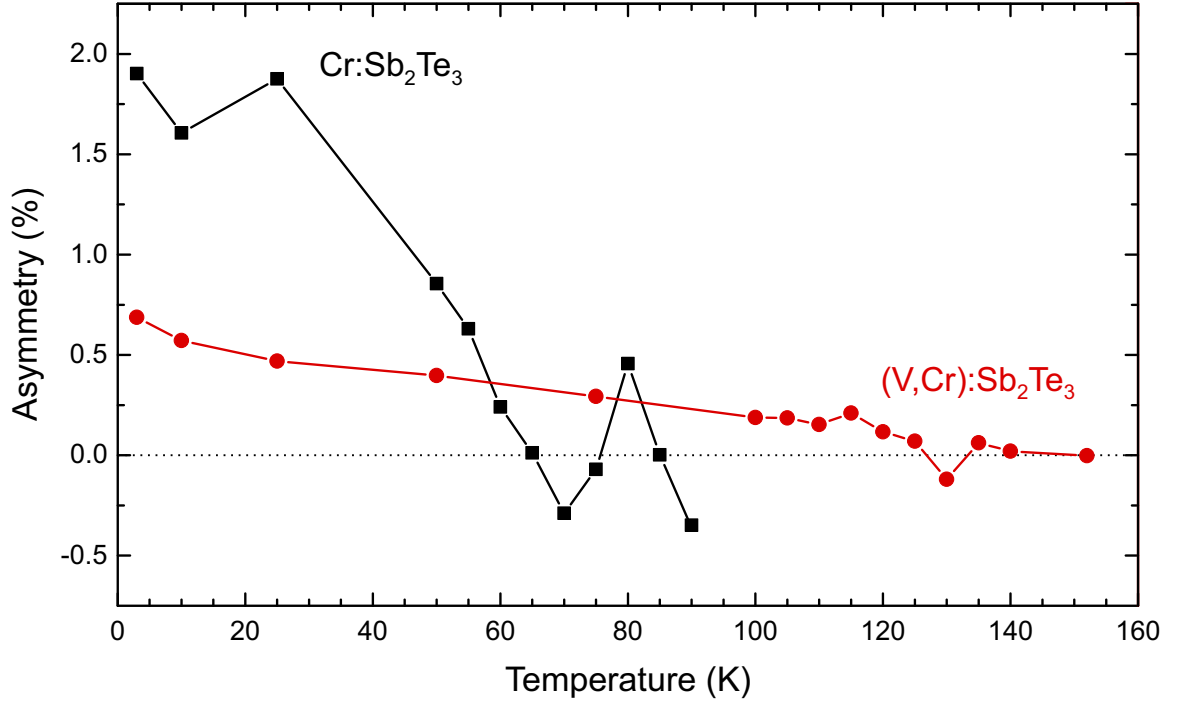


Figure 3.30: XMCD asymmetry (TEY) measured at the Cr L_3 edge in zero field (after saturating the sample in a field of 8 T) at 30° grazing incidence for both the Cr-doped and codoped sample as a function of temperature. The magnetic behaviour of the Cr in both samples follows closely the magnetometry data, shown in Fig. 3.28, demonstrating that the magnetic properties of both samples can be attributed to Cr. For the codoped sample this indicates that V does not appear to have a significant magnetic contribution. Reprinted from ref. [15] with permission from the APS.

from all magnetic species in order to disentangle the individual contributions of each magnetic species. It is clear that for both samples, Cr is mainly responsible for the magnetic bulk properties of the sample. This suggests that for the codoped sample V does not contribute significantly to the ferromagnetic order directly. Note that this is why it is reasonable to convert the measured moment data to the moment per Cr ion for the magnetometry data.

The intensity of the Cr XMCD found at the L_3 edge was also observed as a function of applied magnetic field in order to investigate the element specific behaviour and once again compare it to bulk magnetometry data for each of the samples at a temperature of 5 K. Figure 3.31 shows the XMCD and magnetometry hysteresis

plots for both samples with the field applied in-plane. For the magnetometry data the diamagnetic contribution originating from the Al_2O_3 substrate was subtracted by using a linear field to the high-field region of the magnetisation curve. Figure 3.31(a) shows that the codoped sample has a saturation field of ~ 5 T when measured by magnetometry, however the XMCD data doesn't saturate at the maximum applied field of 7 T. This is consistent with previously reported glassy behaviour of Cr_2Te_3 [123]. The increase in the asymmetry is very gradual beyond 5 T. The saturation magnetisation of the codoped sample is $(0.35 \pm 0.2) \mu_{\text{B}}/\text{Cr}$ with the uncertainty dominated by the determination of the film volume used to convert the magnetisation from emu units. The XMCD data demonstrates a clearly open hysteresis loop which closes at approximately ~ 1.5 T.

Figure 3.31(b) shows that the single doped $\text{Cr:Sb}_2\text{Te}_3$ sample is in comparison saturated by an in-plane applied field at ~ 1.5 T, consistent with Fig. 3.1.3.1. The measured saturation magnetisation moment is $(3.0 \pm 0.2) \mu_{\text{B}}/\text{Cr}$ ion once again in agreement with Fig. 3.1.3.1 with the error originating from the calculation of the volume of the film. In both cases, the XMCD data are slightly offset in comparison to the magnetometry data as the sample was measured 30° from grazing incidence compared to entirely in-plane. It is important to note the difference in the shape of the hysteresis loops for each sample.

The saturation moment for the codoped sample $\text{V,Cr:Sb}_2\text{Te}_3$ is found to be remarkably low. As discussed previously, Cr_2Te_3 is ferromagnetic with a stoichiometry-dependent transition temperature. The magnetic moment in epitaxial thin film of Cr_2Te_3 is $2.8 \mu_{\text{B}}/\text{Cr}$ close to the free ion moment of $3 \mu_{\text{B}}/\text{Cr}$ so does not explain the order of magnitude difference in saturation moment [123]. However, a number of Cr-Te compounds are known to exhibit complex magnetic coupling scenarios where Cr on different lattice sites can couple both ferromagnetically and antiferromagnetically leading to a reduced magnetic moment [124,125]. The Cr-Te phase could also

magnetically couple to the $\text{Cr:Sb}_2\text{Te}_3$ contained within the sample further modifying the magnetic behaviour of the film. The reduced moment seen in the codoped film could also be due to the fact the effective Cr density in the unit cell is not properly taken into account.

The XMCD signal at the Sb $M_{4,5}$ absorption edges was also observed for each sample. Figure 3.32 shows the measured XAS spectra for each helicity of X-ray and corresponding XMCD for both the single doped and codoped sample at a temperature of 3 K and in an applied field of 8 T with each sample still oriented 30° to the incident X-ray beam. The $(\text{V,Cr})\text{:Sb}_2\text{Te}_3$ does not demonstrate an Sb XMCD, even in high magnetic fields showing that there is no magnetic ordering. The Cr-doped sample on the other hand, shows an XMCD signal corresponding to the Sb mediating the long-range ferromagnetic order within the magnetically doped TI through a superexchange interaction with the magnetic ions which substitutionally replace the Sb within the structure of the sample [12, 96]. This is also demonstrated by the Cr and Sb XMCDs for this sample being opposing to one another [12]. The fact that there is no observable Sb XMCD demonstrates that the V and Cr appear to not be substitutionally replacing the Sb sites in the codoped samples, disabling the superexchange mechanism in these samples.

3.3.3.3 Conclusion

This research highlights the difficulties of doping thin films of the $(\text{Bi,Sb})_2(\text{Se,Te})_3$ family of compounds which exhibit a layered structure. Adding very small amounts of another dopant to a usually stable monodoped MTI, in this case V added to $\text{Cr:Sb}_2\text{Te}_3$, leads to the formation of Cr_2Te_3 and prevents substitutional incorporation of the dopants into the TI structure.

There are two possible explanations for these findings. It is possible that the V introduced into the sample is preferentially incorporated as a dopant onto the Sb

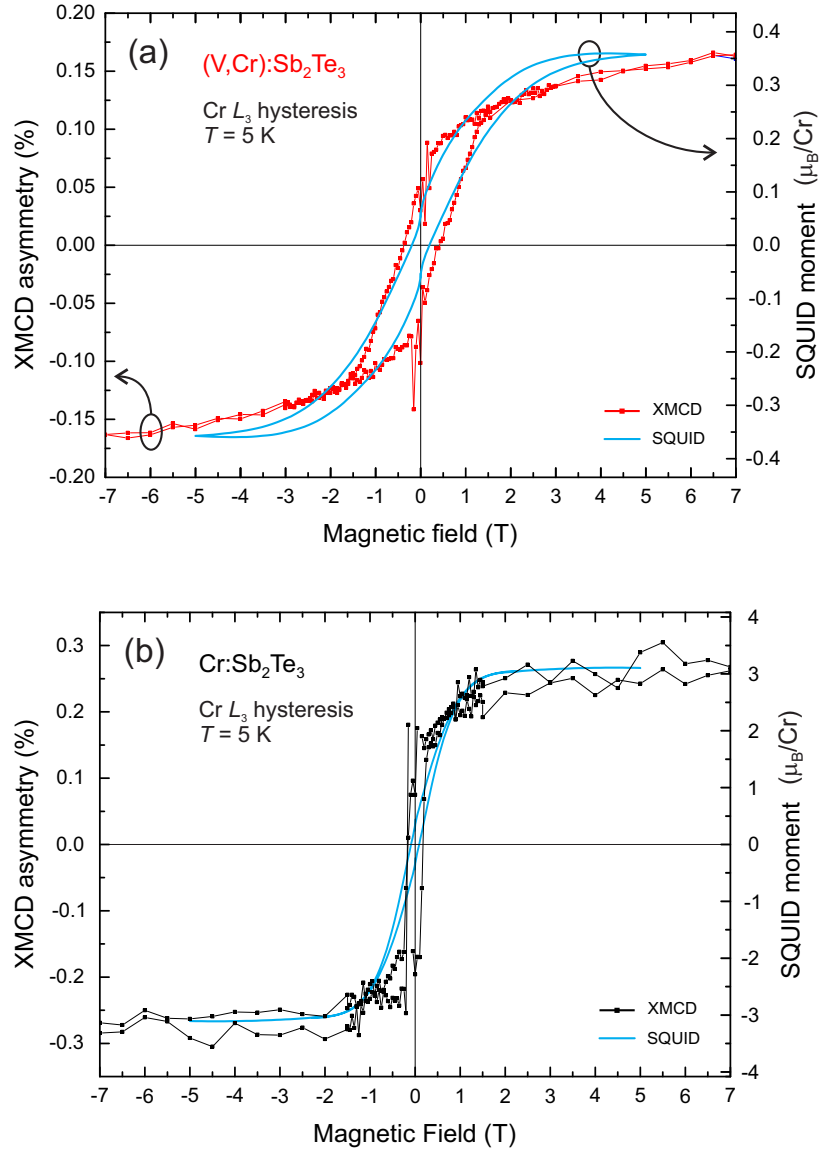


Figure 3.31: Magnetisation as a function of in-plane applied magnetic field, $M(H)$, at 5 K for (a) the codoped and (b) the Cr-doped sample. The plots compare the magnetometry hysteresis with the XMCD asymmetry (TEY) at the Cr L_3 edge with the field applied in-plane recorded at the same temperature. Reprinted from ref. [15] with permission from the APS.

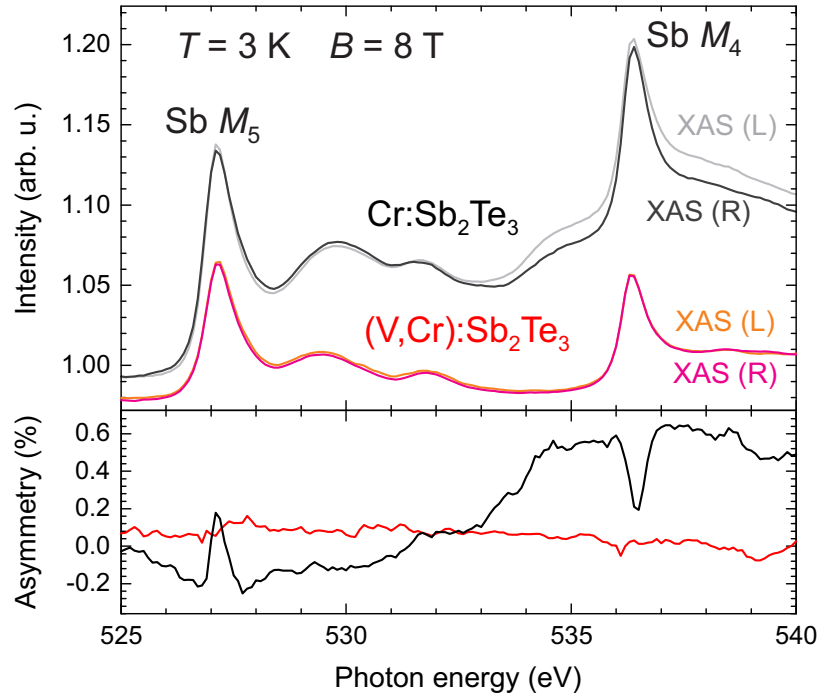


Figure 3.32: XAS and XMCD measurements for both the single doped and codoped samples at a temperature of 3 K and an applied field of 8 T. The Cr-doped samples XAS measurement for both right and left helicities of X-ray are shown in black and grey respectively with the corresponding XMCD shown at the bottom of the plot in black. The (V,Cr): Sb_2Te_3 samples XAS measurements for right and left helicities of X-ray are demonstrated in magenta and orange with the corresponding XMCD shown at the bottom of the plot in red. Reprinted from ref. [15] with permission from the APS.

site, causing the Cr to be forced out into the van der Waals gap or form clusters. The XAS and XRD measurements performed on the sample demonstrate there is no metallic Cr present in the sample. It is possible however, that the Cr forced into the van der Waals gap forms Cr_2Te_3 in the space between Te layers. In this situation the magnetic properties of the film would be dominated by the magnetic properties of $\text{Cr:Sb}_2\text{Te}_3$ as only a maximum of 20% of the Cr dopants should be replaced by V due to the flux ratio of the V and Cr cell during growth. There would also be two transition temperatures witnessed during the temperature dependent magnetisation measurements corresponding to the $\text{Cr:Sb}_2\text{Te}_3$ (~ 70 K) transition temperature and Cr_2Te_3 (~ 170 K bulk value [126, 127]) which is not demonstrated by Fig. 3.28. The film diffraction peaks should also broaden significantly and the c -axis lattice constant would increase significantly due to the disordered formation of Cr_2Te_3 in the van der Waals gap. Once again there is no experimental evidence for this scenario as demonstrated by Fig. 3.25.

It is also possible that the V acts as a surfactant during the film growth such that only a very small amount of the material is incorporated into the Sb_2Te_3 structure but the growth mode of the material is altered. In the surfactant assisted growth scenario the surfactant would be segregated on the surface of the sample after terminating the growth. Both RHEED and XAS measurements shown in Fig. 3.23 and 3.27 confirm the presence of a large concentration of V on the surface of the uncleaved sample. The V is oxidised on the surface of the sample as a result of exposure to air as demonstrated by the line shape which resembles that of V^{5+} corresponding to a stable oxidation state [128–130]. After cleaving the sample, only a small amount of V is detectable at a lower-lying layer of the film in TEY. The less intense peaks are shifted to a lower photon energy corresponding to a lower oxidation state for the V atoms lying lower down in the sample. The line shape of the cleaved sample is consistent with previously reported $\text{V:}(\text{Bi,Sb})_2\text{Te}_3$ [87, 95, 117].

There is sufficient experimental evidence to therefore conclude that V acts as a segregating species that promotes the formation of Cr_2Te_3 . The opposing case of Cr preventing the incorporation of V would cause the formation of a V-Te compound and this is not observed as demonstrated by Fig. 3.25. Cr_2Te_3 also has a compatible hexagonal structure compatible with the Sb_2Te_3 matrix, while the binary V-Te phase diagram would only allow for the formation of V_3Te_4 which is a monoclinic system. The role of the surfactant is to alter the adatom kinetics in order to promote layer by layer growth so it makes sense that for the layered $(\text{Bi,Sb})_2(\text{Se,Te})_3$ -type MTIs, that the V acting as a surfactant would want to improve the Sb_2Te_3 host materials crystalline quality by expelling the Cr dopant from the matrix [131–133].

It is apparent from these results that magnetic doping of a TI with more than one dopant, a method explored in an attempt to enhance the magnetic moment and transition temperature, is not promising in the case of the combination of Cr and V. Using XAS, XMCD, in combination with standard structural and magnetic characterization techniques, we have demonstrated that V has the undesired effect of preventing Cr from substitutionally doping into the TI on Sb sites. Instead it causes the system to form Cr_2Te_3 within the sample, consistent with the much enhanced transition temperature of the codoped sample. V, on the other hand, does not contribute significantly to the magnetic properties of the sample. Note that the effects of this rather undesired doping scenario on the electronic transport properties at very low temperatures may not be affected in a detrimental way, and the observation of the precisely quantised QAH effect may still be possible [122]. Nevertheless, this experiment has demonstrated the importance of XMCD for exploring the origins of magnetic ordering in MTIs.

Chapter 4

Magnetic Topological Insulator Heterostructures

4.1 Proximity Coupling Cr:Sb₂Te₃ to Cobalt

As discussed previously, the breaking of TRS which leads to the introduction of a gap in the TSS Dirac point and allows for the experimental observation of the QAH effect, can be achieved through two different methods. In Chapter 3 of this thesis it was demonstrated how long-range ferromagnetic order can be introduced into the TI through the use of transition metal magnetic dopants such as Cr. Cr doping of (Sb,Bi)₂(Se,Te)₃ has proven to be one of the most promising ways of producing an MTI [13,85,115], even leading to the experimental verification of the QAH effect [31]. It is also possible to break TRS by proximity coupling a ferromagnetic layer to the TI.

These same ferromagnetic layers can be used to further enhance the magnetic properties of MTIs once again through proximity coupling. Mn-doped (Bi,Sb)₂(Se,Te)₃ systems have demonstrated an enhanced ferromagnetic transition temperature by being magnetically coupled to a deposited Fe overlayer [134]. It has previously been

demonstrated for Cr-doped Bi_2Se_3 that the ferromagnetic transition temperature T_C can be enhanced from 7 K to 19 K through the deposition of a Co layer onto the surface of the MTI [90]. Even though in this case the T_C was more than doubled, these temperatures are still well below ones required for practical applications. As demonstrated by the results in section 3.1 magnetic ordering occurs at a much higher temperature for $\text{Cr}_x\text{Sb}_{2-x}\text{Te}_3$ thin films, for example at a doping concentration of $x = 0.42$ a $T_C = 125$ K has been achieved.

This research investigates the magnetic properties of in-situ cleaved $\text{Cr}_{0.32}\text{Sb}_{1.68}\text{Te}_3$ thin films before and after the deposition of a Co overlayer via the use of XMCD. The isothermal magnetisation curves are measured by XMCD as a function of applied magnetic field in order to produce Arrott plots in order to identify the T_C of the sample both before and after the deposition. The film growth and XMCD measurements were carried out by the author in collaboration with Dr. Adriana Figueroa, Prof. Gerrit van der Laan and Dr. Nina-Juliane Steinke. The results were analysed by the author. The research presented in this section resulted in the publication ref. [12].

4.1.1 Thin Film Growth

The same $\text{Cr}_{0.32}\text{Sb}_{1.68}\text{Te}_3$ thin film that was investigated during the XMCD measurements carried out in section 3.1.3.2 was also used to carry out the experiment detailed here. In order to perform the measurements on the Co overlayer sample, an electron-beam evaporator mounted to the measurement chamber of beamline ID32 was used to deposit a thin layer of ferromagnetic Co on the pristine sample surface. In order to prevent clustering of the Co atoms and adverse reactions with the sample surface, the sample was kept at a temperature of 10 K during the growth and the base pressure of the chamber was maintained at $\sim 5 \times 10^{-10}$ Torr [135].

The Co layer needs to be magnetic at remanence, which requires a thickness of 3 nm as determined by the material's characteristic exchange length. The Co layer

also needs to be thin enough that it does not suppress the TEY signal from the underlying MTI layer which has a surface sensitive probing depth of 3 to 5 nm [11]. The growth was then terminated at this XMCD intensity. To ensure the Co layer was magnetic, XMCD measurements were carried out periodically during the different stages of evaporation by flipping the X-ray helicity. The XAS and XMCD line shape and intensity were recorded during this process at both the Co and Cr $L_{2,3}$ edges to ensure they remained consistent with clean Cr and a subsequently grown clean ~ 3 -nm-thick Co film. The intensity of the Co XMCD was compared to a previously grown Co layer estimated to be ~ 3 nm in ref. [90] to ensure the correct thickness.

4.1.2 X-Ray Magnetic Circular Dichroism and X-ray Absorption Spectroscopy

The XAS and XMCD measurements were conducted also at beamline ID32 in the same manner detailed in section 3.1.3.2. In this case the sample was oriented at an angle of 54.7° to the incoming X-ray beam. This angle was selected as, in the uniaxial symmetry scenario of a thin film, the anisotropic contribution in the spin and orbital moments disappear [136, 137]. As Fig. 3.6 demonstrates, the easy axis for the $\text{Cr}_{0.32}\text{Sb}_{1.68}\text{Te}_3$ is out-of-plane and the easy axis for the Co film is likely to be in-plane, so this angle accounts for the perpendicular magnetisation directions of the Co and MTI.

Figure 4.1 shows the Co average XAS and XMCD spectra taken at the $L_{2,3}$ absorption edge at a temperature of 10 K after the sample was magnetised in an applied field of 6 T parallel to the incident X-ray beam and then the field was removed. The clear XMCD signal demonstrates that the Co overlayer is ferromagnetic with a moment aligned parallel to that of the Cr dopants.

Figure 4.2 shows the Cr XMCD recorded at the $L_{2,3}$ absorption edge both before and after the Co overlayers deposition. The two spectra are largely identical apart

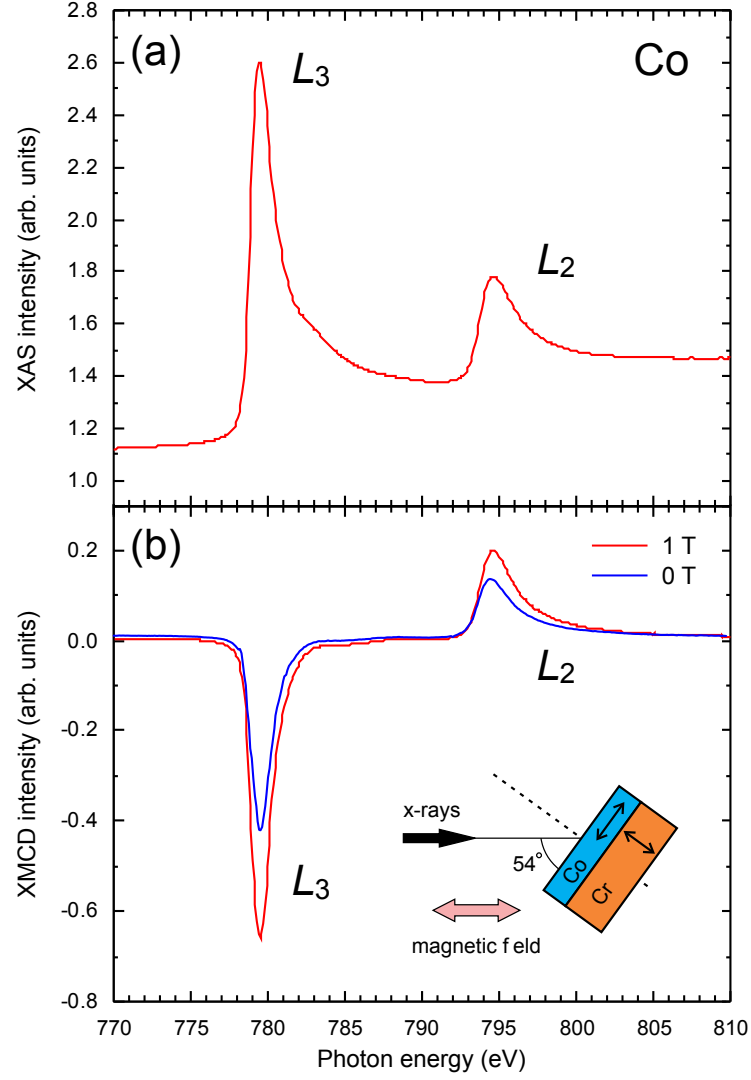


Figure 4.1: XAS and XMCD recorded from the *in-situ* cleaved $\text{Cr}_{0.32}\text{Sb}_{1.68}\text{Te}_3$ film after Co deposition. (a) XAS and (b) XMCD measured at the Co $L_{2,3}$ edge in an applied magnetic field of 1 T (red) and at remanence (blue), at a temperature of 10 K, and with an incident angle of the X-rays of 54° , as shown by the geometry in the inset. Figure adapted from ref. [12].

from a small reduction which is seen at the low-energy shoulder of the XMCD at a photon energy of 575.1 eV. This same effect was also witnessed when Co was deposited on top of Cr-doped Bi₂Se₃ [90]. It is possible that this could be caused by the delocalisation of the Cr 3*d* states after the introduction of the Co overlayer. The difference in XMCD signals demonstrates that there is no significant chemical reaction between the MTI and Co layer. The chemical state of the Cr contained within the TI is not altered by the presence of the Co overlayer and there is no diffusion of either material into the other. The valence state of the Cr dopant remains the same and there is no identifiable presence of the Cr³⁺ valence which would be indicated by a peak ~ 1.5 eV higher than the characteristic Cr²⁺ peak.

The intensity of normalised XMCD for the Cr *L*₃ absorption edge was recorded at a number of different temperatures and fields in order to record a set of isotherms of M^2 versus H/M for the sample before and after the Co overlayer deposition. These Arrott plots allow for the accurate determination of the ferromagnetic transition temperature of the sample in each scenario. Figure 4.3(a) shows the Arrott plot for the as-cleaved sample where M is obtained by using the background corrected Cr *L*₃ XMCD asymmetry. Figure 4.3(b) shows the Arrott plot produced in the same manner for the Co overlayer sample. Both samples demonstrate isotherms that are parallel straight lines in the high field regions. These regions were fitted with parallel straight lines with matching gradients in order to determine the M^2 intercept. The intercept is positive for $T < T_C$ and negative for $T > T_C$. The T_C is equal to the temperature at which the isotherm passes through the origin where the M^2 intercept is zero. The low field regions of the isotherms demonstrate bending owing to the disorder in the films at these applied magnetic fields.

Figure 4.4 shows the M^2 intercepts for each temperatures isotherm for both the as-cleaved and Co overlayer samples. This plot can be used to determine the zero crossings giving a $T_C \approx 87$ K for the MTI which is then enhanced up to a $T_C \approx 93$

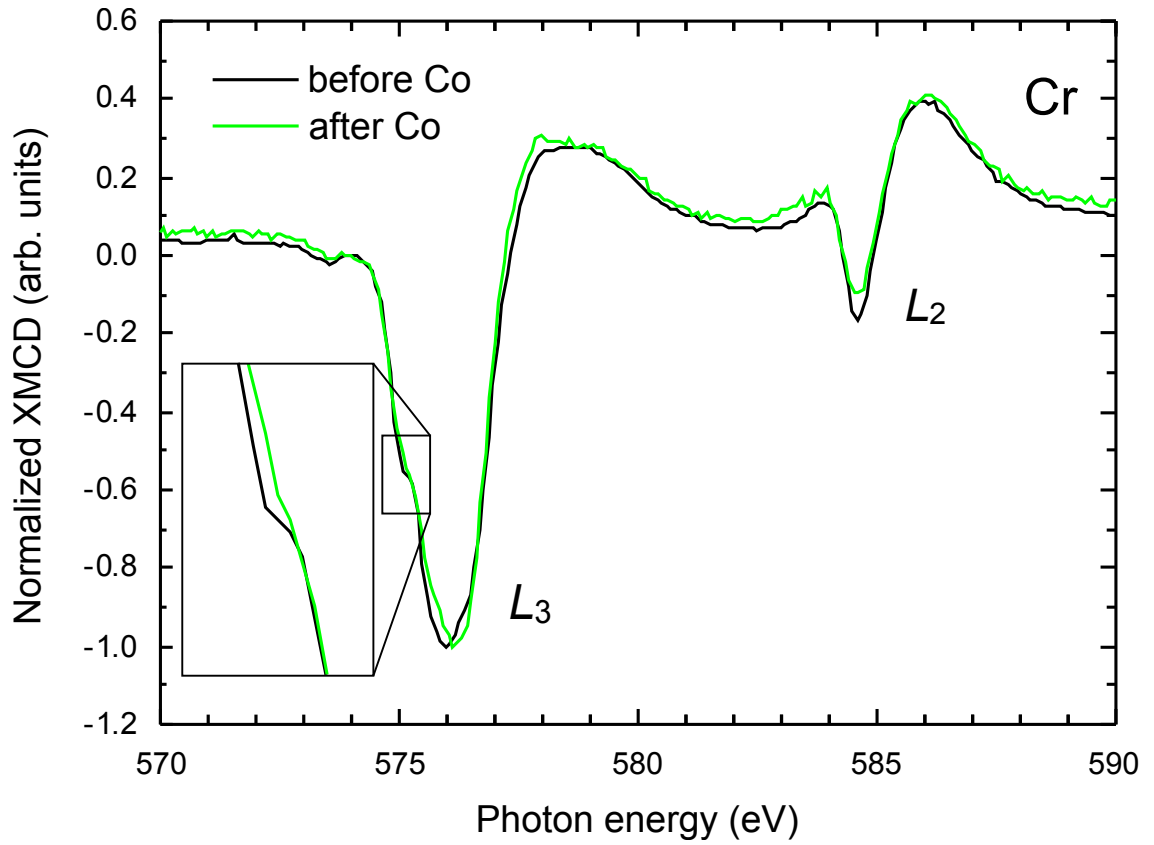


Figure 4.2: Comparison of the Cr $L_{2,3}$ XMCD signals before (black line) and after (green line) Co deposition. The inset shows a blow up of the small shoulder at 575.1 eV. There is no significant alteration of the chemical properties of the Cr dopant caused by the presence of the Co overlayer. Figure adapted from ref. [12].

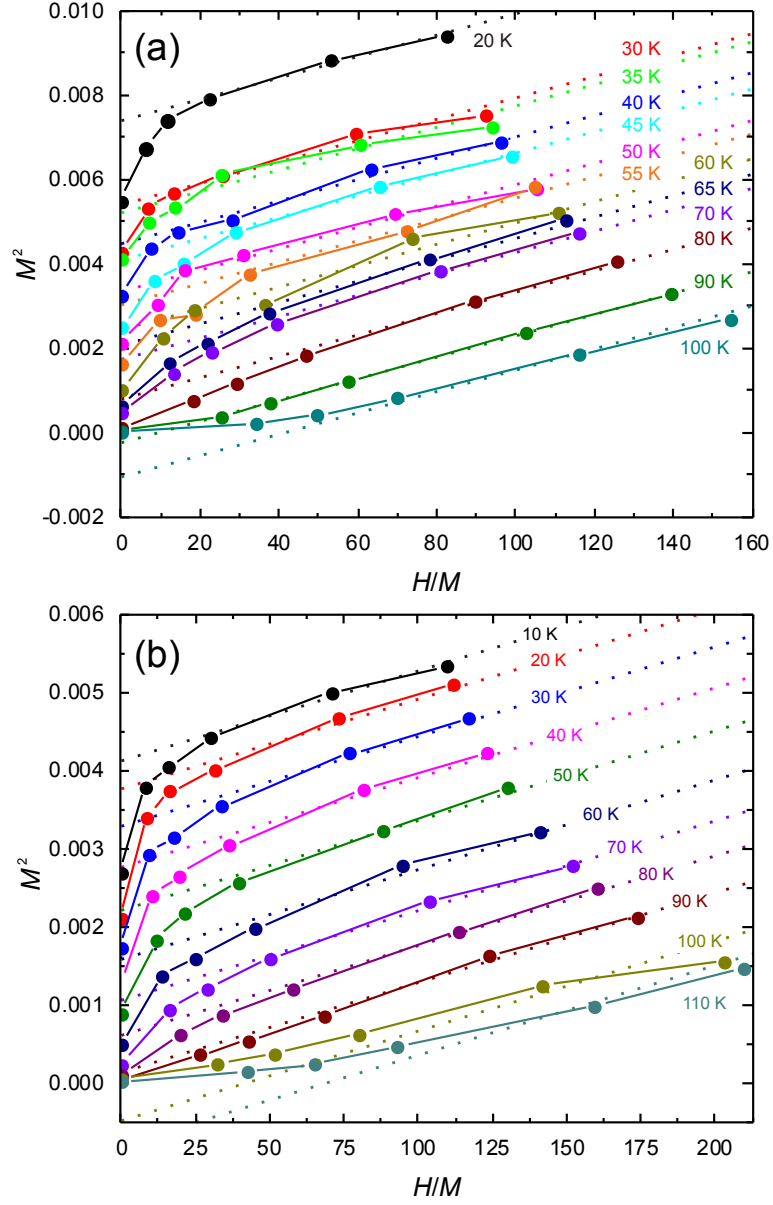


Figure 4.3: Arrott plots for the Cr magnetisation of (a) an as-cleaved $\text{Cr}_{0.32}\text{Sb}_{1.68}\text{Te}_3$ sample and (b) after *in-situ* Co deposition. The isothermal variations of M^2 are plotted as a function of H/M , where H is the applied field and M is the magnetisation as measured by the XMCD asymmetry of the Cr L_3 peak using TEY. In both plots, straight lines were fitted (shown as dotted lines) to the three data points obtained at the highest fields at each temperature. Figure adapted from ref. [12].

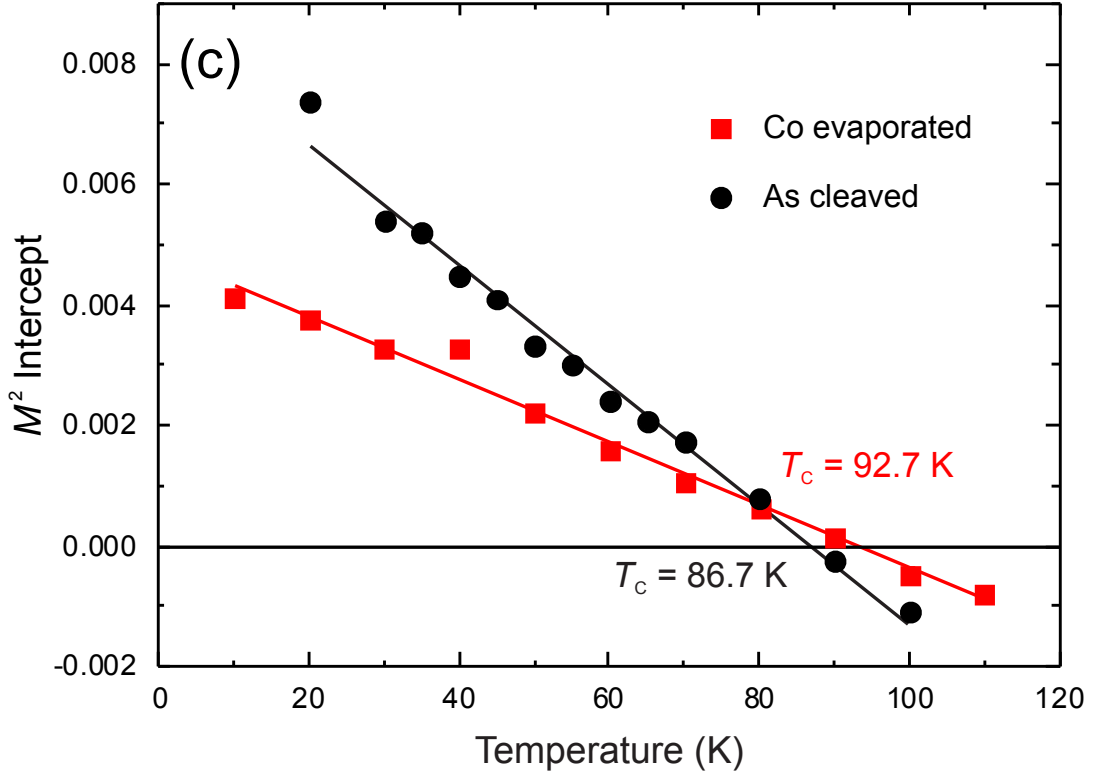


Figure 4.4: The M^2 intercepts, collected from Fig. 4.3 (a) and (b), plotted against temperature. The straight lines are guides to the eye. The temperature at which the M^2 intercept goes through zero corresponds to the ferromagnetic transition temperature. The values for the as-cleaved (black line) and Co decorated (red line) surfaces are 86.7 K and 92.7 K, respectively. The error bars of the data points are smaller than the size of the circles and squares representing the data points. Figure adapted from ref. [12].

K, representing a rather modest increase.

4.1.3 Conclusion

The XMCD spectra for both the Co and Cr $L_{2,3}$ absorption edge demonstrate that the moments of the deposited ferromagnetic Co layer are parallel to those of the Cr dopants. Despite this, the Arrott plots demonstrate only a small enhancement in the ferromagnetic transition temperature of the MTI when it is proximity coupled to the

Co overlayer. This result is unexpected considering that in the case of an Fe overlayer on top of Mn-doped GaAs, where the Fe and Mn moments are antiparallel to one another, a significant enhancement to the T_C is observed [138]. Cr-doped Bi_2Te_3 deposited on the ferrimagnetic insulator $\text{Y}_3\text{Fe}_5\text{O}_{12}$ also demonstrates a large increase in T_C [139]. The enhancement observed in this case is not as large as what is to be expected from a magnetically doped system in proximity to a ferromagnetic material. This is because the strength of the magnetisation of the Co layer would be expected to pull the Cr magnetisation direction into alignment with it, thus enhancing the transition temperature.

The Co layer does not appear to be able to polarise the Cr moments significantly even though Fig. 4.1 shows a Co XMCD which is indicative of good ferromagnetic quality, demonstrating the robustness of the long-range ferromagnetic order present in Cr-doped Sb_2Te_3 . If some of the deposited Co were to diffuse into the MTI, spin-polarised first principles calculations demonstrate the proximity coupling may be weakened. In the case of Co and Fe impurities, due to an occupied minority spin- d state at the Fermi level, the magnitude of the exchange interaction increases but becomes negative because of the large exchange splitting and narrow band character of the occupied d orbitals [97]. Previous research has demonstrated that using Fe as a proximity layer instead of Co would have lead to the Fe atoms partly penetrating into the surface of the MTI, reducing their magnetic moments due to the chemical interaction with the Te and Sb atoms at the topmost layer [140].

Another reduction of the proximity coupling could arise due to magnetic anisotropy. Spin-polarised scanning tunneling microscopy measurements of a $\text{Cr}_{0.05}\text{Sb}_{1.95}\text{Te}_3$ system show that while the bulk bands possess an out-of-plane magnetic easy axis, the TSS is spin polarised in-plane [141]. The T_C of the MTI may not be enhanced purely because the easy axis of the Co overlayer is expected to be in-plane while the MTI has an easy axis out-of-plane. However, the values retrieved from the Arrott plots should

be insensitive to magnetic anisotropy. While for low fields the magnetic anisotropy gives a different magnetisation behaviour along different magnetisation directions, the magnetic anisotropy should not change the value of T_C because this value is defined in zero magnetic field, i.e., where there is no direction of the magnetic field. These results therefore indicate the robustness of the magnetic coupling scenario found in Cr-doped Sb_2Te_3 . This information can be used to further utilise this material in proximity coupled MTI heterostructures as will be demonstrated in the next section of this thesis.

4.2 Transition Metal Doped Sb_2Te_3 and Rare Earth Doped Bi_2Te_3 Proximity Effect Heterostructures

In the previous chapter of this thesis we have seen that doping Sb_2Te_3 with the transition metal Cr leads to structurally well ordered samples that demonstrate long range ferromagnetic order up to relatively high temperature (~ 125 K). This long-range ferromagnetic order is mediated by the conduction band and Cr doping can lead to the formation of impurity bands which need to be frozen out at low temperatures on the order of ~ 100 mK in order for the QAH effect to be experimentally observed in these types of samples despite their much larger ordering temperatures [7]. In an attempt to alleviate this issue, high quality rare-earth doped Dy: Bi_2Te_3 samples were fabricated and investigated as the size of the magnetic gap in the usually gapless TSS which is required to observe the QAH effect is directly dependent on the size of the magnetic moment, where Dy has an effective magnetic moment of $10.6 \mu_B/\text{Dy}$ [4]. No ferromagnetic long-range order has been detected however, despite this, the samples behave as though they are on the verge of becoming ferromagnetic and a gapped

TSS band has been observed [104]. Even more promising is the evidence to suggest that this short-range ferromagnetic coupling is not mediated by the conduction band, suggesting a possible absence of impurity bands.

In order to combine the advantages of the high-temperature order in Cr-doped systems with the high magnetic moments of rare-earth element doped films, yet avoiding the respective shortcomings, this section of the thesis presents an investigation of magnetically doped $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ heterostructures. The structure and electronic properties of undoped $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ multilayer films grown by MBE has previously been investigated [142–144]. High quality magnetic TI heterostructures consisting of multiple bilayers Dy-doped Bi_2Te_3 /Cr-doped Sb_2Te_3 were fabricated and investigated using RHEED, XRR, XRD, XAS and XMCD. Structural characterisation measurements were carried out and analysed by the author. XAS and XMCD measurements were carried out by the author in collaboration with Dr. Andreas Frisk, Dr. David Burns and Prof. Gerrit van der Laan. The data was then analysed by the author. The results presented in this section led to the publication of ref. [16].

4.2.1 Thin Film Growth

The thin film heterostructures were synthesized using established recipes for Dy: Bi_2Te_3 and Cr: Sb_2Te_3 [12–14,61]. The c -axis oriented films were grown on c -plane Al_2O_3 substrates using flux ratios of $\sim 100:10:1$ for Te:(Sb,Bi):(Cr,Dy), as measured by a BFM. To begin the heterostructure an ~ 3 nm thick layer of undoped Bi_2Te_3 was deposited at a substrate temperature of 200°C and was then annealed for 30 minutes at an increased substrate temperature of 250°C in a background flux of Te. The magnetic TI heterostructure was then deposited on top of this layer starting with Dy: Bi_2Te_3 then followed by Cr: Sb_2Te_3 . Each sample grown consists of n bilayer repeats, whereby each bilayer is made of equally thick Dy: Bi_2Te_3 and Cr: Sb_2Te_3 layers. In order to protect the Cr: Sb_2Te_3 top layer for surface sensitive X-ray spectroscopy measurements, the

heterostructures were capped with a layer of Bi with an optimal thickness to both protect the sample from oxidation and allow surface sensitive measurements to be carried out.

4.2.2 Structural Characterisation

4.2.2.1 Reflection High Energy Electron Diffraction

The quality of the layers across the interfaces was monitored using *in-situ* RHEED. As demonstrated by Fig. 4.5 the RHEED patterns exhibit streaks during the growth of each layer indicating smooth, two-dimensional, layers. The two characteristic RHEED patterns of both Bi_2Te_3 and Sb_2Te_3 are obtained along the $[10\bar{1}0]$ and $[11\bar{2}0]$ azimuths of the c -plane Al_2O_3 substrate, are separated by 30° and repeat every 60° revealing the expected space group $R\bar{3}m$. These patterns remain consistent even after a number of interchanging layers have been deposited.

4.2.2.2 X-Ray Reflectometry

XRR measurements were performed in order to determine the roughnesses and thickness of each layers of the grown thin film. The measured data was fitted by generating a model of the sample by using the GenX package. Figure 4.6 demonstrates XRR data measured from a heterostructure sample with 10 bilayer repeats. The best fitting model demonstrates that each bilayer is identical in its structure, consisting of $\text{Cr:Sb}_2\text{Te}_3$ and $\text{Dy:Bi}_2\text{Te}_3$ thicknesses of 3.5 and 3.8 nm, respectively. The root mean square surface roughnesses for each layer are found to be ~ 1 nm demonstrating a heterostructure with well defined interfaces. The model used fixed the film stoichiometries to be $\text{Dy}_{0.72}\text{Bi}_{1.28}\text{Te}_3$ and $\text{Cr}_{0.42}\text{Sb}_{1.58}\text{Te}_3$ which match the doping concentrations seen for samples grown at the flux ratios used during the growth of these samples. The undoped Bi_2Te_3 seed layer was found to be ~ 3 nm thick and was free from the Dy dopant.

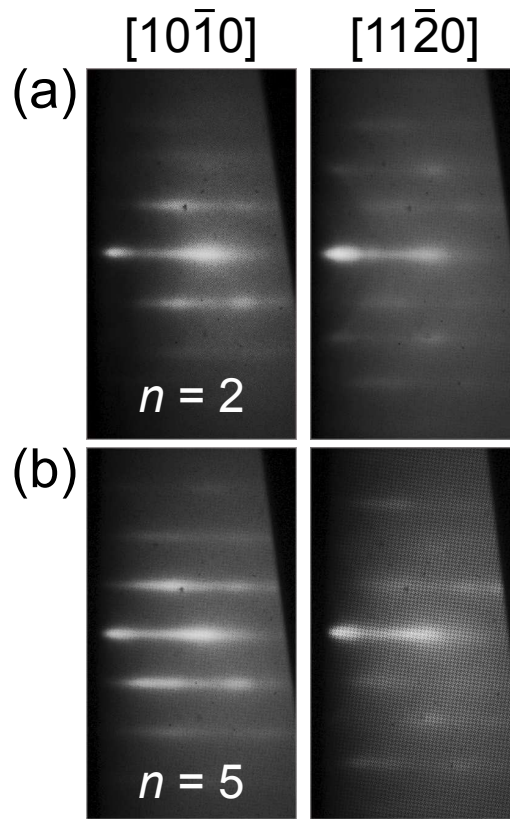


Figure 4.5: RHEED patterns obtained of the $\text{Cr:Sb}_2\text{Te}_3$ surface during growth, after (a) $n = 2$ and (b) $n = 5$ bilayer repeats. Patterns obtained along the $[10\bar{1}0]$ azimuth are shown on the left, and along the $[11\bar{2}0]$ azimuth of c -plane sapphire on the right. Reprinted from ref. [16] with permission from the APS.

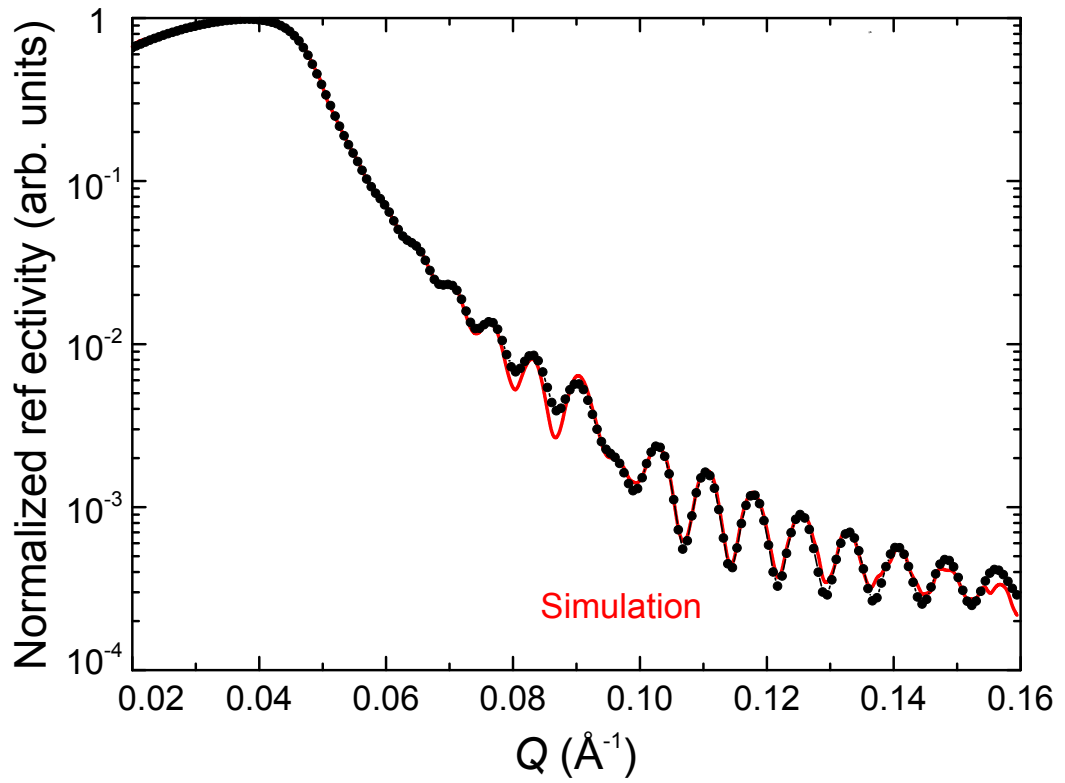


Figure 4.6: X-ray reflectivity scan (black dots) and simulation (red line) as a function of momentum transfer Q . The fitted data was retrieved by using the GenX package. The best fitting model demonstrates that the sample is a heterostructure that consists of 10 bilayer repeats with well defined interfaces between each layer. Reprinted from ref. [16] with permission from the APS.

4.2.2.3 X-Ray Diffraction

The crystalline quality and phase of the layers in the heterostructures were determined using out-of-plane XRD. Figure 4.7 demonstrates the measured XRD data for the same $n = 10$ bilayer sample as previously discussed. The measured $(00l)$ order reflection peaks which indicate the film is entirely c -axis, are indexed according to the Bi_2Te_3 (ICSD 158366) and Sb_2Te_3 (ICSD 2084) unit cells where the peak positions were once again compared to data taken from the ICSD. It is important to note that due to the largely identical structure of both Sb_2Te_3 and Bi_2Te_3 these peaks occur at the same diffraction angles. Note that it has been shown that Dy doping of Bi_2Te_3 can lead to both a percentage of the dopant substitutionally replacing the Bi within the structure as well as an increased c -axis lattice constant (up from the expected 30.43 Å) where the Dy-dopant is found to sit in the van der Waals gap [14,61]. For Cr-doped Sb_2Te_3 a smaller c -axis lattice is found (reduced from 30.458 Å) which is consistent with Cr replacing Sb within the structure [13].

The inset of Fig. 4.7 indicates the presence of superlattice peaks which occur for well-ordered multilayer structures with well-defined interfaces. Using the distance between the Bragg peaks and satellite peaks demonstrated in the XRD data, a bilayer thickness of ~ 8 nm can be estimated, consistent with the previously discussed XRR data. The estimated total thickness of the film ~ 83 nm, calculated from the distance between superlattice peaks is also consistent with model used to fit the XRR data. The $(00l)$ peak positions are also consistent with previously published data on c -axis oriented undoped $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ heterostructure samples [143].

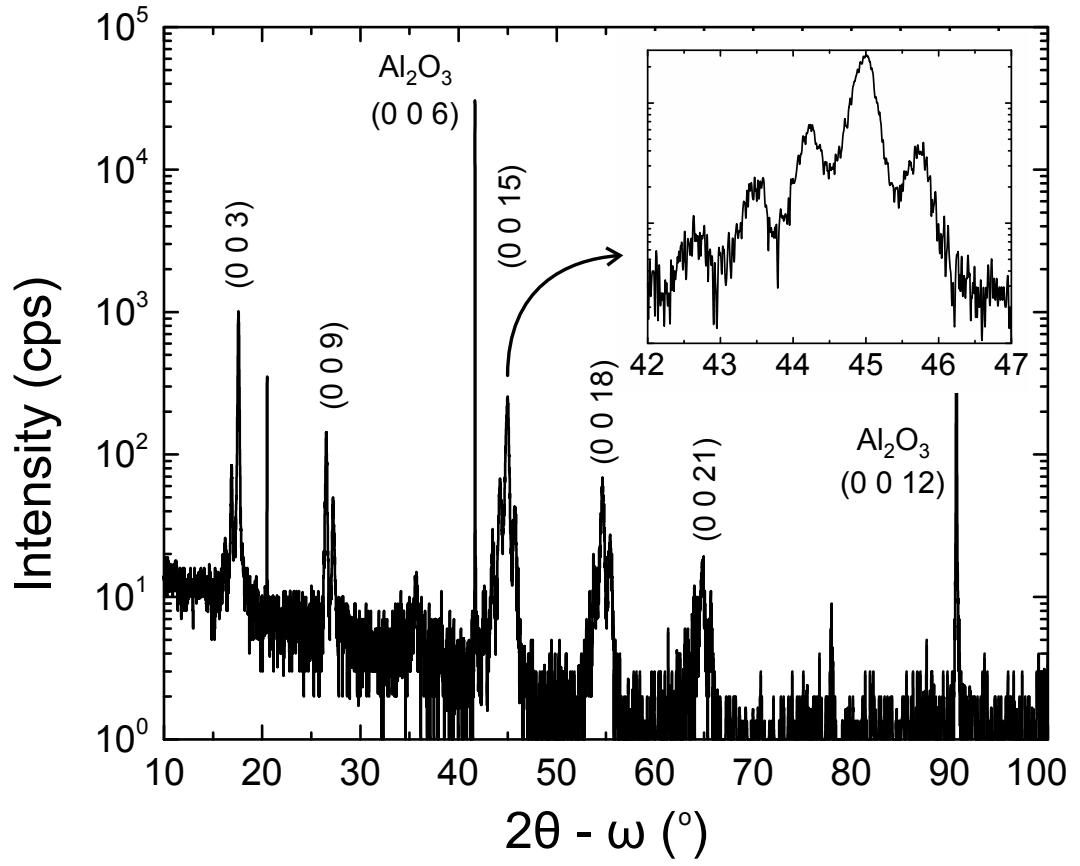


Figure 4.7: X-ray diffraction (2θ - ω scan) of the Dy:Bi₂Te₃/Cr:Sb₂Te₃ heterostructure grown on *c*-plane sapphire. The inset shows the superlattice peaks around the (0 0 15) Bragg peak. Reprinted from ref. [16] with permission from the APS.

4.2.3 Magnetic Characterisation

4.2.3.1 X-Ray Magnetic Circular Dichroism and X-Ray Absorption Spectroscopy

The XAS and XMCD measurements demonstrated in this research were performed at both beamline 29, BOREAS and beamline I10. The measurements were carried out at the Cr $L_{2,3}$ and Dy, Te and Sb $M_{4,5}$ edges in TEY, FY and LY. TEY allows for a probing depth of 3 to 5 nm while FY and LY probe the entire heterostructure stack [11].

Figure 4.8(a) shows the Cr $L_{2,3}$ absorption edges of a heterostructure sample with 5 bilayer repeats as measured by surface sensitive TEY after an applied field of 6 T parallel to the X-ray beam was removed to perform a remanence measurement at a temperature of 3 K. This particular measurement was carried out at beamline I10 with the sample oriented at 54.7° to the incoming X-ray beam, the angle at which the anisotropic contributions to the spin and orbital moments disappear [136, 137]. This was to accommodate for the expected perpendicular magnetisation direction of the Cr:Sb₂Te₃ (easy axis out-of-plane) and Dy:Bi₂Te₃ with expected easy axis in-plane [13, 61]. The spectrum is very similar to that of single-layer Cr:Sb₂Te₃ with the Cr L_3 edge demonstrating a double peak structure. The first peak is found 0.5 eV below the second peak which is more dichroic [12]. Figure 4.8(a) demonstrates a reference spectrum of Cr₂O₃. Oxidation leads to a Cr³⁺ peak which is found at 1.5 eV higher energy than the Cr²⁺ one at the Cr L_3 edge. This peak is not present in the experimental TEY spectrum demonstrating that the heterostructure is free from surface oxidation due to the Bi cap.

The fitting of the XMCD spectrum by atomic multiplet calculations [52] matches those previously published with the same local ground state and octahedral crystal field [12]. The intensities of the L_3 and L_2 peaks are negative and positive as a result

of the $2p$ core spin-orbit interaction. The sloping background of the Cr $L_{2,3}$ XAS spectrum is due to the energy range coinciding with the Te $M_{4,5}$ absorption edge. This sloping background is almost entirely cancelled out in the XMCD apart from a small negative peak that can be found at ~ 573 eV demonstrating the Te M_5 peak. The Te and Cr moments are antiparallel as the azimuthal quantum number for the orbitals in these two electric-dipole transitions are opposite with a transition from $2p$ to $3d$ for Cr and a transition from $3d$ to $5p$ for Te [52, 136].

Figure 4.8(b) shows the Cr $L_{2,3}$ absorption edge for a 10 bilayer sample measured in remanence after an applied field of 6 T at a temperature of 1.6 K in LY mode which averages the Cr spectrum across the entire heterostructure. The LY measurements were carried out at beamline 29 BOREAS with the sample oriented 20° from grazing. The measurement retains all the characteristics discussed above for the TEY spectra demonstrating the homogeneity of the heterostructure samples.

XAS and XMCD measurements taken at the Dy $M_{4,5}$ in LY were also carried out for the $n = 10$ heterostructure sample under the same conditions. The measurements are shown in Fig. 4.9. The XAS spectrum is in good agreement with the characteristic shape of Dy^{3+} , composed of three sharp peaks each separated by ~ 2 eV [61]. The spectra for left-circular and right-circular polarisation are distinctly different, similar to single-layer Dy:Bi₂Te₃ [61, 145]. At remanence there is a small but clear XMCD signal suggesting that the Dy in the heterostructure has ferromagnetic order at 1.6 K. The integrated Dy M_5 XMCD has the same sign as the Cr L_3 XMCD indicating that the averaged Dy moments are aligned along the direction of the Cr moments. By comparing the intensity of the measured Dy M_5 XMCD to the calculated spectra for Dy with the expected $4f$ moment $\mu_{\text{eff}} = 10.65 \mu_{\text{B}}/\text{Dy}$ using atomic multiplet theory for the Hund's rule ground state of single-layer Dy:Bi₂Te₃, a value of $\mu_{\text{eff}} = 0.22 \mu_{\text{B}}/\text{Dy}$ ($\sim 2\%$ of the full moment) at 1.6 K in remanence [14, 61, 145]. The TEY signal from the Dy was found to be too weak to measure due to the Dy:Bi₂Te₃ being

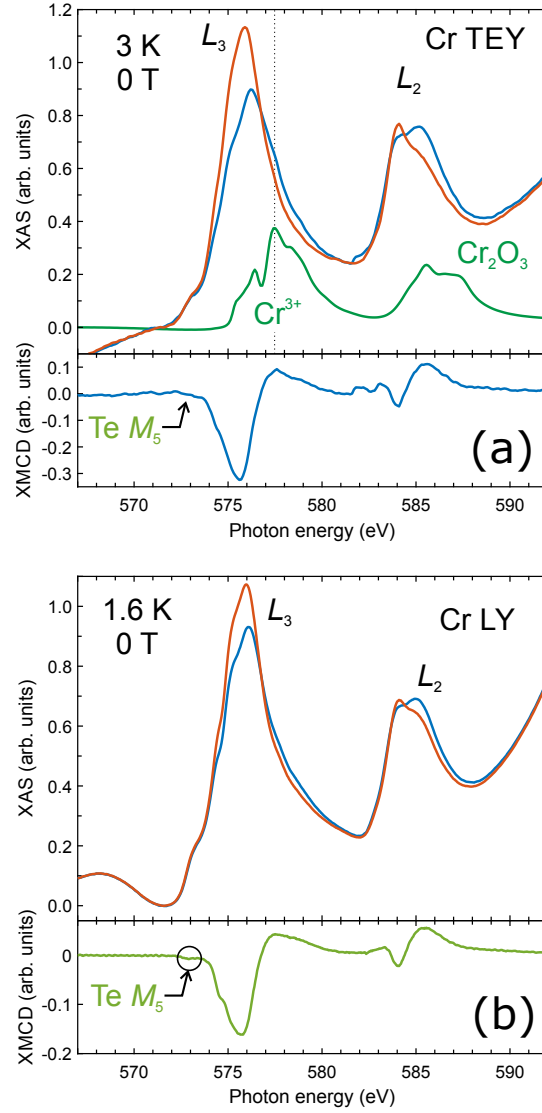


Figure 4.8: XAS and XMCD spectra of Dy:Bi₂Te₃/Cr:Sb₂Te₃ thin film heterostructures for the Cr $L_{2,3}$ absorption edge. The red and blue XAS spectra were measured with right and left circular polarisations respectively. (a) Cr $L_{2,3}$ absorption edge XAS and XMCD in remanence at 3 K, measured in surface-sensitive TEY for a $n = 5$ bilayer heterostructure. Owing to the Bi cap, the spectra do not show a Cr³⁺ oxide peak, which would be 1.5 eV above the predominantly Cr²⁺ peak [as seen from the Cr₂O₃ XAS reference spectrum shown in green]. A small negative peak in the XMCD at 573 eV is indicative of the Te M_5 edge. The spectrum is identical to that of single layer Cr:Sb₂Te₃ [12]. (b) Cr $L_{2,3}$ absorption edge XAS and XMCD in remanence at 1.6 K for a $n = 10$ bilayer sample, measured in LY. The spectrum matches the one measured in TEY demonstrating the homogeneity of the heterostructure samples. Reprinted from ref. [16] with permission from the APS.

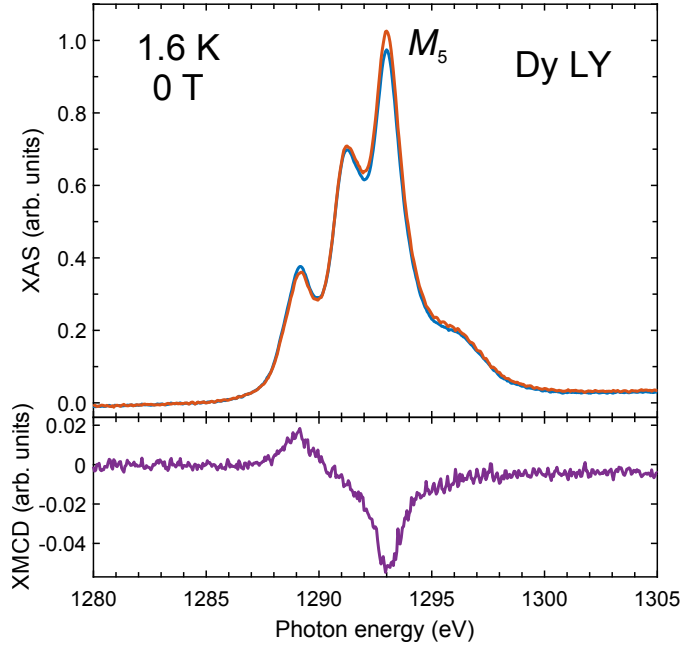


Figure 4.9: XAS and XMCD spectra of Dy:Bi₂Te₃/Cr:Sb₂Te₃ thin film heterostructures for the Dy $M_{4,5}$ absorption edge. The red and blue XAS spectra were measured with right and left circular polarisations, respectively. Dy M_5 XAS and XMCD in remanence at 1.6 K, measured in LY for the $n = 10$ bilayer sample. An XMCD is clearly visible suggesting that the Dy displays ferromagnetic order under these conditions. Reprinted from ref. [16] with permission from the APS.

concealed by the Cr:Sb₂Te₃ and Bi layer on top.

The Sb $M_{4,5}$ absorption edges of the $n = 10$ bilayer heterostructure were also probed in LY in an applied magnetic field of 6 T, parallel to the incident X-ray beam at a temperature of 1.6 K, as shown by Fig. 4.10. There is an ~ 8 eV wide absorption structure, whose onset coincides with the Sb M_4 peak. This originates from the O K edge of the sapphire substrate and is visible in LY but is absent in TEY, consistent with the substrates luminescence process. The XMCD demonstrates sharp peaks indicating the same induced Sb moment found in magnetically ordered single-layer Cr:Sb₂Te₃ [12]. The M_5 and M_4 peak are positive and negative respectively for a $3d$ to $5p$ transition which has an opposing sign to the $L_{2,3}$ absorption edge of Cr representing a $2p$ to $3d$ transition. This means that the Sb moments point along the

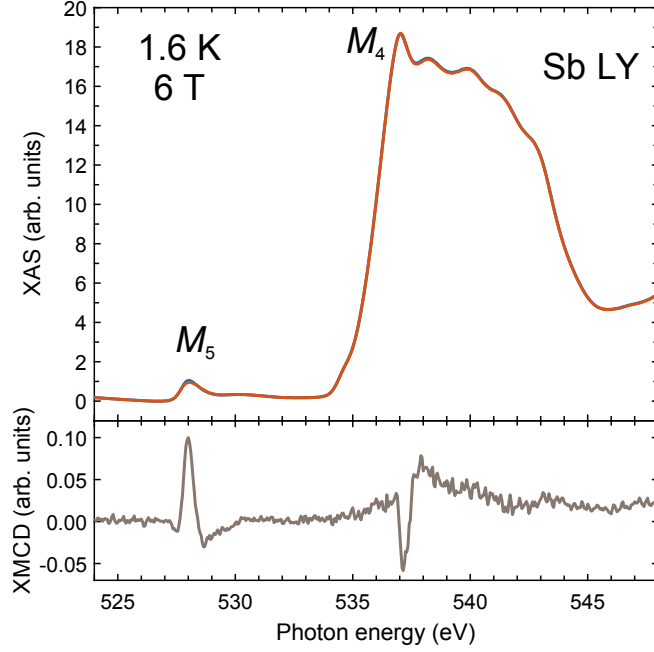


Figure 4.10: Sb $M_{4,5}$ XAS and XMCD at 1.6 K in a field of 6 T, measured in LY for the $n = 10$ bilayer heterostructure. The Sb XMCD is consistent with an induced Sb moment which is found in magnetically ordered single layer Cr:Sb₂Te₃. Reprinted from ref. [16] with permission from the APS.

direction of the Cr moments consistent with the hybridisation between the Cr $3d$ and Sb $5p$ states.

LY measurements were also used to perform element specific XMCD hysteresis loops for the $n = 10$ heterostructure sample at a temperature of 1.6 K by sweeping the applied magnetic field with the photon energy tuned to either the Cr L_3 or Dy M_5 maxima [11]. Figure 4.11(a) shows the Cr hysteresis loop and the Dy hysteresis loop is shown in Fig. 4.11(b). Whereas Cr shows a loop opening with a coercive field of ~ 230 mT, the Dy loop appears to be closed. It is likely that the small Dy loop opening is obscured by an error in the magnetic field during the sweeping of the applied magnetic field of the superconducting magnet as Fig. 4.9 demonstrates a Dy XMCD at remanence. The Cr moment saturates at a field of 3 T whereas the maximum applied field of 6 T was not sufficient to saturate the Dy moments.

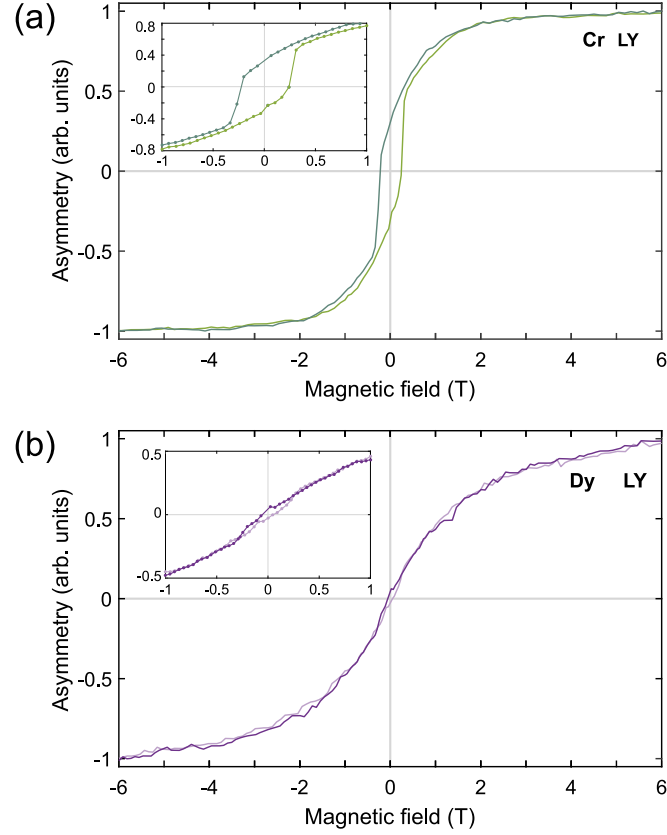


Figure 4.11: Hysteresis loops for Cr and Dy measured at the peak maximum of the Cr L_3 and Dy M_5 absorption edge. (a) Cr L_3 and (b) Dy M_5 hysteresis loops at 3 K, measured in LY. The left-side insets show the low-field behaviour. Reprinted from ref. [16] with permission from the APS.

In comparison, the saturation magnetisation of single-layer Dy:Bi₂Te₃ is only ~ 4 T demonstrating that the presence of the Cr:Sb₂Te₃ strongly influences its magnetic behaviour [61].

In order to accurately determine the ferromagnetic transition temperature for each magnetic layer type, a measure of the element-specific magnetisation, M , as a function of applied field H was observed for a number of different temperatures in order to satisfy the Arrott criterion [54]. The XMCD peak asymmetries measured at the Dy M_5 and Cr L_3 edge were used to measure the magnetisation of each element [90]. The Arrott plot then consists of isotherms of M^2 versus H/M curves.

This method minimises the magnetic contributions from multi-domain states and magnetic anisotropies. Where the applied magnetic field is large enough to overcome the stray fields and domain states, a straight line will be observed for the isotherm, representative of a second-order ferromagnetic phase transition under a mean-field theory assumption. For lower applied magnetic fields, disorder in the system leads to a bending of the isotherms [55].

This set of measurements was carried out at beamline I10 due to the higher magnetic field range which allowed the saturation field of 7 T for Dy to be reached. The set of measurements were performed on a $n = 5$ bilayer sample. The sample was oriented 54.7° from the incident X-ray beam with the applied magnetic field parallel to the direction of the beam. The Cr L_3 XMCD peak was measured using TEY and Dy M_5 edge was measured using FY. Even though the TEY measurements only probe the Cr in the top surface of the sample, LY measurements shown in Fig. 4.8 have demonstrated that the XMCD spectrum is identical to the rest of the heterostructure.

Figure 4.12(a) shows the Arrott plot for the Cr L_3 XMCD peak asymmetry. Parallel straight lines with matching gradients are fitted to the high field region in order to determine the straight line intercept. The ferromagnetic transition temperature can be determined as the temperature at which the isotherm passes through the origin where M^2 and H/M are equal to zero. In this case the H/M intercept was observed. The H/M intercept is seen to be positive for temperatures above the T_C and negative for temperatures below it. Figure 4.12(b) shows the H/M intercepts for the different temperature isotherms giving a T_C of (70 ± 2) K for the Cr dopants. Note that this is also confirmed in Fig. 4.12(a) where the straight line fit to the 70 K isotherm is seen to pass through the origin. This value matches closely to single-layer Cr:Sb₂Te₃ with a similar doping concentration [13].

Figure 4.12(c) shows the Arrott plot measured using the background-corrected Dy M_5 XMCD asymmetry in FY. The straight line fits for the high-field region do not

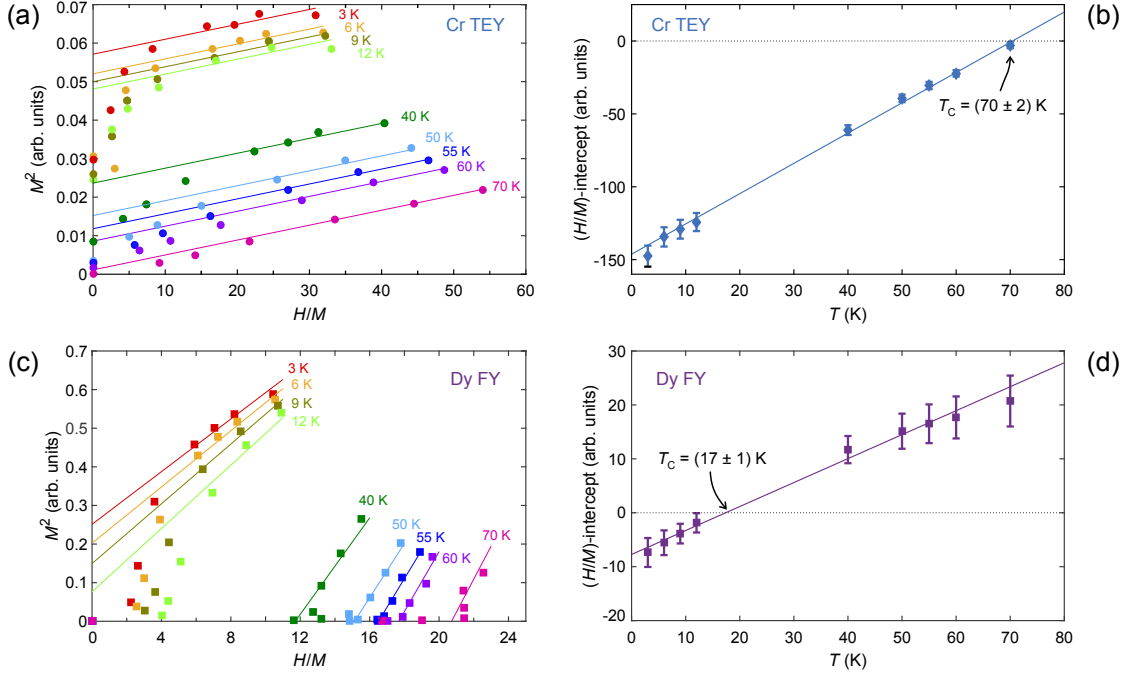


Figure 4.12: Arrott plot analysis of magnetic transition temperatures. Arrott M^2 versus H/M plots where the magnetisation M for a field H is obtained from the XMCD peak asymmetry of the (a) Cr L_3 and (c) Dy M_5 edges, respectively. The error bars are smaller than the symbols representing the data points. The solid lines are linear fits to the high-field data points for each isotherm. The temperature dependence of the H/M intercept allows for the determination of the magnetic transition temperatures of Cr and Dy, and thus the chemically distinct layers in the heterostructure. For Cr the T_C is 70 K (b) and for Dy it is 17 K (d), demonstrating that, through engineering of the heterostructure, the high moment of the rare-earth element can give long-range magnetic order through the presence of the Cr-doped layer. Reprinted from ref. [16] with permission from the APS.

share a global slope in this case likely due to disorder [55]. Linear fits with varying slopes above and below the transition temperature were therefore used. Figure 4.12(c) shows that the ferromagnetic transition temperature for Dy is found to be $(17 \pm 1) \text{ K}$. This is different to single-layer rare-earth doped Bi_2Te_3 where paramagnetic, antiferromagnetic, or near ferromagnetic behaviour has previously been observed [14, 61, 102, 103].

Finally, in order to try to understand the orientation of the moments contained within the heterostructure and thus get a grasp of the coupling mechanism between

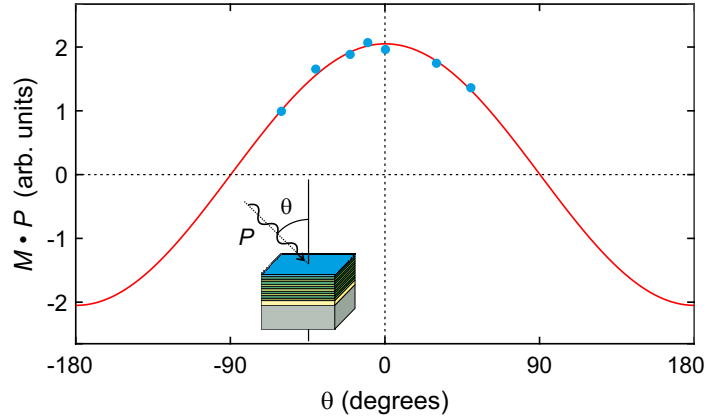


Figure 4.13: Magnetic anisotropy of the Cr dopants at remanence. Cr L_3 XMCD peak asymmetry measured in TEY in zero field as a function of the incidence angle θ of the beam with respect to the surface normal, as shown in the inset. The X-ray helicity vector P is along the beam direction. The blue dots represent the data points for Cr obtained in remanence at 3 K, which are fitted with a sine function (red curve). The angular behaviour shows that the easy direction of the Cr moments is along the surface normal. Reprinted from ref. [16] with permission from the APS.

the different layers, angular dependent XMCD measurements at the Cr L_3 edge were carried out at $T = 3$ K in zero applied field for the $n = 5$ bilayer sample. As previously discussed single layer Cr:Sb₂Te₃ and Dy:Bi₂Te₃ are expected to have their easy axis out-of-plane and in-plane respectively. Figure 4.13 shows the intensity of Cr L_3 XMCD asymmetry as a function of the incidence angle θ of the X-ray beam. The X-ray helicity vector is along the beam direction as demonstrated by Fig. 4.13 inset. The XMCD peak asymmetry is proportional to the Cr magnetisation M onto P . The measurements were fitted onto a sine function which represents the expected changes in the intensity of the component of the magnetisation being resolved. This demonstrates that the orientation of the magnetic anisotropy for the Cr moments is not affected by the layers incorporation into the heterostructure. These same angular dependent measurements could not be carried out for Dy as both LY and FY have a secondary angular dependence due to the positioning of the photodiode that detects the signal.

4.3 Conclusion

Previously investigated heterostructures containing both magnetically doped TIs and antiferromagnetic or ferromagnetic layers where an enhanced proximity coupling was able to introduce interfacial spin textures have used a combination of theoretical modelling and experiment to gain a deeper understanding of the coupling effect between different layers [90, 146–148]. First principle density functional theory calculations were carried out by collaborator Prof. Arthur Ernst for the electronic and magnetic structure of Cr:Sb₂Te₃ and Dy:Bi₂Te₃ single layer films and their interfaces. Details of these calculations can be found in ref. [16]. The calculations demonstrate that the magnetic interaction in a Cr:Sb₂Te₃ single-layer film is predominantly positive with a relatively strong ferromagnetic coupling between the Cr moments. This is in agreement with research conducted on Cr:Sb₂Te₃ thin films with a Co overlayer [12]. The calculations estimate a ferromagnetic transition temperature of 102 K which is higher than the experimentally measured 70 K. It is likely that this discrepancy originates from the presence of vacancies and other imperfections in the real grown sample when compared to the theoretical structure which is free from defects. This results in a substantial reduction of the T_C for the real sample. The calculations also show there is a strong impurity state at the Fermi level in the majority spin channel which suggests Zener type of exchange interaction in the system [98].

In a Dy:Bi₂Te₃ single-layer, holes are formed almost equally in both spin channels leading to paramagnetism in the system. The exchange interaction between the Dy moments is positive and very strong but only within the Bi layer between the nearest neighbours. The magnetic coupling between different layers is very small and cannot force magnetic order throughout the whole structure but according to the calculations each Dy-Bi layer is ferromagnetic with a $T_C = 5$ K. The absence of magnetic coupling between each layer prevents magnetic order in the system and the ferromagnetic layers remain frustrated.

For a $\text{Cr:Sb}_2\text{Te}_3/\text{DyBi}_2\text{Te}_3$ interface, the hole in the majority spin channel of the $\text{Cr:Sb}_2\text{Te}_3$ polarises the hole in $\text{Dy:Bi}_2\text{Te}_3$ leading to an enhancement of the magnetic interaction in the vicinity of the interface. The magnetic coupling between the Dy and Cr moments is strong and negative near the interface, indicating antiparallel alignment of the moments. The exchange interaction also extends over several layers with the Cr moment at the interface interacting with Dy moments in the first and second neighbouring layer forcing them to be antiparallel with the Cr moment but parallel to each other. The proximity to the $\text{Cr:Sb}_2\text{Te}_3$ also enhances the amount of almost free electrons in the $\text{Dy:Bi}_2\text{Te}_3$ which leads to a stronger indirect exchange interaction between the Dy $4f$ electrons via the conduction electrons known as the RKKY interaction. This leads to the corresponding exchange parameters being enhanced on the long-range scale.

The ferromagnetic transition temperature of the $\text{Dy:Bi}_2\text{Te}_3$ in the vicinity of the interface is calculated to be 23 K which is remarkably close to the experimentally obtained 17 K. DFT calculations also show that the interaction between the Cr moments is enhanced by being in proximity to the $\text{Dy:Bi}_2\text{Te}_3$, the largest enhancement being found to be between the second nearest layers. This should lead to a Cr ferromagnetic transition temperature enhancement of 19 K which is not experimentally observed possibly once again due to the presence of defects or other imperfections.

According to the calculations the $\text{Cr:Sb}_2\text{Te}_3$ layers have an out-of-plane magnetisation as confirmed by the angular dependent measurement of the XMCD and the $\text{Dy:Bi}_2\text{Te}_3$ layer has a magnetisation in-plane. At the interface between the layers there is an antiferromagnetic interaction between the Cr and Dy which is very strong and dominated by the Cr so that both layers have an out-of-plane magnetisation. For Dy moments further away from the interface the situation can be different as is also seen in heterostructures of in-plane antiferromagnetic CrSb and out-of-plane ferromagnetically ordered Cr-doped $(\text{Bi,Sb})_2\text{Te}_3$ [146]. Since the XMCD measurements

taken here demonstrate the averaged Dy moment of every layer in the heterostructure, the overall moment is aligned with the direction of the Cr moment.

By the demonstration of the enhancement of the T_C of the usually paramagnetic Dy:Bi₂Te₃, it is clear that the design of TI heterostructures hold the key to progress in the field of QAH effect physics, paving the way for dissipationless spintronics applications.

Chapter 5

Conclusions

This thesis has presented an investigation of both the structural and magnetic properties of magnetically doped 3D topological insulator thin film samples grown by molecular beam epitaxy. The 3D TI chalcogenide based systems of Sb_2Te_3 and Bi_2Te_3 have been monodoped with the transition metal Cr and rare-earth element Dy, respectively, in a single layer form as well as codoped in the case of Sb_2Te_3 with Cr and V dopants. Both basic structural and magnetic characterisation of these systems, as well as more advanced synchrotron and neutron based characterisation techniques in the form of XMCD and PNR, have been used to gain a greater understanding of the growth of these systems, as well as the mechanisms behind their magnetic properties. In the pursuit of further enhancing the magnetic properties of MTI systems, heterostructure systems have also been fabricated consisting of a $\text{Co/Cr:Sb}_2\text{Te}_3$ bilayer and multiple bilayers of $\text{Cr:Sb}_2\text{Te}_3/\text{Dy:Bi}_2\text{Te}_3$.

The pursuit of enhancing magnetic properties of MTIs through the use of codoping is seen to cause a deficiency in the structural quality of $\text{Cr:Sb}_2\text{Te}_3$ when also doped with V, leading to the formation of a Cr_2Te_3 phase. XMCD results demonstrate that long-range ferromagnetic order is mediated by the conduction band in Cr-doped Sb_2Te_3 which is robust enough to withstand the influence of a ferromagnetic Co

layer deposited on top of the grown film. PNR measurements show that rare-earth Dy-doped Bi_2Te_3 , which does not demonstrate long-range ferromagnetic order, has a strong magnetic response in the presence of an in-plane applied magnetic field making it a suitable candidate for providing magnetic enhancement in magnetic heterostructures. These two key findings lead to a systematic study of $\text{Cr:Sb}_2\text{Te}_3/\text{Dy:Bi}_2\text{Te}_3$ MTI heterostructures where the $\text{Cr:Sb}_2\text{Te}_3$ is seen to enhance the magnetic properties of the $\text{Dy:Bi}_2\text{Te}_3$ layers contained within the heterostructure such that a ferromagnetic response can be measured with XMCD. These results have significant implications for the field of MTIs, highlighting the importance of the use magnetic TI heterostructures to further enhance the magnetic properties of MTI systems in the pursuit of realising a QAH effect at device-friendly temperatures.

5.1 Summary of Results

Chapter 3 details the study of single layer thin film chalcogenide TI systems when doped with the transition metals such as Cr and V in the case of Sb_2Te_3 and rare-earth Dy in the case of Bi_2Te_3 .

The magnetic coupling scenario which causes long-range ferromagnetic order in Cr-doped Sb_2Te_3 has long been disputed in the MTI field due to a variation in the quality of samples, requiring further investigation of a structurally sound system using element specific magnetic characterisation via the use of XMCD, and an in-plane magnetic depth profiling of samples using PNR. A structural analysis using basic characterisation techniques demonstrate the Cr-doped Sb_2Te_3 thin films grown on Al_2O_3 to be of high structural quality with a substitutional doping mechanism for the introduction of Cr on Sb sites in the TI. A magnetic easy axis out-of-plane is seen in SQUID VSM measurements with a saturation moment of $(2.8 \pm 0.2) \mu_B$ observed with the ferromagnetic transition temperature of the films seen to increase with Cr-

doping concentration. The highest ferromagnetic transition temperature observed was ~ 120 K for a sample of doping concentration $x = 0.42$. XMCD measurements demonstrate that the exchange interaction occurs due to a carrier mediated coupling mechanism where Cr ions ferromagnetically couple due to an exchange mediated by spin polarised Te valence holes. PNR measurements demonstrate that samples are homogeneously doped with no surface enhancement, and that they behave similarly to dilute magnetic semiconductors. These results provide a greater understanding of how long-range ferromagnetic order is achieved in transition metal doped TI systems. The fact that this magnetic dopant causes the formation of dissipative conduction channels that are detrimental to the observation of the QAH effect led us to the pursuit of other magnetic dopants such as the rare-earths.

Bi_2Te_3 , when doped with the rare-earth dopant Dy, and contrary to other rare-earth dopants such as Ho and Gd, demonstrates a TSS band gap opening which can be observed with ARPES, even though the material appears to remain paramagnetic. The complex microscopic nature of the dopant therefore requires further investigation with both XMCD and PNR. The structural characterisation of Dy-doped Bi_2Te_3 samples grown on Al_2O_3 using an MBE demonstrate a high structural quality where the Dy dopes both substitutionally and interstitially. SQUID VSM measurements down to 5 K show that there is no ferromagnetic transition for the films. Hysteresis loops are consistent with previously published data demonstrating that a higher Dy-doping concentration leads to a reduced saturation moment below the free ion value of $10.64 \mu_B/\text{Dy}$. XMCD measurements demonstrate that unlike transition metal doped TI systems, a conduction-band-mediated magnetic response is not observed. PNR results demonstrate that the films are neither entirely paramagnetic nor fully ferromagnetic, displaying complex, short-range, inhomogeneous magnetic order. This result forms the basis for exploiting this material in MTI heterostructures in an effort to enhance its magnetic order.

The method of codoping TI systems in order to enhance the magnetic ordering temperatures of the single layer MTI systems, as has been previously used in the optimisation of high-performance permanent magnets, is also explored by doping Sb_2Te_3 with both the transition metals Cr and V. Through the use of structural and magnetic characterisation using XRD, SQUID VSM and XMCD, it is apparent that introducing both V and Cr at the same time to Sb_2Te_3 causes the formation of a secondary Cr_2Te_3 phase, whereby V merely acts as a surfactant. The V is likely to prevent the Cr from doping into the Sb_2Te_3 substitutionally. These results highlight the difficulties associated with the codoping process for the chalcogenide based TIs, demonstrating that this method is unlikely to lead to an enhancement of the magnetic properties of MTIs.

Chapter 4 collects the research performed on heterostructure MTIs consisting of both ferromagnetic layers and the single layer MTI systems looked at in the previous chapter in an attempt to enhance magnetic properties through proximity coupling and interfacial effects.

It has previously been demonstrated that depositing a layer of ferromagnetic material onto an MTI can lead to an enhancement of its ferromagnetic transition temperature. For Cr-doped Bi_2Se_3 the T_C has been shown to be enhanced from 7 K to 19 K through the deposition of a Co layer onto its surface. In an effort to further enhance the much greater magnetic ordering temperature of Cr-doped Sb_2Te_3 , a Co layer was deposited onto a single layer thin film in order to form a heterostructure. Element specific magnetic and chemical characterisation using XMCD and XAS reveals that the Co layer demonstrates the expected chemical and ferromagnetic properties of Co while not reacting with the Cr: Sb_2Te_3 layer beneath. Arrott plots, which reveal an accurate measurement of the T_C of the MTI layer both before and after the Co deposition, demonstrate a rather small increase from 86.7 K to 92.7 K. The Co layer appears unable to polarise the Cr moments significantly, indicating the robustness of

the magnetic coupling scenario found in Cr:Sb₂Te₃. These results are significant as they validate the use of the Cr:Sb₂Te₃ layer in a Cr:Sb₂Te₃/Dy:Bi₂Te₃ heterostructure in an effort to enhance the magnetic properties of Dy:Bi₂Te₃.

The previously discussed results led to the fabrication of Cr:Sb₂Te₃/Dy:Bi₂Te₃ heterostructures in an effort to enhance the T_C of the MTIs present within the heterostructure through proximity coupling. Structural characterisation of the samples demonstrate that the layers contained within the heterostructure have well-defined interfaces with each layer being of high structural quality. XMCD measurements of the element specific magnetism contained within the sample demonstrate that the Cr:Sb₂Te₃ layers behave similarly to single layer Cr:Sb₂Te₃ with the magnetic coupling being mediated by conduction electrons. Unlike single layer Dy:Bi₂Te₃, which behaves as if it is on the verge of ferromagnetism, XMCD measurements demonstrate the layers to be ferromagnetic with Arrott plots indicating a T_C for Dy of 17 K, while the Cr:Sb₂Te₃ layers do not demonstrate an enhancement in T_C . The Cr moments are found to be pointing out-of-plane with the XMCD results indicating the averaged Dy moment of every layer within the heterostructure to be largely aligned with the direction of the Cr moments. These results are of great importance to the field of MTIs as they demonstrate how magnetic heterostructures can be used to successfully enhance the magnetic properties of MTIs in the pursuit of a QAH effect device friendly characteristics.

5.2 Perspective and Outlook

It is important to consider the implications of these results and how they can inform suggestions for new studies which can help to progress the field of MTIs. The entirety of the research shown in this thesis concentrates on the chalcogenide based systems of Bi₂Te₃ and Sb₂Te₃. Although research has also been conducted on mixtures of

(Bi,Sb)₂(Te,Se)₃ by other groups in the field, these are chemically quite complex with variations in sample fabrication leading to a wide array of results. A systematic study of the effects of the variations in these chalcogenide mixed samples is likely required which is why the research presented here is conducted on the simplified case of Bi₂Te₃ and Sb₂Te₃. Even in this simplified case, still variations in sample quality are found, caused by for example Te deficiencies. It is therefore important for the field to try to find a single element TI system where these chemical variations which effect the properties of samples are not an issue, such as α -Sn (although it should be noted α -Sn is a topological semimetal which exhibits novel electronic properties, but not a TI). It is then important to try to realise long-range ferromagnetic order in this single element system through the use of magnetic doping or proximity coupling.

It is very important to ensure that if a system does exhibit long-range ferromagnetic order that it does so without the formation of impurity bands. In the case of using transition metals such as Cr, the Cr 3d impurity bands are inherently tied to the exchange interaction mediating the magnetisation of the sample. In order to realise a QAH effect device at practical temperatures these impurity bands cannot be present so it is unlikely that this dopant is suitable. Using the rare-earth dopant Dy is promising, as unlike for Ho and Gd, a gapped TSS is found for much lower doping concentrations than were used in the studies performed in this thesis, despite Dy remaining on the cusp of becoming ferromagnetic. At lower Dy doping concentrations, it is entirely possible that no impurity bands are formed. As these studies have shown, it is feasible to enhance the Dy in Dy:Bi₂Te₃ through proximity coupling in heterostructures in order to cause the layers to become ferromagnetic. Transport measurements are required to verify whether the QAH effect can be observed in the Dy:Bi₂Te₃ layers contained within the heterostructure. It may be possible that without the need to freeze out impurity bands, the QAH effect could be observed at much higher temperatures than has been reported before.

Although 17 K is still not a practical temperature for a QAH effect device, there are a number of avenues this opens up. In the case of the heterostructures demonstrated here, there is evidence to suggest that Cr:Sb₂Te₃ has an easy axis of magnetisation out-of-plane while Dy:Bi₂Te₃ is in-plane. Building a magnetic heterostructure where the coupling layer also has an easy axis in-plane (such as Co) is likely to lead to a larger enhancement, perhaps increasing the T_C of the Dy:Bi₂Te₃ layer further. Although it should be noted that the requirement to deposit Co at low temperatures lead to difficulties in realising Co and Dy:Bi₂Te₃ multilayers. The field could also continue in trying to find a suitable MTI candidate akin to Dy:Bi₂Te₃ where ferromagnetism can be induced without the formation of impurity bands by exploring rare-earth doping of other TI systems.

Similar to the Dy:Bi₂Te₃ sample discussed above, systems such as Mn:Bi₂Te₃ where the TSS gap has been seen to persist up to temperatures well above the ferromagnetic transition temperature of films, have highlighted the need for a greater understanding behind the mechanism which causes the band gap to form. Understanding this mechanism may shed light on new ways to realise exotic quantum effects in TIs suitable for device applications.

Although little progress has been made towards practically realising a QAH effect device, this research demonstrates a significant blue print for how it can be eventually realised. It highlights the importance of using both basic structural and magnetic characterisation techniques as well as synchrotron and neutron based techniques, such as XMCD and PNR, in order to gain a greater understanding of the magnetic behaviour of fabricated MTIs in order to engineer systems to study. Understanding the drawbacks of transition metal dopants led to the pursuit of rare-earth dopants which can be magnetically enhanced through the use of magnetic heterostructures. Use of this same process by the wider field of MTIs with simpler magnetically doped TI systems is likely to eventually lead to the realisation of higher temperature QAH

effect devices.

Appendix A

List of Abbreviations and Acronyms

1D	One Dimensional
2D	Two Dimensional
2DEG	Two Dimensional Electron Gas
3D	Three Dimensional
AFM	Atomic Force Microscopy
AH	Anomalous Hall (effect)
Al₂O₃	Sapphire
ARPES	Angle Resolved Photo-Emission Spectroscopy
BFM	Beam Flux Monitor
CB	Conduction Band
DLS	Diamond Light Source
EMF	Electromagnetic Induction
ESRF	European Synchrotron Radiation Facility
FY	Fluorescence Yield
ICSD	Inorganic Crystal Structure Database

ISIS	ISIS Neutron and Muon Source
LY	Luminescence Yield
MBE	Molecular Beam Epitaxy
MOSFET	Metal-Oxide-Semiconductor Field Effect Transistor
MPMS	Magnetic Property Measurement System
MTI	Magnetic Topological Insulator
M_vH	Magnetisation versus (applied magnetic) Field
M_vT	Magnetisation versus Temperature
PID	Proportional-Integral-Differential
PNR	Polarised Neutron Reflectometry
QAH	Quantum Anomalous Hall (effect)
QH	Quantum Hall (effect)
QSH	Quantum Spin Hall (effect)
RBS	Rutherford Backscattering Spectrometry
RCaH	Research Complex at Harwell
RGA	Residual Gas Analyser
RHEED	Reflection High Energy Electron Diffraction
RKKY	Ruderman-Kittel-Kasuya-Yosida (interaction)
SLD	Scattering Length Density
SOC	Spin Orbit Coupling
SQUID	Superconducting Quantum Interference Device
STM	Scanning Tunnelling Microscopy
T_C	Ferromagnetic Transition Temperature
TEY	Total Electron Yield
TI	Topological Insulator
TRS	Time Reversal Symmetry
TSS	Topological Surface State

UHV	Ultra High Vacuum
VB	Valence Band
VSM	Vibrating Sample Magnetometer
XAS	X-Ray Absorption Spectroscopy
XMCD	X-Ray Magnetic Circular Dichroism
XRD	X-Ray Diffraction
XRR	X-Ray Reflectometry

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