Structural characterisation of L1₀ ordered materials for spintronics

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By
David C. Huskisson

School of Computer Science
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Abstract

L1₀ ordered materials offer considerable promise for enhancing the performance of current and future spintronic technologies, particularly magnetic data storage. The need for greater areal density fuels research into high anisotropy materials, such as L1₀ ordered FePt. MnAl is another L1₀ ordered material which has great potential as an efficient spin polariser for the development of magnetic tunnel junctions due to its low spin-orbit coupling. The magnetic properties of these materials depend on their crystal structure and degree of ordering.

The work presented here concerns the structural characterisation of L1₀ ordered materials and the development of L1₀ ordered MnAl thin films. The additional parameter space offered by remote plasma sputtering was explored with a view to controlling the grain size of FePt thin films by varying the target bias voltage. A semi-automatic grain identification method was identified, improving the repeatability and reliability of the results. The average grain size and grain size distribution was found to increase after annealing, but was robust against variation in the target bias voltage.

The structural properties of FeRh were investigated as a complementary material for next generation magnetic data storage applications. Island type growth was seen with considerable dewetting from the substrate. The degradation of the magnetic properties of these films with decreasing thickness was attributed to the decrease in crystal order as observed in this work.

MnAl thin films were fabricated by co-sputtering. The formation of the metastable L1₀ phase was found to be highly sensitive to the elemental composition and processing temperatures used. Local ordering was observed which improved after annealing to give a maximum saturation magnetisation of 67 emu/cm³. This work provides a strong grounding in the challenges associated with producing ferromagnetic, L1₀ ordered thin films of MnAl, and identifies directions for further research.
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Chapter 1

Introduction

Modern society is dependent on digital information, with vast amounts of data being generated every day. Data storage is intrinsic to many of the electronic devices we take for granted such as personal computers, smartphones and the internet. Since the introduction of the first commercial hard disk drive in 1956 the storage capacity of a hard drive has increased by eight orders of magnitude [1], largely enabled by the development of new magnetic materials.

Electronic circuits are the foundation of the functionality of these modern technologies, powered by the movement of electrons and their electronic charge. However, charge is not the only property electrons possess that may be used to transfer or process information. As fundamental particles, electrons have a quantum mechanical property known as spin. Although it may be thought of as an intrinsic angular momentum, spin has no classical analogue and its exact nature remains unknown [2]. Where a reference axis has been defined by, for example, a magnetic field, the spin of an electron may be described as having one of two directions, conventionally known as either up or down. Spintronics involves the detection and manipulation of electron spins in order to transfer information with or without the movement of charge. Spintronic devices are fundamental to the development of a wide variety of technologies from the read/write heads used in hard disk drives and non-volatile magnetic random access memory (MRAM) to programmable logic gates and position controllers in robotics [2].
1.1 Spintronics and magnetism

The concept of spin is directly related to the field of magnetism. Uncompensated electron spins give rise to magnetic moments in certain atoms [3]. When these moments couple to each other and align in parallel they create a macroscopic magnetic moment and the material is defined as a ferromagnet. As magnetic moments, spins can interact with external magnetic fields which are then capable of influencing the internal magnetisation of a material. In this way, magnetism provides a mechanism for the manipulation of spins and a means to control their direction by the application of a magnetic field.

Spin-polarised currents are a key component of spintronic devices, which may be produced by passing a current through a ferromagnetic material. The internal magnetisation of a ferromagnet causes the spins of passing electrons to align parallel with the direction of magnetisation. This spin-polarised current may then go on to interact with the magnetisation of another material in a different part of the device. Once outside the ferromagnet, the polarisation of the spin current will start to decay, typically within a few tens of nanometres at room temperature [4]. Spintronic devices are therefore necessarily small, most often consisting of layers of thin films with thicknesses ranging from just a few atoms to several tens of nanometres. The development and characterisation of thin films of various magnetic materials are therefore essential for optimising the performance of spintronic devices.
1.1.1 Spintronic devices

The fundamental spintronic device is the magnetic tunnel junction (MTJ), illustrated in figure 1.1. This consists of two ferromagnetic layers magnetised in opposite directions separated by a non-magnetic spacer layer so that the magnetisations of the ferromagnetic layers are not coupled. An electric current is passed through the device perpendicular to the plane of the layers.

The resistance of the device depends on the relative orientation of the two ferromagnetic layers according to the tunnelling magnetoresistance effect, discussed further in section 3.1. The resistance is higher when the magnetisations are orientated anti-parallel, known as the off state, and is lower when the magnetisations are orientated parallel, known as the on state. The efficacy of an MTJ is determined by the ratio of its electrical resistance in the on state versus the off state, known as the magnetoresistance ratio. Initial studies of magnetoresistance investigated the giant magnetoresistance effect in the 1980s, where the spacer layer consisted of a non-magnetic metal. Experiments carried out at low temperatures were able to achieve magnetoresistance ratios of 150% and as high as 65% at room temperature. By the early 2000s MTJs using tunnelling magnetoresistance with an insulating spacer layer acting as a tunnel barrier had achieved tunnelling magnetoresistance ratios (TMR) of up to 70% at room temperature [5]. Current devices use a crystalline tunnel barrier and are capable of room temperature TMRs of several 100% [6]. The efficiency of tunnelling, and hence the TMR, depends strongly on the smoothness of the interfaces between the layers. Structural characterisation is therefore essential in the development of these materials and devices.

An MTJ may be switched on or off by the application of an external magnetic field or by increasing the current passed through the device. The first ferromagnetic layer acts as a spin-polarising layer, or fixed layer, producing a spin-polarised current. This interacts with the magnetisation of the second ferromagnetic layer, or free layer, destabilising its
magnetisation and potentially causing it to reverse direction if the current density is high enough. In order to ensure reliable and convenient switching, the magnetisation of the free layer must be more easily reversed than the fixed layer. The development of high anisotropy materials requiring respectively higher energies to reverse their magnetisation is therefore of interest for use as fixed spin-polarising layers.

1.1.2 Magnetic data storage

One of the main application areas of spintronics is magnetic data storage. This involves recording binary information as the magnetisation directions of regions of a magnetic storage medium, which are known as bits. The storage medium consists of a polycrystalline thin film composed of segregated grains which are magnetically isolated from one another. As there will be a distribution in size, the magnetic properties and the orientation of the grains, each bit must contain a minimum number of grains, typically between ten and one hundred, in order to give a good signal to noise ratio [7]. The capacity of a hard disk drive is determined by the size of the grains, and hence the areal density of the bits.

The trend for higher and higher storage densities, illustrated in figure 1.2, has been boosted by spintronic discoveries such as the giant magnetoresistance effect and MTJs. This enhanced the sensitivity of the sensors used to read the data, enabling storage densities of several tens of Gbit/in\(^2\) [8]. The increase in density continued with the introduction of perpendicular magnetic recording, in which the magnetisations of the grains point out of the plane of the disk rather than in plane as used previously in longitudinal recording. Perpendicular recording allowed storage densities to reach 1 Tbit/in\(^2\). However, the continuation of the trend beyond 1 Tbit/in\(^2\) now relies on increasing the capacity of the storage medium itself by further reducing the grain size and width of the grain size distribution and enhancing the orientation of the medium.
The size of the grains in a given storage medium has a physical lower limit, known as the superparamagnetic limit. Below this size, the volume of the grains for a given anisotropy energy will not be sufficient to maintain thermal stability, causing the magnetisation to randomly flip and hence losing the value of the bit. At this point, the energy required to reverse the magnetisation of a grain, given by $K_u V$, where $K_u$ is the anisotropy of the storage medium and $V$ is the volume of the grain, approaches the thermal energy of $k_B T$, where $k_B$ is the Boltzmann constant and $T$ is the temperature. In order to produce practical devices, the ratio of $K_u V / k_B T$ must be greater than 50 [10]. New materials with very high $K_u$ are therefore required in order to overcome this limit. However, this brings fresh challenges as the magnetic fields used to write data are no longer strong enough to reverse the magnetisation of the grains [11]. This conundrum is often referred to as the magnetic recording trilemma [11]. Technologies incorporating high $K_u$ materials must therefore find innovative solutions to lower the energy barrier to write data when required. Such solutions are known as energy assisted magnetic recording and are discussed further in section 3.2.

Figure 1.2: Progress in areal storage density highlighting key innovations [9].
1.1.3 L1₀ ordered materials

Of particular interest for magnetic data storage and spintronic applications are a class of binary alloys with a chemically ordered crystal structure known as an L1₀ structure. These materials have a high perpendicular magnetocrystalline anisotropy making them promising candidates for spin polarisers and high density storage media. Anisotropies of $5 \times 10^7$ erg/cm$^3$ are possible in L1₀ ordered FePt, potentially allowing thermally stable grain sizes as small as 3 nm [7]. L1₀ ordered materials also have considerable potential for spintronic applications, and in particular MnAl is a most promising material [12]–[15], having the advantage of only consisting of light elements without any heavy metals. This gives it a very low Gilbert damping parameter of just 0.006 making it an efficient spin polariser [16].

The magnetic properties of L1₀ ordered materials are dependent on the crystal structure and degree of ordering. High temperature annealing is often necessary to enhance the chemical ordering by facilitating atomic diffusion. Structural characterisation is therefore complementary to magnetic characterisation in gaining a full understanding of the growth and ordering process of these materials. These materials are discussed further in section 3.3.

1.2 Research aims

This work is primarily concerned with the development and characterisation of L1₀ ordered materials. Determination of their crystalline properties such as grain size, phase identification, degree of ordering and orientation with respect to the substrate was performed using transmission electron microscopy (TEM) and electron diffraction patterns. The potential to control the grain size in FePt thin films using remote plasma sputtering was investigated, along with structural changes associated with the necessary annealing process. Controlling the grain size by varying the process parameters would be extremely beneficial for the production of high density data storage media with a small average grain size and a narrow distribution. The structural characterisation of FeRh as a
complementary material for energy assisted magnetic storage applications was also performed. This is a necessary initial step towards combining it with FePt to enhance the performance of heat assisted magnetic recording.

The development of L1\textsubscript{0} ordered MnAl thin films are a key part of this work. Experimental work on sputtered thin films is sparsely reported, leaving much scope for optimisation. However, as the L1\textsubscript{0} ordered phase in MnAl is metastable at room temperature, the successful nucleation and growth of well-ordered films is extremely challenging. The degree of ordering is sensitive to many experimental parameters, and may be entirely lacking if any one of those parameters is not optimised. This work therefore aims to identify the optimum growth conditions for L1\textsubscript{0} ordered MnAl thin films and evaluate their magnetic and structural properties.

1.3 Thesis outline

The fundamentals of magnetism, magnetic materials and spintronics are introduced in Chapter 2. The interactions of magnetic moments are described and how this leads to different types of magnetic ordering. Magnetic anisotropy is discussed along with the magnetisation dynamics associated with spin polarised currents. This theory will form the basis of understanding for the functionality of the desired applications.

A more in-depth introduction to spintronics and its applications is given in Chapter 3. Also presented is a review of the literature concerning the L1\textsubscript{0} materials studied, focussing on the growth of MnAl thin films and the associated experimental challenges.

The principles of the various experimental techniques used in this work are outlined in Chapter 4. It is important to ensure that the experimental details are understood in order to be aware of the limitations of each technique and fully understand the results. Emphasis is given to transmission electron microscopy (TEM) and the sample preparation necessary as the principle investigative technique used.
Chapter 5 discusses the results of the study of grain sizes in FePt thin films and their crystal ordering. Grain size measurement techniques are evaluated before the TEM and electron diffraction results are given. The effects of the greater parameter space offered by remote plasma sputtering are explored for the sample series before and after annealing.

The structural characterisation of FeRh thin films is presented in Chapter 6. TEM experiments examine the surface morphology, crystal quality and in-plane strain present in single layer films.

Chapter 7 details the results of the MnAl study and the magnetic properties obtained. The calibration and optimisation of the elemental ratio and the deposition and annealing temperatures are given, along with structural analysis performed by X-Ray diffraction, X-Ray reflectivity, high resolution TEM.

Finally, Chapter 8 draws together the conclusions from this work and suggests further avenues of investigation which may build upon and enhance the research performed so far.
Chapter 2

Basic Theory of Magnetism

The historical development of magnetic materials centred on the use of lodestones or quenched iron needles as navigational compasses [17]. The first scientific study published by William Gilbert in 1600 [18] led to the identification of the Earth as a magnet and the source of the magnetic field sensed by compasses. The subjects of magnetism and electricity became linked in 1820 when Hans-Christian Oersted discovered a current-carrying wire creates a circumferential magnetic field [17]. This led rapidly to the invention of the electromagnet, a current-carrying coil of wire equivalent to a normal magnet. This provided the basis of a theoretical understanding of the origin of magnetic fields as the motion of electric charge [19].

Magnetic materials and magnetic fields now underpin much of modern technology, in particular the digital revolution of the last 50 years. An understanding of the theory of magnetism is essential to understanding the operation of the devices and technologies used in this project. This section introduces the important theoretical concepts used later. The cgs system of units is used throughout.
2.1 Magnetic dipoles and moments

Rather than involving a current-carrying wire, magnetic fields may be described by the definition of two magnetic poles, the North pole (N) as the source of the field and the South pole (S) as the sink [19]. This is illustrated in figure 2.1a for a conventional bar magnet, and in figure 2.1b for a current-carrying loop, where iron filings align with the field lines.

![Magnetic field lines](image)

Figure 2.1: Magnetic field lines in (a) a conventional bar magnet, showing field direction from the North (N) to the South (S) poles, and (b) a loop of current-carrying wire, revealed by iron filings [19].

Two magnetic poles, of strength $p_1$ and $p_2$ separated by a distance $r$, exert a force, $F$, on each other, which is empirically found to be [20]

$$F = \frac{p_1 p_2}{r^2} \quad (2.1)$$

Hence the magnetic field, $H$, created by the first pole may be expressed in terms of the force exerted on the second pole as

$$\vec{H} = \frac{p_1}{r^2} \quad (2.2)$$
which is measured in Oersted (Oe). This is also equal to the amount of magnetic flux, \( \Phi \), per unit area, \( A \), perpendicular to the field, hence \( \Phi = HA \) [20].

Unlike electric charge, magnetic poles do not occur in isolation, but always as a pair of opposite polarity, \( +p \) and \( -p \). For the limit of separation distance \( r \to 0 \), these are known as dipoles. A dipole placed in a magnetic field will therefore experience a torque due to equal and opposite forces, \( \vec{F} = \pm p\vec{H} \), acting on each end, illustrated in figure 2.2. The total torque, \( \tau \), is then

\[
\tau = pr|\vec{H}| \sin \theta
\]  

(2.3)

where \( \theta \) is the angle between the axis of the dipole and the external magnetic field. However, the distance \( r \) is uncertain as magnetic poles are not individual point objects. The experimentally relevant factor is the product \( pr \), known as the magnetic moment, \( m \). Equivalently, for a loop of area \( A \) carrying a current \( I \) [20],

\[
m = IA
\]  

(2.4)

Therefore, a dipole not parallel to the external magnetic field has a potential energy, \( E_p \), which is conventionally equal to 0 at \( \theta = \pi/2 \), given by

\[
E_p = \int_{\pi/2}^{\theta} mH \sin \theta \, d\theta = -mH \cos \theta = -\vec{m} \cdot \vec{H}
\]  

(2.5)
This is an important relation for determining the performance of various materials in spintronic devices such as magnetic tunnel junctions. The cgs unit of $E_p$ is the erg. The unit of magnetisation is therefore erg/Oe, known as the electromagnetic unit, or emu [21].

### 2.2 Single atom moments

The origin of macroscopic magnetism lies in the unpaired spins of atomic electrons. Due to the relationship between magnetic fields and moving electric charges, electrons and, to a lesser extent, protons, inside an atom will act as magnetic dipoles. The moment due to the protons is 1000 times less than the electrons, and is most often safely neglected [17]. A classical treatment of an atomic electron consists of a charge, $-e$, orbiting a central potential, moving in a closed loop with orbital velocity, $\omega$. The associated magnetic moment is therefore given by equation (2.4) as,

$$\vec{m} = I \vec{A} = -\frac{e\omega r^2}{2} = -\frac{e}{2} \vec{r} \times \vec{v}$$

(2.6)

The magnetic moment of an electron with mass $m_e$ due to its orbital angular momentum, $\vec{L} = m_e \vec{r} \times \vec{v}$, is given by

$$\vec{m} = -\frac{e}{2m_e} \vec{L}$$

(2.7)

However, the orbit of an electron around a nucleus is a quantum mechanical system. The solution to the Schrödinger equation for a single electron atom dictates quantised values of $\vec{L}$ such that $|\vec{L}| = \sqrt{l(l+1)}\hbar$ where $l$ is the orbital quantum number, an integer $0 \leq l \leq n - 1$ where $n$ is the principle quantum number characterising the electron orbit energy level [22]. These represent the electron orbitals known as s ($l = 0$), p ($l = 1$), d ($l = 2$), f ($l = 3$) etc. Therefore, electrons in s orbitals do not have any orbital angular momentum.
Experimentally measurable expectation values are actually projections on a chosen z axis, \( L_z \), typically parallel to the applied magnetic field. These projections are also quantised in units of \( \hbar \) by a magnetic quantum number \( m_l \), which is an integer \(-l \leq m_l \leq l\). Hence the projection of the magnetic moment is,

\[
m_z = -\frac{e\hbar}{2m_e}m_l = \mu_B m_l
\]

where \( \mu_B \) is the Bohr magneton, the smallest unit of electronic magnetism [17].

However, the orbital angular momentum operator does not commute with the Dirac Hamiltonian for a central potential, \( H_D^{(V)} \), which is a linearised form of the Schrödinger equation for relativistic particles, ie. \( [\vec{L}, H_D^{(V)}] \neq 0 \) [23]. This violates the law of conservation of angular momentum, indicating that there is another form of angular momentum present. Dirac introduced a spin operator,

\[
\vec{S} = \frac{\hbar}{2} \vec{\sigma}
\]

where \( \sigma \) is the set of Pauli matrices. The commutator of \( \vec{S} \) with the Dirac Hamiltonian is equal and opposite to \( [\vec{L}, H_D^{(V)}] \), hence the quantity \( \vec{L} + \vec{S} \) commutes with the Dirac Hamiltonian, conserving the angular momentum. Hence the concept of spin becomes necessary as an intrinsic form of angular momentum for all elementary particles [23].

Using the appropriate Pauli matrix, the projection of the spin angular momentum on the z axis, \( S_z \), is quantised by a spin quantum number, \( s \), such that

\[
S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \hbar s
\]

Electrons have just two possible spin states, which may therefore be described by \( s = \pm \frac{1}{2} \) [22]. The total angular momentum of an electron is therefore due to a combination of its
orbital motion and intrinsic spin, which provides another contribution to the magnetic moment of an electron. This is therefore projected on the z axis as

\[ m_z = -\frac{e\hbar}{m_e} = -2\mu_B s \]  

(2.11)

The factor of 2 is referred to as the g-factor, which relates the magnetic moment in units of \( \mu_B \) to the angular momentum in units of \( \hbar \) [17]. The total magnetic moment due to orbital motion and spin is therefore,

\[ m_z^{\text{tot}} = -\mu_B(2s + m_I) \]  

(2.12)

From the frame of reference of the electron, the orbiting nuclear charge creates a magnetic field. This interacts with the spin moment of the electron, leading to spin-orbit coupling. equation (2.5) gives an interaction energy of,

\[ E_{SO} = \frac{Z^*e^2}{2\pi m_e^2 \hbar^3} \]  

(2.13)

where \( Z^* \) is the effective nuclear charge due to screening by electrons in lower energy levels [23]. This becomes increasingly important for lower energy levels in higher \( Z \) elements.

In many-electron atoms, the interactions between electrons becomes extremely complex. The Pauli exclusion principle states that no two electrons may occupy the same state uniquely identified by all four quantum numbers, \( n, l, m_l \) and \( s \) [24]. Electrons confined to the same orbital will therefore have antiparallel spins, which cancels out the combined magnetic moment. However, for a simplified two-electron system, the electrons will prefer to occupy different orbitals in order to minimise the Coulomb repulsion between them, and hence have parallel spins. This is known as the intra-atomic exchange interaction, which tends to maximise the overall spin of the atom, \( \tilde{S} \), which is therefore only composed of the unpaired electron spins [25]. The arrangement of electrons in
energy levels and orbitals is summarised by Hund's rules, which state that the total angular momentum of the atom, $\vec{L}$, as well as $\vec{S}$, will be the maximum permitted by the Pauli exclusion principle, which will also maximise the total atomic magnetic moment [25].

2.3 Magnetic Ordering

Magnetic moments within a material will arrange themselves with respect to each other depending on their interaction. The arrangement of non-zero atomic moments in a material leads to the categorisation of materials as presented in figure 2.3.

A collection of magnetic dipoles will have a moment equal to the sum of the individual moments. This gives the total magnetisation of the material, $\vec{M} = \frac{\vec{m}}{V}$, where $V$ is the volume of the material. This contributes to the magnetic induction field, $\vec{B}$, which is the response of the material to an applied magnetic field, given by

$$\vec{B} = \vec{H} + 4\pi\vec{M} \quad (2.14)$$

The ratio of these fields is known as the permeability of the material, $\mu = \frac{\vec{B}}{\vec{H}}$. The different categories of materials have different permeabilities and ratios of flux density out-side the material, $\Phi_{\text{out}}$, to inside the material, $\Phi_{\text{in}}$ [20] as detailed below.
### 2.3 Magnetic Ordering

**Paramagnetic:** Internal moments are randomly oriented, giving $|\bar{M}| = 0$. $\Phi_{out} < \Phi_{in}$ and $\mu > 1$.

**Ferromagnetic or ferrimagnetic:** Internal moments are mostly parallel (ferrimagnetic) or entirely parallel (ferromagnetic) and aligned in the same direction, leading to a non-zero magnetisation. $\Phi_{out} \ll \Phi_{in}$ and $\mu \gg 1$.

In addition, materials with no atomic moment are known as diamagnetic, which have $\Phi_{out} > \Phi_{in}$ and $\mu < 1$.

These different systems of magnetic ordering are caused by interactions between the atomic moments, known as inter-atomic exchange. In general the energy of exchange coupling between two spins, $\mathbf{s}_a$ and $\mathbf{s}_b$, separated by a distance $r$, can be expressed as

$$E_{ex} = -2\mathcal{J}_{ab}(r) \mathbf{s}_a \cdot \mathbf{s}_b$$

(2.15)

where $\mathcal{J}_{ab}(r)$ is the exchange interaction integral [26]. For $\mathcal{J}_{ab} > 0$, the lowest energy state is obtained by parallel alignment of the spins, leading to ferromagnetic ordering and a non-zero overall magnetic moment, known as spontaneous magnetisation, even without an applied magnetic field. For $\mathcal{J}_{ab} < 0$ the spins will align anti-parallel, creating two intersecting sub-lattices of oppositely orientated parallel spins. In the case of anti-ferromagnetism, the moments exactly compensate each other, leading to an overall zero magnetisation. For the more general case of uncompensated moments, ferrimagnetic ordering is obtained.

The band structure in a magnetised ferromagnet creates the spin polarisation as shown in figure 2.4. Spins aligned with the majority of other spins, conventionally described as pointing up, have a lower energy than anti-parallel spins, conventionally described as pointing down. The exchange interaction therefore reflects the splitting of the bands as shown in figure 2.4b, with a lower occupation of the down spin states.
The Stoner condition describes the conditions for spontaneous ferromagnetism as,

\[ JD(E_F) > 1 \quad (2.16) \]

where \( E_F \) is the Fermi energy and \( D(E_F) \) is the Density Of States (DOS) at the Fermi energy without any exchange interaction, as in figure 2.4a. Transition metals such as Fe, Ni and Co have a very large \( D(E_F) \) due to the 3d band [27]. In these materials, the electrostatic potential of the crystal lattice ions quenches the magnetic moment due to the orbital angular momentum, hence only the spins contribute to the magnetisation of the material [26].

The sign of \( J_{ab} \) can be seen from the Bethe-Slater curve, shown in figure 2.5, which relates \( J_{ab} \) to the ratio of \( r \) over the radius of the d orbital of the atoms, which overlap in the materials shown to allow the direct exchange interaction to occur [28]. The magnitude of this interaction is typically of the order of 0.1 eV [26].

Figure 2.4: Difference in Density Of States (DOS) and band structure between (a) a non-magnetic metal and (b) a ferromagnet, where exchange coupling leads to partially spin polarised bands [27].

Figure 2.5: The Bethe-Slater curve relating the exchange coupling integral, \( J_{exch} \), with the ratio of the atomic separation \( r_{ab} \) and the radius of their d orbitals, \( r_d \). For the materials shown, positive \( J_{exch} \) gives ferromagnetic ordering, and negative \( J_{exch} \) gives anti-ferromagnetic ordering [28].
For a critical temperature, \( T_{\text{crit}} \), corresponding to a certain thermal energy, \( k_B T_{\text{crit}} \geq E_{\text{ex}} \), the direct exchange interaction is overcome, leading to a breakdown of the magnetic order as \( T \) approaches \( T_{\text{crit}} \) and \( \vec{M} = 0 \) for \( T > T_{\text{crit}} \). Beyond this point, the material becomes paramagnetic. For ferromagnetic materials, this critical point is known as the Curie temperature, \( T_C \). For anti-ferromagnetic materials, it is known as the Neel temperature, \( T_N \). Using the Weiss molecular field approximation, \( T_C \) is more rigorously related to a constant \( J \) between \( z \) nearest neighbours by

\[
T_C = J \frac{2zJ(J+1)}{3k_B}
\]  

(2.17)

where \( J = S + L \) is the total angular momentum [28]. For the typical energy associated with the direct exchange interaction described above, \( T_C \) is of the order of 1000 K.

Direct exchange, given by equation (2.15), assumes that electrons remain localised around their respective nuclear potentials. However, ferromagnetic materials are most often metallic. Metallic systems rely on mobile electrons in the conduction band, which facilitate indirect exchange coupling between orbital electrons confined at large \( r \) relative to the radius of their wavefunctions, where direct exchange is very weak. Conduction electrons become polarised in the vicinity of the atomic magnetic moment, which causes exchange interactions with neighbouring atoms [29]. This long range interaction is known as RKKY coupling, which oscillates about 0 at large \( r \) as \( \frac{\cos x}{x^3} + \frac{\sin x}{x^4} \) [30], [31]. This becomes important when considering a multilayer structure composed of different materials. RKKY coupling between a hard and a soft ferromagnet, or between an anti-ferromagnet and a ferromagnet, can be used to help define the direction of magnetisation of a ferromagnetic layer. Depending on the separation between the layers, this coupling will either lead to ferromagnetic ordering or anti-ferromagnetic ordering across the interface. This can be used to pin a ferromagnetic layer, increasing the energy required to alter its magnetisation, and/or to create a synthetic anti-ferromagnet, consisting of two anti-ferromagnetically coupled ferromagnetic layers separated by a non-magnetic spacer layer of appropriate thickness [32].
2.4 Magnetisation of materials

The overall magnetic moment in a ferromagnetic material creates its own magnetic field, which, inside the material, acts in the opposite direction to the magnetisation. This is therefore known as the demagnetising field, $H_d$, which is given by

$$\vec{H}_d = -N_d \vec{M} \quad (2.18)$$

where $N_d$ is the demagnetisation factor [17]. This factor is shape dependant, and leads to a preferred direction of magnetisation, which can be expressed as a shape anisotropy, discussed in section 2.5.1. A ferromagnetic material with positive exchange coupling prefers parallel alignment of its moments. However, this creates a stronger demagnetising field. At zero applied field, a minimum energy state is reached by the formation of magnetic domains. Each domain consists of a region of parallel moments, having a single overall magnetisation. The magnetisation of each domain is orientated such that the material has an overall minimum magnetisation. Domains are separated by domain walls, where the moments continuously vary from one orientation to the next.

Once a magnetic field is applied, the domain orientated closest to the direction of the field will grow at the expense of the other domains, hence the domain walls will move [33]. As the strength of the applied field increases, appropriately orientated domains will coalesce, eliminating non-orientated domains. The overall magnetisation will increase due to the increased number of parallel moments. Once the applied field is strong enough, the entire material will consist of a single domain, which will then rotate away from the preferred direction of magnetisation to align itself parallel with the applied field. Higher fields will not be able to increase the magnetisation any further [34]. This point is known as the saturation magnetisation, $M_S$, shown in figure 2.6, and is an important fundamental property of a material which determines many aspects of its performance in spintronic devices.
A plot of $\overrightarrow{M}$ against applied field, $\overrightarrow{H}$, for a ferromagnetic material will reveal a hysteresis loop, as seen in figure 2.6. Starting from saturation with decreasing field, the magnetisation will remain high due to the exchange coupling. As $H$ is reduced, the magnetisation in the direction of the applied field reduces as the magnetisation rotates back to its preferred direction. Domains of random orientation will start to nucleate around crystal and/or structural defects in the material, further reducing $M$ as they grow by domain wall motion. As $H$ becomes increasingly large and negative, domains aligned with the negative field direction start to grow, and eventually dominate at $M_S$. The value of $H$ where the loop crosses the axis is known as the coercive field, $H_C$, or coercivity. This is the field required to reduce the magnetisation of a material to zero. By convention, materials with high coercivity, such as figure 2.6 (dashed), are described as magnetically hard, requiring large fields to reach saturation, whereas those with lower coercivities, such as figure 2.6 (solid), are magnetically soft [33]. The remanence, $M_r$, is the value of the magnetisation at zero applied field, and is often used as a measure of the strength of a permanent magnet.

2.5 Magnetic anisotropy

A material is magnetically anisotropic when its magnetisation has a preferred direction. The magnetic anisotropy is the energy barrier associated with rotating the direction of magnetisation away from the preferred direction to a non-preferred direction. Magnetic
anisotropy has a variety of causes, the most significant of which are due to the shape of
the material, known as shape anisotropy, its crystalline structure, known as
magnetocrystalline anisotropy and distortions of the crystal lattice, known as strain
anisotropy. These contribute to an effective overall anisotropy field, $H_k$, expressed as

$$H_k = H_d + H_m + H_s$$

(2.19)

where $H_d$ is the effective field due to the shape anisotropy, $H_m$ is the effective field due
to the magnetocrystalline anisotropy, and $H_s$ is the effective field due to the strain
anisotropy. The overall anisotropy of a material will be a combination of these effects.

2.5.1 Shape anisotropy

Any magnetised material will have
a demagnetising field, as
introduced in section 2.4,
consisting of the stray field arising
from any free magnetic poles. This
is related to the magnetostatic
energy, which will be minimised
by the formation and orientation of
magnetic domains to eliminate
free poles as shown in figure 2.7, known as flux closure domains [35]. As this is
dependent on the geometry of the material, the associated energy is known as shape
anisotropy. Shape anisotropy will act in opposition to any applied magnetic field which
may attempt to alter the flux closure domain structure.

In order to magnetise a material along a certain direction, the shape anisotropy and
demagnetising field in that direction must first be overcome. In three dimensions, the
magnitude of this demagnetising field in any one dimension is proportional to the
magnetisation in that direction. Hence there are three demagnetising factors, $N_a$, $N_b$ and
$N_c$, one for each orthogonal dimension, the sum of which is $4\pi$ [21]. For a perfectly
2.5 MAGNETIC ANISOTROPY

symmetric sphere, \(a = b = c\), therefore \(N_a = N_b = N_c = 4\pi/3\), leading to a uniform, isotropic field \([30]\). However, for a long, thin rod where \(a = b \ll c\), \(N_c \to 0\) and \(N_a = N_b \to 4\pi/2\). This gives a preferred direction, \(c\), in which the demagnetising field, and hence the energy required to magnetise the material in that direction, will be at a minimum, known as the easy axis. For a flat disk, \(a = b \gg c\), therefore \(N_a = N_b \to 0\) and \(N_c = 4\pi - 2N_a \to 4\pi\). Therefore, less energy is required to magnetise the disk in the plane of the disk, which is known as an easy plane. A much higher field is required to magnetise the disk in the out-of-plane direction, which is therefore known as a hard axis. The shape anisotropy, \(K_s\), of a flat disk may therefore be expressed as

\[
K_s = 4\pi M_s^2
\]  

(2.20)

2.5.2 Magnetocrystalline anisotropy

Materials may experience magnetocrystalline anisotropy due to the anisotropic crystal lattice structure. This may also arise at interfaces in multilayer structures, which may be considered as a special case of an artificially created lattice. Spin-orbit coupling creates an energy landscape defined by the localisation of orbitals to the crystal lattice sites. The potentials created by the ionic lattice will lift the degeneracy of the orientation of the

![Figure 2.8: Magnetocrystalline anisotropy directions in (a) Fe with a body-centred-cubic structure, (b) Ni with a face-centred-cubic structure and (c) Co with a hexagonal-close-packed structure showing the zenith angle θ and the azimuthal angle φ [21].](image)

35
electron orbitals, creating lower energy states with a preferred direction with respect to the crystal lattice. Easy axes will therefore exist at points of minimum energy, whilst spin-orbit coupling energy will be maximised at hard axes. The easy and hard axes of various crystalline structures are illustrated in figure 2.8.

**Simple cubic:** For a simple cubic lattice with direction cosines $\alpha, \beta$ and $\gamma$, the energy of this interaction is given by

$$E_{cub} = K_1 (\alpha^2\beta^2 + \alpha^2\gamma^2 + \beta^2\gamma^2) + K_2 \alpha^2\beta^2\gamma^2 + \cdots$$  \hspace{1cm} (2.21)

where $K_1$ and $K_2$ are the empirical anisotropy constants [36]. The behaviour of the material is determined by the sign of $K_1$. For $K_1 > 0$, the energy minima, $E_{cub} = 0$, exists at the $\langle 100 \rangle$ axes. For $K_1 < 0$, $E_{cub}$ is maximally negative at the $\langle 111 \rangle$ axes.

**Hexagonal:** The $c$ axis of a hexagonal unit cell is a high symmetry axis, and may either be an easy axis or a hard axis [36]. The magnetocrystalline anisotropy energy may therefore be expressed as

$$E_{hex} = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta + \cdots$$ \hspace{1cm} (2.22)

where $\theta$ is the zenith angle from the $c$ axis, and $\phi$ is the azimuthal angle [37] as shown in figure 2.8. In practice, the first two terms are generally sufficient to match experimental values.

2.5.3 Strain anisotropy

High anisotropy may be achieved by tetragonally distorted cubic materials where $K_2$ becomes significant. This is due to inverse magnetostriction, where the strain creates additional anisotropy in the direction of the effective stress [26]. Thin films grown epitaxially on cubic substrates with a slightly different lattice parameter may therefore have increased anisotropy perpendicular to the plane of the material. Although this is not expected to be a significant effect in this work, it is mentioned here for completeness.
Strain anisotropy can be two orders of magnitude larger than magnetocrystalline anisotropy, altering the easy axis from in-plane to out-of-plane [36]. The magnetic properties are therefore dependent on the magnitude of the distortion, often quantified as the ratio of \( c/a \). A cubic substrate with a lattice constant much greater than the material will lead to dislocations, disrupting the atomic ordering. It is therefore desirable to use a substrate which has a relatively small lattice mismatch of no more than a few percent.

2.5.4 Uniaxial anisotropy

Technologically useful materials are most often considered to have one overall easy axis, which is therefore known as uniaxial anisotropy, with \( E = K_u \sin \theta \), where \( \theta \) is the angle away from the easy axis [21]. The anisotropy energy is defined as the energy required to turn the magnetisation from an easy axis to a hard axis. Materials with high anisotropy therefore often have high coercivities. The value of \( K_u \) may be evaluated from a hysteresis loop measured with the field applied parallel to the hard axis of the sample. The field required to overcome the anisotropy is the applied field at which the hard loop saturates, known as the anisotropy field, \( H_k \). The uniaxial anisotropy is then given by

\[
K_u = \frac{M_s H_k}{2}
\]  

(2.23)

2.6 Magnetisation dynamics

A magnetic moment in an applied magnetic field will experience a torque as shown in figure 2.2, which will reach a static equilibrium. However, the time evolution of the magnetisation of a material in an effective applied field, \( H_{eff} \), taking into account factors such as the demagnetising field, is described by the Landau-Lifshitz equation [38],

\[
\frac{d\vec{M}(t)}{dt} = -\gamma \vec{M}(t) \times \vec{H}_{eff}(t)
\]  

(2.24)
where $\gamma$ is the gyromagnetic ratio, which is equal to $e/m_e$ for a free electron with a charge of $e$ and a mass of $m_e$. The magnetisation will therefore precess around the direction of the effective field, as shown in figure 2.9a. In order to align parallel with the field, damping must occur, shown in figure 2.9b, which Gilbert [39] described phenomenologically by a dissipative field orientated towards the axis of the applied field,

$$H_{diss} = -\frac{\alpha}{\gamma M_s} \frac{d\vec{M}(t)}{dt} \tag{2.25}$$

where $\alpha$ is the dimensionless Gilbert damping constant [40]. Combining this with equation (2.24) yields the Landau-Lifshitz-Gilbert (LLG) equation,

$$\frac{d\vec{M}(t)}{dt} = -\gamma \vec{M}(t) \times \left( \vec{H}_{eff}(t) - \frac{\alpha}{\gamma M_s} \frac{d\vec{M}(t)}{dt} \right) \tag{2.26}$$

which is the most commonly used form for studies of magnetisation dynamics. For numerical simulations, it is often assumed that the magnetisation, $\vec{M}$ is uniform throughout the material. This approximation is known as the macrospin model, and is valid for thin films of a magnetic material. Neglecting the damping term, the LLG equation can therefore be solved for a thin film to find the macrospin precession frequency,
2.7 Spin Transfer Torque

Just as the magnetisation of a material exerts a torque on the spin of an electron, a spin polarised current will exert a torque on the magnetisation of a ferromagnet as required by Newton’s third law of motion. This is known as Spin Transfer Torque (STT), and was first predicted by Slonczewski [42] and Berger [43] in 1996. As STT involves a transfer of spin angular momentum, the efficiency of the process is decreased in materials with strong spin-orbit coupling, where spin angular momentum is not conserved [44]. MnAl in particular is therefore a very promising material for achieving high spin transfer torque efficiency due its lack of heavy metals and low spin-orbit coupling.

Spin transfer torque (STT) may be modelled in the macrospin approximation by adding a spin torque term, known as the Slonczewski term, to the LLG equation, which is given by

\[
\frac{d\hat{M}_s t}{dt} = \frac{\eta(\theta) \mu_B j}{ed} \hat{M} \times (\hat{M} \times \hat{M}_{fixed})
\]

(2.28)

where \(\eta(\theta)\) is a polarisation efficiency factor related to the angle, \(\theta\), between the magnetisation and the spin polarisation direction, \(j\) is the current density per unit area, \(d\)

\[\omega_0 = \gamma \sqrt{(H_{eff} + 4\pi M_s)H_{eff}}\] (2.27)

which is known as the Kittel equation, and forms the basis of most analyses of ferromagnetic resonance (FMR) [38]. For nano-scale thin films, this is of the order of 1 – 10 GHz. In real systems, the damping term may be overcome by the application of a pulsed applied field anti-parallel to the magnetisation, leading to a ferromagnetic resonance when the pulse frequency matches \(\omega_0\). For high anisotropy materials such as the L10 thin films discussed above, this resonance may have a room temperature linewidth of the order of 0.1 Oe [41].
is the thickness of the free layer and $\vec{M}$ and $\vec{M}_{\text{fixed}}$ are unit vectors in the directions of the magnetisation of the free layer and the fixed layer respectively [46].

STT contributes a driving force to the magnetisation precession, which may compensate for the damping, allowing steady-state precession at zero applied field, as shown in figure 2.10a. The magnetisation is first perturbed by the STT and precesses around the easy axis, labelled $x$, before settling into steady-state precession around the $z$ axis. Complete switching of the magnetisation may be achieved with a slightly larger current, as shown in figure 2.10b. Once the precession reaches a critical amplitude, marked by the saddle point $S_1$, the magnetisation will irreversibly flip, aligning with the $-x$ direction. For in-plane magnetisation, the theoretical threshold current density for destabilising the magnetisation from the parallel configuration is,

$$J_c = \frac{2e\alpha M_s d}{\hbar \eta} (H + H_k + 2\pi M_s) \quad (2.29)$$

where $\alpha$ is the Gilbert damping coefficient, $H$ is the applied field and $H_k$ is the effective field due to the anisotropy of the ferromagnetic layer [47]. This gives a nominal value for $J_c$ of the order of $10^8$ A/cm$^2$ [48]. Much effort continues to be devoted to reducing this threshold for the sake of power efficiency.
Chapter 3

Spintronic applications and materials

3.1 Spintronic devices

The field of spintronics began with the discovery of the Giant Magneto-Resistance (GMR) effect in 1988 [49] sparking the rapid development of magneto-resistive technologies, as shown in figure 3.2, becoming essential components of computer memory systems.

Magnetic multilayer structures were discovered to have a large difference in electrical resistance depending on the relative orientation of the magnetisation of the layers. Layers of Fe were separated by a layer of Cr with a thickness (~ 0.8 nm) suitable for anti-ferromagnetic RKKY coupling between the Fe layers. At zero applied field and low temperature (T = 4.2K) these anti-parallel aligned layers exhibited up to twice the resistance measured when the layers were forced to be parallel by the application of a saturating magnetic field. Devices are characterised by their ratio of high to low resistance, or GMR ratio, defined by equation (3.1). GMR ratios as high as 150% have [50]since been observed at low temperature [51], and as high as 65% at room temperature.
The GMR effect is attributed to spin-dependent scattering at the interface of the layers, illustrated in terms of the band structure in figure 3.1. Electrons with minority spin (down) have a higher density of states at the Fermi energy, leading to a higher scattering cross section and a lower resistance due to the greater availability of excited states. The

![Diagram of spintronic applications and materials](image)

**Figure 3.2:** The development of magneto-resistive devices, one of the most important application areas of spintronics [52].

![Diagram of band structure](image)

**Figure 3.1:** Band structure of ferromagnetic layers either side of a non-magnetic spacer layer, showing (a) parallel alignment and (b) anti-parallel alignment. Parallel alignment leads to lower resistance due to more states of the same spin being available on the far side of the spacer layer [28].
magnetic moment of an electron passing through a ferromagnetic material will experience a torque due to the magnetisation, as described in section 2.1.

This creates a spin-polarised current through the non-magnetic spacer layer, which is incident on the second ferromagnetic layer, where the spin-dependent scattering occurs.

The GMR effect may be described by the two-current model, illustrated in figure 3.3, where the total resistivity, $\rho_T$, is given by,

$$\rho_T = \frac{\rho_1 \rho_\uparrow}{\rho_1 + \rho_\downarrow}$$  \hfill (3.1)

where $\rho_1$ is the resistivity of the spin up channel and $\rho_\downarrow$ is the resistivity of the spin down channel [27]. Strong polarisation leads to the assumption that $\rho_1 \ll \rho_\downarrow$. For a current perpendicular to the plane of the layers, the total resistance of two layers in series for parallel, $\rho_p$, and anti-parallel, $\rho_{AP}$, configurations is therefore

$$\rho_p = \left( \frac{1}{\rho_1 + \rho_\uparrow} + \frac{1}{\rho_\downarrow + \rho_\uparrow} \right)^{-1} \approx 2\rho_\uparrow$$  \hfill (3.2)

$$\rho_p = \left( \frac{1}{\rho_1 + \rho_\downarrow} + \frac{1}{\rho_\uparrow + \rho_\downarrow} \right)^{-1} \approx \frac{\rho_\downarrow}{2}$$  \hfill (3.3)

Therefore $\rho_p < \rho_{AP}$. As GMR is a conduction phenomenon, only electrons near the Fermi energy, $E_F$, will contribute. The degree of polarisation is therefore defined as,

$$P = \frac{N_\uparrow(E_F) - N_\downarrow(E_F)}{N_\uparrow(E_F) + N_\downarrow(E_F)}$$  \hfill (3.4)
where $N_\uparrow(E_F)$ is the number of electrons with spin up at the Fermi energy and $N_\downarrow(E_F)$ is the number of electrons with spin down at the Fermi energy. This polarisation will persist until scattering events perturb the spin direction enough to lose any correlation with the original magnetisation direction. The spin diffusion length is related to the spin-orbit coupling of the material, and is thus much shorter in ferromagnetic metals than non-magnetic materials, of the order of $1–10$ nm, especially those containing heavy metals such as FePt [53]. This gives MnAl a strong advantage for efficient polarisation as it is free from such heavy metals giving it sufficiently low spin-orbit coupling, motivating the scientific interest in exploring the material. Experimentally determining the polarisation is challenging, although strong polarisation is generally assumed for ferromagnetic materials over short length scales up to the spin diffusion length. Devices must therefore consist of appropriately thin layers.

3.1.1 Magnetic Tunnel Junctions

Although the development of GMR ushered in a period of rapid increase in the areal density of data storage, the size of bits has decreased sufficiently that GMR ratios no longer provide enough signal-to-noise for reliable reading. Replacing the metallic spacer layer of a GMR trilayer with an insulating tunnel barrier leads to Tunnelling Magneto-Resistance (TMR), creating a device called a Magnetic Tunnel Junction (MTJ). MTJs using an amorphous Al$_2$O$_3$ barrier layer are capable of TMR ratios of up to 70% at room temperature, and have been used until the last decade in the read heads of HDDs [5], [6], [50]. The origin of TMR is again due to the spin-polarised band structure of ferromagnetic materials. However, the probability of tunnelling, and hence the resistance of the device, is related to the density of states in both ferromagnetic layers, as illustrated in figure 3.1. In the anti-parallel configuration, there is a relatively low density of states on the far side of the tunnelling barrier for incident electrons in both spin up and spin down states. However, in the parallel configuration, there is a large density of states for spin up electrons on both sides of the barrier, leading to a large increase in transmission probability, and hence a large decrease in electrical resistance.
Julliere's model for spin-dependant tunnelling transmission gives the magneto-resistance as,

\[ MR = \frac{2P_1P_2}{1 - P_1P_2} \] (3.5)

where \( P_1 \) and \( P_2 \) are the polarisations of the two ferromagnetic layers \([6], [54]\). Although this relation gives good agreement between experimentally measured polarisations and TMR ratios, it differs significantly from band structure calculations. This is a result of not accounting for the differences in transmission probability between different Bloch states \([55]\), as shown in figure 3.4. Preservation of the spin polarisation across the tunnel barrier is key to achieving a high TMR. Theoretical calculations of band structures in crystalline tunnel barriers, in particular MgO, suggest TMR ratios of up to 1000% are possible \([6]\). This is due to the \( \Delta_1 \) Bloch state from an iron polarising layer having a very slow rate of decay in magnesium oxide \([56]\). This state is also only available for majority spin electrons, resulting in a very large difference in conductance. Experimental MTJs with a single crystal MgO barrier layer have achieved TMR ratios of 200 – 400% at room temperature, an example of which is shown in figure 3.5 \([50]\). The challenge remains to produce atomically clean interfaces to match the theoretical predictions and simulations, as intermixing

![Figure 3.4: Transmission of Bloch states across (a) an amorphous Al\(_2\)O\(_3\) and (b) a crystalline MgO tunnel barrier. The \( \Delta_1 \) Bloch state allows efficient tunnelling not predicted by the incoherent, amorphous model \([50]\).](image)
between the layers will disrupt the coherent transfer of the $\Delta_1$ Bloch state. Lattice mismatch at the tunnel barrier will also degrade the TMR, which is a key issue in devices using MnAl with MgO tunnel barriers, where there is a noticeable difference in lattice spacing [57]. However, this may be somewhat relieved and the TMR improved by inserting a very thin buffer layer with an intermediate lattice parameter, such as cobalt [59] or chromium.

In order to separate the switching of the two layers so as to achieve the different configurations, MTJs are typically fabricated with a hard, or fixed layer, and a soft, or free layer. The fixed layer may be thicker so as to increase its coercivity, and/or it may be exchange biased by additional pinning layers. This is typically done using a layer structure similar to the one shown in figure 3.6.

Through exchange coupling at the interfaces, an anti-ferromagnetic material is used to bias a synthetic anti-ferromagnet, which creates a magnetically stiff structure which does not easily reverse in an applied magnetic field. The top layer of the synthetic anti-

**Figure 3.5:** Giant TMR in an MTJ with a MgO tunnelling barrier at room temperature and at 20K. The high resistance state corresponds to anti-parallel alignment of layers [58].

**Figure 3.6:** TEM cross section image of an MTJ, showing the anti-ferromagnetic PtMn biasing the synthetic anti-ferromagnet (SyF), the fixed (pinned) layer, the MgO tunnel barrier and the free layer [50].
ferromagnet then forms the fixed layer. The free layer is most often no more than a few nanometres thick in order to allow switching with minimum activation energy. This binary behaviour makes MTJs very suitable for memory storage applications such as Magnetic RAM (MRAM), which potentially represents a non-volatile, solid-state universal computer memory [48]. This initial proposition involved the writing of bits by using nearby pulsed currents to create a magnetic field to flip the free layer. Data would be read by the resistance state of the MTJ itself. However, the need for stray fields from the writing currents limited its scalability to high densities, prompting the shift to writing using STT.

In order to be suitable for the majority of technological applications, spintronic devices must be able to function without an external applied magnetic field. Instead, STT is used as the principle activation mechanism, leading to STT-MRAM. In this way, the free layer may be switched between parallel and anti-parallel states by reversing the direction of current. The positive direction of current is defined as being from the fixed layer to the free layer. When applying negative current, electrons will pass through the free layer without acquiring significant polarisation due to its small volume. Minority spin electrons with respect to the fixed layer will therefore be reflected from the tunnel barrier back into the free layer, whereas majority spin electrons will be transmitted. This creates an excess of minority spin electrons in the free layer, which will then apply STT. This asymmetry in switching mechanism leads to a predicted asymmetry in switching current, although the experimentally observed asymmetry is less than expected [46]. Theoretically, asymmetry may be avoided by including a second fixed layer on top of the free layer, orientated anti-parallel to the first fixed layer [60]. This would also reduce the threshold current as STT would now be applied both directly and via reflection for both current directions. For appropriate thicknesses of the central free layer, resonance conditions may be satisfied which are predicted to increase the effective STT by an order of magnitude [61].
3.2 Energy assisted magnetic recording

The greater sensitivity of tunnel magnetoresistance devices as compared with giant magnetoresistance devices has allowed a dramatic increase in the storage density of magnetic recording media in hard disk drives. This was further accelerated by the transition from longitudinal recording, in which the magnetisation is orientated in-plane, to perpendicular recording, in which the magnetisation points out of the plane of the disk [11]. However, for storage densities greater than 1 Tbit/in², this trend is no longer sustainable, and the industry now faces a problem known as the magnetic storage trilemma [11]. This reflects the conflicting requirements of thermal stability, the ability to write a bit, and the storage density. The size of the grains in recording media are now approaching a lower limit of just a few nanometres below which they would no longer be thermally stable. At this point, the volume of the grains, $V$, is small enough that the anisotropy energy per grain, $K_uV$, is comparable with the thermal energy at room temperature, $k_B T$. This is known as the superparamagnetic limit [62]–[64]. The industry standard is that data should be thermally stable for at least 10 years, leading to the more restrictive condition that $\frac{K_u V}{k_B T} > 60$ [65]. The simple solution to this problem would be to use a magnetically stiffer recording medium with a higher anisotropy which retains thermal stability at smaller grain sizes. However, the strength of the magnetic field currently used to write bits would no longer be enough to reverse the magnetisation of such a bit [66]–[68]. As such, all three conditions of the magnetic storage trilemma cannot be simultaneously satisfied by current technologies. New solutions are therefore required in order to further increase the storage density of hard disk drives.

3.2.1 Heat assisted magnetic recording

The main contender for solving the magnetic storage trilemma is known as heat assisted magnetic recording (HAMR), illustrated in figure 3.7 [66], [68]. The recording medium has extremely high anisotropy to allow very small grain sizes whilst maintaining thermal stability. In order to write a bit, localised heating is used to temporarily reduce the anisotropy of the bit prior to writing. Heating to close to the Curie temperature reduces
the magnetic field required to reverse the bit to technologically achievable values. The bit then cools, freezing the new orientation in place. With its high anisotropy, FePt is a strong contender for a HAMR storage medium [7], [70], [71]. Grains of FePt may be as small as 3 nm before reaching the superparamagnetic limit, so such a system may be able to achieve storage densities of several Tbit/in² [72].

As the anisotropy is reduced by localised heating applied by a laser, heat dissipation is a major concern in a HAMR system. Heating to the Curie temperature of FePt, ~750 K, places very high demands on the thermal stability of the disk lubricant and overcoat, requiring new materials to mitigate the effects of thermal degradation [66]. The thermal conductance of the disk must be enhanced to dissipate the heat from the point of application within 1 nanosecond or less, or the bit may demagnetise and lose its new direction before freezing in place [66], [73]. This timescale also places an upper limit on the writing rate. Repeated thermal cycling places additional mechanical stress on the disk as a whole.

A simple way to minimise the heat dissipation problems of HAMR is to use a lower temperature. FePt is an exceptional candidate for the storage medium, but requires heating
to the high temperature of approximately 500°C to write a bit [67]. Using a different material with a lower Curie temperature may seem to be the solution, which has been attempted by adding Ni to FePt, but this also reduces the anisotropy [66]. However, the level of heating required may be conveniently reduced without such chemical modification by pairing FePt with FeRh in an exchange-spring bi-layer structure [63], [67].

An exchange spring consists of two magnetic layers in epitaxial contact [74]. One layer has high anisotropy and low saturation magnetisation, the other has low anisotropy and high saturation magnetisation. Exchange coupling at the interface ensures the magnetisation of both layers are aligned parallel. Under the increasing influence of an opposing external magnetic field, the low anisotropy layer is reversed and saturated first. However, a non-saturated transition region will exist on both sides of the interface where the exchange energy is minimised by maintaining parallel spins. This exerts extra torque on the high anisotropy layer, causing it to reverse in a lower external field than a single high anisotropy layer would with this additional torque contribution. The coercivity of the bi-layer system is therefore lower than that of a single high anisotropy layer.

The binary alloy FeRh is anti-ferromagnetic at room temperature at close to equi-atomic composition, with a body-centred cubic structure. However, when heated to approximately 100°C, FeRh undergoes a first-order phase transition and becomes ferromagnetic, accompanied by a cubic lattice expansion of ~1% [75]. When heated beyond the transition temperature, an FeRh layer in the ferromagnetic state would then form an exchange spring structure when paired with an FePt storage layer. This reduces the coercivity of the resultant bi-layer system by ~60% when heated to the reasonable temperature of 150°C (~420 K) compared with just a 10% reduction in anisotropy in a single layer of FePt at this temperature [63]. The exact transition temperature may be tuned and optimised by varying the stoichiometry, or doping FeRh with iridium [67], [75]. As this transition occurs much below the typical Curie temperature of the storage layer, this significantly reduces the temperature required to write the bit, improving the efficiency and reliability of such a HAMR system.
3.2.2 Microwave assisted magnetic recording

The magnetic storage trilemma may be resolved by temporarily reducing the coercivity of the bit to be written. The previous section provided an overview of how this might be achieved using temperature. However, this is not the only method by which additional energy can be supplied to the magnetic media. Energy can also be introduced by instigating precession of the storage media grains, destabilising the magnetisation. Microwave assisted magnetic recording (MAMR) proposes to use a spin torque oscillator (STO) of microwave frequencies to generate an oscillating magnetic field, illustrated in figure 3.8 [76].

A spin-polarised input current will exert spin transfer torque on a magnetically soft layer, known as the field generating layer, causing precession of its magnetisation. This oscillating magnetisation will create an oscillating stray field which will then excite precession in the storage media, leading to ferromagnetic resonance. At this point, energy

![Figure 3.8: The operating principle of microwave assisted magnetic recording (MAMR). An oscillating stray field from a spin torque oscillator excites precession in the storage medium [76].](image)

51
is absorbed from the oscillating field at a higher rate than energy is lost to damping, overcoming some fraction of the anisotropy energy barrier. A reduction in coercivity of approximately $1/3$ is calculated for broadband oscillations with an amplitude of $0.1H_k$ where $H_k$ is the anisotropy field of the grain [76]. As the magnetisation of the storage media precesses, the usual quasi-static field used to write the bit is applied, completing the reversal of the bit.

Although STOs hold great potential for the generation of an oscillating magnetic field, many challenges remain before they can actually be used in practical MAMR systems. There are few experimental realisations of spin torque oscillators suitable for MAMR which meet the requirements for high anisotropy perpendicular polarising layers and perpendicular field generation layers. L1$_0$ ordered FePt would be a good candidate, but has high spin-orbit coupling and strong magnetic damping making it inefficient as a spin polariser. High temperature annealing up to 800°C is also required which would cause undesirable diffusion between the complicated layers of an STO [77]. MnAl does not require such high temperatures, and would be more power efficient, although forming the L1$_0$ ordered phase is highly non-trivial, as discussed in section 3.3.3. It is difficult to experimentally observe the oscillations of such a perpendicular STO as the relative angle between the magnetisations of the polarising layer and the field generating layer does not change with time [77]. Most work on STOs has been done with in-plane materials where large variations in the magnetoresistance can be observed as the free layer precesses. Due to these experimental difficulties in developing suitable STOs, MAMR is more likely to be a successor to HAMR rather than be directly used as the next generation technology in hard disk drives.

3.3 L1$_0$ ordered materials

High intrinsic anisotropy in magnetic materials is related to the crystal structure, whether this be natural or artificially created by fabricating multilayers. Certain binary alloys, some of which are listed in table 3.1 with typical bulk properties, can form a highly
3.3 L10 ORDERED MATERIALS

<table>
<thead>
<tr>
<th>L10 alloy</th>
<th>$K_u \ (10^7 \text{erg/cm}^3)$</th>
<th>$M_s \ (\text{emu/cm}^3)$</th>
<th>$T_c \ (\text{K})$</th>
<th>$a(\AA)$</th>
<th>$c(\AA)$</th>
</tr>
</thead>
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<td>7</td>
<td>1140</td>
<td>750</td>
<td>3.85</td>
<td>3.71</td>
</tr>
<tr>
<td>FePd</td>
<td>1.8</td>
<td>1100</td>
<td>760</td>
<td>3.85</td>
<td>3.72</td>
</tr>
<tr>
<td>FeNi</td>
<td>1.3</td>
<td>1270</td>
<td>820</td>
<td>3.58</td>
<td>3.61</td>
</tr>
<tr>
<td>CoPt</td>
<td>4.9</td>
<td>800</td>
<td>840</td>
<td>3.80</td>
<td>3.70</td>
</tr>
<tr>
<td>MnAl</td>
<td>1.7</td>
<td>560</td>
<td>650</td>
<td>3.94</td>
<td>3.58</td>
</tr>
</tbody>
</table>

*Table 3.1: Typical magnetic and structural properties of some bulk L10 ordered alloys, taken from [73], [78]–[80].*

ordered phase with long range chemical ordering in the form of monoatomic layers, known as an L10 structure. The L10 crystal structure is shown in figure 3.9, which may be considered as a tetragonally distorted face-centered-cubic (fcc) structure. This structure may also be described by a reduced unit cell consisting of a tetragonally distorted body-centred cubic (bcc) structure, shown in figure 3.9 by the dashed unit cell with axes $a/\sqrt{2}$ and $c$.

Care must be taken to ensure consistency with the choice of unit cell, as different publications may use either. Moments at the corners couple ferromagnetically with each other, but antiferromagnetically with any magnetised atoms at the $c/2$ sites. The magnetisation and anisotropy are therefore strongly dependent on the atomic ordering. The magnetisation is also

*Figure 3.9: L10 crystal structure of FePt, showing the tetragonally distorted body centred cubic reduced unit cell (dashed) [81].*
dependent on the degree of tetragonal distortion, making fabrication a delicate and non-trivial process.

The choice of substrate and/or seedlayers can promote the successful formation of the L1_0 phase. Cubic substrates or seed layers provide an epitaxial template for the fct structure. Magnesium oxide single crystal substrates are commonly used, cut along the (001) planes. MgO has a B1 structure with a lattice parameter of 4.212 Å. As this is larger than the a parameters of L1_0 magnetic materials, interfacial strain promotes the larger a parameter of the L1_0 phase over the smaller a parameter of the disordered cubic phase without the tetragonal distortion. This strain also promotes perpendicular alignment of the crystallites, essential for application in high density storage media or perpendicular STOs, as the larger a parameter is preferred over the smaller c parameter. Single crystal substrates are expensive and not practical for technological applications, leading to research into sputtered MgO seed layers as well as other potential materials [7]. However, these are inevitably polycrystalline, which create defects and define the grain size of subsequent films. All samples in this work are therefore made with single crystal MgO substrates unless otherwise specified.

3.3.1 Iron platinum

As can be seen from table 3.1, FePt has the largest anisotropy of the L1_0 materials two orders of magnitude greater than Fe alone. This is due to the strong spin-orbit coupling of the Pt as well as the hybridisation of the spin polarised d bands from the Fe atoms [33]. The high anisotropy makes FePt very attractive for data storage applications, allowing nanoscale grain sizes before the superparamagnetic limit is reached.
The bulk phase diagram for FePt is shown in figure 3.10. At high temperatures, equiatomic FePt forms a face-centred-cubic (fcc) phase with an A1 structure, known as the $\gamma$ phase. This is a chemically disordered phase with no preferential sites for the iron or platinum atoms. Despite the high temperature in the phase diagram, this phase is commonly obtained when depositing the material at room temperature due to the high energy barriers associated with the atomic diffusion necessary to achieve long range chemical ordering [86]. Although the A1 phase has a similar saturation magnetisation and Curie temperature as the L1$_0$ phase, its anisotropy is two orders of magnitude lower, making it useless for the advanced technological applications discussed in section 3.2.1. Transforming the as-deposited material into the high-anisotropy L1$_0$ phase is therefore essential for realising those applications.

Elevated temperatures of more than 550°C, and often as much as 700°C, are required in order to form the desired L1$_0$ phase in reasonable time scales of no more than a few hours.
This may be during deposition on a heated substrate or applied afterwards as annealing. The enhanced atomic mobility at high temperatures causes the grains to grow, which is undesirable for the formation of high density storage media. Segregation of the grains in practical storage media is a key requirement, not only to magnetically decouple bits from each other, but also to limit this growth. This segregation may be achieved by adding carbon, which is insoluble in FePt and does not form any carbide phases [87]. Isolating the nucleation sites enhances the ordering of the growing grains, reducing the chance of crystal defects and anti-phase boundaries [64]. Higher temperatures may yield more ordering more quickly, but this would not be practical for industrial processes. Various dopants such as Cu, Ag or Au have been found to reduce the ordering temperature to lower values [7], [88]. The addition of Cu has been found to be most effective, with significant ordering achieved at just 350°C, although it also decreases the anisotropy and increases the surface roughness of the films, both of which are undesirable [88].

Ordering occurs via a first-order phase transformation from the A1 phase to the L1\textsubscript{0} phase [89]. The reduction in symmetry may result in up to two different translational domains each with three possible orientations of the atomic ordering. This gives rise to many new anti-phase boundaries which are expected to affect the local magnetic properties and act as pinning sites for magnetic domains [90]. Large scale ordering occurs via the nucleation and growth of L1\textsubscript{0} grains at the expense of parent A1 grains. Successful formation of the L1\textsubscript{0} phase after annealing is therefore greatly enhanced by having pre-existing nuclei created during deposition. Without such nuclei, the L1\textsubscript{0} phase formation is more sensitive to the annealing temperature and longer annealing times are required, or the phase may not form at all [71].

3.3.2 Manganese aluminium

Manganese aluminium (MnAl) has a ferromagnetic L1\textsubscript{0} phase, known as the $\tau$ phase. A bulk phase diagram is shown in figure 3.11, and crystalline information for the principle phases is shown in table 3.2. Data for low temperature bulk phases is very difficult to acquire due to the extremely long timescales associated with atomic diffusion [78].
Table 3.2: Structure and lattice constants of bulk MnAl phases [91], [92].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Spacegroup</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>A3</td>
<td>P6$_3$</td>
<td>194</td>
<td>2.70</td>
<td>4.37</td>
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<tr>
<td>($\beta$Mn)</td>
<td>A13</td>
<td>P4$_1$32</td>
<td>213</td>
<td>6.32</td>
<td></td>
</tr>
<tr>
<td>$\tau$</td>
<td>L1$_0$</td>
<td>P4</td>
<td>123</td>
<td>3.94</td>
<td>3.56</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>A7</td>
<td>R3$m$</td>
<td>166</td>
<td>10.1</td>
<td>7.63</td>
</tr>
</tbody>
</table>

Figure 3.11: Bulk phase diagram for MnAl showing the ferromagnetic metastable $\tau$ phase, which may easily decompose into the surrounding equilibrium $\gamma_2$ or ($\beta$Mn) phases [93].

Relatively few studies have been done on MnAl thin films, with most previous work being focussed on developing the material for bulk permanent magnets [94].
The τ phase is metastable at room temperature, as well as having a narrow window of acceptable atomic composition between 49-59% Mn, making fabrication a challenge. However, spin-polarised band calculations predict a highly desirable magnetisation of 2.4 μ_B per Mn atom and a magnetocrystalline anisotropy constant of $1.5 \times 10^7$ erg/cm$^3$ [95]. In contrast to other L1$_0$ materials, MnAl does not contain any heavy metals or rare earth elements, making it economically attractive as well as more efficient for spin transport due to low spin-orbit coupling. The variation of magnetic moment and total energy with the tetragonal distortion ratio, c/a, is shown in figure 3.12. The system settles in the minimum energy configuration at $c/a = 0.9058$, or $c/a = 1.28$ if the axes of the reduced bcc unit cell are used [95]. However, the magnetisation may be increased if the system is strained to lower values of c/a.

### 3.3.3 MnAl τ phase formation

The key challenge to making use of the promising properties of τ phase MnAl lies in first fabricating the material itself. Although the theoretically predicted properties are very attractive, experimentally achieving such good quality material is particularly challenging [96], [97]. Due to the meta-stable nature of the τ phase, the fabrication process must be carefully controlled and optimised in order to achieve the desired phase.

Numerous studies have been carried out on MnAl alloys fabricated by mechanical methods such as casting, grinding or milling [98], as well as by heat treatment techniques such as sintering, arc melting and melt-spinning [91], [94], [99]. Samples are typically
prepared at high temperatures of over 1000°C and then quenched to form the ε phase with a hexagonal close packed (hcp) structure. Annealing between 400 – 600°C then yields the required τ phase. It has been previously suggested, first by Kojima et al [101], and later supported by references [99], [100], [102], [103] that this occurs via a two stage process, as illustrated in figure 3.13.

The disordered hcp structure first undergoes an ordering reaction within the close-packed planes, resulting in a reduced-symmetry orthorhombic B19 structure, sometimes known as the ε′ phase [101]. This then experiences a martensitic shear along the close packed planes, giving the L1₀ face centered tetragonal unit cell inclined at 55° to the original hexagonal unit cell.

In-situ annealing experiments using a Transmission Electron Microscope (TEM) have directly observed the accumulation of stacking faults, shearing and associated changes in the electron diffraction patterns, as shown in figure 3.14 [100], [103]. These dark field images, taken from a B19 super-lattice diffraction spot, provide evidence of the growth of the intermediate B19 phase [100]. Figure 3.14a shows that small nuclei are already present in the otherwise A3 ordered as-quenched material. These nuclei become well
defined with antiphase boundaries after annealing to 450°C, also evidenced by the sharper B19 super-lattice diffraction spots shown in figure 3.14b. Stacking faults are seen to cross the antiphase boundaries of the B19 nuclei, visible as broad, dark stripes parallel to the close-packed planes seen in figure 3.15. Further shearing along these planes results in the formation of the L1\(_0\) phase.

However, NMR data [47], as well as other electron microscopy, diffraction and thermal kinetic studies [97], [104]–[108] suggested that the \(\varepsilon \rightarrow \tau\) phase transition can occur without going through any intermediate phases. This has led to alternative kinetic mechanisms being suggested, independent of the formation of the B19 ordered \(\varepsilon'\) phase.

---

**Figure 3.14:** In situ annealing of MnAl, showing the growth of the B19 intermediate phase from (a) the as-quenched state to (b) after heating at 450°C. Super-lattice diffraction spots become sharper and better defined, evidencing increasing crystal ordering [100].

**Figure 3.15:** Close-packed planes of the B19 intermediate phase, with stacking faults in the broad, dark regions [100].
Figure 3.16: TEM images showing the nucleation and growth of the τ phase. (a) BF-TEM micrograph showing clearly faceted phase grain growing from a ε phase grain boundary. (b) BF-TEM micrograph with associated electron diffraction patterns. The phase grain is orientated to the ε₁ grain, and grows into the ε₂ grain. (c) High resolution TEM micrograph of atomic-scale facets of the developing τ phase grain (right) into ε phase (left). Arrows indicate (020) steps between (111) ledges [104].

It is now believed that the phase grows from the grain boundaries through a compositionally invariant nucleation mechanism, or massive transformation, growing by the diffusion of interphase interfaces rather than the transformation of an intermediate phase [104], [107]. As can be seen in figure 3.16, the τ phase grain grows from ε phase grain boundaries. The developing grain exhibits well-defined facets over a range of length scales, from the meso-scale, through the nano-scale to the atomic scale. A well-defined orientation relationship is established with one of the parent grains, (0001)ₑ(111)ₑ and [1120]ₑ[110]ₑ, illustrated in figure 3.16b. The interface with this parent grain has very low mobility. The phase grain preferentially grows at the expense of the other parent grain, with which there is no crystallographic orientation relationship. Despite the faceted nature of the interphase interface, the movement of the growth interface is facilitated by quasi-continuous random atomic migration across the incoherent phase boundary from the parent phase to the product phase rather than any step-wise growth pattern [105]. This random attachment process results in a high density of defects in the resulting L₁₀ grain. The presence of carbon is known to stabilise the formation of the τ phase by inhibiting the diffusion of the Mn and Al atoms, thereby slowing the decomposition into the stable (βMn) and γ₂ phases [100], [109], [110]. However, it also hinders the formation of the τ
phase when present above the solubility limit [102], found to be 1.4 – 2.1 atomic percentage proportional to the Mn content [109], [111]. Huang et al attributed this to carbide precipitates inhibiting the shear action of the assumed martensitic transformation [102]. It is not yet clear how this may be explained by the massive transformation process, or even what influence carbon might have on the diffusion kinetics [104].

3.3.4 Magnetic properties of bulk MnAl

A comparison of the magnetic properties obtained from a variety of bulk fabrication methods is presented in table 3.3. Remanence, $M_r$, is proportional to the volume of $\tau$ phase material present, whilst coercivity, $H_c$, is inversely proportional to the grain size and density of domain-wall-pinning defects. Although the hot-extrusion process has superior properties, the process itself is expensive in energy requirements and equipment [94]. Extrusion results in a small grain size with high anisotropy, giving high coercivity up to $H_c = 4$ kOe as reported in reference [109]. Smaller grains are also given by the rapid quenching method of reference [94] rather than conventional water quenching, with higher coercivity as a result. It should be noted that absolute comparison of coercivity between different publications is difficult due to the volume dependency.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Composition (at%)</th>
<th>Method</th>
<th>$M_r$ (G)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
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<tr>
<td>[109]</td>
<td>Mn$<em>{52.9}$Al$</em>{45.3}$C$_{1.8}$</td>
<td>Extrusion</td>
<td>6100</td>
<td>3000</td>
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<tr>
<td>[98]</td>
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<td>Mechanical alloy</td>
<td>2500</td>
<td>3400</td>
</tr>
<tr>
<td>[94]</td>
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<td>1500</td>
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<tr>
<td>[99]</td>
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<td>3030</td>
<td>1310</td>
</tr>
<tr>
<td>[98]</td>
<td>Mn$<em>{53.3}$Al$</em>{46.7}$</td>
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<tr>
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<td>[94]</td>
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</tr>
<tr>
<td>[99]</td>
<td>Mn$<em>{52.6}$Al$</em>{47.4}$</td>
<td>Arc-melted</td>
<td>1990</td>
<td>730</td>
</tr>
</tbody>
</table>

Table 3.3: Comparison of magnetic properties from a variety of bulk fabrication methods.
As can be seen from table 3.3, some of the best magnetic properties appear in materials in which a small amount of carbon has been introduced. The trends in coercivity, magnetisation and Curie temperature with carbon content are presented in figure 3.17. Studies typically investigate the effects of adding carbon around its solubility limit, not more than 4 at%, or 2 wt%. As mentioned in section 3.3.3, this is caused by carbon stabilising the formation of the ferromagnetic \( \tau \) phase. This is due to the carbon atoms preferentially occupying \((1/2, 1/2, 1/2)\) sites in the \( \text{L}_{10} \) unit cell, preventing Mn atoms from occupying this site where they would couple antiferromagnetically to the Mn atoms at the \((0, 0, 0)\) sites \[102\], \[111\].

However, the marked increase in the \(c\) axis of the \( \text{L}_{10} \) unit cell with carbon doping suggests that the carbon atoms occupy octahedral interstitial sites in the Mn layer, i.e. \((1/2, 0, 0)\) \[112\], \[113\]. Optimum carbon content at the solubility limit in bulk samples maximises the stability of the \( \tau \) phase, resulting in a higher coercivity and a higher saturation and remnant magnetisation. In mechanically milled samples the high density of defects limited the formation of both the \( \varepsilon \) and \( \tau \) phases \[113\]. As such, carbon doping
was not able to stabilise the $\tau$ phase and did not lead to a higher magnetisation. A high coercivity was obtained in C-free samples due to the high density of defects and equilibrium ($\beta$Mn) and $\gamma_2$ phases acting as domain-wall pinning sites.

Adding carbon over the solubility limit creates non-magnetic Mn$_3$AlC precipitates, decreasing both the grain size and the volume of $\tau$ phase material present [102], [114]. This greatly increases the coercivity but decreases the saturation and remnant magnetisation. However, at even higher carbon concentrations, the precipitates may also act as nucleation sites for the decay into the equilibrium ($\beta$Mn) and $\gamma_2$ phases, decreasing the coercivity, or at least preventing its increase, as well as further decreasing the magnetisation [94]. The addition of carbon also decreases the Curie temperature, as shown in figure 3.17c. Although this may prove problematic for high temperature applications, the decrease is only \(~20\%\) before the trend saturates at the solubility limit of carbon [109].

The most common heat treatment process used to produce $\tau$ phase MnAl is annealing of the quenched $\epsilon$ phase, typically between 300 – 600°C. The temperature and duration of annealing must be sufficient to facilitate the thermally activated boundary diffusion of the developing $\tau$ phase. However, too high a temperature or too long a duration leads to the accelerated decomposition of the $\tau$ phase into the equilibrium ($\beta$Mn) and $\gamma_2$ phases, degrading the magnetic properties [113].

### 3.3.5 MnAl thin films

Despite the interest in developing MnAl for bulk permanent magnets, efforts to develop thin films have been moderated by experimental challenges in fully realising the potential of the $\tau$ phase. Some studies have used MBE to deposit a few monolayers of Mn and Al to directly create the atomically ordered L1$_0$ structure which acted as a template for subsequent growth [13], [115]–[117]. This template was amorphous in the as-deposited state, but crystallised on annealing at approximately 200°C [13]. Thicker template layers required a higher annealing temperature, but this often led to the decomposition of the $\tau$
phase into the equilibrium $\gamma_2$ or ($\beta$Mn) phases [13]. It was found that a template thickness of two L1$_0$ unit cells was optimal. Subsequent $\tau$ phase film growth proceeded at the same elevated temperature by the co-deposition of Mn and Al until surface layers containing the equilibrium phases were observed by in-situ reflection high-energy electron diffraction. Higher substrate temperatures allowed the growth of thicker films before the equilibrium phases became dominant up to a maximum thickness of 60 nm, beyond which the $\tau$ phase could not form at all [117].

The remnant magnetisation was found to increase when the finished sample was rapidly annealed for 30s at temperatures up to approximately 500°C, as shown in figure 3.18 [116]. This allowed films up to 100 nm thick to be produced as the ordering was improved after deposition. The magnitude of the increase was very sensitive to the film thickness and annealing temperature. This was accompanied by a large reduction in coercivity due to the improved crystalline ordering and the reduction

Figure 3.18: Remanence and coercivity trends in different thicknesses of MnAl films deposited by MBE after annealing [116].

Figure 3.19: XRD spectra of epitaxial MnAl thin films after annealing at various temperatures [115].
in equilibrium phase pinning sites. Annealing at higher temperatures reduced the magnetisation and coercivity due to the degradation of the film into the equilibrium phases. This is evident in XRD spectra, shown in figure 3.19, where the \( \tau \) phase peak completely disappears above 550°C and the \( \varepsilon \) phase peak grows more intense [115].

All these studies used GaAs substrates grown with a terminating layer of AlAs which had a lattice parameter of 5.66 Å. This closely matches the (110) distance of the MnAl L1\(_0\) unit cell of 5.57 Å, with a difference of 1.6%. The L1\(_0\) film therefore grew epitaxially with the \( c \) axis orientated out of plane, giving perpendicular anisotropy [115], [116]. Interfacial diffusion and reactivity between the AlAs and the MnAl was minimal due to the large proportion of Al in MnAl [13].

An MgO substrate, rather than GaAs, is preferred for technological applications such as the MTJs described in section 3.1.1. The templating effect provided by the substrate strongly affects the resultant structure of the L1\(_0\) film. The lattice parameter of MgO is 4.212 Å, representing a difference of 6.7% with that of L1\(_0\) MnAl. This large difference produces a highly strained film. Biased target ion beam deposition has been used to deposit quasi-monomlayers of Mn and Al on MgO substrates with total film thicknesses varying between 3.4nm and 10.2 nm [118]. The substrate was heated to 500°C and etched with an ion beam for 30 minutes prior to deposition to remove surface contaminants. The ion beam energy was kept low at 35 eV to prevent roughening of the substrate. The films were deposited at room temperature as elevated deposition temperatures were found to decrease the ordering, presumably as the ordering was already optimised by the monolayer deposition method. XRD analysis revealed that the films were strained such that the bcc reduced unit cell, normally with a tetragonal distortion ratio \( c/a \sim 1.2 \), was no longer tetragonal but cubic, with \( c/a \sim 1 \). The value of \( c/a \) reduced with increasing film thickness, reducing \( K_u \) and even creating in-plane anisotropy for the thickest film. The 10.2 nm thick film had a saturation magnetisation of 394 emu/cm\(^3\). A Ta capping layer had been added to prevent oxidation. However, the saturation magnetisation reduced with decreasing film thickness due to the presence of a 2.7 nm magnetically dead layer caused by intermixing with the Ta cap layer. Although the use of a cap layer may
<table>
<thead>
<tr>
<th>Layer</th>
<th>Substrate/Seed (nm)</th>
<th>Thickness (nm)</th>
<th>Annealing Temperature (°C)</th>
<th>Deposition Temperature (°C)</th>
<th>$H_c$ (Oe)</th>
<th>$M_s$ (emu/cm$^3$)</th>
<th>Composition</th>
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<td>00</td>
<td>400</td>
<td>0000</td>
<td>250</td>
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<td>[12]</td>
</tr>
<tr>
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<td>030</td>
<td>000</td>
<td>300</td>
<td>30</td>
<td>Mn$<em>{60}$Al$</em>{40}$</td>
<td>[12]</td>
</tr>
<tr>
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<td>050</td>
<td>000</td>
<td>300</td>
<td>60</td>
<td>Mn$<em>{60}$Al$</em>{40}$</td>
<td>[12]</td>
</tr>
<tr>
<td>W$_{55}$/Cr (40)</td>
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<td>0</td>
<td>000</td>
<td>000</td>
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<td>20</td>
<td>Mn$<em>{60}$Al$</em>{40}$</td>
<td>[12]</td>
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<tr>
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<td>000</td>
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</tr>
<tr>
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<td>000</td>
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</tr>
<tr>
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<td>000</td>
<td>000</td>
<td>010</td>
<td>Mn$<em>{60}$Al$</em>{40}$</td>
<td>[12]</td>
</tr>
</tbody>
</table>

Table 3.4: Fabrication properties and magnetic results of various sputtered MnAl thin films. (a) No data available. (b) Annealed in a magnetic field of 4 kOe applied perpendicular to the plane of the film. (c) A 5 nm dead layer was subtracted from this in order to calculate $M_s$. 

Magnetic field of 4 kOe applied perpendicular to the plane of the film.  $M_s$ was calculated from this in order to calculate.
be deemed necessary, it represents a potentially undesirable additional degree of freedom in an already complex experimental process.

The ability to manufacture L1₀ ordered thin films of MnAl using sputtering is essential for their integration with new and existing technologies. However, a wide range of process parameters must be optimised to achieve good ordering. Some key properties and results of sputtered MnAl thin films from the literature are summarised in table 3.4. Each entry represents the best result from each study. The variety of values of the parameters therefore highlights the complex dependencies present in this system, making process optimisation highly non-trivial.

The sputtering targets used so far have mostly either been alloys [14], [15], [96], [119] or composites made from strips of Mn overlaid on an Al target [12], [120], [121]. Composite targets represent a convenient way to control the effective target elemental composition. Systematic investigations of the composition using this method were able to produce the τ phase in the range of 40-60 at% Mn, although only the film with 50 at% Mn gave strong ordering. Films with ±6 at% Mn contained the non-magnetic equilibrium phases and consequently had a much reduced magnetisation [120]. However, the precision of this composite target control is fairly poor and not suitable for long term use. On the other hand, alloy targets restrict investigations to a single composition ratio, which is unlikely to be reproduced in the film itself due to the difference in momenta of the two different atoms when interacting with the sputtering working gas. Careful calibration and tight process control is therefore required before deciding on the final target composition in order to achieve the optimal Mn to Al ratio at the substrate. An alternative approach is to emulate the initial layered deposition of MBE on a nanometer scale, relying on post-deposition annealing to then complete the ordering process of the multilayers of Mn and Al via atomic diffusion [122], [123]. A simpler variation of this is the continuous co-deposition of Mn and Al as done with MBE. This has the advantage of allowing convenient control over the elemental ratio by altering the power applied to each target, which is able to dynamically compensate for the difference in elemental ratio observed at the substrate from alloy targets.
Glass substrates are commonly used in sputtering studies \([12], [96], [120], [121]\). However, the amorphous surface provides no templating effect, which has previously been shown to promote the formation of the \(\tau\) phase. Despite this, the conditions may still be optimised to produce good ordering, although the films investigated were rather thick at 600-800 nm. It was found that the films deposited at lower substrate temperatures had a greater degree of \(\varepsilon\) phase crystal ordering, allowing them to realise the best conversion to the \(\tau\) phase after annealing \([120]\). This emphasises the importance of achieving good crystallinity in the as-deposited films, as annealing is not able to produce the \(\tau\) phase without well-ordered regions of the precursor \(\varepsilon\) phase, or better still nuclei of the \(\tau\) phase itself.

![Image](image.png)

**Figure 3.20:** Saturation magnetisation and anisotropy trends in 30 nm MnAl thin films sputtered onto Si/TiN(10 nm) and annealed at 350°C \([15]\).

Silicon substrates have also been used as MnAl thin films have poor adhesion to glass \([15], [96], [119], [123], [124]\). Various seed layers have been used, most notably MgO \([124]\) and TiN \([15]\), requiring the native oxide to be stripped from the Si substrate by hydrofluoric acid immediately prior to deposition. As shown in figure 3.20, the cubic texture of these seed layers gave well-ordered films just 30 nm thick with a saturation magnetisation of approximately 600 emu/cm\(^3\) when deposited at 425°C and annealed at 350°C. This is higher than the typical bulk value given in table 3.1, but still well within the ideal theoretical limit of approximately 740 emu/cm\(^3\) \([125], [126]\). However, the highest anisotropy was observed for films deposited at 400°C, which had a lower \(M_s\) of approximately 400 emu/cm\(^3\) \([15]\). This emphasises the incredibly sensitive nature of the \(\tau\) phase formation to the process conditions. Due to the strong templating effect of single crystal MgO substrates, it is not expected that crystallographic trends will
directly translate to other substrates, which will affect the deposition and annealing temperatures required to achieve well-ordered L1₀ films.

In order to reduce the lattice mismatch of 6.7% between MgO and L1₀ MnAl, a Cr buffer layer has been used on a single crystal MgO substrate [14], [57], [127]. However, it is not clear how the beneficial templating effect of the MgO substrate may propagate through the relatively thick 40nm Cr buffer layer. Despite this, XRD results shown in figure 3.21 indicate good ordering in films deposited at 200°C. Evaluating a variety of alloy targets suggested an optimal film composition of approximately Mn₅₄Al₄₆ obtained from a target composition of Mn₄₈Al₅₂. Deposition conditions for the sample series shown in figure 3.21a, produced by Hosoda et al. [14], and figure 3.21b, produced by Saruyama et al. [57], were almost identical apart from a different type of target, a lower base pressure and a higher growth rate for the series produced by Hosoda et al. These differences appear to be enough to affect the ordering temperature and resultant saturation magnetisation. Annealing at 450-500°C is required for the samples produced by Hosoda et al., who
achieved an $M_s = 600$ emu/cm$^3$, whereas the $\tau$ phase is immediately present in the as-deposited films produced by Saruyama et al. Annealing the films of Saruyama et al. has no affect up to the relatively low temperature of 400°C, although they found a maximum saturation magnetisation of 530 emu/cm$^3$ in films deposited at 250°C. Although the targets used in both studies were nominally of the same composition, Saruyama et al. used a molten target, giving a film composition of Mn$_{56.9}$Al$_{43.1}$, whereas Hosoda et al. used a sintered target giving a film composition of Mn$_{54.1}$Al$_{45.9}$. The composition given by the sintered target yielded superior magnetic properties, although impurities in the target increased the surface roughness of the film [127]. It is likely that the excess Mn in the films grown by Saruyama et al. stabilised the $\tau$ phase even in the as-deposited state, which also reduced the saturation magnetisation due to the antiferromagnetic coupling of Mn occupying Al sites in the L1$_0$ lattice.

3.4 Summary

Spintronic devices form key components of many modern technologies, especially current and future magnetic data storage solutions. Although great progress has been made with the development of magneto-resistive technologies, the continued need for higher storage areal densities requires new innovations and magnetic materials with high perpendicular magnetocrystalline anisotropy.

L1$_0$ ordered materials are promising candidates, having high anisotropies of the order of $10^7$ erg/cm$^3$. The magnetic properties of these binary alloys are dependent on their chemical ordering and crystal structure, requiring structural characterisation to fully understand their behaviour. High temperature processes are often required to facilitate the atomic diffusion necessary for the chemical ordering to take place.

L1$_0$ ordered FePt has a very high anisotropy of $7 \times 10^7$ erg/cm$^3$ [73], [128], making it an excellent candidate for use as a storage medium in heat assisted magnetic recording. Strict control of the ordering and grain size is required to fully realise its potential in practical devices. MnAl is of particular interest as an L1$_0$ ordered material with the advantage of
low spin-orbit coupling and low magnetic damping. This makes it ideal for use as a spin polariser in magnetic tunnel junctions. However, in order to produce such nano-scale devices, the material must be fabricated as thin films. Previous studies have mostly focussed on bulk samples or epitaxial thin films, but optimisation of thin film growth by sputtering is required for mass production. The metastable nature of the L10 ordered $\tau$ phase makes its stabilisation at room temperature a challenge, requiring delicate calibration and simultaneous optimisation of the fabrication conditions. Care must be taken to prevent the nucleation and growth of the non-magnetic equilibrium phases. The ordering is especially sensitive to the elemental composition, the deposition temperature and the annealing conditions.
Chapter 4

Experimental techniques

This project utilises a variety of experimental techniques to characterise magnetic thin films. Structural properties are of paramount importance, including crystal structure, orientation and interface quality. All of these are directly responsible for the magnetic properties and behaviour of the component materials in a spintronic device. It is thus essential to be able to verify the structure in order to evaluate the functionality of the device and ensure the fabrication methods are working as expected and to a good enough standard. Sputtering is used as a convenient deposition method, providing high purity, homogenous deposition of multiple materials simultaneously. Transmission Electron Microscopy (TEM) provides direct observation for structural characterisation at sub-nanometre resolution, as well as other complimentary techniques for crystal structure and elemental analysis. X-ray diffraction and reflectivity are useful techniques for the inspection of the overall crystalline and layer structure as well as interface roughness. Magnetic measurements with techniques such as Vibrating Sample Magnetometry (VSM) are essential for evaluating the overall magnetic properties of thin films and hence their potential performance in devices.
4.1 Sputtering

Fabrication by sputtering has several advantages over other thin film growth methods, such as molecular beam epitaxy or thermal evaporation commonly used for atomic layer deposition. It is a relatively rapid process, requiring only minutes of deposition and preparation time, making it suitable for high throughput production. Sputtering is also a versatile method, seamlessly allowing many high purity materials to be deposited simultaneously or consecutively to form high quality alloys or multilayer structures respectively.

Sputtering refers to the process by which a target surface is eroded by high energy incident particles, creating a plume of ejected target material which coats the sample substrate. A high base vacuum is necessary, typically $10^{-7} - 10^{-9}$ Torr, to prevent contamination [57], [96]. A sputtering gas, typically Ar, known as the working gas, is then introduced into the chamber, reaching an operating pressure of approximately 3-10 mTorr. The purity of this gas, ideally 99.9999% pure, is important for ensuring the high quality of the films. A negative bias is applied to the target, typically 100 V, establishing an electric field between the target and the grounded substrate. Mobile electrons ionize the Ar, creating a plasma. The positive ions are accelerated towards the target, impacting with sufficient energy, $E$, to cause displacement and ejection of the target atoms. As a first approximation, the sputtering yield, $S$, is given by elastic collision theory as [129]

$$S = \frac{k}{\lambda(E) \cos \theta (M_i + M_t)^2} E$$  \hspace{1cm} (4.1)

where $k$ is a constant related to the target material, $\lambda(E)$ is the mean free path near the target as a function of ion energy, $\theta$ is the angle of incidence from the normal of the ions, $M_i$ is the mass of the bombarding ion and $M_t$ is the mass of the target atom. The sputter rate is therefore controlled by the target bias, which affects the incident ion energy. The deposition rate is further influenced by the mean free path of sputtered atoms in the space between the target and the substrate, typically a few millimetres [129], controlled by the operating pressure, as well as the atomic mass of the target material. Materials with a
higher mass will lose less momentum when interacting with the working gas, and will therefore reach the substrate at a higher rate than materials with a lower mass. Sputtered atoms have a large angular and energy distribution due to the inelastic nature of collisions inside the target and also with the working gas, making analytical calculations challenging.

Conductive materials may be sputtered using a Direct Current (DC) target bias. To prevent charge build-up, insulating materials require an alternating bias, a technique known as Radio Frequency (RF) sputtering [130]. Due to the difference in mobility between the Ar ions and electrons, a reverse bias applied for a short enough time will not result in sputtering of the sample surface. Care must be taken with materials with poor thermal conductivity, such as ceramics, to avoid rapid heating, potentially causing cracking of the target. Such problems can be mitigated by using a copper backing plate to improve the thermal contact with the bias terminal.

The sample substrate may be heated for a variety of reasons. It is useful to bake the substrate prior to deposition in order to evaporate any residual impurities. High temperatures may be required for the formation of certain crystal phases, either during the deposition process or as a post-deposition anneal. However, the surface roughness of the sample increases at higher deposition temperatures due to the higher mobility of the target atoms on the growing sample surface. For efficient thin films multilayer devices based on electron tunnelling, atomically flat interfaces are ideally required, making the deposition temperature a critical condition.

The initial growth of the film and surface coverage of the substrate proceeds via a nucleation process. Incident atoms are fairly mobile over the substrate surface depending on the substrate temperature and will interact with each other to form clusters. As these clusters grow they form islands, known as Volmer-Webber type growth [129]. As more material arrives at the substrate these islands grow laterally in order to minimise their surface energy until they begin to coalesce. At this point, grain boundaries will be formed, creating a polycrystalline film if the orientation of the growing nuclei was random, or an epitaxial film if they were orientated parallel.
4.1.1 Magnetron sputtering

In order to increase the efficiency of ionisation, a technique known as magnetron sputtering may be used, in which a magnetic field is applied parallel to the target surface [130]. The principle mechanism is illustrated in figure 4.1. Electrons move under the influence of the Lorentz force due to the perpendicular electric and magnetic fields, following a closed circular path above the target. This confines the electrons to a small volume just above the target surface, creating a higher density plasma and increasing the sputtering rate. The magnetic field also prevents electrons from reaching the substrate, where they might otherwise lead to unwanted heating effects or exposure of lithographic resist.

Although magnetron sputtering increases the sputtering rate, allowing lower Ar operating pressures, the target is not uniformly eroded due to the localisation of the electrons by the magnetic field, creating a ring shaped groove in its surface. Magnetic materials with a large susceptibility strongly attenuate the magnetic field, causing lower relative sputtering.

Figure 4.1: The mechanism of magnetron sputtering. A magnetic field near the target traps electrons, creating a plasma with the Ar gas. Ar$^+$ ions are accelerated into the negatively biased target, causing erosion of the target material (Tg) which condenses as a film on the sample.
rates. These effects may be minimised by using a thin target with less material and removing the central magnet to divert the field to the edges of the target.

4.1.2 Remote plasma sputtering

An alternative technique for plasma confinement is known as remote plasma sputtering, or high target utilisation sputtering [131]. In this configuration, the plasma is generated outside the main chamber then guided on to the target by magnets, shown in figure 4.2. The plasma is produced via the interaction of electrons with an RF antenna operated at 13.54 MHz in a DC magnetic field. The long spiralling paths of the electrons as they are guided down onto the target ensure a uniformly high density plasma reaches the target. The plasma is thus able to erode the entire target surface, dramatically improving the target use efficiency when compared with the small fraction used by the ring-shaped plasma in magnetron sputtering. However, the plasma alone does not have sufficient energy to sputter the target, requiring a separate bias voltage to accelerate the ions towards the target. This decouples the plasma generation from the sputtering process, allowing independent control over the plasma energy and the incident energy of the bombarding ions.

![Figure 4.2: Remote plasma sputtering. The Ar plasma is generated externally then guided onto the target by magnets, causing erosion of the target material (Tg).](image)
ions. This may then influence the energy of the sputtered atoms and their eventual crystal structure. However, due to the close proximity of the plasma to the substrate, this technique may not be suitable for materials sensitive to electron exposure such as lithography resist which may be exposed by the electrons in the plasma.

4.2 Transmission Electron Microscopy

Transmission Electron Microscopes (TEM) were first developed to overcome the resolution limit of visible-light microscopy. They consist of a parallel beam of high-energy electrons accelerated to approximately 200 kV impacting on a thin sample. A high vacuum of approximately $10^{-8}$ Torr is required to prevent contamination of the delicate sample and system components. The transmitted beam is magnified and focused onto either a fluorescent screen or a CCD camera. An image or a diffraction pattern may be formed depending on the projection system settings. A major variation is Scanning-TEM (STEM), in which the beam is focused to a point probe and raster scanned across the sample, rather than parallel illumination, giving several advantages for atomic resolution imaging. The incident beam causes the emission of characteristic X-rays from the sample, giving rise to techniques such as Energy-Dispersive X-ray spectroscopy (EDX), which, in a STEM system, allows spatially-resolved elemental analysis.

4.2.1 Electron Optics

An image of a point-like object will not resolve to a point, but rather consist of a central maximum haloed by secondary maxima of diminishing intensity. This is due to diffraction caused by the finite size of the objective lens, and is known as the Airy disk [132]. The smallest separation of two objects at which they can still be distinguished, $\delta$, is thus governed by the size and overlap of their Airy disks. This is known as the resolving power of a microscope and is generally defined by the Rayleigh criterion.
\[
\delta = \frac{0.61 \lambda}{\eta \sin \beta}
\]  \hfill (4.2)

where \(\lambda\) is the wavelength of radiation, \(\eta\) is the refractive index of the viewing medium and \(\beta\) is half the collection angle of the objective lens [133]. This defines the limit as the distance at which the central maximum of the first Airy disk coincides with the first minimum of the second [132]. The denominator of equation (4.2) is also known as the numerical aperture, and is fixed by the design of the lenses. For practical microscopes, this does not generally exceed 1.3, making wavelength the deciding factor. Even using blue light with \(\lambda = 400\) nm, this makes the best realistic resolution of a visual-light microscope no more than approximately 200 nm.

The concept of wave-particle duality allows us to think of using electrons as the radiation, which have much smaller wavelengths than visible-light photons. The de Broglie relation gives the wavelength of a particle as

\[
\lambda = \frac{h}{p}
\]  \hfill (4.3)

where \(h\) is Planck’s constant and \(p\) is its momentum. Electrons are given momentum by accelerating through a potential difference, \(V\), converting this potential energy, \(eV\), into kinetic energy. Most TEMs operate with \(V = 100 – 300\) kV, giving velocities of the order of half the speed of light, necessitating relativistic calculations. The total energy of the electron is given by

\[
E = \sqrt{p^2c^2 + m_0^2c^4}
\]  \hfill (4.4)

where \(c\) is the speed of light in a vacuum and \(m_0\) is the rest mass of an electron. Rearranging for \(p\) and substituting into equation (4.3) gives

\[
\lambda = \frac{hc}{\sqrt{E^2 - m_0^2c^4}}
\]  \hfill (4.5)
The total energy may also be thought of as the simple summation of the kinetic energy, \( eV \), and the rest mass energy, \( m_0c^2 \). Substituting these values gives

\[
\lambda = \frac{hc}{\sqrt{(eV + m_0c^2)^2 - m_0^2c^4}}
\]

\[
= \frac{hc}{\sqrt{e^2V^2 + 2eVm_0c^2 + m_0^2c^4 - m_0^2c^4}}
\]

\[
= \frac{hc}{\sqrt{eV(2m_0c^2 + eV)}} \quad (4.6)
\]

This defines the relationship between the accelerating voltage of the microscope and the wavelength of its electrons. Wavelengths and velocities for commonly used accelerating voltages are given in table 4.1.

<table>
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<th>Accelerating voltage (kV)</th>
<th>Wavelength (nm)</th>
<th>Velocity (c)</th>
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<tr>
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<tr>
<td>300</td>
<td>0.00197</td>
<td>0.777</td>
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*Table 4.1: Electron properties of some commonly used accelerating voltages for TEM microscopes.*

The electron beam is focused by magnetic lenses, such as the dipole lenses shown in figure 4.3. The magnetic field is established between two soft-iron polepieces, created by either one or two solenoids. A split polepiece design, shown in figure 4.3b allows convenient insertion of an aperture or sample into the plane of the lens.

Despite the pico-metre scale of electron wavelengths, practical TEMs are limited to a resolution of approximately 0.1 nm by various aberrations introduced by these lenses, including spherical, chromatic and astigmatism [133].
Spherical aberration is the most critical, having the greatest detrimental effect at high resolutions. This is caused by a lens focusing electrons more strongly the further away they are from the optic axis, causing a broadening of the Gaussian image formed by a point object. For paraxial incident rays, the radius is given by 

\[ \delta = C_s \beta^3 \]

where \( C_s \) is a constant aberration factor and \( \beta \) is the collection angle of the lens, shown in figure 4.3. \( C_s \) is a unit of length, normally approximately equal to the focal length of the lens, and is related to the cyclotron frequency of the electrons, \( \omega_c \), by

\[ C_s = \frac{\pi m v}{e B} = \frac{\pi v}{\omega_c} \quad (4.7) \]

where \( m \) is the electron mass, \( v \) is its velocity, \( e \) is the electron charge and \( B \) is the induction field of the magnetic lens. For the objective lens in most TEMs, this is 1-3 mm [133]. However, advanced modern instruments are now able to correct for this aberration with extra lenses to introduce compensating magnetic fields, allowing sub-Ångstrom probe sizes in STEM.

Chromatic aberration refers to electrons with more energy being more weakly focused than those with less energy. This leads to a similar spread of the Gaussian image as with spherical aberration, expressed as

\[ C_s = \frac{\pi m v}{e B} = \frac{\pi v}{\omega_c} \]

Figure 4.3: Magnetic dipole lenses used for focusing the electron beam. (a) single coil, (b) split polepiece coil allowing the insertion of an aperture to limit the collection angle of the lens, \( \beta \).
\[ \delta = C_c \frac{\Delta E}{E_0} \beta \]  

(4.8)

where \( C_c \) is the chromatic aberration coefficient, which is again roughly equal to the focal length of the lens, \( \Delta E \) is the width of the energy distribution and \( E_0 \) is the initial energy. One possible source of this effect is the electron source, or gun. Older, or more basic TEMs use thermionic emission to extract electrons. Due to the high temperature required, tungsten used to be the material of choice, operating at 2700 K. Lanthanum hexaboride, LaB\(_6\), is now used for these guns due to its lower work-function, allowing two orders of magnitude higher current density and a lower emission temperature of 1700 K, giving ten times the operating life-time. The energy distribution width is also halved from 3 eV to 1.5 eV at an accelerating voltage of 100 kV [133]. However, the best sources are Field Emission Guns (FEGs), which use an extremely high electric field concentrated at a very fine tungsten tip to extract electrons through tunnelling, often assisted by moderate heating. These sources require much better vacuums to keep the surface free of contaminants, however, they give an energy distribution width of less than 1 eV. For all sources, the width of the energy distribution is clearly a very small proportion of the magnitude, making this aberration only important if \( C_s \) has already been corrected. However, inelastic scattering within the sample introduces the main source of energy variation, which could be up to 25 eV for a typical 100 nm metal film. It is therefore important to make samples as thin as possible.

Astigmatism is caused by electrons experiencing a non-uniform magnetic field at different azimuthal positions within the column. This can be caused by microscopic imperfections in the polepieces, or by charged contamination on the apertures. This aberration is easily corrected by octopole stigmator lenses introducing a compensating field.

4.2.2 Electron Scattering

TEM relies on the electron beam interacting with the sample during transmission, causing scattering to produce regions of higher or lower intensity in the transmitted beam, giving
contrast. As electrons are charged particles, interaction primarily occurs via the Coulomb force with both the nuclei and electrons in the sample, which is the major difference compared to X-ray diffraction. The amplitude of this interaction may be quantified for high energy electrons by a scattering cross section per atom, \( f(\theta) \), given by

\[
 f(\theta) = \frac{1 + \frac{E}{m_0 c^2}}{8\pi^2 a_0} \left( \frac{\lambda}{\theta \sin \frac{\theta}{Z}} \right)^2 (Z - f_x)
\]

(4.9)

where \( \theta \) is the scattering angle, \( E \) is the beam energy, \( m_0 \) is the rest mass of an electron, \( c \) is the speed of light in a vacuum, \( a_0 \) is the bohr radius, \( \lambda \) is the wavelength of the electrons, \( Z \) is the atomic number of the target atom and \( f_x \) is the scattering factor for X-rays [133]. This is derived from the Rutherford scattering cross-section, including relativistic corrections. The amplitude of a scattered beam is given by \( |f(\theta)|^2 \). The significance of this complex equation may be summarised by noting the proportionality relations. The function decreases with \( \theta \), thus beams scattered to higher angles will have a lower intensity. This forward bias is important for diffraction phenomena. The function increases with \( \lambda \), so a less energetic electron with a larger wavelength will be scattered more strongly. However, a lower electron energy will reduce the overall intensity of the transmitted beam. The function also scales linearly with \( Z \), meaning a sample of heavier elements will scatter the electron beam more strongly. All the materials used in this project have sufficiently high \( Z \) to ensure good interaction, with carbon being the usual lower limit for convenient TEM study.

The majority of contrast in low-to-medium magnification images of crystalline samples is caused by diffraction of the electrons away from the optic axis, resulting in lower intensity regions in the directly transmitted beam.

Inelastic scattering will also occur, although with a cross section up to four orders of magnitude smaller than elastic scattering [133]. The main mechanisms include ionisation and X-ray production, secondary electron emission, phonons and plasmons. Characteristic X-rays are of great interest, and are discussed further in section 4.2.4,
whilst most TEMs ignore secondary electrons and regard thermally activated diffuse scattering mechanisms such as phonons sources of background noise.

Diffraction techniques are essential for examining the micro-structure of crystalline materials. Diffraction patterns provide invaluable information on crystal quality, phase, orientation and lattice dimensions. The basis of diffraction can be briefly explained in the following way. Consider two atoms as scattering points with separation \( \vec{a} \) as shown in figure 4.4. An incident beam with wavevector \( \vec{k} \) will scatter from each point and re-radiate, with wavevector \( \vec{k}' \), in all directions, but will only interfere constructively and form a diffracted beam when the path difference is an integer multiple of the wavelength, \( \lambda \) [134]. For the geometry shown in figure 4.4, this is given by

\[
AB - CD = a \cos \theta_1 - a \cos \theta_2
\]

\[
= \vec{a} \cdot (\vec{n} - \vec{n}')
\]

\[
= h\lambda \tag{4.10}
\]

where \( \vec{n} \) and \( \vec{n}' \) are the unit direction vectors of the wavevectors \( \vec{k} \) and \( \vec{k}' \) respectively and \( h \) is an integer. For elastic scattering,
The von Laue condition may therefore be written in terms of the wavevectors as

$$|\vec{k}| = |\vec{k}'| = \frac{2\pi}{\lambda} \tag{4.11}$$

Equivalent equations may be written for the other two dimensions, typically using indices $k$ and $l$ in place of $h$. These indices, known as Miller indices, describe a reciprocal lattice of points which is a spatial Fourier transform of the crystal lattice [135]. Points in the reciprocal lattice are given by

$$\vec{g} = h\hat{a}^* + k\hat{b}^* + l\hat{c}^* \tag{4.13}$$

For the simple one dimensional example given here, the reciprocal lattice vector, $\hat{a}^* = 2\pi\lambda/\hat{a}$, hence a diffraction beam will only form if $\vec{k} - \vec{k}' = \vec{g}$.

Alternatively, the condition for diffraction may be derived by considering the crystal lattice as a set of parallel planes separated by a distance $d$ [134]. Beams incident at an angle of $\theta_B$ will reflect and interfere constructively if the path difference is an integer multiple of the wavelength. This produces Bragg’s law,

$$2d \sin \theta = n\lambda \tag{4.14}$$

where $n$ is an integer, which is equivalent to equation (4.12).

The conditions for diffraction may be visualised using the Ewald sphere construction. Consider a sphere in reciprocal space of radius $2\pi/\lambda$ centred at position $\vec{k}$ [134]. The diffraction conditions are met for a reciprocal lattice point if it intersects the boundary of the Ewald sphere. Ordinarily, the reciprocal lattice consists of an array of infinitesimal points. However, due to the finite thickness of TEM samples, the reciprocal lattice points are extended in the direction perpendicular to the plane of the sample into reciprocal
lattice rods, or ‘relrods’ [136]. This allows many more points to intersect the Ewald sphere. A wedge sample has two different sample planes, producing two relrods for each reciprocal lattice point and two diffraction spots in the pattern on either side of the central position for a planar sample [133]. The intensity of a diffracted beam is related to the distance, $s$, or deviance parameter [137], of its reciprocal lattice point from the Ewald sphere, and is proportional to the sinc function, $\sin(\pi s z_0) / \pi s z_0$ where $z_0$ is the thickness of the sample. A diffraction pattern from a twin boundary is shown in figure 4.5, showing the ring of intensity associated with the Ewald sphere from each twin.

The kinematic theory of diffraction, which is often used for quick simulations, relies on the assumption that samples will only cause incident electrons to scatter once [138]. However, electrons passing through a single crystal sample will most often experience multiple diffraction events, a process known as dynamical diffraction. Diffracted beams thus act as the incident beams of further coherent constructive diffraction events. This can lead to otherwise forbidden diffraction spots being present in the resultant diffraction pattern for a particular crystal structure. This is especially true for thicker samples as the interaction cross section increases. Samples are made as thin as possible to minimise the complex effects of dynamical diffraction.

For reliable analysis and indexing of diffraction patterns, it is important to align the sample with the beam such that it is parallel to a low-order axis of the crystal lattice, known as the zone axis. Once this alignment is achieved, the Ewald sphere and associated

Figure 4.5: A diffraction pattern from a twin boundary of MgAl$_2$O$_4$ showing the two rings of intensity where each Ewald sphere intersects the reciprocal lattice [133].
ring of high intensity is centred around the direct beam. The diffraction pattern would otherwise be distorted.

Another very useful tool for checking crystal alignment is the Kikuchi pattern, an example of which is shown in figure 4.6. This is formed of pairs of apparently parallel lines in the diffraction pattern, one bright and one dark, caused by diffusely scattered electrons then undergoing Bragg diffraction, as shown in figure 4.7. The lines are formed at an angle of $\pm \theta_B$ from the diffracting crystal plane. Due to scattering being biased in the forward direction of the incident beam, the scattered beam which is closer to its initial direction will have a higher intensity [135]. However, once this is Bragg diffracted, it will then appear at a higher angle in a region of lower diffuse background as a bright line. Conversely, the lower intensity beam is diffracted into a region of higher diffuse background, appearing as a dark line [136].

The deviance parameter is related to the separation of a Kikuchi line from the corresponding diffraction spot [137]. As these lines are fixed to the crystal planes, their position is very sensitive to the sample orientation. A low index zone axis may be
identified by a point of high symmetry in the Kikuchi pattern. Once the zone axis is aligned, one might expect the Kikuchi lines would disappear, being symmetrically distributed about the optic axis and therefore of equal intensity to the background. However, the lines are still evident, although a more detailed theoretical treatment, involving Bloch wave theory, is needed to explain their contrast mechanisms [133]. As these patterns are caused by dynamical diffraction effects, they are generally more visible in thicker regions where the spot pattern fades into the diffuse background.

This discussion holds for single crystal specimens, which produce patterns of well-defined spots. Many crystalline samples will instead be polycrystalline, with many crystal orientations presented to the beam at once. These samples therefore produce a simple diffraction pattern of concentric rings, one for each \( d \) spacing.

From Bragg’s law, crystal lattice spacings, \( d \), may be calculated using the camera length, \( L \), the electron wavelength and a calibrated scale for measuring distances in the pattern, \( R \), according to

\[
d = \frac{\lambda L}{R}
\]  

(4.15)

If the crystal structure is known, the pattern may then be indexed. Comparison with known standard patterns or simulations is also an extremely useful identification method. A camera length of 430 mm was used for the diffraction patterns in this study.

4.2.3 The Microscope

The combination and arrangement of lenses inside a practical TEM column is extremely complex, including quadrupole, hexapole and octupole magnets for tilting, shifting and shaping the electron beam. Simplified versions containing the principle focusing lenses and apertures for the most common operating modes are shown in figure 4.8 and figure 4.9. The simplest technique is known as bright field TEM, shown in figure 4.8a, which is discussed first.
Figure 4.8: Ray diagrams for (a) bright field TEM and (b) diffraction, showing principle lenses, focal planes and apertures. Coloured rays are a guide to the eye.
Figure 4.9: Ray diagrams for (a) dark field TEM and (b) scanning TEM, showing principle lenses, focal planes and apertures. Coloured rays are a guide to the eye.
The first lens is a simple electrostatic lens within the electron gun. This is either the Wehnelt cylinder for thermionic sources, or the anodes for a FEG source [133]. Its primary function is to localise the emission from the source in order to direct a beam down the column, forming a virtual point-source at the gun crossover which becomes the source subsequent lenses will focus on. This is further demagnified by the first condenser lens, known as ‘C1’. The second condenser lens, known as ‘C2’, may be adjusted to control the spread of the beam, forming the parallel beam necessary for TEM.

The objective lens is a split polepiece lens either side of the sample. The split polepiece design not only allows convenient sample loading, but also allows auxiliary instruments access to the sample, such as X-ray spectrometers or secondary/backscattered electron detectors.

The diffraction pattern is formed at the Back Focal Plane (BFP) of the lower objective lens. In order to improve the diffraction contrast in an image, an aperture may be inserted in the BFP, known as the objective aperture, to exclude strongly scattered electrons, producing a bright field image. Although a small objective aperture may improve the diffraction contrast, the resolution of the image is decreased due to excluding higher angle diffraction beams which have been formed by the smaller scale features of the sample. A larger aperture would not exclude this information, selecting more than one beam which would form a phase contrast image. Contrast is given by the periodic crystal lattice potential causing a phase difference between the previously coherent electrons, forming fringes, such as Moiré fringes, related to the atomic structure of the sample. Interpretation of these images is often challenging, as the fringes do not necessarily form a direct image of the sample, but are simply optical effects related to the size and orientation of the crystal lattice [133].

The intermediate lens is used to switch between imaging, as in figure 4.8a, and diffraction, as in figure 4.8b, modes. In imaging mode, this lens magnifies the image formed by the objective lens in the primary image plane. In diffraction mode, the focussing power of the intermediate lens is weakened by reducing the current in the electromagnetic coils to focus on the BFP of the objective lens. An aperture may also be inserted into the primary
image plane of the objective lens to select an area on the sample from which the
diffraction pattern should be formed, which is therefore known as the selected area
aperture. Diffraction patterns formed in this way are known as Selected Area Diffraction
Patterns (SADP). This can be useful in isolating a single crystal area of a polycrystalline
sample.

Alternatively, the objective aperture may be ‘moved’ to only select electrons from a
certain diffraction condition, forming a dark field image. In practice, to maintain
alignment of the aperture with the optic axis, the beam is tilted before reaching the sample
such that the diffracted electrons are directed down the optic axis as shown in figure 4.9a.

The final projector lens magnifies and focuses the image or diffraction pattern onto a
fluorescent viewing screen or CCD camera.

A major variation of TEM is scanning TEM (STEM), in which the source is demagnified
and focussed to a point probe and then raster scanned across the sample, as shown in
figure 4.9b. The transmitted intensity is used to build up an image of the sample pixel by
pixel. As such, this mode is only affected by lenses which influence the beam above the
sample, known as the illumination system. Lenses below the sample, known as the
projection system, are therefore excluded from figure 4.9b.

The size of the electron source is typically very large for thermionic sources,
approximately 10 µm [133], requiring the first condenser lens, to demagnify it in order to
form nano-scale point probes for STEM. The C2 lens is weakened to remove the
crossover. The objective lens now forms an image of the C1 crossover, which is more
strongly demagnified due to its greater distance. The size of the C2 aperture controls the
convergence angle of the STEM probe, and is useful for excluding excessive spherical
aberrations from the edges of the beam.

In order to achieve a focused probe for STEM, the upper objective lens acts as another
condenser lens, often called ‘C3’. In order to switch back to a parallel beam for TEM
without disturbing the objective lens, an extra ‘mini’ lens may be switched on above the objective lens to form a crossover at the front focal plane of the upper objective lens.

Scan/tilt coils are used to raster scan the beam across the sample in STEM mode, as well as tilting the beam for dark field imaging, shown in figure 4.9a. For scanning in STEM mode, the beam is tilted around the front focal plane of the upper objective lens to maintain a perpendicular beam at the sample.

To overcome the resolution limits of bright field TEM due to exclusion of the diffracted beams, Z-contrast images may be used to achieve sub-atomic resolution, which are given contrast by only collecting electrons scattered to high angles. A High Angle Annular Dark Field (HAADF) detector with a large central hole, thus ignoring the direct beam, is used to record the spike in intensity when the STEM probe is diffracted from one atom at a time [139]. Due to the Z dependency of equation (4.9), the signal is sensitive to the elemental structure and variation of the sample, providing qualitative elemental mapping [133].

4.2.4 Energy-Dispersive X-ray spectroscopy

As the sample is irradiated with high energy electrons, ionisation inevitably occurs. When an electron in a core shell is excited to a continuum state, an orbital electron from a higher shell fills the gap, releasing a photon with an energy equal to the difference in the electron energy levels. These are known as characteristic X-rays, and form a well-defined unique spectrum for each element. Analysis of these emitted X-rays is known as Energy-Dispersive X-ray Spectroscopy (EDX), and allows both qualitative and quantitative elemental analysis of a sample [138]. For quantitative measurements, a ratio of composition, $c_A/c_B$, for a binary alloy may be derived from the ratio of intensity peaks, $I_A/I_B$ by

$$\frac{c_A}{c_B} = k_{AB} \frac{I_A}{I_B}$$

(4.16)
Measurement of the calibration factor, known as the k-factor, is thus essential, requiring known calibration standards of each element [140]. A STEM probe is used to provide sufficiently intense electron flux to generate a high X-ray count, giving practical acquisition times of a few minutes to an hour. A larger C2 aperture is often used to allow a higher beam current, although this increases the probe size and sacrifices some resolution. Practical EDX is possible with probe diameters down to approximately 1 nm, although the interaction volume will be slightly larger due to scattering [140]. If the probe is used to scan a certain area, a spatially-resolved nano-scale elemental map may be obtained, providing invaluable characterisation for structures such as core-shell nanoparticles and interface analysis of multi-layer structures. Due to electrons scattering in all directions, many X-rays are also emitted from the copper support grid, the sample holder and the TEM column itself. Using a low-background grid and sample holder, typically made of beryllium, can help to reduce these unwanted signals [133].

4.3 TEM sample preparation

The quality of a TEM image and its analysis is directly dependent on the quality of the sample, regardless of the quality of the microscope [133]. As such, sample preparation may be regarded as a key aspect of TEM, and is where the most time and effort should be invested.

A general prerequisite of transmission microscopy is that the sample must be transparent. For electron transparency, samples must be typically no more than 100 nm thick, and ideally should be less than this [141]. There are a variety of sample preparation techniques that can satisfy this condition, either by directly producing sufficiently thin samples, or by thinning bulk materials. This project does not use any materials with light elements that would not interact with the electron beam, making contrast-enhancement techniques such as heavy-metal staining unnecessary [141]. All samples used in this project are also inherently conductive, avoiding charging problems and any need to apply a conductive coating.
Due to the limited size of the sample holder in the microscope, the lateral sample dimensions must be no larger than 3 mm [141]. A metal washer, typically copper, may be used as a support structure for smaller, fragile samples. Some washers contain a fine metal or carbon mesh, which in turn supports any sample placed upon it, allowing inspection through the holes in the mesh. Washers without meshes are used for self-supporting samples that may simply be glued to the edge of the washer, overhanging the central hole.

Some materials, such as vapour-deposited materials or nanoparticles, may already be sufficiently thin for inspection. However, they most often require a continuous, solid substrate, such as a silicon wafer, making meshes impractical. Back-etched silicon nitride membranes are commonly used as TEM support structures, and are commercially-available with window sizes of 500 μm square from 10-200 nm thick in a 3 mm silicon chip. Samples may be deposited directly onto the polished front surface, as long as the total combined thickness of sample and membrane does not preclude electron transparency.

However, depositing samples onto a silicon nitride membrane is not always possible, either because the sample is a bulk material or because a different substrate material is required. In these cases, the sample must be thinned after fabrication to achieve electron transparency. A variety of techniques are available to suit specific materials, each of which have certain advantages and disadvantages. The correct technique should ideally be efficient whilst incurring minimal change, damage and artefacts in the sample. Preliminary preparation of bulk samples involves cutting, sawing or, for crystalline materials, scribing and cleaving to fit within the 3 mm diameter sample holder. Initial thinning is often done by mechanical polishing, which involves placing the sample on a flat, spinning, abrasive disk, or lapping film, as illustrated in figure 4.10. The sample is moved radially.

![Figure 4.10: Diagram showing the layout of the wedge sample, polished in the direction of the large arrow.](image-url)
to utilise the full area of the disk. These lapping films consist of abrasive granules, typically silica or diamond, bound to plastic sheets, which may be fixed to a spinning platen. Decreasing grades of coarseness are used sequentially to achieve a finer and finer finish, with each grade removing the scratches caused by the last. A general rule of thumb is that each grade should remove a layer of material three times thicker than the previous granule size [141]. Water or some other appropriate lubricant is used to cool the sample and remove loose debris. Rather than polishing parallel-sided samples, a slight wedge angle can be included to maintain structural integrity via a variation known as tripod polishing. This can vary from 0.2° - 2° or more depending on the required size of the electron transparent area [142]. The sample is typically aligned with respect to the direction of rotation of the disk so that the thinnest edge of the wedge is trailing, and therefore protected from any chunks of debris that might impact with the leading edge.

Another very commonly used technique is ion milling. This is a versatile technique utilising a beam of high energy ions, typically ~30 keV, to remove material by sputtering the sample [143], [144]. This may be applied to almost any material, achieving a large, electron-transparent area of the order of 100 µm wide of uniform thickness. Focused Ion Beam (FIB) milling is the most precise technique for selecting a particular area of interest, with a spatial resolution of ~20 nm [144]. This makes it an invaluable tool for preparing cross-section samples of nano-scale, multi-layer films.

Mechanical polishing is often only used to reach a sample thickness of the order of 10µm, with Focused Ion Beam (FIB) milling used for final thinning [141]. However, this introduces defects such as implantation of the ions and an amorphous surface layer [144]. Localised heating can also induce phase changes in crystalline materials, further limiting its suitability for the samples considered in this project [145]. Using a low incidence angle (~ 1°) and a lower ion energy (~1 keV) can greatly reduce ionic damage [144]. However, the amorphous surface layer remains non-negligible, and lower ion energies can even increase the surface roughness of the sample [143].
Figure 4.11: HRTEM images showing a comparison of sample preparation techniques: (a) ionic thinning, showing the amorphous surface layer and (b) mechanical polishing [145].

The specific technique used is a further modification of tripod polishing. The sample is moved radially over the disk by an automatic arm, with the wedge angle maintained by the sample holder attachment. This is done using an Allied High Tech Multiprep polishing system, shown in figure 4.12. This system also allows control of the disk rotation speed and the downward force applied to the sample, as well as using digital micrometres to monitor the amount of material removed.

Figure 4.12: Allied High Tech Multiprep polishing system used for sample preparation in this project [146].

Figure 4.11 shows a comparison of FIB thinning and a sample prepared only by mechanical polishing all the way to electron transparency for a crystalline SrTiO$_3$ substrate. Wedge polishing was able to achieve a lower surface roughness with no amorphous layer, allowing easier image interpretation and even atomic resolution [145]. Mechanical polishing is also typically a faster, less expensive thinning technique, albeit requiring a more hands-on approach. A simple, plan-view sample may be prepared in a matter of hours, avoiding potentially lengthy ion milling times of up to a few days [141]. Its efficiency and lack of severe artefacts makes mechanical polishing the technique of choice for this project. No ionic polishing was used for sample preparation in this project.
The specific procedure used for preparing a thin film plan-view sample is as follows:

1. **To trim the sample.** A small scratch is made with a fine-tip diamond scribing pen on the backside of the substrate. Glass running pliers are used to cleave the sample.

2. **Preparing the sample holder.** Prior to mounting the sample, the sample holder must be planarised to ensure eventual flatness of the sample itself. This is done by polishing the sample holder at 0° angle on the 15 µm lapping film, and again on the 6 µm lapping film.

3. **To mount the sample.** The sample holder is heated on a hot plate to 150°C. A small drop of mounting wax is deposited with a toothpick at the front edge. The sample is placed film-side-down on the drop, aligned parallel to the edge and gently pressed down to eliminate any bubbles. This protects the film from damage during polishing. The setup is shown in figure 4.10.

4. **To set the angle.** The desired wedge angle is set by adjusting the micrometers on the Multiprep attachment. This is typically 2°, although more brittle samples require a steeper angle to maintain structural integrity.

5. **To polish the sample.** The following polishing steps are taken, monitoring the amount of material removed throughout to achieve the target thickness at each step. The sample thickness is periodically checked under a calibrated visible-light microscope by first focusing on the top surface of the wedge tip, then focusing on the sample holder surface. Water is used as a lubricant, and loose debris is removed by a sponge held against the lapping film.
Optical thickness fringes should become apparent once this is complete. The sample is briefly polished a few times on the 0.5 μm lapping film to remove scratches with extra lubrication. This caution is mostly due to the fragility of the lapping film itself.

6. **Finishing steps.** The lapping films are replaced by a felt platen to carry out the following final steps.

<table>
<thead>
<tr>
<th>Finishing step</th>
<th>RPM</th>
<th>Duration (mins)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica suspension (200nm)</td>
<td>30 → 80 → 50</td>
<td>2</td>
</tr>
<tr>
<td>Cleaning with soap</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Rinsing with water</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Rinsing with DI water</td>
<td>50</td>
<td>5</td>
</tr>
</tbody>
</table>

7. **To unmount the sample.** The sample holder is placed face-down on a tissue and immersed in acetone to dissolve the mounting wax. The sample is allowed to fall free onto the tissue. The tissue is removed from the acetone and placed upside-down over a second clean, dry tissue. As the acetone evaporates, any sediment is absorbed by the wet tissue until the sample falls free to the dry tissue. This hand-free process avoids damaging the now very fragile sample.

8. **To re-mount the sample.** A small drop of epoxy glue is placed onto the edge of a 3 mm copper washer using a toothpick. The washer is held in a pair of tweezers and the glued region brought down on the thicker edge of the sample such that the
thinnest edge overhangs the central hole. The washer and sample are placed on a hot plate to cure. Care should be taken to ensure only just enough glue is used, as too much may smother the sample or allow the sample to drift before the glue hardens.

**Figure 4.13:** Sandwich technique used for preparing cross-section samples. (a) Two slices of the substrate (grey) are glued (black) together face-to-face, protecting the sample (red). (b) The sandwich is then polished flat on one side, and (c) wedge polished on the other side, creating an electron transparent region of interest.

Cross section samples may be prepared by a method known as the sandwich technique, shown in figure 4.13 [141]. This involves gluing two slices of the sample face-to-face, such that the thin film is protected between two layers of substrate. The sandwich is then polished flat on one side to prevent electron scattering from surface roughness, and wedge polished from the other side to create the electron transparent region.

The potential difficulties of mechanical polishing lie in the mechanical properties of the sample. A sample made of different materials, such as a dispersion embedded in resin, or a cross-section sandwich glued together, may be abraded at different rates, leading to different thicknesses or even loss of the region of interest. Preferential polishing of the glue line in a cross-section sandwich may be regarded as desirable, as it further thins the region of interest. To avoid this effect causing drastic thickness contrast, and prevent the loss of any valuable material, the glue line should be made as thin as possible (∼50 nm) [145]. Brittle materials, such as the single crystal MgO substrates used in this project, are also challenging due to their tendency to fracture and crumble rather than be smoothly
eroded. This fragility can be reduced by polishing in a direction that is not perpendicular to any crystal planes, thus reducing its tendency to cleave and fragment.

Sample preparation is crucial to the success of any TEM study. Care must be taken to ensure the sample preparation technique does not alter or damage the sample. The mechanical polishing technique described here is capable of preserving the crystallinity of the sample, and provides large regions of uniformly electron transparent material in just a few hours. This makes it the technique of choice for the crystalline materials investigated in this study.

4.4 X-ray diffraction

X-ray diffraction is an ideal technique for the analysis and evaluation of the overall structural properties of crystalline thin films. Compared with TEM, it allows a non-destructive, relatively quick and simple identification of the crystal phases present and analysis of the crystalline quality and orientation. Although it is an indirect observation technique, typical wavelengths used in the laboratory are in the single angstrom range, in principle allowing the exact atomic structure to be investigated and modelled. In contrast with the limited field of view of TEM, a beam of X-rays may cover the entire sample surface, penetrating to a typical depth of several hundred nanometres dependent on the electron density of the sample material [147]. This provides a convenient overview of the average properties of a sample.

As electromagnetic waves, X-rays interact with the electrons of a material. The electric field of the wave excites orbital electrons, causing either ionisation by ejection of the electron, known as the photoelectric effect, or scattering of the wave as the electron relaxes and re-radiates the wave [148]. The scattered wave may or may not have the same energy as the incident wave, which is known as elastic or inelastic scattering respectively. Inelastic scattering, also known as Compton modified scattering, produces an incoherent, diffuse background in measurements [147]. However, elastically scattered waves from a crystal may coherently interfere with each other, leading to constructive interference and
a peak in the reflected intensity whenever the incident angle satisfies Bragg’s law, given by equation (4.14). This allows determination of the spacing of the crystal planes from the angular position of the measured peaks, similar to electron diffraction measurements.

The most common laboratory X-ray source is a copper anode target, which is bombarded by a beam of electrons extracted from a heated tungsten filament by an accelerating voltage. This is commonly 40 kV with an extracted current of 30-45 mA, giving an overall power of 1.2-1.8 kW. The incident electrons ionise the target atoms causing emission as target electrons from higher energy levels relax to fill the vacated state. The X-ray spectrum is therefore characterised by a broad background due to Bremsstrahlung radiation with sharp peaks arising from the specific electron energy levels in the target atom. The strongest of these is the $K_\alpha$ wavelength at approximately 1.54 Å, corresponding to the energy released when an electron relaxes from the 2p state to the 1s state [148]. The $K_\beta$ wavelength, corresponding to the gap between the 3p state and 1s state, is very similar, requiring a monochromatic filter for high-resolution measurements to isolate the more intense $K_\alpha$ radiation.

The $K_\alpha$ peak is split into two, known as $K_{\alpha 1}$ and $K_{\alpha 2}$, due to spin-orbit coupling, although the energy difference is just 20 eV [149] giving a small angular separation of 0.072° according to Bragg’s law. A narrow band monochromator is needed to distinguish between these wavelengths to provide the best resolution measurements. These consist of a single, high-purity crystal, normally of silicon or germanium [147]. This is orientated such that the X-ray beam reflects off it at an angle that satisfies the Bragg condition, causing constructive interference of the desired wavelength and destructive interference of undesired wavelengths. The precision of the orientation and the mosaicity of the crystals must be less than the angular separation of $K_{\alpha 1}$ and $K_{\alpha 2}$ in order to differentiate between them. Two identical crystals may be used together at the same orientation like a periscope, known as a double-bounce monochromator, in order to preserve the original direction of the beam and cancel out any divergence [147].
To measure the position of the diffraction peaks, the X-ray source and detector are rotated around the sample to cover a range of angles. In practice, the sample stage may be rotated through an angle \( \theta \), whilst the detector is rotated through an angle \( 2\theta \) in order to maintain symmetry, as shown in figure 4.14. Alternatively, the sample may be held flat and the source rotated clockwise by \( \theta \) and the detector rotated anti-clockwise by \( \theta \). This is more desirable for delicate samples such as loose powders.

The area of the sample illuminated by the beam will increase as the incident angle decreases. Care must therefore be taken to restrict the size of the beam using slits such that it does not exceed the total size of the sample. Any excess could interact with the stage material, leading to false readings and higher background at lower angles. To further help avoid this, smaller samples may be placed onto a large amorphous glass slide, which will not produce any spurious diffraction peaks.

Certain materials will fluoresce under specific wavelengths of X-ray radiation, typically those two or three less in atomic number than the target material [150]. This creates a high level of background with a very weak signal, and makes reliable analysis impossible. For a copper target this is cobalt, iron, and, to a much lesser extent, manganese as another transition element [150]. For very detailed studies of large quantities of these materials a different target material is required, most commonly iron, chromium or cobalt [147], [150].

The divergence of the incident beam may be conveniently compensated for by focussing the beam onto the detector via reflection from the sample, known as parafocusing [151].
However, this requires that the source, detector and sample all lie on the perimeter of a circle. This is clearly not possible for the entire surface area of a flat sample as it can only be tangential to the circle, leading to broadening of the peaks at small $\theta$ [147]. Any slight offset of the sample from the circle, whether by position or transparency, will also cause shifts in the peak position [147], [152]. These problems can be eliminated by using a parallel beam with very small divergence created by additional incident optics at the cost of some intensity [147].

In order to fully characterise a crystalline sample, all crystallographic orientations must be sampled. The diffracted beams from an ideal polycrystalline sample will form a cone with $\theta$ as the angle of inclusion. As $\theta$ is varied the corresponding circles will build a ring pattern similar to electron diffraction in TEM. However, due to the point-like, limited window of most X-ray detectors, as well as the symmetry of the source and detector angles with respect to the sample, diffraction will only be detected from a cross section of the ring pattern corresponding to sets of planes parallel to the sample stage. Diffraction peaks may therefore be missed from textured samples where there is a preferred crystal orientation, or where the number of illuminated grains is not statistically significant, as the rings would be incomplete and may not fall on the detected solid angle. This can be used as an indication of crystal alignment, or may be resolved by producing a powder sample or polycrystalline film such that all possible crystal directions are simultaneously perpendicular to the plane of the sample stage. A two dimensional detector with a larger angle of acceptance reduces the chance of missing these peaks, allowing the full pattern to be observed. However, these detectors are not particularly common as this level of detail is rarely required and presents unnecessary expense and complications in data analysis. At the time of writing they are beginning to be introduced to lab based equipment. A one-dimensional detector may be used to improve data acquisition times by sampling a small range of $\theta$ simultaneously with separate pixels.
4.5 X-ray reflectivity

The thickness and interfacial roughness of thin film structures are of paramount importance for determining their magnetic characteristics and suitability in applications. As discussed in section 3.1.1, magnetic tunnel junctions require atomically flat interfaces for efficient tunnelling with precise layer thickness control. Reflectivity measurements offer an ideal method for determining the thickness, layer structure and roughness of thin film systems. In contrast to transmission electron microscopy, and much like XRD, the sample does not require any special preparation and is thus a fast, convenient and non-destructive technique.

4.5.1 Refraction and reflection

Grazing incidence X-rays undergo refraction and reflection from layer interfaces, as shown in figure 4.15, interfering to reveal information about the thickness and refraction index of the layers. For X-rays, the refractive index, \( n \), is slightly less than 1, given in complex form by

\[
n = 1 - \delta - i\beta \quad (4.17)
\]

where \( \delta \) is the real part of the deviation from 1 and \( \beta \) is the complex part, related to the attenuation of the wave as it passes through the material. The form of \( \delta \) can be understood by modelling the material electrons as a series of damped harmonic oscillators excited by the electric field of the incident wave, yielding

\[
\delta = \frac{\lambda^2 r_e \rho_e}{2\pi} \quad (4.18)
\]
where $\lambda$ is the wavelength of the incident wave, $r_e$ is the classical radius of the electron and $\rho_e$ is the electron number density [147].

The angle of the transmitted beam, $\theta_t$, is given by Snell’s law relating the refractive index with the incident angle, $\theta_i$, as

$$\cos \theta_i = n \cos \theta_t \quad (4.19)$$

Below a certain angle of incidence, known as the critical angle, $\theta_i = \theta_c$, total external reflection will occur as the transmitted beam is parallel to the sample surface, hence $\theta_t = 0$. Combining equations (4.17) and (4.19), neglecting absorption and using the small angle approximation for $\theta_c$ gives

$$\theta_c = \sqrt{2} \delta \quad (4.20)$$

From equation (4.18) it can therefore be seen that the critical angle will increase with increasing material density, allowing the determination of the material density from the measurement of the critical angle.

The Fresnel equation for the intensity of a beam reflected from a single interface gives

$$I_R = \frac{|\theta_i - \theta_t|^2}{|\theta_i + \theta_t|^2} = \frac{\theta_i^2 + |\theta_t|^2 - \sqrt{2}\theta_i \sqrt{|\theta_t|^2 + \theta_t^2}}{\theta_i^2 + |\theta_t|^2 + \sqrt{2}\theta_i \sqrt{|\theta_t|^2 + \theta_t^2}} \quad (4.21)$$

which, as expected, goes to unity as $\theta_i \to 0$. For $\theta_i \gg \theta_c$ beyond the critical angle the reflected intensity will decrease rapidly according to $I_R \propto \theta_i^{-4}$ as the incident beam is transmitted through the interface and enters the material. Including the effects of absorption slightly softens the transition between the region of total external reflection and the decrease beyond the critical angle, as shown in figure 4.16.
A non-zero roughness will accelerate this decrease as intensity is lost due to diffuse scattering. This can be modelled by including a factor of $e^{-\sigma^2 Q^2}$ in equation (4.21), where $\sigma$ is the root-mean-square roughness of the interface and $Q = \frac{\sin \theta}{4\pi \lambda}$ [147].

3.4.1 Reflection from a thin film

The inclusion of a thin film on top of a substrate creates multiple interfaces, leading to multiple reflected beams. These beams interfere to create periodic maxima in the reflected intensity, occurring when the phase difference, $\Delta$, between the reflected and refracted beams equals a multiple of the wavelength, $\Delta = m\lambda$, where $m$ is an integer. Combining equations (4.17) and (4.20) with Snell’s law, ignoring absorption, allows $\theta_i$ to be defined in terms of $\theta_i$ and $\theta_c$ as $\sqrt{\theta_i^2 - \theta_c^2}$. Applying the small angle approximation, Bragg’s law for reflection from a layer with thickness $t$ is therefore

$$m\lambda = 2t \sqrt{\theta_i^2 - \theta_c^2} \quad (4.22)$$

The angular position of each maximum, $\theta_m$, may therefore be defined relative to the critical angle by [147]

$$\theta_m^2 = \theta_c^2 + \left(\frac{\lambda}{2t}\right)^2 m^2 \quad (4.23)$$
The thickness of the film may therefore be derived from the measured angular position of these fringes. In practice, the measured curve is fitted with simulations to extract the density, roughness and thickness of the layer. Thicker films give higher frequency fringes. The angular resolution of the instrument therefore defines the maximum thickness layer that may be measured, typically no more than 100 nm [147].

Reflection from multiple layers creates patterns with multiple frequencies of fringes. Many substrates and metal thin films have a naturally occurring oxide surface layer with a thickness of the order of a few nanometres. A Fourier transform may give a good initial indication of the layers present in a sample, but is no substitute for a full fitting in order to reliably understand the physical origin of the data.

4.5.2 Fitting the reflectivity data

The modelling and fitting of the data is performed by a specialised software package called GenX [154]. This builds upon equation (4.21) using the Parratt recursive algorithm [155]. Parameters such as layer thickness, interface roughness/width and layer density may be modelled and extracted once the fit is deemed to have converged with the data. Layer thicknesses and interface roughness are given in Ångstroms. For density calculations, GenX uses the scattering length density, given by multiplying the density in relative atomic mass units per Å³ by the total scattering length in units of the Thomson scattering length or classical electron radius [156]. The scattering lengths of each element are included in a built-in database in GenX. The scattering length density of each material can therefore be calculated from their chemical stoichiometry and lattice parameters as an initial starting point for the fitting procedure.

It is important to ensure the initial simulation is in reasonable agreement with the experimental data before starting the automatic fitting algorithm, or the fit may reach an unphysical solution, or fail to converge at all. A genetic optimisation algorithm is used to simultaneously test many values of the fit parameters, selecting those which minimise the figure of merit and give the best global fit. Reasonable bounds are set on the tested values in order to ensure the physical credibility of the fitted result. An iterative approach is often
required, optimising only one or two parameters at a time and fixing others before moving on to the next few parameters in order to prevent convergence on local minima or unphysical solutions. The log figure of merit was used to determine the quality of the fit, defined as the average of the absolute difference between the logarithms of the data and the simulation. Using the logarithm figure of merit makes the fitting algorithm sensitive to minima in the reflected intensity, where the beam is probing deeper into the sample stack [157]. A fit was deemed to have converged when the figure of merit reached less than 0.1.

4.6 Elemental analysis

The successful formation of the desired high-anisotropy L1\textsubscript{0} ordered crystalline phase requires the correct elemental composition and stoichiometric ratio of the alloy. In order to verify the composition of the films, inductively coupled plasma optical emission spectroscopy has been used as a sensitive, accurate and reliable technique, giving better than 1% precision [158]. This level of precision is necessary for optimising MnAl films within the narrow window of composition that forms the desired L1\textsubscript{0} ordered \( \tau \) phase. The sample is dissolved off the substrate into solution, vaporised and passed into an Ar plasma. The plasma excites the sample atoms, causing them to emit their characteristic emission spectra. Calibration standards allow the concentration of each element in the sample to be quantified by measuring the intensities of their characteristic emission peaks.

This analysis is offered as a central service provided by Mr Martin Jennings in the Microanalysis laboratory of the Chemistry department.
4.7 Magnetic measurements

Vibrating sample magnetometry (VSM) is a versatile technique for the precision measurement of the magnetic moment of a sample [159]. Quantities measured typically include the saturation magnetisation and the coercivity from a $M(H)$ hysteresis loop. Thin film samples with large surface areas can be conveniently measured in a VSM as a function of the angle of the applied field and the angle of the magnetic response.

The principle workings of a VSM are shown in figure 4.17, and involve mechanically vibrating a sample between two pickup coils [21]. An oscillating magnetic sample will induce a current, or electromotive force (emf) in the detector coils according to Faraday’s law of electromagnetic induction. This states that the normal component of a time-varying magnetic flux, $\Phi$, passing through a loop will induce a voltage, $V$, in the loop proportional to the rate of change of the flux, given by

$$V = -N \frac{d\Phi}{dt}$$  \hspace{1cm} (4.24)
where $N$ is the number of turns in the loop or detector coil. The signal is given by the change in the measured voltage as the sample becomes magnetised by the applied field. This can be used to measure hysteresis loops giving the magnetisation of a material in response to the applied field.

The magnetisation response, $M(H)$, is sensed via the magnitude of the emf in the lower pickup coils. Feedback from a reference magnet in an upper set of pickup coils is used to keep the amplitude of the vibration constant. A vector VSM has two sets of pick-up coils orientated perpendicular to each other to allow the direction of the magnetisation to be determined with respect to the plane of the sample and the angle of the applied field [160], [161].

As the measured signals can be extremely small, on the order of $\mu$V, lock-in amplifiers are needed to improve the signal to noise ratio. The detection of the magnetic signal is improved by mixing the measured signal with the reference frequency of the mechanical vibrations. Signals of the appropriate frequency can then be extracted, improving the signal to noise ratio by approximately 30 dB.

VSM requires calibration for quantitative measurements, typically carried out using a Ni standard of known magnetisation. The proportionality factor between the voltage signal and the sample magnetisation can therefore be determined. Calibration in both the perpendicular and in-plane directions with respect to the applied field gives any necessary corrections due to mechanical and electrical differences in the two sets of pick-up coils. The standard must be the same shape and size as experimental samples to ensure validity. For this study, an ADE Technologies Mk II Vector VSM was used with a sensitivity of the order of 1 emu.

Samples are cut into 8 mm disks by an annular drill bit which uses silicon carbide slurry to abrade the sample. The cutting is done from the back side of the substrate to protect the thin film sample. Each disk is then mounted on a glass sample holder. The linear diamagnetic response of the glass sample holder must be subtracted from the data in order to isolate the magnetisation of the sample. This can be measured by fitting the slope of
the signal once the sample has saturated. Knowledge of the sample volume then allows calculation of the saturation magnetisation in emu/cm$^3$.

The maximum applied field generated by the electromagnet used in this study was 20 kOe. However, at high fields greater than 18 kOe, the vibrations begin to couple with the pickup coils due to the imperfect mechanical isolation of the vibrating components, causing an artificial loss of signal. Although the maximum field may be applied to saturate the sample, the range of data analysed was therefore restricted to applied fields of 15 kOe or less.

Two loops are often measured for perpendicular anisotropy thin films, one where the sample plane is parallel to the applied field and another where it is perpendicular. For well-aligned perpendicular anisotropy materials, the perpendicular loop should show a higher coercivity with sharper switching transitions, which verifies the direction of the easy axis. Extrapolation of the out-of-plane gradient to the saturation magnetisation of the in-plane loop gives the anisotropy field $H_k$, used for the calculation of the uniaxial anisotropy by equation (2.23).

#### 4.8 Atomic force microscopy

The surface profile of a sample may be measured with nanometre precision by scanning probe microscopy techniques [162]. This allows determination of step heights in thin films with single nanometre resolution which may be used to calibrate the rate of deposition of a sputtering system.

Atomic force microscopy (AFM) uses a flexible cantilever with a probe tip to trace the sample surface, as shown in figure 4.18. The sample is raster scanned, typically at approximately 0.5 Hz depending on the field of view, underneath the tip by a piezoelectric stage and the deflection of the cantilever is monitored by the reflection of a laser beam. As the various attractive and repulsive forces deflect the cantilever, the position of the reflected laser spot is monitored on a segmented photodiode. The topography of the
sample surface is then determined by raising or lowering the sample or cantilever to maintain a constant deflection, and hence a constant displacement from the sample surface [162]. Single nanometre resolution can be achieved in the vertical direction, with a lateral resolution of a few nanometres depending on the sharpness of the tip.

In conventional contact mode the cantilever is in direct contact with the sample surface. However, this can easily damage the fragile tip and/or the sample. Instead, the cantilever may be held away from the surface and oscillated by a piezo-electric actuator at its base, typically near its resonant frequency. The frequency and/or amplitude of the tip oscillations will then be influenced by the various interatomic or longer range forces acting between the sample and the tip, depending on the distance maintained away from the surface [162]. This non-contact mode can allow the sensing and mapping of various long range forces such as magnetic domains or electric fields with appropriately functionalised tips. However, the resolution of such techniques are reduced to several tens of nanometres depending on the distance the cantilever is held away from the sample surface.

Intermittent contact, or tapping mode, is most commonly used for measurements of the surface topography. The cantilever oscillates as in non-contact mode, but is allowed to touch the sample surface during each oscillation. This removes any dependency on the potentially variable tip-sample interaction forces and ensures the measured profile is purely due to the surface topology [162]. Due to the limited tip-sample contact time, tapping mode is much less likely to damage the tip or the sample, allowing more reliable
measurements with nanometre resolution. For this project, all AFM measurements were carried out using a Bruker Dimension Icon microscope operated in tapping mode.
Chapter 5

Grain size studies in FePt

Iron platinum (FePt) is a leading contender for the next generation of high-density storage media above 1 Tbit/in$^2$ [7]. Its strong perpendicular anisotropy of $7 \times 10^7$ erg/cm$^3$ together with a high saturation magnetisation of 1140 emu/cm$^3$ [72], [163], [164] makes it highly suitable for use in heat assisted magnetic recording, introduced in section 3.2. Its strong anisotropy allows the necessarily small grains to remain thermally stable down to grain sizes of approximately 3 nm [72], [164]. The high saturation magnetisation ensures good signal to noise ratio. In order to be suitable for storage applications, the grain size distribution must be carefully controlled to within about $\pm 10\%$, allowing consistent switching under thermal excitation and the write field [165], [166].

5.1 Grain size distributions

Grain size is an important material parameter for magnetic thin films governing properties such as anisotropy and reversal mechanism. Higher coercivity is often caused by a smaller grain size, providing a higher density of domain wall pinning sites. It is therefore desirable to be able to produce thin films with a reliable grain size characterised by a narrow distribution, which is particularly required for data storage applications. Grain size distributions are most often modelled by a log-normal function, which represents a variable whose logarithm is normally distributed. The coalescence of neighbouring grains...
proceeds multiplicatively, such that the size of each grain independently increases by a random fraction of its size. As such, the logarithm of this change is then represented by a summation of independent random variables, which, according to the central limit theorem, approximates a normal distribution [167]. For a log-normally distributed variable \( x \), the mean and standard deviations of \( \ln(x) \) are known as \( \mu \) and \( \sigma \) respectively. The normalised probability density function is therefore

\[
P = \frac{1}{\sqrt{2\pi\sigma x}} e^{-\frac{(\ln x - \mu)^2}{2\sigma^2}} \tag{5.1}\]

with an average value of

\[
\langle P \rangle = e^{\mu + \frac{1}{2}\sigma^2} \tag{5.2}\]

and a standard deviation of

\[
SD = \langle P \rangle \sqrt{e^{\sigma^2} - 1} \tag{5.3}\]

Average grain sizes reported in the rest of this work are values extracted from the fitted distributions given by equation (5.2).

The standard deviation is used as a measure of the grain size distribution width. The uncertainty in the average grain size is the larger of either the conventional standard error, given by \( SD/\sqrt{N} \), where \( N \) is the total number of grains counted, or the error derived from the fitting of the log-normal distribution to the data. In practice, the fitting error is most often larger than the standard error.
5.2 Grain size analysis techniques

Grains will appear as darker spots in a bright field TEM image due to diffraction, and are typically identified manually by outlining the appropriate regions. However, this is extremely time-consuming for any statistically significant total count, and sensitive to user bias and experience. Some grains may not be as readily visible as others, and smaller

Figure 5.1: A comparison of grain size distributions from three grain identification techniques with log-normal fits and optimised grain selection criteria. (a) a bright field TEM image of the 10 nm iron platinum sample sputtered onto a silicon nitride membrane. The fit from manual outlining, (b), is far inferior to both automatic methods, (c) and (d). Trainable Weka segmentation, (d), represents a reliable, objective method that can be easily applied to many images.
grains may go entirely unnoticed. Figure 5.1 shows a TEM bright field image of a 10 nm thick FePt thin film sputtered onto a 50 nm thick silicon nitride membrane, and the grain size distributions obtained from three different outlining techniques. The performance of each technique was evaluated by fitting the distribution histogram to a log-normal curve and comparing the adjusted $R^2$ values.

Figure 5.1b shows the results obtained by manually outlining three hundred grains. This number was chosen to match the typical order of magnitude used in previous studies [86]. The distribution does not fit well to a log-normal curve, with an adjusted $R^2 = 0.69623$. Although this may be increased by counting more grains or allowing the histogram bin size to increase, manual outlining is clearly a time-consuming, impractical method for consistent, high through-put experiments.

Figure 5.1c and d show the best fit results of the automatic selection techniques, called “direct thresholding” and “trained segmentation” respectively. The grains responsible for figure 5.1c were identified by applying a threshold to the image, creating a binary image by only selecting areas with an intensity above a certain grey level. The best fit is vastly improved (adjusted $R^2 = 0.86193$) and the total count instantly reaches a far more statistically significant level, decreasing the measurement uncertainty by an order of magnitude. This technique removes most of the user bias associated with manual outlining.

To separate adjoining or overlapping grains, a process known as “watershed” may be applied in ImageJ, which splits large selections. Single pixel gaps are drawn between neighbouring centres-of-mass, separating the convex regions of the selection from each other. This reduces the occurrence of exceptionally large selections which would otherwise create an abnormally large tail in the grain size distribution.

Figure 5.1d was taken from grains selected by a plugin for ImageJ called Trainable Weka Segmentation [168]. This is a machine-learning algorithm by which a user may select a region of interest and the software will automatically select similar regions in the image. The process may be refined by adding additional user-defined selections. Once the
classifier algorithm is `trained', it may then be applied to other, similar images for instant grain selection, making it a convenient, objective and thorough technique. The results reflect these advantages, showing an improved best fit over the thresholding method (adjusted $R^2 = 0.936$) with a slightly lower average grain size uncertainty.

For automatic outlining, various criteria are available for altering the selection. The minimum size may be specified, which is useful for eliminating noise and stray pixels which would otherwise artificially decrease the average size. The minimum circularity may also be specified in order to eliminate conglomerates or other unreasonable selections. For each of the automatic methods, these two parameters were varied from $0 - 3 \, \text{nm}^2$ for the area and $0 - 0.5$ for the circularity. Figure 5.2 shows the adjusted $R^2$ values obtained across this parameter space. All values show a better fit than the manual outlining method. The results presented in figure 5.1c and d are from the combination of minimum area and circularity that were found to give the best fit.

Figure 5.2 also demonstrates the consistency of the trained segmentation method, with far less dependency on the minimum circularity and minimum area, which would otherwise represent another form of user bias. In particular, the adjusted $R^2$ value does not show any dependence on circularity, so no circularity restriction was placed on any future measurements. The improvement due to the minimum area threshold appears to saturate above $2 \, \text{nm}^2$, defining the minimum threshold required. Trainable Weka Segmentation is used for all further grain size analysis in this project as an objective, reliable and efficient automatic outlining method.
Various schemes exist for the expression of the size of irregularly shaped grains as a one dimensional parameter. Conventional grain identification techniques require the user to match each grain with a circle of equal area, giving the grain size as the diameter of projected area. Martin’s diameter is the diameter of the grain at a point which divides the grain into two halves of equal area [169]. However, in this work, Feret’s diameter is used as a convenient measure of the grain size built in to the ImageJ software. This is a common measure of particle size also known as the calliper diameter, representing the distance between two parallel lines drawn tangentially to each side of the particle [169].

5.3 Grain size of iron platinum thin films

The extra process parameter space offered by remote plasma sputtering, introduced in section 4.1.2, has been explored to investigate the possibility of grain size control in FePt thin films, as found in certain other materials, most notably Cr thin films [170], [171]. If a similar effect is present for FePt then this would provide an additional degree of freedom in optimising the grain size. As part of her PhD, Dr. Zygridou investigated this effect via XRD and VSM analysis, simultaneously verifying the good ordering and magnetic properties of the films produced. Average grain sizes were extracted using the Scherrer equation, relating the width of the XRD diffraction peak to the average size of the appropriate crystallites [148]. However, this does not reveal the grain size distribution, and so direct TEM observations of the grains were made.

Selected area diffraction patterns also further verified the crystal structure and ordering. As deposited FePt is expected to have the A1 fcc crystal structure with no chemical ordering between the lattice sites [7], [64], resulting in the smallest distance observed in reciprocal space corresponding to the (200) spacing. In contrast, the L10 ordered phase gives rise to (100) reflections due to the superlattice created by the chemical ordering.

In collaboration with Dr. Zygridou, three samples of 10 nm of Fe50Pt50 were deposited at room temperature using remote plasma sputtering with a target bias voltage of 200 V, 600 V and 1000 V. Single crystal MgO (001) substrates were used to promote crystal
alignment and create perpendicular anisotropy. Annealing was necessary to achieve the desired L1\textsubscript{0} ordered crystal phase which was done at 800°C for one hour in a Thermcraft tube furnace in an atmosphere of 10% H in Ar to prevent oxidation. The samples were observed in both the as-deposited state and after annealing in order to investigate any grain growth caused by annealing. The degree of ordering may be quantified using the order parameter, \( S \), which describes the ratio of Fe and Pt atoms occupying the correct crystal sites. This varies between \( S = 0 \) for a completely random arrangement and \( S = 1 \) for a perfectly ordered crystal [148]. This value can be determined experimentally from XRD \( \theta - 2\theta \) scans by comparing the relative integrated intensities of the fundamental (002) and superlattice (001) peaks, given by \( I_{002} \) and \( I_{001} \) respectively, such that

\[
S = \left( \frac{I_{001}}{I_{002}} \frac{F_{002}}{F_{001}} \frac{(LAD)_{002}}{(LAD)_{001}} \right)^{1/2}
\]

Where \( F \) is the structure factor, \( L \) is the Lorentz polarisation factor, \( A \) is the absorption factor and \( D \) is the temperature factor [172]. However, difficulties in reliably determining these experimental factors, along with a broad background signal from the MgO substrate, prevented determination of \( S \) in this way, with all efforts yielding \( S > 1 \). The good ordering of the films was instead evidenced by the strong intensity of the superlattice peak and the disappearance of the disordered A1 FePt 200 peak after annealing [173].

Samples were thinned to electron transparency using the polishing process described in section 4.3. The Phillips CM20 and the FEI Tecnai T20 microscopes were used for the as-deposited and annealed samples respectively, both of which have a LaB\textsubscript{6} source and an accelerating voltage of 200 kV.

Dark field TEM images were used to identify grains as these are more selective, illuminating only those grains which satisfy the chosen diffraction conditions and ignoring any non-crystalline material. This simplifies grain identification and measurement. A (200) FePt spot was chosen as this reflection had a strong intensity and is given by both the disordered, as-deposited FePt and by the L1\textsubscript{0} ordered phase.
Figure 5.3a, figure 5.4a and figure 5.6a show the results for the as-deposited films deposited with a target bias voltage of 200 V, 600 V and 1000 V respectively. Figure 5.3b, figure 5.4b and figure 5.6b show the results for the corresponding annealed films. Grains are outlined by the trained segmentation algorithm discussed in section 5.2. The minimum area threshold was set at 7 nm$^2$, corresponding to the minimum diameter of a circular grain of 3 nm. The diffraction patterns consist of discrete spots rather than rings, evidencing the high level of crystalline ordering in the sample. The patterns were indexed by comparison with simulations using the MgO substrate as a built-in reference. Epitaxial FePt is expected to have very similar lattice spacing and azimuthal alignment as the MgO substrate, which is verified by the overlap in the observed patterns. No observable change in the lattice spacing is seen between the as-deposited and annealed films. The extra, smaller spots seen around each major reflection are due to a phenomena known as double diffraction, which occurs when the sample consists of two crystals with slightly different lattice spacing, in this case FePt and MgO. The diffracted beams from the first crystal act as incident beams on the second crystal, producing small sub-patterns with a spacing equal to the difference between the lattice parameters. The exact appearance depends on which way up the sample is, as this dictates which crystal the electron beam encounters first. This explains the slightly different appearance of the sub-patterns obtained from the 1000 V annealed sample.

The normalised grain size distributions of the as-deposited samples are fitted with log-normal curves. Due to the disperse nature of the grains in the 200 V sample, additional images were required to reach a count of at least 500 grains in order to produce fits with a good uncertainty of less than 1 nm. No significant dependence on target bias voltage is observed, with all values being within one standard deviation of each other.
5.3 Grain size of iron-platinum thin films

Figure 5.3: Dark field TEM images with outlined grains of the sample deposited with a target bias voltage of 200 V. Inset grain distributions and diffraction patterns showing MgO (green) and FePt (red) indices.
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Figure 5.4: Dark field TEM images with outlined grains of the sample deposited with a target bias voltage of 600 V. Inset grain distributions and diffraction patterns showing MgO (green) and FePt (red) indices.

(a) As-deposited

(b) Annealed

100 nm

50 nm
5.3 Grain size of iron platinum thin films

Figure 5.5: Dark field TEM images with outlined grains of the sample deposited with a target bias voltage of 1000 V. Inset: grain distributions and diffraction patterns showing MgO (green) and FePt (red) indices.

(a) As-deposited
(b) Annealed
After annealing, the successful growth of the desired L1₀ phase is evidenced by the strong (100) spots in the diffraction patterns. A preferential direction can be observed where the grains appear to form lines. This is attributed to step edges formed by the angle of the crystal cut acting as nucleation sites for grain growth. Significantly more counts of at least 2000 were required to reach the same range of uncertainty as the as-deposited samples due to the increased scatter in the data. This is reflected in the increased fitting uncertainties, as well as the larger standard deviations and broader distributions which have increased from an overall average of 2.4 ± 0.2 nm before annealing to 7.5 ± 0.9 nm. The average grain size also consistently increases after annealing for all samples, from an overall average of 6.7 ± 0.2 nm to 12.5 ± 0.5 nm, with no statistically significant correlation with target bias voltage.

The overall trend in average grain size is shown in figure 5.6. All average grain sizes and standard deviations are summarised with fitting uncertainties in table 5.1.

Although the average grain sizes measured previously by XRD agree well for the as-deposited samples with an overall average of all three samples of 6.3 ± 0.1 nm, the increase after annealing is not as great as that measured by TEM, with an overall average of all three samples of just 9.2 ± 0.3 nm. This is due to the fact that, as a surface reflectivity technique, XRD is only sensitive to out-of-plane distances, while TEM measures the lateral dimensions of grains. Vertical grain growth is limited by the overall thickness of the film, whereas lateral grain growth has no such restriction.

Figure 5.6: Overall trend of average grain size for FePt thin films deposited at different target bias voltages measured in both the as-deposited state and after annealing.
<table>
<thead>
<tr>
<th>Target bias voltage (V)</th>
<th>Average grain size (nm)</th>
<th>Standard deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>As-deposited</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>6.7 ± 0.2</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>600</td>
<td>6.3 ± 0.3</td>
<td>2.2 ± 0.2</td>
</tr>
<tr>
<td>1000</td>
<td>7.0 ± 0.2</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td><strong>Annealed</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>11.4 ± 0.5</td>
<td>6.4 ± 0.7</td>
</tr>
<tr>
<td>600</td>
<td>13.6 ± 0.6</td>
<td>8.5 ± 1.2</td>
</tr>
<tr>
<td>1000</td>
<td>12.6 ± 0.6</td>
<td>7.6 ± 1.0</td>
</tr>
</tbody>
</table>

Table 5.1: Average and standard deviation of the grain size distributions from FePt thin films deposited at different target bias voltages measured in both the as-deposited state and after annealing.

5.4 Summary

The additional parameter space offered by remote plasma sputtering has been explored with a view to controlling the grain size of FePt thin films. Electron diffraction patterns show a good epitaxial relationship between the film and the substrate, with strong L1₀ spots evidencing a good degree of ordering. This sample series shows that grain size in FePt thin films is not affected by the target bias voltage used in remote plasma sputtering. However, a significant increase in grain size and a broadening of the grain size distribution is observed after annealing. It should be noted that these films are prototypes without the required segregation of grains to form usable storage media with independent, de-coupled bits. Grain growth would also be affected by other dopants such as Cu or Ag designed to reduce the required annealing temperature, decreasing production costs as well as altering the mobility of the material, and hence the ability of the grains to grow [64]. Much research has already been devoted to the development of FePt storage media, grain segregation and ordering [7], [64], [71]–[73]. Future work using remote plasma...
sputtering may continue this trend, benefiting from higher target utilisation without being affected by the accelerating voltage used.
Iron Rhodium thin films

Iron rhodium has exceptional promise for improving the next generation of magnetic data storage through heat assisted magnetic recording (HAMR) [63], [67]. It also has potential for low power spintronics and artificial multiferroic logic systems [174]. In order to achieve higher density storage media, the grains of the storage medium must be made smaller. This necessitates using a storage medium with high anisotropy in order to retain thermal stability at very small grain sizes. However, the field required to write bits in such stable media exceeds that available from current read/write heads [66]. In order to write a bit, HAMR uses localised heating to reduce the magnetocrystalline anisotropy, as discussed in section 3.2.1. However, heating magnetic media to high temperatures creates a number of undesirable effects to both the media structure and to the near-field antenna used to concentrate the optical power for heating. The protective overcoats and lubricants are essential to ensure that the stable flying of the head within a few nm of the disk surface and it follows that any disruption to these layers risks a head crash.

The performance of a HAMR drive can be enhanced by pairing FeRh with an FePt storage layer in an exchange spring structure [63], [67]. In the chemically ordered, B2-type body-centred-cubic phase, FeRh undergoes a ferromagnetic-antiferromagnetic phase transition at a temperature of approximately 100°C (370K). This can be used in HAMR to generate a destabilising field with localised heating beyond the transition temperature, reducing the level of heating necessary to enable writing of a bit. Most work in the literature to date has focussed on the properties of films with a thickness of several 10’s of
nanometers, similar to the bulk material. However, to be suitable for use in applications such as HAMR the total media thickness is severely limited by the recording spacing loss [175], and so the thickness of the films must be less than 10 nm.

6.1 Structural characterisation of FeRh

A sample series of various thicknesses of FeRh was made in order to investigate the low-dimensionality effects of very thin films and verify their structural properties. The samples were produced by Dr Craig Barton using DC magnetron sputtering of an alloy target with an atomic percentage composition of Fe$_{50}$Rh$_{50}$. The base pressure was kept below $5 \times 10^{-9}$ mBar. Single crystal MgO $(001)$ substrates were used to promote crystal alignment. In order to produce the required chemically bcc ordered crystal phase, samples were deposited at a temperature of 650°C and then immediately annealed at 750°C in the vacuum of the sputtering chamber. The sample thicknesses were nominally set to 2.5 nm, 5 nm, 7.5 nm and 10 nm. Samples were thinned to electron transparency using the polishing process described in section 4.3. A Tecnai T20 microscope was used for TEM measurements with a LaB$_6$ source and an accelerating voltage of 200 kV.

FeRh has a body-centred cubic structure with a lattice parameter of 2.984 Å at room temperature. This matches well with the $(110)$ distance of MgO of 2.978 Å, derived from its lattice parameter of 4.212 Å. As such, it is expected that FeRh will grow epitaxially on MgO with a 45° azimuthal rotation, such that MgO $(110)$ is parallel to FeRh $(100)$, as shown in figure 6.1. Some slight strain may be present in the film due to the difference in lattice

Figure 6.1: Epitaxial relationship between FeRh and MgO, where the FeRh lattice is rotated 45° relative to the MgO substrate.
parameters with the substrate. However, this will lead to dislocations in the film during the initial growth stages in order to help relax the strain and achieve the lowest energy state.

Figure 6.2: Bright field plan view TEM images of FeRh thin films on MgO. Nominal film thicknesses are (a) 2.5 nm, (b) 5 nm, (c) 7.5 nm and (d) 10 nm. Significant de-wetting is observed with Volmer-Webber type island growth until the islands begin to coalesce in the 10 nm sample. Continuous films are required for applications such as HAMR.
Figure 6.2 shows bright field plan view TEM images of the samples, revealing de-wetting of the FeRh film from the substrate. The large scale variation in contrast, particularly evident from the top-left to the bottom-right of figure 6.2c, is due to diffraction from the substrate, caused by a combination of bending, variable thickness, and imperfections in the MgO crystal. The images were taken off-axis with respect to the crystallography of the substrate in order to minimise diffraction contrast, otherwise the visibility of the small scale features of the FeRh film was severely limited.

The apparent de-wetting of the substrate may be described as Volmer-Webber type island growth for most of the samples due to the slight mis-match in lattice parameter with the substrate. Once the nominal thickness reaches 10 nm, the islands start to coalesce, forming a web-like structure leaving holes in the film. However, continuous films with thicknesses of the order of a single nanometre will be required for HAMR applications. Seed layers and/or different processing conditions, such as the deposition and annealing temperature, will be required to improve the wetting of the films before they can be incorporated into multi-layer structures. The growth of these islands was measured using the same Trainable Weka segmentation technique that was used for studying grain growth of FePt as described in Chapter 5. This also enabled determination of the percentage area of the substrate covered by the film.

At a nominal FeRh film thickness of 2.5 nm, the islands appear rather sparse. The unavoidable diffraction contrast from the substrate in figure 6.2a obscures many of the islands from view. Image analysis was therefore limited to a smaller region of this figure with less diffraction contrast to avoid overtly misrepresenting the sample. The average island size was small at 13.1 ± 0.7 nm and coverage was just 9% of the analysed area.

For nominal film thicknesses of 5 nm and 7.5 nm, well-defined islands are clearly observed. Their average size is significantly larger at 48 ± 2 nm and 62 ± 2 nm respectively. The surface area coverage has also dramatically improved, with the 5 nm sample covering 56% of the substrate and the 7.5 nm sample covering 55% of the substrate. The near-identical area coverage despite larger island size indicates that there is more space between the islands in the 7.5 nm sample than in the 5nm sample. This is
attributed to the island height increasing, which, under the assumption of a constant volume, cancels out any expected increase in area coverage.

Once the nominal thickness of the FeRh film reaches 10 nm, the islands begin to coalesce, forming a semi-continuous, web-like film structure. This leaves voids through which the substrate is visible. This inversion of morphology is further confirmed by energy dispersive X-ray mapping, identifying the regions rich in Fe and Rh as shown in figure 6.3. Island size is obviously now meaningless as the islands have coalesced, but the area coverage increased only slightly to 58%, which is again attributed to the de-wetting causing the film thickness to increase at the expense of area coverage.

Selected area electron diffraction patterns for each sample, shown in figure 6.4, reveal a very good epitaxial relationship between the film and the substrate. Simulated patterns for FeRh rotated at 45° with respect to MgO fit well with the experimental data. This evidences the successful growth of the bcc chemically ordered phase required for the antiferromagnetic-ferromagnetic phase transition.

No FeRh spots are visible in the pattern from the 2.5 nm sample. This is partially due to the decreased volume of diffracting material in the sample. More significant, however, is the decreased crystal quality of the material present, as evidenced by X-ray diffraction

Figure 6.3: EDX map of 10 nm FeRh film on MgO, confirming that Fe and Rh make up the web-like structure with holes through which the substrate is visible.
The ordering parameter derived from analysis of the (001) and (002) peaks of the XRD measurements for the thinnest sample is just 0.68, compared with approximately 0.81 for the others. These measurements also indicate increasing out-of-plane strain as the film thickness is reduced, with a difference of 0.65% between the
Figure 6.5: Line profile across the diffraction pattern from the 10 nm FeRh thin film on MgO (inset). FeRh peaks are highlighted in red, MgO peaks are highlighted in green.

Figure 6.6: Measured FeRh lattice parameters compared with literature values and the (220) distance of the MgO substrate for reference of the epitaxial relationship. There is no data for the 2.5 nm sample due to low crystal ordering, hence no observable FeRh diffraction spots to analyse.
thickest and thinnest samples. These differences cause the phase transition temperature to increase as the film thickness decreases.

In order to investigate the possible presence of in-plane strain in the films, the FeRh lattice parameter was determined from the separation of the spots in the diffraction patterns. This was done for all samples except the 2.5 nm film, due to the lack of FeRh spots. The separation of spots is inversely proportional to the appropriate \( d \) spacing, as seen in equation (4.15), normally requiring calibration with a known standard. However, these patterns were individually calibrated by using the known lattice parameter of the MgO substrate as a built-in standard, eliminating the need for absolute calibration of distances in the pattern and any associated systematic error. Multiple line profiles were taken from each pattern at four different orientations, horizontally, vertically, 45° and -45°, including higher and lower order spots such as the profile shown in figure 6.5. Peak positions were identified as local maxima. The MgO spot separation corresponds to the \( \langle 200 \rangle \) spacing, or \( \langle 220 \rangle \) spacing when rotated \( \pm 45^\circ \). As such, the average of half the \( \langle 200 \rangle \) separation and \( 1/2\sqrt{2} \) of the \( \langle 220 \rangle \) separation was defined as corresponding to 4.212 Å in order to set the scale for each pattern.

The average FeRh lattice parameter, shown in figure 6.6, was measured from the separation of the FeRh spots relative to the scale established by the MgO spots. Slightly different separation distances were observed in each direction. However, this was consistent between the substrate and the FeRh film, indicating the substrate itself was slightly warped rather than the film being strained. This is due to the extreme thinness of the sample leading to slight bending or even slight thickness variations in the polished substrate. FeRh lattice parameters measured separately in each direction using the appropriate scaling factor from the substrate in the same direction yielded the same value within statistical uncertainties. Therefore, to improve the overall uncertainty associated with the statistic error in the peak positions, all directions were averaged to produce a single FeRh lattice parameter for each sample.

All measured FeRh lattice parameters agree well with the literature value for the antiferromagnetic, B2 ordered phase. The MgO \((220)\) distance also lies within the
statistical uncertainty bounds, and is shown to provide a reference of the epitaxial relationship with the substrate. Also shown in figure 6.6 is the expanded lattice parameter corresponding to ferromagnetic FeRh, representing an example of 0.5% strain from the antiferromagnetic phase. As can be seen, no overlap is observed with experimental data, indicating that the FeRh in all samples has a strong epitaxial relationship with the substrate with minimal in-plane strain. The resolution of the strain measurement is given by the magnitude of the uncertainties, which are smaller than the 0.5% example presented. It is therefore concluded that there is no in-plane strain in these films within the detectable limit of 0.5%. This matches well with the theoretical model developed to explain the XRD results, where increasing out-of-plane strain and decreasing chemical ordering contributes to a higher transition temperature in thinner films [176].

6.2 Summary

The structural properties of ultrathin FeRh films have been investigated. Island type growth was observed, with surface coverage no more than 60% for a nominal film thickness of 10 nm. Seed layers and/or different processing temperatures will be required before these films can be incorporated into multilayer structures.

The crystalline ordering decreased with decreasing film thickness, as evidenced by the decreasing intensity of the FeRh spots in electron diffraction patterns. This correlates with the degradation of the magnetic

![Figure 6.7: Thermal hysteresis loops of the FeRh films investigated in this study as measured by VSM, showing the antiferromagnetic (shaded green) to ferromagnetic (shaded red) phase change and the decrease in magnetisation for thinner films [176].](image-url)
properties shown in figure 6.7. Thermal hysteresis loops measured by Dr. Craig Barton using VSM reveal the change in magnetisation associated with the antiferromagnetic – ferromagnetic phase transition. The sample was saturated in the in-plane direction using an applied field of 1 kOe. The temperature was varied in intervals of 3 K with a soak time of 60 seconds by passing hot Ar gas over the sample. The magnetisation signal was determined from an average of 50 measurements at each temperature interval. The maximum magnetisation achieved in the ferromagnetic state decreases as the film thickness decreases. No evidence of in-plane strain was found in these films within the detectable limit of 0.5%, supporting the assumption that strain accommodation takes place in the out-of-plane direction [176].
Chapter 7

Manganese Aluminium

\textit{L1}_0 ordered manganese aluminium (MnAl) has received much attention for use as bulk permanent magnets. It has a high perpendicular magnetocrystalline anisotropy of $1.5 \times 10^7$ erg/cm$^3$ and a saturation magnetisation of approximately 500 emu/cm$^3$ \cite{14}. As well as these attractive magnetic properties, MnAl does not contain any heavy metals or rare earths normally found in other high anisotropy materials. This makes it a very economical material for mass production. More significantly, the lack of heavy metals gives MnAl low spin orbit coupling, leading to a low Gilbert damping parameter of just 0.006 and a longer spin diffusion length than other high anisotropy ferromagnetic materials \cite{124}. This makes it a potentially excellent candidate for use as an efficient spin polariser in spintronic devices such as magnetic tunnel junctions and spin torque oscillators. Its moderate saturation magnetisation and low damping parameter also lead to a low critical current for spin torque transfer as demonstrated by equation (2.29), making it attractive for use in applications such as STT-MRAM.

In order to be incorporated in spintronic devices, MnAl must be produced in thin film form. The production of the ferromagnetic \textit{L1}_0 ordered $\tau$ phase is challenging even as a bulk material due to it being metastable at room temperature. The reduced dimensionality of thin films may be expected to alter the formation mechanisms and structural properties of the material away from bulk values. Precise calibration of parameters such as the elemental composition and the process temperatures are therefore vital to enable good ordering.
7.1 Elemental composition analysis

Accurate and precise calibration of the elemental composition of MnAl thin films is essential for successfully realising their good magnetic properties. The phase diagram shown in figure 3.11 reveals a narrow window of just ±5 at% in which the desired, L10-ordered τ phase may form. This necessitates careful calibration of the elemental composition ratio before any magnetic properties may be investigated.

The use of an equi-atomic alloy target was initially investigated as a convenient starting point. The manufacturing process chosen was vacuum melting rather than hot pressing, as this was expected to produce targets of much higher purity. However, the MnAl alloy is extremely brittle, which invariably caused the target to shatter during the two attempts made by the Kurt J. Lesker company, rendering it unusable. Following the unsuccessful attempts to produce an alloy target, hot pressed targets were considered. However, these targets have a higher risk of impurities inherent from the manufacturing process. Given the difficulty of creating high quality MnAl, this approach was rejected. A co-sputtering approach was adopted, using two separate high purity targets, 99.95% pure, one of each element, which gave a fine degree of in-situ control over the elemental composition ratio. For all depositions discussed in this chapter, high purity (99.9999%) Ar working gas was used with a pressure fixed at 3mTorr.

In order to calibrate the elemental ratio of the film in the co-deposition system, it was first necessary to calibrate the rate of deposition of each elemental component. These rates could then be independently manipulated by varying the power applied to each target and re-checked in order to achieve different elemental ratios within a single deposition window. The thickness of single-element films was measured by analysing the profile of step edges using atomic force microscopy (AFM). Previous work has created such steps by using a small piece of silicon to mask part of the substrate during deposition. However, on the microscale, this produces a broad step with very shallow gradients, requiring very large scans to unambiguously measure the difference in height. In order to refine this process, previous work has used photolithography to define structures in the film. This
produced very sharp edges with well-defined steps, allowing a good average measurement of the step height.

Films deposited by sputtering conform to the substrate surface due to the variety of incident energies and angles of the sputtered material as well as the rotation of the sample. In a single-layer positive resist system, this would make removal of the resist after deposition very challenging, as the solvent would be unable to penetrate the film coating the sides of the exposed pattern. Using a bi-layer of resist overcomes this problem. The lower resist, PMGI, is more soluble in the developing solution than the upper layer, creating a cavity underneath the mask of the upper layer. The sputtered film is then unable to conform to the walls of this cavity, leaving only the desired structure on the substrate surface.

The standard bi-layer recipe used was composed of SF6 PMGI [177] for the lower layer and Microposit S1805 [178] for the upper layer. The substrate is heated on a hot-plate after each layer to remove residual solvent in a process known as soft-baking. The layers were spin-coated onto the substrate using the following procedure.

1. Spin-coat SF6 PMGI at 4000 RPM for 60 seconds. Nominal thickness of 250 nm.
2. Soft-bake at 190°C for 5 minutes.
3. Spin-coat S1805 at 4000 RPM for 60 seconds. Nominal thickness of 460 nm.
4. Soft-bake at 110°C for 60 seconds.

This was then developed for 60 seconds in MF319 and rinsed in de-ionised water prior to deposition, after which the resist was removed using Microposit Remover 1165 and the sample rinsed again in de-ionised water. The photolithography exposure was performed using a Microtech Laserwriter LW405, with a wavelength of 405 nm. The ideal dose was calibrated by exposing multiple times at different arbitrary gains.
AFM measurements were performed using a Bruker Dimension Icon operated in tapping mode using a silicon RTESP-300 probe with a nominal tip radius of 8 nm. For each element, four samples were prepared with sputtering durations of 2, 4, 6 and 8 minutes in order to calibrate the rate of deposition. Si substrates were prepared by ultrasonic cleaning in acetone for 5 minutes followed by IPA for 5 minutes. The base pressure of the sputtering chamber was below $5 \times 10^{-8}$ mBar. Figure 7.1 shows optical micrographs of representative patterned structures in both Al and Mn. Figure 7.2 shows AFM images and average height profiles of the films from 4 minute depositions. Each structure was measured in three different locations to ensure an accurate representation. Overall the 4 minute aluminium film exhibited an average height of $14.2 \pm 0.1$ nm, whilst the 4 minute manganese film had an average height of just $4.8 \pm 0.1$ nm.

Figure 7.1: Optical micrographs of photolithography structures of (a) aluminium and (b) manganese.
7.1 Elemental Composition Analysis

Figure 7.2: AFM images and height profiles of 4 minute depositions of (a), (b) Manganese and (c), (d) Aluminium.
Figure 7.3 shows the average heights from the depositions of all durations. The film thickness is linear with respect to deposition time, allowing the rate to be extracted from the fitted gradient. The gradients give a deposition rate of $2.7 \pm 0.1$ nm/minute with an intercept of $3.8 \pm 0.5$ nm for Al and $4.5 \pm 0.6$ nm/minute with an intercept of $-13 \pm 3$ nm for Mn. A positive intercept is expected due to the non-linearity in rate during the initial stages of film growth. Despite the apparent higher rate of Mn, the absolute thicknesses measured were less than those of the Al depositions. However, from equation (4.1), it is expected that the sputtering rate of Mn should be higher than that of Al. Additionally, the greater momentum of the sputtered Mn atoms should allow them to reach the substrate more quickly, as mentioned in section 4.1. The 2 minute deposition of Mn repeatedly failed to fully develop, and was often not visible at all, hence it could not be reliably analysed.

Clearly, material is being lost from the Mn depositions, leading to the negative intercept, large uncertainties and large deviations from the linear trend seen in figure 7.3. This was attributed to the reactivity of Mn, leading to corrosion and removal of the metal by the solvents used in the lithography processing. Evidence of this can also be seen in figure 7.1b, where the Mn structure has reduced optical contrast and faded extremities. In order
to shield the Mn from the solvents a 10 nm capping layer of Al was added to a 4 minute deposition of Mn, shown in figure 7.4. However, the reduced optical contrast attributed to corrosion is still seen as the Mn is exposed at the sides of the structure. Figure 7.4b shows how this sample becomes increasingly corroded by the solvents towards the edges of the structure, where the film becomes discontinuous.

Attempting to calibrate the deposition rate of Mn by measuring step heights is therefore not feasible. Rather than calibrating elemental composition by physical measurements of single-element films, a more direct chemical approach would be expected to yield more reliable data not influenced by sample processing artefacts. Inductively coupled plasma optical emission spectrometry (ICP) was therefore used to directly measure the chemical composition of continuous alloy films with a precision of 1 at%. These measurements were performed by Mr. Martin Jennings using a Thermo iCAP 6300 Duo instrument.

A series of samples were sputtered on Si substrates at room temperature using a fixed Al power of 100 W and varying Mn powers of 120, 130 and 140 W. A relatively large mass of material, of the order of 500 μg, is required in order to provide sufficient signal. This

Figure 7.4: (a) Optical micrograph and (b) AFM image of highlighted region of manganese with aluminium cap layer. Corrosion is visible as the faded regions in (a) and the increasing roughness towards the right hand side of (b).
necessitated long deposition times of 3.5 hours, based on the rate data gathered from AFM measurements. In-situ monitoring of the deposition was not available to check any variations in composition or sputtering rate over such long deposition times, limiting calibration to measurements taken before and after each deposition. Substrates were weighed before and after deposition using a quartz crystal microbalance with a precision of 1 μg. The films were dissolved off the substrate into a solution of nitric, perchloric and sulfuric acids and compared with a control solution of equal volume for the ICP measurement.

Figure 7.5 shows the atomic percentage of Mn and Al present in these films as measured by ICP. A linear trend was observed with lower concentrations of Mn found in the films deposited using a lower Mn power as expected. All films were rich in Mn. Extrapolating the linear fits gave the 50:50 atomic percentage cross-over point at a Mn power of 87 W. This power was therefore chosen as a starting point for further investigation.

A further series of samples was created to optimise the elemental composition by evaluating the magnetic properties of the films. The Al power was again maintained at
100 W and the Mn power varied to yield ±5 at% either side of 50:50 in 2.5% intervals using the gradient obtained from figure 7.5, giving powers of 63, 75, 87, 98 and 110 W. A film thickness of 50 nm was chosen in order to ensure good magnetic signal. Assuming equal quantities of Mn and Al are deposited by using a Mn power of 87 W allows the same deposition rate to be used for both elements. The deposition time required for a particular film thickness may therefore be calculated using the aluminium rate data obtained from figure 7.3, although this will be doubled for the alloy as there are two targets used simultaneously. Samples deposited using higher Mn powers will yield more Mn, which may be expected to give slightly thicker films and hence a larger volume for the calculation of the saturation magnetisation. This difference may be at least partially compensated for by slightly altering the deposition time of each sample with a percentage time offset equal to half the elemental percentage difference from the median.

In order to produce the L1₀ ordered τ phase in thin films, elevated deposition temperatures and post-deposition annealing are required, as discussed in section 3.3.5. Based on values from the literature, a deposition temperature of 300°C was chosen [57]. Samples were analysed in their as-deposited state, after annealing for 30 minutes in a reducing atmosphere of 10% H in Ar at 375°C and again after annealing at 450°C. Silicon substrates were used rather than single crystal MgO as perpendicular alignment of the films promoted by the cubic MgO template was not essential at this stage. The substrates had a thick oxide layer of 290 nm to prevent the formation of manganese silicides at high temperatures.

These initial samples were prepared for VSM analysis by cutting them into 8mm disks, giving a nominal film volume of $2.5 \times 10^{-6}$ cm$^3$. However, no ferromagnetism was observed for any of the samples in the as-deposited state or after annealing. Two more samples, using Mn powers of 63 and 87 W, were therefore prepared for ICP analysis to confirm the expected elemental composition. Despite the previous ICP data, it was found that the 50:50 ratio had drifted, and that a Mn power of 87 W gave a film composition of 60 at% Mn, whereas a Mn power of 63 W gave a film composition of 54 at% Mn. The origin of this drift is discussed further in section 7.3. Although the film compositions had changed from the expected values, the sample with 54 at% Mn coincided with the window
in which \( \tau \) phase formation was possible. The fact that this sample was not ferromagnetic indicated that the deposition and/or annealing temperatures required optimisation. The use of silicon oxide substrates rather than single crystal MgO is thought to contribute to the lack of \( \tau \) phase observed so far. The absence of any templating effect from the amorphous oxide surface likely altered the optimum temperatures adopted from the literature where MgO substrates were used [14], [57], [127].

### 7.2 Temperature optimisation

Due to the metastable nature of the L1\(_0\) ordered \( \tau \) phase in MnAl, the temperature conditions are critical to its successful formation and stabilisation. Deposition temperature governs the energy available to atoms which have arrived at the substrate, and hence their mobility within the growing crystal structure. Sufficient energy is essential to allow the atomic diffusion necessary to achieve the L1\(_0\) ordering. However, too high a temperature will promote the breakdown of the \( \tau \) phase into the equilibrium \( \gamma_2 \) and (\( \beta \)Mn) phases. There therefore exists an optimum window of deposition temperatures within which the \( \tau \) phase may form.

The degree of ordering and volume of any \( \tau \) phase nuclei may be enhanced by post-deposition annealing. Annealing is a more controlled process than high-temperature film growth as the duration may be set and the structure is not disrupted by additional incoming material. However, the energy barriers for diffusion may be higher as the material is constrained by its surroundings, rather than being freely mobile as during the growth process. Again, this is a balance requiring sufficient thermal energy to facilitate atomic diffusion whilst not providing too much so that the L1\(_0\) ordering is lost.

The literature suggests that the optimum windows for both deposition and annealing temperatures are rather narrow, with an almost total loss of saturation magnetisation \( \pm 100^\circ\text{C} \) of the optimum values [12], [15]. The value of the optimum temperatures appears to depend on other parameters that affect the stability of the \( \tau \) phase such as the substrate...
7.2 TEMPERATURE OPTIMISATION

used and the exact elemental composition of the films. Consistency is therefore essential in optimising the deposition and annealing temperatures.

Single crystal (100) MgO substrates were used to take advantage of the templating effect derived from their cubic structure. A film thickness of 50 nm was again chosen to provide a good magnetic signal. The target powers were set to 100 W and 63 W for Al and Mn respectively, which was expected to yield films with an ideal composition of \( \text{Mn}_{54}\text{Al}_{46} \) according to the most recently taken ICP measurements. Four samples were deposited using a range of substrate temperatures, room temperature (20°C), 250°C, 350°C and 400°C. Magnetic hysteresis loops were measured by VSM in the as-deposited state and after annealing at 300°C, 350°C, 400°C and 450°C for 30 minutes at each temperature.

Figure 7.6 shows a cross section of a film deposited on a SiO\(_2\) substrate with the same deposition time as the main series as a check of the film thickness. The measured thickness agrees well with the nominal value of 50 nm.

Figure 7.7 shows plan view bright field TEM images of the samples deposited at room temperature and at 400°C before annealing. The grain size is clearly seen to increase at

![Figure 7.6: Bright field TEM cross section of MnAl thin film on SiO\(_2\) substrate.](image)

![Figure 7.7: Bright field TEM images of MnAl thin films deposited on single crystal MgO substrates deposited at (a) room temperature and (b) 400°C.](image)
the highest deposition temperature. This evidences the increased mobility of the material over the substrate at higher deposition temperatures.
7.2 Temperature Optimisation

Figure 7.8 shows the maximum saturation magnetisations measured for all process steps and conditions employed. The peak value obtained was 67 emu/cm³, observed for the sample deposited at 250°C and annealed at 350°C. These deposition and annealing temperatures were chosen for further optimisation and will be discussed further in section 7.3. The sharpness of this single-value peak, where all neighbouring samples had negligible magnetisation, highlights the sensitivity of the processing conditions.

Figure 7.9 shows the hysteresis loops measured in both the in-plane and out-of-plane geometries. In both cases, the magnetisation was measured parallel to the applied field. This data shows that the coercivity in both geometries is close to zero. The anisotropy field, $H_k$, is the point at which the hard axis loop, in this case in the out-of-plane direction, reaches the saturation magnetisation. This occurs at approximately 8 kOe. The uniaxial anisotropy, $K_u$, may then be calculated using equation (2.23). Once shape anisotropy, calculated using equation (2.20), has been subtracted, this gives a small in-plane magnetocrystalline anisotropy of $2.4 \times 10^5$ erg/cm³, two orders of magnitude smaller than expected.

In order to directly observe the crystalline ordering of this film, a TEM sample was prepared. Figure 7.10a shows a high resolution TEM image of a small nuclei of L1₀ ordered material, measuring approximately 15 nm across. The measured magnetism is thus attributed to a small number of such nuclei. Figure 7.10b shows a selected area electron diffraction pattern from this sample, with indices confirming the presence of L1₀ MnAl. The pattern is polycrystalline, indicating the L1₀ nuclei have no preferred orientation.

Strong fringes are observed in figure 7.10a due to interference between the direct beam and the diffracted beam(s) from the crystalline grain. The presence of weaker fringes located in between the higher contrast fringes, visible in the inset line profile, suggests that this pattern arises from the alternate monatomic layers in an L1₀ grain. Due to the complex dependence of contrast and fringe spacing on axial tilt, especially on a crystalline substrate where moiré patterns may form, fringes are not necessarily a direct image of the atomic lattice [179]. However, they do reflect the presence of dislocations, and may
provide useful information on the relative lattice spacing and orientation relationships between adjacent grains. A full understanding of the relationship with the lattice would require image simulations of the sample and substrate to reproduce the observed fringe spacing and contrast, which is beyond the scope of this work.

Although a clear peak in saturation magnetisation was observed in this sample series, the value obtained was low, just 13% of the bulk value. This, together with zero coercivity and an apparent anisotropy which is two orders of magnitude lower than the bulk, suggested that this was unlikely to represent the optimum conditions. Another check of the elemental composition with ICP using the same target powers revealed that the expected ratio had shifted again, with a measured composition of Mn$_6$Al$_{39}$. This raised uncertainty over how consistent the elemental composition was throughout the sample series. However, now that a deposition and annealing temperature had been identified at which some level of ordering was observed, the elemental composition of the films could be more reliably optimised by maximising the saturation magnetisation and anisotropy.

Figure 7.10: (a) High resolution TEM image of crystalline nuclei in 50 nm MnAl thin film on single crystal MgO deposited at 250°C and annealed at 350°C. Line profile of highlighted region inset with background removed. (b) Diffraction pattern from same sample showing polycrystalline $L1_0$ MnAl indices.
7.3 **Elemental ratio optimisation**

A further series of samples was created in order to optimise the elemental composition. The temperature conditions were fixed as a deposition temperature of 250°C and annealing temperature of 350°C, as identified in section 0. Films were deposited on single crystal MgO substrates to maintain consistency and the applicability of the temperature calibration. The power applied to the Al target was again kept constant at 100 W. Five samples were deposited with Mn powers of 100 – 60 W in 10 W intervals. The base pressure was kept below $2 \times 10^{-7}$ Torr.

The crystallinity of the as-deposited samples was investigated with XRD. For this work, all X-ray measurements were done using a Rigaku SmartLab system using a copper anode operated at 1.4 kW. A two-bounce Ge (220) monochromator was used to isolate the Cu Kα1 radiation and enhance the resolution of the measurements. A parallel beam geometry was used with a 5 mm incident slit and a 5 mm receiving Soller slit for collimation.

Figure 7.11 shows the $\theta - 2\theta$ scans for all the samples in the as-deposited state. The MgO (002) peak is very clear at 42.9°, accompanied by satellite peaks at $\pm 1^\circ$. Additional shoulders are observed with a constant width of 3.7° but variable position with respect to the main peak. These satellite peaks and shoulders are attributed to terracing and crystal defects in the substrate. The rise in intensity at 90° is the edge of the MgO (004) peak. The MnAl L10 (001) and (002) peaks are expected at approximately 25° and 51° respectively [124], and the $\epsilon$ phase peak at approximately 20°. However, no peaks are visible apart from those arising from the substrate, suggesting the films are largely amorphous. Figure 7.12 shows the $\theta - 2\theta$ scans for the sample deposited using a Mn power of 70 W in the as-deposited state and after annealing at 350°C for 30 minutes. The shoulders of the substrate peak have shifted due to the different in-plane orientation of the sample with respect to the incident beam. Beyond this there is no change in the spectrum after annealing.
Figure 7.11: XRD $\theta - 2\theta$ scans for MnAl thin films deposited on single crystal MgO substrates with five different powers applied to the Mn target.

Figure 7.12: XRD $\theta - 2\theta$ scans for a MnAl thin film deposited on a single crystal MgO substrate before and after annealing at 350°C.
The thicknesses and layer structure of the films were investigated using X-ray reflectivity. The same instrument and experimental setup as the XRD measurements was used. GenX was used to simulate the sample and fit the data. Figure 7.13 shows a representative fit from the sample deposited using a Mn power of 70 W after annealing at 350°C. All samples showed a similar structure apart from minor variations in surface roughness. The sample model consisted of the MgO substrate, a MnAl layer and a low-density oxide surface layer.

The average MnAl film thickness of 47 nm was then used to calculate the volume used to determine the magnetic moment per volume. The standard error in the thicknesses was the same as the average roughness of 1 nm. The saturation magnetisations both before and after annealing are plotted in figure 7.14. Once again a single peak is observed, although its value of 35 emu/cm³ remains much lower than expected for a fully ordered and optimised sample, and lower than previously observed in figure 7.8. The peak is from the sample deposited using a power of 70 W applied to the Mn target, which is close to the 63 W used during the temperature optimisation series shown in figure 7.8. This smaller $M_s$ from an applied power difference of just 7 W highlights the sensitivity of the ordering to the elemental composition, and suggests the need for an even more detailed exploration of this parameter space if the optimum conditions are to be found.
Figure 7.14: Saturation magnetisation of MnAl films deposited on single crystal MgO substrates at 250°C using different target power ratios before and after annealing at 350°C. Error bars are within the symbols.

Figure 7.15: Bright field TEM images of the MnAl thin film deposited at 250°C using a Mn power of 70 W. (a) As-deposited. (b) After annealing at 350°C.
7.3 Elemental Ratio Optimisation

As previously, TEM images were taken to investigate the microstructure and ordering of the films. Figure 7.15 shows bright field TEM images of the peak sample deposited using a Mn power of 70 W and a deposition temperature of 250°C before and after annealing. A very similar grain structure is observed in both, indicating annealing has little effect on facilitating grain growth. No grain size measurements were performed as the growth and annealing conditions have not yet been fully optimised for crystal ordering. Different conditions might be expected to affect the grain size, but achieving L1₀ ordering is the first priority.

Figure 7.16 shows high resolution TEM images of an L1₀ ordered grain before and after annealing. In the as-deposited state, the L1₀ grain can be seen adjacent to another grain on the right with a different orientation, evidencing its formation by nucleation at grain boundaries. Due to the unknown grain orientation with respect to the substrate and optical axis, it is not clear whether this other grain is hexagonally ordered or a cubic phase orientated along its (111) axis. In the annealed sample however, no such adjacent grains are observed. Crystalline ordering has now propagated, creating regions of homogenous orientation. The dislocation visible in the centre of figure 7.16b matches well with the random attachment grain boundary diffusion process discussed in section 3.3.3, which

![Figure 7.16: High resolution TEM images of ordered grains in MnAl thin films on single crystal MgO substrates deposited at 250°C. (a) As-deposited. (b) Annealed at 350°C.](image)
leads to many defects. However, the overall size of the grains has not increased, suggesting growth beyond the immediate environment of the nuclei is restricted by other means such as impurities or defects in the crystalline quality of the substrate.

7.4 Discussion

The drift in the elemental ratio is attributed to the uneven erosion of the sputtering targets during the deposition process. In the magnetron configuration, the sputtering plasma is confined to a ring by the magnets under the target. This creates a racetrack shape groove as material is sputtered away. As this groove gets deeper the stronger magnetic field confines the plasma to a smaller volume, reducing the sputtering rate. This is correlated with a decrease in the applied voltage necessary to maintain a constant power \[180\], illustrated in figure 7.17. The long sputtering times illustrated were performed to deposit sufficient mass for the ICP measurements discussed in section 7.1. The rate of erosion will be different for each material due to the difference in sputtering yield as described by equation (4.1). This difference causes the elemental ratio of the sputtered films to drift.

![Figure 7.17: Decrease in voltage required to sustain an applied power of 100 W on the Al target over time.](image)
with target wear. Based on the qualitative similarity of the decrease in voltage and the decrease in sputtering rate, maintaining a constant applied voltage rather than a constant applied power may compensate for this, but a full understanding of the plasma physics involved would require simulations, which is beyond the scope of this work. It is therefore important to limit deposition times to a minimum to prevent significant drift. The remote plasma sputtering method described in section 4.1.2 does not suffer from this drift, however, only one target may be exposed to the plasma at a time, preventing co-sputtering of multiple targets at once.

As well as the elemental calibration, the deposition and annealing temperatures are critical, requiring detailed optimisation before any ordering may be obtained rather than simply using temperatures chosen from the literature [57]. As these films are deposited directly on the MgO substrate without a buffer layer it is not surprising that the ideal temperature conditions may differ from the literature. A Cr buffer layer is described as providing a very smooth surface, whereas for this work, XRD $\theta - 2\theta$ scans revealed a high level of terracing and crystal defects in the MgO substrate, disrupting the formation and growth of the $\tau$ phase.

Maintaining a good base pressure is important for reliable calibration of other process parameters. For MnAl this goes beyond simply ensuring the base pressure is low enough. A repeat of the sample deposited at 250°C using a Mn target power of 70 W was done at a much lower base pressure of $8.2 \times 10^{-9}$ Torr. In the first sample a saturation magnetisation of 35 emu/cm$^3$ was measured after annealing at 350°C as shown in figure 7.14. However, the repeat sample showed a negligible saturation magnetisation of 7.5 emu/cm$^3$. This is attributed to fewer impurities providing fewer nucleation sites for the formation of the $\tau$ phase.

In order to confirm this base pressure dependence a third sample was deposited at a higher base pressure of $5.8 \times 10^{-8}$ Torr, which was closer to the base pressure used for the first sample. A cap layer of Ta was also added to limit the surface oxidation layer observed in the XRR scans and prevent a decrease of the magnetically active volume. This cap layer was deposited at room temperature after the sample had cooled in the sputtering chamber.
in order to prevent intermixing with the MnAl layer. Figure 7.18 shows the VSM hysteresis loops measured from this sample with the field applied in plane and out of plane. An enhanced saturation magnetisation of 54 emu/cm$^3$ is seen, with a similar in-plane magnetocrystalline anisotropy of $2.3 \times 10^5$ erg/cm$^3$ as the best sample from the temperature optimisation series discussed in section 0 and zero coercivity.

Although it is not clear if the enhancement in saturation magnetisation is caused by the higher base pressure or by the cap layer preventing oxidation, it can be safely concluded that the magnetic properties are not negatively affected by the cap layer. Intermixing of the Ta cap layer with the MnAl during annealing does not appear to be a problem, although this may change at different temperatures. The use of cap layers is therefore suggested for all future work.

Lower base pressures are desirable for high purity films. The crystal quality may be expected to be higher at lower base pressures with fewer impurities to disrupt the growth during deposition. Growth of $\tau$ phase nuclei may therefore be enhanced, although initial nucleation may require different temperature conditions. A sample series exploring the
effects of varying base pressure is therefore suggested. Due to the highly interdependent nature of all process parameters for the successful formation of \( \tau \) phase MnAl, care must be taken to ensure all parameters are tightly controlled during calibration.

7.5 Summary

MnAl thin films have been fabricated by sputter deposition. A co-sputtering approach was used, giving greater flexibility and control over the elemental composition than an alloy target. Attempts to calibrate the elemental composition via conventional step height measurements using AFM were thwarted by the chemical reactivity of Mn which led to dissolution of the film in the lithography solvents. A more direct measurement of the elemental composition was made using ICP with a precision of 1 at%. Such precise calibration of the elemental composition is vital for the successful formation of the L1\(_0\) ordered \( \tau \) phase.

The maximum degree of L1\(_0\) ordering observed was very small, leading to a maximum measured saturation magnetisation of just 67 emu/cm\(^3\) and an in-plane magnetocrystalline anisotropy of 2.5 \( \times \) 10\(^5\) erg/cm\(^3\). The specific degree of ordering is too small to reliably quantify as there are no peaks in the XRD \( \theta - 2\theta \) scans. The final degree of ordering achievable appears to be determined by the as-deposited crystal quality. TEM images show increased grain size at higher annealing temperatures, but no grain growth after annealing. If large regions of well-ordered material are present grain boundary diffusion may proceed efficiently, allowing the L1\(_0\) grains to grow. However, if there is a high density of defects or regions of amorphous material, grain growth will be severely limited. More aggressive annealing at higher temperatures or for longer durations may overcome these energy barriers and nucleate L1\(_0\) grains without pre-existing nuclei, but the risk of nucleating the non-magnetic equilibrium phases will increase.

The process of calibrating process parameters for the successful formation of the MnAl \( \tau \) phase is iterative, requiring detailed and carefully controlled studies. This work has confirmed that L1\(_0\) ordered MnAl is achievable in a co-sputtering system and has
identified appropriate process parameters and conditions. The ordering may be optimised further by iterating the studies carried out thus far, whilst maintaining awareness of the sensitivity of the material on all other parameters which must be kept constant. The ordering should be optimised before any other studies are carried out such as grain size analysis, magnetic dynamics or magnetoresistance measurements.
Spintronic devices form essential components of a number of modern technologies. Their continued development is crucial for the advancement of technologies such as the read heads used in hard disk drive magnetic data storage and MRAM non-volatile solid state memory.

$L1_0$ ordered materials offer considerable promise for current and future developments in spintronics and are the material system of choice for advanced data storage media. The high perpendicular anisotropy is dependent on the tetragonal distortion of the unit cell. Structural characterisation is essential in order to understand the relationship between the physical arrangement of the atoms and the magnetic properties of these materials. The grain structure of remote plasma sputtered $L1_0$ FePt thin films and the crystal ordering of ultrathin FeRh films have been investigated and their structural properties examined with TEM. The potential of MnAl to form a ferromagnetically ordered $L1_0$ phase in thin films has also been explored, highlighting the sensitivity of the formation of the $L1_0$ ordered $\tau$ phase on the process parameters.
8.1 Grain size of remote plasma sputtered FePt thin films

High density magnetic storage media greater than 1 Tbit/in² will require new materials and technologies to overcome the superparamagnetic limit. The most likely candidate is heat assisted magnetic recording, which uses a very high anisotropy storage medium to retain thermal stability at grain sizes less than the currently used 8 nm. L1₀ ordered materials have a very high perpendicular magnetocrystalline anisotropy, the highest of which is FePt at $7 \times 10^7$ erg/cm³ [73]. In order to be used as a reliable storage media, the grain size of FePt thin films must be tightly controlled to an average size of approximately 5 nm with a distribution no greater than 10%. TEM provides direct observations of the grains, allowing their average size and distribution to be measured.

Measuring the grain size from TEM images requires some method of identifying grains in the images. Conventional particle size analysers rely on the user to identify and match grains with a circle of equivalent area. However, the need to individually identify at least several hundred grains makes this laborious and prone to user bias. Several alternative techniques were evaluated including manual outlining of grains in the image, thresholding of the image and a machine learning algorithm called “Trainable Weka Segmentation” [168]. Manual outlining suffered similar drawbacks to conventional methods, whereas thresholding was insensitive to variations in background contrast. The trainable segmentation technique produced the best fits to the expected lognormal distribution, as well as providing a repeatable, automatic method without user bias once the algorithm had been trained.

The additional parameter space offered by remote plasma sputtering has been previously explored as a potential method of controlling the grain size in thin films [170]. Previous XRD results on continuous FePt thin films, where the peak width was determined using the Scherrer analysis [148] suggested that the grain size was robust against variations in the target bias voltage. However, the grain size increased slightly after the annealing process necessary to form the desired high anisotropy L1₀ ordered phase. TEM observations provide an unambiguous measure of the grain size characteristics and quantify the conclusions of the XRD analysis. No dependence on the target bias voltage
was observed in the average grain size or in the grain size distributions. This is similar to work reported on Co/Pd multilayers [181] where again no dependence on bias voltage was observed. Together, these results provide significant evidence that any effect of bias voltage on grain size is quite material specific. The overall average grain size of the samples deposited using target bias voltages of 200 V, 600 V and 1000 V was $6.7 \pm 0.2$ nm in the as-deposited state, which increased to $12.5 \pm 0.5$ nm after annealing. The distributions were relatively wide, increasing from $2.4 \pm 0.2$ nm in the as-deposited films to $7.5 \pm 0.9$ nm after annealing. It should be noted that these were prototype films without additives to segregate and magnetically decouple the grains. Such additives may also affect the grain size distribution and grain growth during annealing.

8.2 Structural characterisation of ultra-thin FeRh films

FeRh undergoes an antiferromagnetic-ferromagnetic phase transition at the technologically useful temperature range of approximately 100°C (370 K). This can be used to lower the temperatures needed for the successful implementation of HAMR HDDs. In order to combine FeRh with an FePt storage layer in a HAMR medium, FeRh must be fabricated as thin films less than 10 nm thick. However, almost all the studies reported in the literature have used films of the order of 50 nm thick, with properties approaching that of the bulk material. The crystal structure and surface morphology of FeRh films less than 10 nm thick were therefore investigated using TEM to study the increased role of interfaces in such thin films. Previous work characterising the magnetic properties of these films found decreasing saturation magnetisation with decreasing film thickness.

Electron diffraction patterns revealed the expected epitaxial relationship between the FeRh films and the single crystal MgO substrate, where (100) MgO was parallel to (110) FeRh. Images revealed dewetting of the film from the substrate, leading to an island-like growth in the thinner films. Once the film thickness reached 10 nm the islands coalesced, forming a semi-continuous web-like structure. Using a seed layer or different process temperatures may mitigate this dewetting.
The intensity of the FeRh spots in the diffraction patterns decreased with decreasing film thickness. This was mostly attributed to the decreasing crystalline order, although the decreasing volume and surface coverage were also responsible. The decreased crystalline order was thought to be the main cause of the decreased saturation magnetisation in the thinnest films. This corresponds with an increase in the temperature and width of the antiferromagnetic-ferromagnetic phase transition [176].

8.3 Fabrication and characterisation of MnAl thin films

The high magnetocrystalline anisotropy of L1₀ ordered materials make them ideal for spintronic applications. MnAl has a L1₀ ordered phase but does not contain the heavy metals found in other L1₀ ordered materials, giving it a longer spin diffusion length and making it a very attractive and economical material for mass production. Most previous work has focussed on bulk applications of MnAl as permanent magnets. However, thin films are required in order to utilise MnAl in spintronic devices. The L1₀ ordered τ phase is metastable at room temperature and only forms within a narrow window (10%) of elemental compositions, requiring careful calibration of the chemical ratio and processing temperatures.

A co-sputtering approach was adopted in order to give the greatest control and flexibility over the elemental composition ratio by varying the powers applied to each sputtering target. Initial calibration of the elemental ratio was carried out with ICP optical emission spectrometry with a precision of ±1%. Initial samples did not show any L1₀ ordering due to the processing temperatures and Si substrates used. Subsequent samples were deposited on single crystal MgO substrates to take advantage of the cubic templating effect which helps promote the growth of the L1₀ τ phase. All samples were annealed for just 30 minutes at each annealing step in order to limit the decomposition of the τ phase in to the equilibrium (βMn) and γ₂ phases. Various deposition temperatures and annealing temperatures were investigated, identifying the optimum conditions as a deposition temperature of 250°C and an annealing temperature of 350°C. Bright field TEM images revealed larger grain sizes at higher deposition temperatures. High resolution TEM
images of the optimised sample showed the \( \tau \) phase nucleating at grain boundaries with increased ordering after annealing, although the observed grain size remained small at approximately 15 nm. The highest measured saturation magnetisation was 67 emu/cm\(^3\) with an in-plane anisotropy of \( 2.5 \times 10^5 \) erg/cm\(^3\), suggesting that the ideal conditions had not been achieved. A check of the elemental composition revealed that the ratio had drifted between the start and end of the sample series. This drift was attributed to the difference in the erosion rates of the two targets, which caused the individual sputtering rates to decrease unevenly.

Further optimisation of the elemental composition ratio was carried out, identifying a similar optimum ratio as that nominally used in the temperature optimisation series. The highest measured saturation magnetisation remained only 10 – 15% of the expected bulk value. XRD patterns revealed that the films were mostly amorphous, with the only detectable diffraction peaks arising from the MgO substrate. The shoulders on the MgO peaks indicated there was significant terracing and many crystalline defects in the substrates. This is thought to inhibit grain growth and disrupt the propagation of the L1\(_0\) ordering. Bright field TEM images showed negligible grain growth after annealing, although high resolution images suggested that ordering within individual grains had improved.

A repeat sample at a lower base pressure failed to produce any ordering at all. This was attributed to the reduction in nucleation sites provided by impurities. A second repeat sample was made at a higher base pressure and with a Ta cap layer to prevent oxidation. This restored the ordering and the saturation magnetisation. It is not clear what significance the cap layer may have had in enhancing the saturation magnetisation, but it is clear that it does not have any negative effect due to potential intermixing during annealing. The use of a cap layer is therefore suggested for future work, although higher annealing temperatures or longer durations may lead to intermixing.

Iterating these calibration procedures will isolate the optimum conditions for the growth of the L1\(_0\) ordered \( \tau \) phase in MnAl. This work has identified conditions which can lead to local ordering, although further optimisation is needed to achieve fully ordered films.
Due to the inter-connected, dependent nature of the system, care must be taken to ensure all experimental factors remain tightly controlled whilst systematically exploring individual parameters.

### 8.4 Future work

Understanding the kinetics of grain growth and the ordering process in FePt during annealing is important in achieving well-ordered films with a tightly controlled grain size suitable for data storage applications. In situ TEM annealing experiments would allow direct observation of the grain growth with simultaneous monitoring of the electron diffraction patterns to investigate the ordering. High resolution cross section images of FePt thin films would be able to characterise the orientation of the $L_1_0$ lattice, which is vital for achieving the perpendicular magnetisation necessary for high density data storage. Much work has already been carried out on the segregation of grains necessary for achieving a useable storage medium, typically using carbon, and dopants to reduce the ordering temperature, typically silver [64]. Remote plasma sputtering may be used to further these efforts by increasing the target utilisation without the accelerating voltage affecting the grain size.

In order to enhance the performance of HAMR with FeRh, bi-layer films must be produced in combination with an FePt storage layer. This work has focussed on single layer films of FeRh in order to understand their structural characteristics in the thin film limit. Future work must consider how these properties may be affected by being brought into epitaxial contact with FePt. X-ray reflectivity and cross section TEM images would be important for characterising the interface roughness and investigating any intermixing between the layers. Improving the surface wetting of the growing FeRh film is essential for incorporating the material in multi-layer devices. Island-type Volmer-Webber growth occurs when the substrate-vapour interfacial free energy, $\gamma_{SV}$, is less than the sum of the film-substrate and film-vapour interfacial free energies, $\gamma_{FS}$ and $\gamma_{FV}$ respectively, such that [182]
8.4 Future work

\[ \gamma_{FV} \leq \gamma_{FS} + \gamma_{SV} \]  

(8.1)

Growing the FeRh on top of the FePt layer would alter \( \gamma_{FS} \). Wetting may be improved and Volmer-Webber type growth suppressed if the new \( \gamma_{FS} \) is sufficiently small to reverse the inequality in equation (8.1). Plan view TEM images of bi-layer films, supported by EDX mapping, would help to characterise the surface coverage and confirm the continuous distribution of both materials.

Continued development of MnAl films is highly desired given the potential of the material. The work reported here provides a thorough grounding in the challenges associated with growing MnAl thin films and highlights the direction for future research. Deposition rates and times must be kept low in order to prevent significant drift of the elemental composition. It would be beneficial to investigate methods of compensating for the drop in rate with increasing target wear. As the target thickness decreases the strength of the magnetic field felt by the plasma increases, confining the plasma more strongly and reducing the area of the target which is sputtered. In the conventional constant applied power mode, the applied voltage decreases in a similar fashion to the deposition rate. However, maintaining a constant applied voltage may help to offset the increased confinement of the stronger magnetic field by increasing the kinetic energy of the plasma. Simulations would be required to gain a deeper understanding of the complex plasma physics of the magnetron sputtering gun and quantify the exact relationship between the applied voltage, target wear and sputtering rate.

Optimised deposition conditions are crucial for enhancement of the L1\(_0\) ordering. Without good crystalline ordering and the presence of the precursor \( \varepsilon \) phase in the as-deposited films, annealing is unlikely to be able to form the L1\(_0\) ordered \( \tau \) phase without risking the nucleation of the non-magnetic (\( \beta \) Mn) and \( \gamma_2 \) equilibrium phases. The next sample series would investigate the role of base pressure in dictating the availability of nucleation sites for the formation of the \( \tau \) phase. It may be that deliberately seeding the substrate with controlled nucleation sites would prove beneficial. However, it is expected that optimising all process conditions at consistently lower base pressures would lead to a higher degree of ordering due to the lower density of disrupting impurities. Careful
evaluation of the terracing and defects in the single crystal MgO substrates would help to understand their role in disrupting the atomic diffusion necessary for the growth of the τ phase. Different XRD measurements such as pole figures and in-plane $\theta - 2\theta$ scans would help to establish the quality and orientation of the crystal nuclei. In situ XRD and TEM annealing measurements would also help to determine the optimum annealing temperature and duration by detecting the nucleation of the equilibrium phases.
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