**Magnetic and transport
properties of electronically spin
polarised double perovskites
and Heusler intermetallics**

by

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ABSTRACT

Half-metallic ferromagnets with 100 % electronic spin polarisation are an interesting class of materials for new spin transport electronics applications. Some of the double perovskites and Heusler alloys are predicted to be half-metallic with Curie temperatures above room temperature. This thesis presents the results from an experimental study of polycrystalline double perovskites $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ and $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$, and ordered and disordered epitaxial thin films of Co_2MnSi Heusler alloys. A magnetothermopower was observed in $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ and $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$. This magnetothermopower can be explained in terms of a spin-tunnelling contribution to the thermopower between grains that changes in an applied magnetic field. The results from the high temperature (above 400 K) magnetisation studies on $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ in the paramagnetic region reveal that a localised electron model with antiferromagnetic coupling to itinerant electrons can account for the carrier concentration dependent effective moments. The correlation between the bare itinerant electron susceptibility and the Curie-Weiss temperature supports the kinetic energy driven model that has been used to account for the electronic spin polarisation and high Curie temperatures.

Antisite disorder is evident in the Co_2MnSi thin films that leads to a reduction in the saturation magnetisation. The resistivity of the ordered Co_2MnSi thin film is linear in temperature whereas the resistivity of the disordered film increases at low temperature due to weak localisation. A magnetoresistance is observed in ordered and disordered films. At low fields (below 0.1 T) the magnetoresistance is

likely to be due to domain wall scattering. For magnetic fields greater than 0.1 T there is likely to be a contribution from a magnetic-field-induced suppression of the weak localisation resistivity. Similar magnetoresistance behaviour was observed for ordered and disordered films. There is a large anomalous Hall resistivity observed in the ordered and disordered Co_2MnSi thin films. In the case of the ordered film it is found that the anomalous Hall effect is dominated by skew scattering.

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INTRODUCTION

Spintronics is a technology that utilises the transport of the intrinsic spin of the electron in addition to its charge. This field involves the study of the properties of electron spin in order to improve the efficiency of electronic devices. There has been recent interest in compounds that display a degree of electronic spin polarisation because they can lead to new spintronics devices including improved giant magnetoresistance (GMR) devices and spin polarised charge injectors. Half-metallic ferromagnets with 100 % electronic spin polarisation are an interesting class of materials for new spin transport electronics applications. Some of the double perovskites and Heusler alloys are predicted to be half-metallic with a high Curie temperature. $\text{Sr}_2\text{FeMoO}_6$ and $\text{Ba}_2\text{FeMoO}_6$ double perovskites have Curie temperatures of around 410 K and 310 K respectively, and Co_2MnSi Heusler alloys around 985 K. This thesis presents the results from an experimental study of polycrystalline double perovskites $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ and $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$, and ordered and disordered epitaxial thin films of Co_2MnSi Heusler alloys.

Chapter 2 introduces and explains the theoretical concepts necessary to understand the work presented in this thesis. It includes a discussion of magnetism, half-metallicity, thermopower, magnetothermopower, resistivity, magnetoresistance and the Hall effect. The experimental methodologies are described in chapter 3. Most of the experiments described in this thesis were done using the different options of the Physical Property Measurement System.

Chapter 4 describes the experimental results obtained from magnetic, resistivity, magnetoresistance, thermopower, magnetothermopower, thermal conductivity and Hall effect measurements on the double perovskite $\text{Sr}_2\text{FeMoO}_6$. The measurements were done on polycrystalline samples of pure $\text{Sr}_2\text{FeMoO}_6$ and electron doped, $\text{Sr}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$ and $\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$. The main focus is on the results from magnetothermopower measurements. The appearance of antisite disorder (ASD) makes it difficult to fully interpret the magnetothermopower that is only linear up to ~ 50 K. Therefore it is interesting to study a similar double perovskite, $\text{Ba}_2\text{FeMoO}_6$, where the ASD is low.

Chapter 5 reports the results from measurements on another polycrystalline double perovskite $\text{Ba}_2\text{FeMoO}_6$ and its La doped siblings $\text{Ba}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$ and $\text{Ba}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$. Magnetisation, resistivity and magnetoresistance, thermopower and magnetothermopower, and Hall effect measurements were carried out. The important results in this chapter are from high field magnetisation measurements in the paramagnetic phase in magnetic fields above 2 T, thermopower and magnetothermopower measurements. In polycrystalline samples, there is a significant contribution from the intergrain regions to the electrical transport. So it is interesting to study the bulk behaviour in high quality thin films. This was not possible in BFMO because good quality thin films were not readily available and it was not feasible to grow them in the given time. However, Co_2MnSi thin films were available and they too are known to have a high degree of electronic spin polarisation.

In chapter 6 the results from experimental studies of epitaxial thin films of Co_2MnSi Heusler alloys are presented. The experiments performed included magnetisation, resistivity and magnetoresistance,

and Hall effect measurements. The comparative study of ordered and disordered films is of particular interest.

THEORY

2.1 MAGNETISM

Every material acquires a magnetic moment when placed in an external field. The magnetic behaviour of a material can be classified according to their response to the applied field. The volume magnetic susceptibility (χ) is given by, $\chi = \frac{M}{H}$ with M the magnetisation of the material and H the external magnetic field strength. The different types of magnetism depending on the magnetic susceptibility values are diamagnetism, paramagnetism, ferromagnetism and antiferromagnetism.

In diamagnetic materials, the magnetic response opposes the applied magnetic field and the susceptibility is small and negative ($\chi \approx -10^{-5}$). In the case of paramagnetism, the magnetisation is weak but in the direction of the applied field. For paramagnets, χ is small and positive and typically ($\chi \approx 10^{-3} - 10^{-5}$). Some materials exhibit spontaneous magnetisation in zero applied field. This happens when the atomic magnetic moments tend to align parallel to each other and is known as ferromagnetism. Ferromagnets have positive susceptibility and the χ values range from 50 to 10,000. Above a critical temperature which is the Curie temperature (T_C) the magnetic moments become disoriented and the material exhibits paramagnetic behaviour. The antiparallel alignment of nearest neighbour magnetic moments results in antiferromagnetism or ferrimagnetism. If the opposing magnetic moments cancel each other resulting in zero net magnetisation,

the material is an antiferromagnet. But if the intensities of the neighbouring moments are different, the material can exhibit spontaneous magnetisation as in the case of a ferromagnet and it is called a ferrimagnet. Antiferromagnetic ordering is observed below a critical temperature called the Néel temperature (T_N).

The quantum mechanical exchange interaction is responsible for spontaneous ordering of atomic magnetic moments, *i.e.*, ferromagnetism, antiferromagnetism and ferrimagnetism. The exchange force is a consequence of the Pauli exclusion principle, which makes sure that the electrons with spins parallel to each other, if they belong to the same energy band, hence having otherwise the same set of quantum numbers, do not come too close to each other. This leads to a reduction in the Coulomb repulsion of particles of like charge, and consequently there is a gain in the potential energy (ΔE_{pot}) for the system given by $\Delta E_{pot} \approx E_{pot}(\uparrow\downarrow) - E_{pot}(\uparrow\uparrow)$. But this reduction in potential energy is accompanied by an increase in the kinetic energy of electrons for most materials as the space available to each electron becomes restricted. But for some materials, the reduction in potential energy is higher than the increase in kinetic energy and there is a net gain in energy for the ordered state. And we observe ferromagnetic or antiferromagnetic behaviour [1]. There are different exchange interaction mechanisms which create the magnetism in different ferromagnetic, ferrimagnetic, and antiferromagnetic substances. These mechanisms include direct exchange, Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange, double exchange, and super exchange.

2.1.1 Band Magnetism

Figure 1: Model density of states for the appearance of band ferromagnetism in accordance with the Stoner criterion (Reproduced from [1]).

If the Fermi level (E_F) lies within a distinct peak of the density of states, then it is easier for electrons to flip from spin-down to spin-up without gaining too much kinetic energy. The 3d transition metals have a density of state (DOS) similar to the one shown in [Figure 1](#) which satisfies the Stoner criterion for ferromagnetism, $N(E_F)I \geq 1$, where $N(E_F)$ is the density of states at the Fermi energy E_F and I is the Stoner exchange integral which measures the strength of the exchange interaction.

2.1.2 *Direct Exchange*

Direct exchange operates between electrons of the neighbouring magnetic ions without the need for an intermediary. The moments are close enough to have sufficient overlap of their wavefunctions. When the atoms are very close together, we typically get the antiparallel alignment and negative exchange (antiferromagnetism). According to Bethe and Slater the electrons spend most of their time in between neighbouring atoms when the interatomic distance is small in order to minimise their kinetic energy [21]. This requires the electrons to be at the same place in space at the same time, and therefore Pauli's exclusion principle requires their spin quantum numbers to be different. If the atoms are far apart the electrons spend their time away from each other in order to minimise the electron-electron repulsion resulting in positive exchange (ferromagnetism). Figure 2 shows the Bethe-Slater curve for a Fe-rich amorphous alloy, showing experimentally determined fluctuations in interatomic distances and resulting fluctuations in the exchange interactions [2]. But very often direct exchange cannot be an important mechanism in controlling the magnetic properties because there is insufficient direct overlap between neighbouring magnetic orbitals [22, 23].

Figure 2: Bethe-Slater curve for a Fe-rich amorphous alloy, showing experimentally determined fluctuations in interatomic distances and resulting fluctuations in the exchange interactions (Reproduced from [2]).

2.1.3 RKKY Exchange

The RKKY exchange (after Rudermann, Kittel, Kasuya and Yosida) is the indirect exchange interaction between magnetic ions mediated by the conduction electrons [24]. A localised magnetic moment spin polarises the conduction electrons and this polarisation in turn couples to a neighbouring localised magnetic moment a distance away. The interaction is long range and has an oscillatory dependence on the distance between the magnetic moments resulting in ferromagnetic or antiferromagnetic interactions. Figure 3 is the pictorial representation of RKKY mechanism which shows the interaction between local moments I_α and I_β , mediated by free charge carriers with local spin-density S [3].

Figure 3: Pictorial representation of the RKKY mechanism (Reproduced from [3]).

2.1.4 Super Exchange

The super exchange mechanism can be defined as an indirect exchange interaction between non-neighbouring magnetic ions which is mediated by a non-magnetic ion which is placed in between the magnetic ions. This can be understood using the schematic representation shown in Figure 4 where two transition metal ions (in this example Mn^{3+}) are separated by an oxygen ion. A Mn^{3+} ion has four unpaired electrons. When these atoms bond, electrons are donated from the oxygen to the manganese ions. Hund's first rule ensures that the spin of the electron donated to the left Mn-ion must be the same as the spins in the Mn-ion, which leaves an electron of the opposite spin in the oxygen p-orbital to be donated to the right Mn-ion. This can happen only if the spins of the right Mn-ion are opposite to the left Mn-ion. Hence this oxygen mediated bonding leads to a collective antiparallel spin alignment of nearest neighbour Mn-ions resulting in antiferromagnetism. Super exchange interaction can also be ferromagnetic but in such cases it is weaker and less common than

Figure 4: Schematic representation of the super exchange mechanism in LaMnO_3 (Reproduced from [4]).

the antiferromagnetic exchange [22, 4]. This unusual ferromagnetic super exchange is observed in CdVO_3 [25].

2.1.5 Double Exchange

When the magnetic ion can exist in more than one oxidation state, we can have a ferromagnetic exchange interaction called double exchange. Schematic representation of the double exchange mechanism in $\text{Mn(III)}_8\text{Mn(IV)}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4$ is shown in Figure 5 [5]. In this compound, manganese can have oxidation states of Mn^{3+} or Mn^{4+} . One spin up electron is transferred from the intermediate oxygen to the Mn(IV) , and is then replaced by another electron from Mn(III) . The electron that is replaced on the oxygen site also has to be spin up to satisfy the Pauli exclusion principle. This in turn requires the spins on the neighbouring Mn ions to be aligned in the same direction resulting in ferromagnetism. The electron conduction proceeds by this double step process by which one of the electrons on the Mn-sites jumps back and forth across the oxygen. This electron hopping

reduces the kinetic energy of the system resulting in overall energy reduction [22, 4].

Figure 5: Schematic representation of double exchange in $Mn(III)_8Mn(IV)_{12}O_{12}(CH_3CO_2)_{16}(H_2O)_4$ (Reproduced from [5]).

2.2 HALF METALS

In a nonferromagnetic material, energy levels are normally independent of spin and occupation of spin-up ($\uparrow$) and spin-down ($\downarrow$) states is equal. In a ferromagnetic metal, this degeneracy is broken and more states of one spin channel (the “majority” channel) are occupied than the other (“minority” channel), leading to non-zero net spin polarisation. Half metals are ferromagnets whose density of states shows only one occupied spin polarised sub-band at the Fermi energy E_F . Figure 6 illustrates the electronic density of spin up and spin down states in a non-ferromagnetic metal, a ferromagnetic metal, and a half metal. Half metals were first discovered by de Groot et al. in a com-

putational study on NiMnSb [26]. The spin polarisation P is defined by

$$P = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}},$$

where $N_{\uparrow}$ and $N_{\downarrow}$ are the number of $\uparrow$ spin and $\downarrow$ spin states at E_F , respectively. $P = 100\%$ for a half metal whereas for typical ferromagnets $P = 40 - 50\%$ at room temperature.

Figure 6: Spin resolved density of states of non-ferromagnetic, ferromagnetic and half metallic materials.

2.3 THERMOELECTRIC POWER AND MAGNETOTHERMOELECTRIC POWER

When two points of certain materials are maintained at different temperatures, an electric potential difference develops across the low and high temperature regions. The thermoelectric power (TEP or thermopower or Seebeck coefficient) of a material is the thermoelectric voltage developed per unit temperature difference. If a small temperature difference of ΔT induces a thermoelectric potential difference of ΔV , then the thermopower represented as S is given by,

$$S = -\frac{\Delta V}{\Delta T} \quad (1)$$

The thermopower of a material is a function of the temperature. The sign of S denotes the electric potential of the cold side with respect to the hot side. If we consider the simple classical description of diffusion of mobile charge carriers, negative (positive) thermopower is observed when electrons (holes) diffuse from the hot end of the sample to the cold end. This is because the charge carriers moving to the cold end leave behind their oppositely charged and immobile nuclei at the hot end thus giving rise to a thermoelectric voltage. However, the observed thermopower even in the case of simple metals is much more complicated than this simple explanation implies. A better description is obtained within the semiclassical model of electron dynamics where the diffusion thermoelectric power in metals is given by the Mott formula [27, 28],

$$S = -\frac{\pi^2 k_B^2 T}{3e} \left(\frac{\partial \ln \sigma_{xx}}{\partial E} \right)_{E_F} \quad (2)$$

where k_B is the Boltzmann constant, T is the temperature, E_F is the Fermi energy and e is the charge of an electron. The conductivity σ_{xx} is given by,

$$\sigma_{xx}(E, T) = \frac{e^2}{4\pi^3 \hbar^2} \iint \left(\frac{\partial E}{\partial k_x} \right)^2 \frac{\tau(\mathbf{k}) dA}{\nabla_{\mathbf{k}} E} \quad (3)$$

where E , E_F , τ , and k_x are, respectively, the energy, the Fermi energy, the relaxation time, and the x component of the wave vector of the conduction electrons, $\hbar$ is the reduced Planck's constant, dA is a surface area element. Figure 7 shows the temperature dependent thermopower of some metals.

Figure 7: The temperature dependence of the thermoelectric power of some metals (Reproduced from [6]).

In addition to the diffusion term, there is also a component of thermopower arising out of the temperature gradient in the lattice. There will be a higher density of phonons at the hotter end of the metal than at the colder end. This results in a net flow of phonons down the temperature gradient. These phonons can impart energy and momentum to the electrons via the phonon-electron interaction. The diffusion and phonon drag contributions to thermopower can be treated independently, so

$$S = S_{diffusion} + S_{phonon-drag} \quad (4)$$

There can also be magnetic contributions to thermopower. The electronic spin entropy contribution (if there is any) to the thermopower can vary in a magnetic field when the spin degeneracies are lifted by the applied field. There have been recent reports of this complete suppression of spin entropy term in a longitudinal magnetic field [29]. In the case of ferromagnetic materials, the effect of magnetic field on TEP could be attributed to a magnon drag effect where momentum is transferred to the electrons from quantised spin waves or magnons

[30, 31, 32]. These magnons are suppressed in a magnetic field resulting in a reduced contribution from this drag effect [33, 34].

2.4 RESISTIVITY

The Drude model of electrical conduction was developed considering metals to be a classical gas of electrons whose properties were governed by Maxwell-Boltzmann statistics. He applied the kinetic theory of gas to these conduction electrons moving between ions without interacting with each other. The expression for electrical conductivity (σ) according to this model is $\sigma = \frac{ne^2\tau}{m}$ where n is the number of electrons per unit volume, τ is the relaxation time (average time between the two consecutive scattering events), m is the mass of an electron and e is the electronic charge. Sommerfeld recognised the fact that free electrons in metals were quantum particles that obeyed Fermi-Dirac statistics and derived the free electron model of metals. This model gives a linear dependence of resistivity with temperature. Bloch showed that the wave function of a conduction electron in the periodic potential of the crystalline arrangement of the nuclei can be described in the form of a plane wave modulated by a periodic function with the period of the lattice. The Bloch theory was extended by Grüneisen which gives a linear temperature dependence of resistivity at high temperature and a T^5 dependence at low temperatures [35, 36, 37].

The T^5 behaviour for the electrical resistivity of pure metals is due to inelastic electron-phonon scattering. In addition to this there is also a contribution from impurity scattering to the resistivity. An empirical rule by Matthiessen states that the contributions to the resistivity of an impure metal are additive, *i.e.*, $\rho(T) = \rho_0 + aT^n$ where ρ_0 is

the temperature independent residual resistivity from impurities and aT^n is the pure metal contribution from phonons[36]. In ferromagnets, magnon scattering can cause a T^2 dependence in the low-temperature resistivity [38]. The conduction electrons can also be scattered by magnetic impurities leading to the Kondo effect [39].

In disordered metals, quantum corrections to the conductivity (QCC) are required to account for the anomalous resistivity behaviour. This includes the weak localisation (WL) effect which is caused by coherent interference of the conduction electron wavefunctions due to intense elastic scattering by the defects of the system. Figure 8 illustrates the weak localisation mechanism. The dots represent the impurities which causes electron scattering. The black arrow indicates the injection of an electron. If the electron traces the path indicated by blue arrows, then the red path, which is the time-reversed path of the blue one, should also be present quantum mechanically with the same probability amplitude as the blue path. Since the lengths of the two paths are exactly equal, constructive interference can occur at the endpoint of the two paths (the position of the green impurity). This increases the backscattering probability resulting in enhanced resistivity [40, 7]. The following equation can be used to fit the temperature dependent resistivity in materials where quantum corrections to the conductivity (QCC) like WL and renormalisation of the effective electron-electron interactions (REEI) were applied in 3D [41, 42].

$$\rho(T) = \frac{1}{\sigma_0 + a_1 T^{\frac{p}{2}} + a_2 T^{\frac{1}{2}}} + bT^n \quad (5)$$

where $\sigma_0 = \frac{1}{\rho_0}$ is the residual conductivity and ρ_0 is the residual resistivity, $a_1 T^{\frac{p}{2}}$ is the WL term with $p = 2$ or $p = 3$ for electron-electron or electron-phonon interactions, $a_2 T^{\frac{1}{2}}$ is the REEI correction term and

bT^n is the high temperature phonon scattering term where n is an integer with typical values of 1 or 2.

Figure 8: Illustration of the weak localisation effect (Reproduced from [7]).

2.5 MAGNETORESISTANCE

The magnetoresistance ratio, which is the change of resistivity of a material in an applied magnetic field, is generally expressed as,

$$MR = \frac{\Delta R}{R} = \frac{\rho(B, T) - \rho(0, T)}{\rho(0, T)} \quad (6)$$

where $\rho(B, T)$ and $\rho(0, T)$ represent the electrical resistivities at temperature T with and without the applied magnetic field B , respectively. Transverse magnetoresistance is observed when the applied magnetic field is perpendicular to the electric current whereas longitudinal magnetoresistance occurs when the applied magnetic field is parallel to the current. There are different forms of magnetoresistance effects.

2.5.1 Ordinary magnetoresistance

The ordinary magnetoresistance (OMR) arises from the increased Lorentz force on the charge carriers in the presence of an applied

magnetic field. The conduction electrons get deflected from their trajectories resulting in an increase in resistance and hence a positive MR. In general the ordinary magnetoresistance in the case of non-magnetic metals is, $\frac{\Delta R}{R} = aH^2$ where H is the applied magnetic field and a is the proportionality constant [43]. The transverse OMR is normally larger than the longitudinal one. Also, the relationship between the ordinary magnetoresistance and the applied magnetic field gets more complicated at low temperatures and high magnetic fields [44]. The magnitude of the OMR effect is quite small ($< 1\%$ in laboratory fields) making it unsuitable for most technological applications.

2.5.2 Anisotropic magnetoresistance

Anisotropic magnetoresistance (AMR) is where the change in resistivity in an applied magnetic field depends on the relative orientation between the direction of the electric current and the magnetisation direction. An example of the anisotropic magnetoresistance behaviour is shown in Figure 9 where the MR is positive when the current is parallel to the magnetic field and negative in perpendicular field. The resistivity of a material depends on electronic scattering processes and the angular dependence of these processes results in AMR. In ferromagnetic metals, it arises from spin-orbit coupling and its influence on s-d scattering. If $\rho_{\parallel}$ is the resistivity when the magnetic field is parallel to current and $\rho_{\perp}$ is the resistivity when the magnetic field is perpendicular to current, then the anisotropic magnetoresistivity ($\Delta\rho$) is the difference between these two resistivities given by, $\Delta\rho = \rho_{\parallel} - \rho_{\perp}$. The anisotropic magnetoresistivity ratio is the normalised quantity $\frac{\Delta\rho}{\rho_{av}}$ where $\rho_{av} = \frac{1}{3}\rho_{\parallel} + \frac{2}{3}\rho_{\perp}$ [43].

Figure 9: Anisotropic magnetoresistance of Au:Tb alloy at different temperatures (Reproduced from [8]).

2.5.3 Giant magnetoresistance

Giant magnetoresistance (GMR) arises from spin dependent scattering of charge carriers. GMR is observed in structures consisting of alternating ferromagnetic and nonmagnetic layers and as the name suggests a large increase in magnetoresistance is observed for even a

small applied magnetic field. The GMR effect in three Fe/Cr magnetic superlattices at 4.2 K is shown in Figure 10 [9].

Figure 10: GMR effect in three Fe/Cr magnetic superlattices at 4.2 K (Reproduced from [9]).

The decrease in resistance in the GMR effect can be explained by the two-current model [10]. Figure 11 is a schematic illustration of electron transport in a multilayer magnetic film showing how different spin scattering for parallel and antiparallel magnetisations result in a difference in resistance. The ferromagnetic (FM) layers are depicted to have magnetic moment facing up or down by the right or left arrows inside the multilayer. If the magnetic moments in FM layers are anti-parallel resulting in antiferromagnetic coupling as shown in Figure 11 (a), both up-spin and down-spin electrons will be strongly scattered. In contrast, up-spin electrons will only be slightly scattered

while down-spin ones will be strongly scattered if the magnetic moments in FM layers are parallel (ferromagnetic coupling) as shown in [Figure 11](#) (b). The GMR ratio is defined as $GMR = \frac{R_{AP}-R_P}{R_P}$, where R_P and R_{AP} are the resistances in parallel and antiparallel states. An external magnetic field is used to switch the coupling of layers from ferromagnetic to antiferromagnetic and vice versa.

Figure 11: Illustration of electron transport in magnetic multilayers for (a) antiparallel and (b) parallel magnetisations (Reproduced from [10]).

2.5.4 Tunnelling magnetoresistance

When two ferromagnetic metal layers are separated by a thin insulating layer, electrons can tunnel preferentially in one direction through this barrier if a bias voltage is applied. This tunnelling current depends on the relative orientation of the magnetisations of the two ferromagnetic layers, which can be changed by an applied magnetic field. This change in resistance of a magnetic tunnel junction (MTJ) in an applied magnetic field results in the phenomenon of tunnelling magnetoresistance (TMR). [Figure 12](#) shows the TMR effect in a CoFe/Al₂O₃/Co magnetic tunnel junction. The magnitude of TMR depends on the spin asymmetry of the density of states at the Fermi level (spin-dependent tunnelling or SDT). Similar to GMR, the tunnelling probability is more when there is ferromagnetic coupling and less when the layers are antiferromagnetically coupled [11].

In the Julliere model, the electron spin is assumed to be conserved during the tunnelling process [45]. The tunnelling of up-spin and down-spin electrons can be considered to be two independent processes and the interpretation is then based on the two-current model as in the case of GMR. When the magnetisations of the films are parallel, the minority spins tunnel to the minority states and the majority spins tunnel to the majority states. In the case of antiparallel magnetisation, the majority spins of the first film tunnel to the minority states in the second film and vice versa. The second assumption of the Julliere model is that the conductance for a particular spin orientation is proportional to the product of the effective (tunnelling) density of states of the two ferromagnetic electrodes. According to these assumptions, the conductance for the parallel and antiparallel alignment, G_P

Figure 12: Large room temperature magnetoresistance in a CoFe/Al₂O₃/Co magnetic tunnel junction. The arrows indicate the relative magnetisation orientation in the CoFe and Co layers (Reproduced from [11]).

and G_{AP} , is given by $G_P \propto \rho_1^\uparrow \rho_2^\uparrow + \rho_1^\downarrow \rho_2^\downarrow$ and $G_{AP} \propto \rho_1^\uparrow \rho_2^\downarrow + \rho_1^\downarrow \rho_2^\uparrow$ where $\rho_i^\uparrow$ and $\rho_i^\downarrow$ (layer index $i = 1, 2$) are the tunnelling DOS of the ferromagnetic electrodes for the majority and minority spin electrons. If TMR is defined as the conductance difference between antiparallel and parallel magnetisations, normalised by the antiparallel conductance, then $TMR = \frac{G_{AP} - G_P}{G_P} = \frac{R_P - R_{AP}}{R_{AP}}$. Substituting the values of G_P and G_{AP} , we arrive at the Julliere formula for TMR, $TMR = \frac{2P_1 P_2}{1 + P_1 P_2}$, where P_1, P_2 are the conduction electrons' spin polarisations of the two ferromagnetic layers [45, 11].

Slonczewski formulated a theoretical model for TMR [46]. In this model, the ferromagnetic layers are described by two parabolic bands shifted rigidly with respect to one another separated by a rectangular potential barrier. The tunnel conductance is determined as a function of the relative magnetisation alignment of the ferromagnetic films and is given by $G(\theta) = G_0(1 + P^2 \cos \theta)$. P is the effective spin polarisation of the tunnel junction given by $P = \frac{k^\uparrow - k^\downarrow}{k^\uparrow + k^\downarrow} \frac{\kappa^2 - k^\uparrow k^\downarrow}{\kappa^2 + k^\uparrow k^\downarrow}$ where $k^\uparrow, k^\downarrow$ are the electron momentum for the spin up and spin down electrons and $\kappa = \sqrt{\frac{2m}{\hbar^2}(U - E_F)}$ is the decay constant of the wave function into the barrier. U is the height of the potential barrier and E_F is the Fermi level. The spin polarisation of the tunnelling current thus depends on the barrier height as well in addition to the spin polarisation of electrons in the ferromagnetic layers [11].

TMR is also observed in granular systems with metallic grains separated by insulating grain boundaries [47]. When the magnetic moments of the adjacent FM granules are anti-parallel, high resistance is observed and when the magnetic moments are parallel, then there is a decrease in tunnelling resistance.

2.5.5 Colossal magnetoresistance

Colossal magnetoresistance (CMR) is a property of some materials in which the electrical resistance changes by an order of magnitude or more when an external magnetic field is applied. CMR is normally observed in manganese-based perovskite oxides [12]. The temperature dependence of the MR ratio for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_x$ films is shown in Figure 13.

Figure 13: Three MR ratio versus temperature curves for $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_x$ films. Curve 1, as deposited; curve 2, heated to 700°C for half hour in O_2 atmosphere; and curve 3, heated to 900°C for 3 hours in O_2 (Reproduced from [12]).

These hole-doped materials display a transition from a high-temperature paramagnetic insulator phase to a low-temperature ferromagnetic metallic phase and large magnetoresistance is observed near the phase transition temperature. Strong electron-phonon coupling and double-exchange interactions are contributing factors towards CMR in manganite perovskites. $\text{Ti}_2\text{Mn}_2\text{O}_7$ and some Cr chalcogenide spinels are other systems that exhibit CMR [48]. Similar effects are also observed in the ferromagnetic semiconductor EuO which can display a magnetoresistance ratio as large as 10^4 close to the Curie temperature of ~ 70 K [49].

2.5.6 *Magnetic Impurity Scattering and Spin Fluctuations magnetoresistance*

In systems containing isolated magnetic moments spin-dependent scattering can give a negative contribution to the magnetoresistance [50]. When a conduction electron scatters from a magnetic impurity the spin of the electron can flip, with a corresponding change in the impurity spin. An applied magnetic field tends to align the impurity spins, thereby restricting the possible scattering events to only those which increase the component of the impurity moment along the field. The reduction in possible scattering mechanisms corresponds to a decrease in resistivity.

Enhanced scattering from magnetic fluctuations can also occur close to T_C in a ferromagnet [51]. A magnetic field suppresses such fluctuations, leading to a negative magnetoresistance that is largest near T_C .

2.6 HALL EFFECT

When a current carrying conductor is placed in a magnetic field, a transverse voltage develops across the conducting material. One component of this voltage is due to the Lorentz force (F_L) given by $F_L = q \cdot (v \times B)$ where q is the electron charge, v is the drift velocity of the electron, and B is the magnetic field strength. This force acting on the charge carriers results in the normal Hall effect. This normal hall voltage is given by $V_H = \frac{R_H IB}{d}$ with I as the current, B as the magnetic field strength, d the depth of the sample, and $R_H = -\frac{1}{ne}$ the material specific normal Hall coefficient where n is the charge carrier density and e is the elementary charge. The other contribution to the Hall effect is the anomalous Hall effect (AHE) which is usually observed in ferromagnetic materials and it depends directly on the magnetisation of the material. Hence the Hall resistivity (ρ_{xy}) in ferromagnetic materials is empirically given by [13],

$$\rho_{xy} = R_H \mu_0 H_z + R_S \mu_0 M_z, \quad (7)$$

where R_H is the normal Hall coefficient, H_z is the perpendicular magnetic field, R_S is the anomalous Hall coefficient, μ_0 is the permeability of free space and M_z is the magnetisation. The first term in Equation 31 corresponds to the normal Hall contribution and the second term is the anomalous part. R_H depends mainly on the carrier concentration. The anomalous Hall effect can be either an extrinsic effect due to spin-dependent scattering of the charge carriers, or an intrinsic effect related to their Berry's phase curvature [52]. In the case of the extrinsic AHE, $R_s \sim \rho_{xx}^n$ where ρ_{xx} is the longitudinal resistivity with $n = 1$ for skew scattering from impurities and $n = 2$ if the domin-

ant mechanism is side jump deflection from impurities. Using these, Equation 31 may be rewritten as,

$$\rho_{xy} = R_H \mu_0 H_z + \alpha \rho_{xx}^n \mu_0 M_z, \quad (8)$$

where α is the proportionality constant. The three contributions to the anomalous Hall effect are shown in Figure 14.

Figure 14: Illustration of the three main mechanisms that can give rise to an AHE (Reproduced from [13]).

EXPERIMENTAL DETAILS

3.1 X-RAY DIFFRACTION (XRD)

Powder x-ray diffraction was used to determine the phase composition and purity of the polycrystalline samples. If an x-ray with a wavelength close to the lattice spacing, d_{hkl} , is incident on the crystalline sample, the in-phase diffracted x-rays undergo constructive interference. The Bragg condition for constructive interference is $2d_{hkl} \sin \theta_{hkl} = n\lambda$ where d_{hkl} is the lattice spacing between the planes described by the Miller indices h , k , and l , θ_{hkl} is the angle between the incident x-rays and scattering planes, n is the diffraction order and λ is the x-ray wavelength.

A Philips PW 1729 diffractometer equipped with a Co K α X-ray tube was used to record the XRD patterns. The XRD measurements were all done at room temperature and pressure. The samples were abraded uniformly using fine sandpaper and then mounted on an aluminium holder. The powder diffraction pattern was analysed using EVA (DIFFRACplus EVA from Bruker-AXS) software. The diffraction peaks were matched against the reference patterns obtained from the International Centre for Diffraction Data database.

3.2 RESISTIVITY AND MAGNETORESISTANCE

The different measurement options of the Physical Property Measurement System (PPMS 9 T, Quantum Design) was used to perform most of the magnetic and transport measurements (Figure 15). The PPMS is a flexible system that can be used to perform a variety of automated measurements. The measurements can be done in magnetic fields up to 9 T and at temperatures ranging from 1.9 to 400 K [53].

Figure 15: Physical Property Measurement System from Quantum Design.

The resistivities of the samples were measured in a 4-terminal mode using the dc resistivity option of the PPMS [14]. The four-wire method was used to avoid the contribution of the current leads and contacts to the resistance measurement. Two current leads were used to pass current through the sample, and a potential difference across the sample was measured using two separate voltage leads as shown in Figure 16. The very high impedance value of the voltmeter means that the voltage leads draw very little current. Hence both the current and

the voltage drop across the sample can be measured to a high degree of accuracy.

Figure 16: Current and voltage lead connections for four terminal resistivity measurement.

The samples were mounted on a resistance bridge sample holder board (Figure 17) to be used with the PPMS horizontal rotator. The horizontal rotator was used so that the sample could be rotated around an axis perpendicular to the magnetic field of the longitudinal PPMS magnet to get the preferred orientation of the applied magnetic field and current during magnetoresistance measurements. Channel 2 of the sample holder was used for our measurements. When the sample is mounted along the direction of the contact pads of this channel and the horizontal rotator is at the 90° position, the applied magnetic field would be parallel to the current.

The sample dimensions should ideally be less than 7.5 mm (length) $\times$ 7.5 mm (width) to fit within the sample space of the board. The polycrystalline samples were cut into rectangular shaped pieces using a diamond wire cutter. The approximate sample dimensions were 7 mm (length) $\times$ 4 mm (width) $\times$ 1 mm (height). Silver was deposited on the surface using a dc sputtering system to form the four parallel contacts for the measurement. Current and voltage leads were then soldered on to the silver pads. Low temperature solder was used in order to avoid damaging the sample holder board. In some cases, sil-

ver paint was used to make the electrical contacts. The PPMS sample wiring test station was used to test the contacts once the wiring was completed. The sample holder board was then attached to the horizontal rotator probe and inserted into the PPMS sample chamber for measurements. Appropriate configuration files were sent to the PPMS system to initialise the horizontal rotator. This step also activates the rotator thermometer for temperature control. The rotator thermometer was deactivated on completion of the experiment.

Figure 17: Resistance bridge sample holder board with two samples mounted for four-wire resistance measurements (Reproduced from [14]).

The PPMS MultiVu interface was used to programme and run the measurements from a Windows PC. The desired measurement steps were entered in a sequence file and then executed using MultiVu. The measurements were done in standard mode of the PPMS resistivity option. In the standard mode of operation, hardware linearity errors, drift, and offset errors were compensated using calibration resistors. Also, AC drive mode was employed to remove DC offset voltage errors. DC excitations were applied both in the forward and reverse directions and the potential drops across the sample were read. The

absolute values of these voltages were averaged to get the accurate reading. The resistivity measurements were typically done from 10 K up to 360 K.

Magnetoresistance (MR) is the change in electrical resistivity of a material in an external magnetic field. The 9 T PPMS magnet was used to perform resistivity measurements in a magnetic field. As described earlier, the horizontal rotator was set to the 90° position so that magnetic field was applied parallel to current.

3.3 HALL COEFFICIENT

The Hall coefficient measurements were done using the AC Transport Measurement System (ACT) of the PPMS [15]. The measurements were done in five-wire mode. Also, the horizontal rotator probe was utilised so that Hall voltages could be measured in two different orientations. Samples were wired on to the horizontal rotator ACT board in five terminal configuration (Figure 18) and attached to the horizontal rotator following the same procedure as in the case of resistivity measurements.

Figure 18: PPMS five-wire Hall sample-wiring diagrams (Reproduced from [15]).

Normally only two voltage leads are required to measure the Hall voltage produced as the result of an applied magnetic field. But if these two voltage leads are not perfectly perpendicular to the bias field from the two current leads, then the measured voltage can have a component that is dependent on the magnitude of this electric bias field and the sample resistance. This offset voltage is shown in [Figure 19 A](#). A fifth voltage lead in parallel to one of the other voltage leads was used to overcome this difficulty ([Figure 19 B](#)). While the magnetic field is turned off, a $100\ \Omega$ potentiometer between these two parallel voltage leads was used to null the offset. Measurements were done at both 0° deg and 180° deg positions so that the magnetoresistive component could be subtracted from the measured transverse voltage. A current of 100 mA at a frequency of 13 Hz was used for the measurements in magnetic fields up to 8 T. The Hall voltages as a function of magnetic field were measured at a number of temper-

atures from 10 K to 360 K to obtain the temperature dependence of normal and anomalous Hall coefficients.

Figure 19: Comparison of four-wire and five-wire Hall coefficient measurements (Reproduced from [15]).

If V_0 and V_{180} are the transverse voltages measured at 0° deg and 180° deg positions respectively in a given magnetic field, the Hall voltage is given by, $V_H = \frac{(V_0 - V_{180})}{2}$.

3.4 THERMOELECTRIC POWER AND THERMAL CONDUCTIVITY

The thermoelectric power and thermal conductivity was measured using the thermal transport option (TTO) of the PPMS [54]. The TTO option enables measurement of thermal conductivity and thermopower of samples from 2-400K under an applied magnetic fields of up to 9T (Figure 20). The disk shaped gold-plated copper leads were used to mount samples in two-probe lead configuration. The typical sample dimensions were 3 mm (l) $\times$ 3 mm (w) $\times$ 2 mm (h). The two-component Silver-filled H20E epoxy was used to attach the sample to the leads. The sample was baked at around 150° C to cure the epoxy resulting

in good thermal and electrical contact. The puck-mounting station of the TTO was used to hold the puck in place in order to conveniently mount the sample. One of the sample leads was clamped on to the cold foot of the puck and the other three leads were inserted into the appropriate heater/thermometer shoes. The assembly was inspected carefully to make sure that neither the shoes nor their wires were touching each other or any part of the puck, and that the sample was contacting the puck only at the clamp of the coldfoot. The copper isothermal radiation shield was screwed into the base of the puck to minimise radiation between the sample and the environment. As a final check, the radiation shield cap was removed to verify that no wires, shoes, or that the sample touches the shield. The cap was then put back on and the sample puck assembly was inserted into the PPMS chamber.

Figure 20: PPMS TTO sample puck with sample.

The thermal transport option was activated using the MultiVu software interface and the installation procedure was followed to get the system ready for measurements in high vacuum. The measurements were normally done in continuous mode where thermal transport data could be acquired simultaneously as the temperature or magnetic field were slowly varied. This is the fastest way of data acquisition as an adaptive software built into the system adjusts parameters such as heater power and period to optimise the measurements. The limits for these parameters were set using thermal tab in the thermal transport measurement window. A relatively short heat pulse was applied to one end of the sample resulting in a temperature differential between the two thermometer shoes accompanied by a voltage drop.

These temperature and voltage responses were measured simultaneously and modelled using a sophisticated curve-fitting algorithm to determine the thermopower and thermal conductivity.

3.5 MAGNETISATION

DC magnetisation measurements were mostly done using the Quantum Design Vibrating Sample Magnetometer (VSM) option for the Physical Property Measurement System (PPMS) [16]. The PPMS VSM is a fast and sensitive DC magnetometer. The VSM operates based on the principle that when a sample placed in a uniform magnetic field vibrates sinusoidally, a sinusoidal voltage is induced in the suitably placed pick-up coils. Figure 21 is a schematic diagram of the PPMS VSM linear motor transport used to vibrate the sample and the detection coilset. The PPMS VSM is able to resolve magnetic moment changes of less than 10^{-6} emu at a data rate of 1 Hz [16].

Figure 21: (a) PPMS VSM linear motor transport and (b) detection coilset (Reproduced from [16]).

The paddle-shaped sample holders were used to mount samples for VSM measurements from 5 K down to 360 K. The typical sample dimensions were 4 mm (l) by 2 mm (w) by 0.5 mm (t). The sample was weighed so that the magnetic moment per formula unit could be calculated. The special sample-mounting fixture was used so that the sample was mounted at 35 ± 2 mm from the bottom of the sample

holder. The actual distance from the centre of the sample to the bottom of the sample holder was measured to an accuracy of 0.5 mm to get the sample offset. The samples were glued on using GE Varnish and then held in place using a clear plastic heat-shrink tube. Then the sample holder (with the mounted sample) was removed from the mounting station and was screwed onto the end of the VSM sample rod. The VSM option was activated using the MultiVu interface and VSM sample installation procedures were followed to get the system ready for measurements. During the installation step, a scan for sample offset was performed in a magnetic field of around 1 T. The scan was repeated in a higher magnetic field if the signal was weak. The sample offset obtained from the scan should be close to the value measured earlier using the sample mounting fixture. The measurement type and parameters were specified using the Settings tab of the VSM Measurements dialog. The continuous measuring option was selected and the averaging and logging times were normally set to one second.

For high temperature magnetisation measurements from 300 K to 800 K, the VSM oven option was used. For these measurement, a carbon fibre sample rod with wire feedthroughs for the heater, thermocouple and a thermistor was used. The zirconia sample holder had heaters on the front side and a thermocouple at the back. The heated region, including the sample, was wrapped in low emissivity copper foil to minimise heat leak from the hot region to the surrounding coil-set and the measurements were done in high vacuum.

Some of the more sensitive magnetic measurements were done using the Magnetic Property Measurement System (MPMS 7 T, Quantum Design). MPMS utilises the superconducting quantum interference device (SQUID) technology [55]. Samples were mounted

in the middle of a plastic straw and then inserted into the MPMS chamber for measurements.

The magnetic moments were reported in electromagnetic units (emu). The volume susceptibility of the sample is given by,

$$\chi_V = \frac{\mu_0 m^{[emu]} \rho \times 10^3}{mass \times B}$$

where μ_0 is the permeability of free space, $m^{[emu]}$ is the magnetic moment in *emu*, ρ is the density of the sample in $g.cm^{-3}$, the *mass* measured in *g* and B is the magnetic flux density in *Tesla*. Also the magnetic moment per formula unit is given by,

$$m = \frac{m^{[emu]} M_r}{mass \times N_A}$$

where M_r is the relative atomic weight in grams for one formula unit and N_A is the Avogadro number.

DOUBLE PEROVSKITE $\text{Sr}_2\text{FeMoO}_6$

4.1 INTRODUCTION

The double perovskite $\text{Sr}_2\text{FeMoO}_6$ (SFMO) has generated quite a bit of interest recently since it is predicted to have a high degree of electronic spin polarisation even at room temperature [56]. It also exhibits a high Curie temperature of around 410 K. The polycrystalline SFMO sample also exhibits a colossal magnetoresistance of around -40% at low temperatures [56]. SFMO has an ordered double perovskite structure. The unit cell is tetragonal with alternating Fe and Mo sites surrounded by oxygen octahedra. Sr occupy every hole created by eight MoO_6 octahedra [57] (Figure 22).

Figure 22: $\text{Sr}_2\text{FeMoO}_6$ structure

The spin-resolved partial density of states (DOS) of SFMO is shown in Figure 23 [17]. In the up-spin band, the band extending from -8.0 eV to -2.0 eV below the Fermi level is composed mainly of Fe 3d and O 2p states. The band whose main contribution is from Fe e_g states is localised between the O 2p band and the Fermi level. The sharp narrow band just above the Fermi level is mostly of Mo t_{2g} state origin. In the down-spin band, the O 2p band is fully occupied and the band from -1 eV to 1.5 eV is contributed by Fe t_{2g} and Mo t_{2g} states, which is followed by the Fe e_g band centred at 2 eV and the Mo e_g band starting from 4 eV. the Fermi level is within a spin-down band comprising of Fe($t_{2g}\downarrow$)-O(2p)-Mo($t_{2g}\downarrow$) sub-band orbitals [56, 17] (Figure 23).

Figure 23: The density of states of $\text{Sr}_2\text{FeMoO}_6$ [17].

Various models have been proposed to account for the half-metallicity and the high Curie temperature in SFMO. The observed half-metallic DOS can be attributed to the strong Hund's-rule energy stabilisation due to the high-spin $3d^5$ configuration at the Fe site [58] (Figure 24).

Figure 24: SFMO schematic electronic structure

Conventional double-exchange as in the case of manganites is ruled out because the fully filled Fe $3d^5$ up-spin orbitals makes it impossible for Hund's rule coupling between the itinerant down-spin Mo $4d^1$ electron and the localised up-spin electrons on the Fe site [59, 57]. Mo is normally a non-magnetic site. Many studies have attributed the origin of negative spin polarisation at such a site to a kinetic-energy-driven mechanism [59, 60]. Within this framework, a two-sublattice model, in which hopping interactions involves jumps between Fe and Mo sublattices, was used to explain the magnetic and electronic structure [61, 62, 63, 64].

It is of interest to study the effect of electronic doping on the magnetic and electronic properties of these compounds. Replacing the Sr ions in SFMO with trivalent cations such as La would result in electron doping. Earlier studies have found that the Curie temperature increases from around 400 K for $\text{Sr}_2\text{FeMoO}_6$ to about 490 K for SrLaFeMoO_6 [65, 66]. The saturation magnetisation decreases from $2.2 \mu_B/f.u.$ in $\text{Sr}_2\text{FeMoO}_6$ to about $0.8 \mu_B/f.u.$ in $\text{Sr}_{1.5}\text{La}_{0.5}\text{FeMoO}_6$

due to an increase in Fe-Mo antisite disorder [67]. Photoemission spectroscopy data indicates an increasing density of states [68], and Mössbauer spectra support the reduction in Fe-Mo ordering with La doping [69]. Previous studies have also shown that the thermoelectric power systematically increases with electron doping in this double perovskite compound whereas the magnetoresistance decreases [68, 70]. There have also been first-principles studies of the electronic structure of La-doped SFMO [69, 71].

4.2 EXPERIMENTAL DETAILS

A series of polycrystalline $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 0.2$ and 0.4) samples were prepared by a solid-state reaction method from stoichiometric mixes of $\text{Sr}(\text{NO}_3)_2$, Fe_2O_3 , MoO_3 , and La_2O_3 . The powder was denitrated at 700°C in air. After pressing the powder at 20 MPa, the pellets were placed in air at 1200°C for 8 h. The pellets were about 10 mm in diameter and about 2-3 mm thick. The samples were then ground, pressed into pellets, and then sintered at 1150°C in an atmosphere of 5% H_2 – 95% N_2 for 3 h. The last step in the synthesis process was repeated until all the minority phases are removed and homogeneous samples were obtained. The phase composition and purity were determined from x-ray diffraction measurements using $\text{Co K}\alpha$ radiation. XRD measurements show that all the $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ samples are single phase. The magnetisation measurements were performed using the Vibrating Sample Magnetometer (VSM) option of the physical property measurement system (PPMS 9T, Quantum Design). The electrical resistances were measured in four-terminal configuration using the resistivity option of PPMS. The thermoelectric power and thermal

conductivity were measured using the thermal transport option and the Hall effect using the AC transport option of PPMS.

4.3 XRD

The x-ray diffraction measurements for all the samples were done at room temperature. Figure 25 shows the XRD patterns for single phase $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ samples after the final sinter. The degree of Fe-Mo anti-site disorder (ASD in %) was estimated from the ratio (R in %) of the (101) peak intensity at 22° divided by the (200) peak intensity at 37° using the relation $R = 0.001365(\text{ASD})^2 - 0.136592(\text{ASD}) + 3.417842$ [72]. ASD values obtained were 14%, 22% and 30% respectively for $\text{Sr}_2\text{FeMoO}_6$, $\text{Sr}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$, and $\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$.

Figure 25: XRD patterns of $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$

One of the reasons for the increase in ASD on substitution of Sr ions by La ions is that the doped electrons mainly occupy the Mo orbitals [68, 73]. This reduces the charge difference between Fe and Mo cations which is required for ordering [74].

4.4 MAGNETISATION

Magnetisation measurements under an applied magnetic field of up to 8T at 50 K are plotted in Figure 26. The coercive fields are 0.0089 T, 0.0164 T, and 0.0111 T for $\text{Sr}_2\text{FeMoO}_6$, $\text{Sr}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$, and $\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$ samples respectively. $\text{Sr}_2\text{FeMoO}_6$, $\text{Sr}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$, and $\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$ samples were found to have T_C values of around 410 K, 420 K, and 430 K respectively.

Figure 26: Magnetisation curves at 50 K for $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ samples.

If we consider a simple ferrimagnetic arrangement of the moments corresponding to Fe^{3+} and Mo^{5+} , the total saturation magnetic moment M_s (in $\mu_B/\text{f.u.}$) is given by, $M_s = M_{\text{Fe}} - M_{\text{Mo}} = 5 - 1 = 4 \mu_B/\text{f.u.}$. The experimental saturation magnetisation value obtained for even the undoped SFMO is only $2.66 \mu_B/\text{f.u.}$ which is much less than expected. The reduction in saturation magnetisation is primarily

attributed to Fe-Mo anti-site disorder and ASD can be estimated from the saturation magnetisation (M_s) according to the equation [70] ,

$$M_s = 4.0 - 9.0 \times ASD. \quad (9)$$

There is also a systematic decrease in the high field magnetisation with increasing La-concentration as reported earlier [65]. The M_s values are $1.74 \mu_B/f.u.$ for $Sr_{1.8}La_{0.2}FeMoO_6$ and $1.13 \mu_B/f.u.$ for $Sr_{1.6}La_{0.4}FeMoO_6$. From Equation 9, Sr_2FeMoO_6 , $Sr_{1.8}La_{0.2}FeMoO_6$, and $Sr_{1.6}La_{0.4}FeMoO_6$ samples were found to have ASD values of 15%, 25%, and 32% respectively. But this does not take into account the fact that injected electrons prefer Mo sites which could also lead to reduced saturation magnetisation. Hence a La-doping fraction (x) dependent saturation magnetisation $M_s(x)$ could be defined as, $M_s(x) = M_{Fe} - (M_{Mo} + (3 - 2)x)$, since La^{3+} ions are used to substitute Sr^{2+} ions. The difference in saturation magnetisation with doping from this effect assuming all the doped electrons go to Mo site could be given by,

$$\Delta M_s(x) = -x. \quad (10)$$

This contribution should be corrected when using Equation 9 and now the ASD is 23% for $Sr_{1.8}La_{0.2}FeMoO_6$ which is comparable to the ASD obtained from XRD. But the ASD of 27% for $Sr_{1.6}La_{0.4}FeMoO_6$ is lower than the one obtained from XRD. This may be due to the fact that at higher La concentrations, some of the doped electrons are localised on Fe sites as well.

4.5 MAGNETORESISTANCE

The magnetoresistance, which is the change of resistivity in applied magnetic field, is expressed as,

$$MR = \frac{\rho(B, T) - \rho(0, T)}{\rho(0, T)} \quad (11)$$

where $\rho(B, T)$ and $\rho(0, T)$ represent the electrical resistivities at temperature T with and without the applied magnetic field B , respectively.

Figure 27: Resistivity versus temperature for $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ samples in zero magnetic field (black squares) and in an applied magnetic field of 8 T (red stars).

The temperature dependent resistivities were measured from 360K down to 5K for pure as well as La-doped samples and are shown in [Figure 27](#). The room temperature resistivity for undoped SFMO is about 5 m Ω . cm which is an order of magnitude larger than single crystal SFMO [\[75\]](#). All the samples exhibit an initial decrease in the resistivity with decreasing temperature and then a gradual increase in resistivity as we cool down further. This is due to a metallic resistivity regime at higher temperatures and a crossover to a tunnelling-like behaviour at lower temperatures where the resistivity increases with cooling [\[76\]](#). When a high magnetic field of 8T is applied, the resistivity for the undoped SFMO is significantly reduced over the entire temperature range in particular in the low temperature region where tunnelling dominates. The low temperature upturn in the resistivity is not pronounced now because the spin polarised electrons are now aligned in the magnetic field and there is an increased tunnelling probability which offsets the temperature dependent increase in tunnelling resistivity. For single crystals, the resistivity has a Fermi liquid T^2 dependence and does not increase at low temperatures [\[77\]](#).

Figure 28: Resistivity versus T^2 from 100 K for $\text{Sr}_2\text{FeMoO}_6$ in a magnetic field of 8 T (black circles) and a linear fit to the data above 100 K (red line).

It is seen here that the resistivity increase at low temperature has nearly disappeared at 8 T for $x=0$, and follows a T^2 dependence from around 100 K. This is clearer in Figure 28 where the resistivity is plotted against T^2 . It is likely that this low temperature upturn will disappear for even higher magnetic fields. Thus, for high magnetic fields, the resistivity for polycrystalline SFMO may be written as $\rho = \rho_0 + \rho' T^n$. This is analogous to single crystal behaviour with the residual resistivity (ρ_0) being much higher for polycrystalline samples due to the effect of grain boundaries. With La-doping, initially there is a decrease in resistivity for $\text{Sr}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$ and the resistivity minimum is also lowest for $\text{Sr}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$. If we increase the La concentration ($\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$), there is no further increase in conductivity. This could be an effect of increased antisite disorder at higher

doping concentrations or a grain boundary effect. Hence there seems to be no direct correlation between resistivity and electron doping.

Figure 29: Magnetoresistance as a function of temperature measured at 8T for $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ samples

For La-doped samples, the magnetoresistance decreases with La-doping (Figure 29). Serrate *et al* [76] attributed the decrease in resistivity to the opening of new conduction channels that may not be spin dependent. The shift in crossover temperature could be due to a resistance decrease of the tunnel barriers at the grain boundaries. There is also a suggestion of filling of the minority spin states of the conduction band upon electron doping [78]. In effect there is a reduction in the degree of spin polarisation with La-doping resulting in reduced magnetoresistance and there is no net effect of magnetic field on the scattering of electrons passing through the new conduction channels. Hence though the Curie temperature increases with electron doping which is a desirable effect [65] [66], it is accompanied by a reduction in magnetoresistance. This would mean that La-doping SFMO may not be advantageous from perspective of technological applications.

The magnetoresistance values of SFMO at fields of up to 8 T is shown in Figure 30. The sample shows a negative magnetoresistance of about -5% at room temperature which increases to -24% at low temperatures. These values are close to those reported for high quality polycrystalline SFMO samples [56]. There is a sharp increase in the magnetoresistance response at low fields and the MR value does not saturate even at a field of 8 T which is much higher than the saturation magnetisation field (Figure 26). The La-doped samples show similar magnetoresistance behaviour with field but the values are lower than those observed for pure SFMO.

Figure 30: Magnetoresistance of SFMO at different temperatures

The large magnetoresistance in ceramic SFMO is understood to originate from the tunnelling of spin polarised electrons at grain boundaries. The polycrystalline SFMO consists of grains with low resistance but the grain boundaries themselves could be insulating. These grain boundary regions are small enough for charge carriers to tunnel across. Due to the high degree of spin polarisation in these materi-

als, electrons can tunnel across only if there are states with the same spin orientation across the barrier. When the sample is not magnetised, magnetisations in adjacent grains may not be parallel. Hence the resistivity is higher since there are limited states available for electrons to tunnel into. In the presence of an applied magnetic field, the spins align themselves in the field. This results in neighbouring grains having parallel spin orientation enabling increased tunnelling current [76]. The absence of significant magnetoresistance in SFMO single crystals provides further support to the idea that an extrinsic mechanism is responsible for the large MR in polycrystalline samples [79] [75]. Using the Inoue and Maekawa's theory [80] of the origin of the magnetoresistance in granular magnetic films, it can be shown that,

$$MR = \frac{-P^2 m^2}{1 + P^2 m^2} \quad (12)$$

where $P = \frac{(n_{\downarrow} - n_{\uparrow})}{(n_{\downarrow} + n_{\uparrow})}$ is the degree of spin polarisation with $n_{\downarrow}$ the no. of spin-down charge carriers and $n_{\uparrow}$ the no. spin-up charge carriers, m is the normalised magnetisation of the sample. But when we attempt to fit this direct tunnelling model (Equation 12) to our magnetoresistance data Figure 30, it is clear that the MR does not saturate even at a field of 8 T which is quite a long way above the saturation magnetic field Figure 26. Hence the bulk magnetisation cannot be used directly to model the observed the magnetoresistance in polycrystalline double perovskites.

But it was found that if we use the magnetisation of the region in the vicinity of the grain boundary in Equation 12 instead of the bulk normalised magnetisation, the magnetoresistance data could be explained better [81]. The Equation 12 now becomes,

$$MR = \frac{-P^2 m_{gb}(H)^2}{1 + P^2 m_{gb}(H)^2} \quad (13)$$

where $m_{gb}(H)$ is the magnetisation of the grain boundary region where H the applied magnetic field. Since there is no direct way to measure the magnetisation of the grain boundary region, we should fit using an appropriate function for $m_{gb}(H)$. There is also a component of MR which is linear in field at high fields as seen in previous reports [82]. This linear contribution could be due to antiphase boundaries [83], intrinsic spin disorder contribution [81] or the magnetic nature of the grain boundary region [76]. Adding this linear term to Equation 13, we get

$$MR = \frac{-P^2 m_{gb}(H)^2}{1 + P^2 m_{gb}(H)^2} - \alpha H \quad (14)$$

where α is a fitting parameter. The magnetoresistance data from $(\text{Ba}_{0.8}\text{Sr}_{0.2})_2\text{FeMoO}_6$ was modelled using a functional form for the magnetically disordered region near the grain boundary that is widely used in ferromagnets with weak random anisotropy, $m_{gb}(H) = (1 - \frac{a}{\sqrt{H}})$ [81]. Hemery *et al* [84] used a phenomenological tanh-function correction, $m_{gb}(H) = \gamma \tanh(H/H_0) + [(1 - \gamma) - a/\sqrt{H}]$ (γ , H_0 and a are fitting parameters), at low fields to model the magnetoresistance data in polycrystalline $\text{Sr}_{2-x}\text{Ba}_x\text{FeMoO}_6$ samples. We have attempted to fit the magnetoresistance data for pure SFMO using Equation 14. Fisher *et al* [85] found that magneto-conductivity data for SFMO goes as $\exp(-(H_0/H)^{\frac{1}{2}})$. High field magneto-conductivity measurements on $(\text{Ba}_{0.8}\text{Sr}_{0.2})_2\text{FeMoO}_6$ shows the same behaviour [81]. Guided by this behaviour the magnetoresistance data for SFMO was fitted by modelling grain boundary magnetisation using an exponential term, $m_{gb}(H) = \exp(-a/\sqrt{H})$ [72]. The fits to the magnetoresistance data at 10 K, 77 K, 150 K and 300 K using Equation 13 and Equation 14 with the exponential model for the magnetisation in the vicinity of the grain boundary region is shown in Figure 31.

Figure 31: Field dependent magnetoresistance fits for SFMO at different temperatures using Equation 13 (blue dashed line) and Equation 14 (red solid line).

It can be clearly seen that Equation 13 gives a reasonably good fit for field-dependent magnetoresistance at 10 K ($a = 0.62757$), 77 K ($a = 0.63558$) and 150 K ($a = 0.58092$). From this model, we get a spin polarisation of about 60% at 10 K. But the room temperature data requires Equation 14 in order to get a good fit with fitting parameters $a = 0.44747$, $P = 0.14571$, and $\alpha = 0.00397$. This is similar to the magnetoresistance for $(\text{Ba}_{0.8}\text{Sr}_{0.2})_2\text{FeMoO}_6$ where a spin disorder term was used to model the data above 200 K [81]. The existence of a spin-glass (SG) like phase near the grain surface could be another reason for a change in magnetoresistance behaviour at higher temperatures [86]. The estimated T_g of the SG-like skin from ac susceptibility studies is around 183 K [87]. The degree of spin polarisation obtained from the fits is shown in Table 1. The degree of spin polarisation increases with decreasing temperature which can be attributed to weak spin thermal fluctuation at low temperatures [88]. Apart from the degree of spin polarisation effects like thermal reduction of magnetic moment, inelastic tunnelling due to electron-magnon scattering and thermally assisted hopping conductance could also contribute to the temperature dependence of tunnelling magnetoresistance [89].

Temperature (K)	P from fit to Equation 13	P from fit to Equation 14
300	0.32	0.15
150	0.44	0.37
77	0.58	0.50
10	0.69	0.61

Table 1: Degree of spin polarisation for SFMO from magnetoresistance fits.

4.6 THERMOELECTRIC POWER

The thermoelectric power (TEP) or Seebeck coefficient gives the thermoelectric voltage developed per unit temperature difference applied across a material. The temperature dependent thermoelectric power measurements from 10 K to 300 K were done on pure as well as La-doped SFMO in zero magnetic field and in a magnetic field of 6 T (Figure 32).

Figure 32: Thermoelectric power versus temperature for $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ samples in zero magnetic field (black squares) and in an applied magnetic field of 6 T (red stars)

Earlier studies have shown that the room temperature thermopower values increase with La-doping [67]. This was compared to the change in TEP of superconducting cuprates on electron-doping and the systematic change in the thermoelectric power of SFMO with increasing La concentration was explained using a phenomenological equation which contains a phonon drag component that saturates at high temperatures and a diffusion component that is linear in temperature.

In addition to this change in thermopower with La-doping, we find that there is a change in thermopower in an applied magnetic field as well. The thermopower values become more negative when a magnetic field is applied. This change in thermopower is observed from low temperatures up to room temperature. Also, the effect is observed even for electron doped samples with varying amounts of antisite disorder. The magnetothermopower in a applied magnetic field of 6T, is calculated as, $\Delta S = S(6T) - S(0T)$. It can be seen in Figure 33 that there is no significant variation in the maximum magnetothermopower of SFMO with electron doping. Since the thermopower values go to zero as we approach absolute zero temperature, ΔS is small at low temperatures. As we increase temperature, the magnetothermopower values reaches a maximum around 100 K and then decreases on further warming. There is a small change in the low temperature gradient for $\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$ sample that will be discussed later.

Figure 33: Plot of the $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ thermopower at 6 T minus the thermopower at 0 T for $x=0$ (filled circles), $x=0.2$ (filled up triangles) and $x=0.4$ (filled down triangles). The lines are guides to the eye.

The field-dependent thermopower measurements done at 77 K and 200 K show the variation of thermopower as a function of applied magnetic field (Figure 34). There appears to be a sharp drop at lower fields and the thermopower values tend to saturate at higher fields. The change in thermopower does not follow the magnetisation which saturates at much lower fields (Figure 26).

Figure 34: Thermoelectric power versus applied magnetic field for $\text{Sr}_2\text{FeMoO}_6$ at 77 K and 200 K.

There have been earlier reports of magnetic-field dependent changes in thermopower of strongly correlated materials. In transition metal oxides, this effect was explained in terms of spin entropy suppression [29]. If the electron-electron interactions are large enough then there will exist a narrow band and the spin degrees of freedom can result in a spin-entropy thermopower, $S = -\sigma_s/e$,

where $\sigma_s = k_B \ln(g_s g_c)$ is the entropy per electron with g_s and g_c the spin and configuration degeneracies. For high applied magnetic fields g_s will tend towards 1 and hence there will be a reduction in the spin-entropy thermopower. This is unlikely to occur in $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ because the conduction band is too broad and the magneto-thermopower strongly depends on temperature.

Another magnetic contribution to thermopower in ferromagnetic materials is the magnon drag effect [30, 90, 33, 31, 32]. It is analogous to phonon-drag in non-magnetic metals. At low temperatures, the magnon drag thermopower increases with temperature as the magnon density increases and it will decrease at high temperatures due to magnon-magnon and magnon-phonon scattering. It has been argued that the magnon populations will be low when the applied magnetic field is parallel to the magnetisation and high when it is antiparallel to the magnetisation. The net result will be a reduction in the magnon-drag thermopower at high magnetic fields and when all magnetic domains are aligned in the direction of the applied magnetic field. At low temperatures the magnon-drag thermopower is $S_{MD} \propto \frac{T^{3/2}}{nD^{3/2}}$ where T is the temperature, n is the carrier concentration and D is the spin stiffness constant [34]. This predicts that S_{MD} will be proportional to $T^{3/2}$ at low temperatures and S_{MD} should decrease with increasing carrier concentration. However, it is apparent in Figure 33 that ΔS is nearly linear below 50 K rather than $T^{3/2}$, and ΔS is still finite at 250 K, and ΔS is not correlated with x . A quenching function $F(y)$ is defined which gives the effect of an applied magnetic field on the magnon drag component of thermopower [34] [33].

$$F(y) = \int_0^\infty x^{\frac{3}{2}}(x+y) \frac{e^{(x+y)}}{[e^{(x+y)} - 1]^2} dx \quad (15)$$

Figure 35: Quenching Function fit for magnon drag thermopower at 150 K. Red line indicates the measured region.

with $x = Dq^2/k_B T$ and $y = g\mu_B B_{eff}/k_B T$. D is the spin stiffness constant, q is the magnon wave vector, k_B is the Boltzmann constant, T is the temperature, g is the g factor, and μ_B is the Bohr magneton. $B_{eff} = B_{ext} + \mu_0 M$ is the effective magnetic field [33] [90] where B_{ext} is the external magnetic field induction, M is the magnetisation and μ_0 is the permeability of free space. For SFMO $g \approx 2$ [91][92], and $D \approx 140 \text{ meV } \text{\AA}^2$ [93]. The quenching function fit shows that it will saturate only at very large magnetic fields and for the measured magnetic field range the magnon drag contribution should be linear. Hence this effect cannot account for the observed effect where the magneto-thermopower seem to saturate at much lower field and is not linear even for an applied magnetic field of up to 2 T. These suggests that magnon-drag thermopower is not the origin of the magneto-thermopower in $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$. Further support for the absence of a magnon-drag thermopower can be seen in Figure 55 where the magnetothermopower ($S(8 \text{ T}) - S(0)$) from $\text{Ba}_2\text{FeMoO}_6$ is plotted. It can be

seen that it is linear up to ~ 260 K. This is not expected if the magnetothermopower was due to magnon-drag.

There have been recent reports of giant magnetothermoelectric effect in magnetic tunnel junctions [94]. Since the region around the grain boundary acts as a tunnel junction, the observed magnetothermopower could be attributed to the increased tunnelling probability in an applied magnetic field. We propose that the magneto-thermopower from polycrystalline $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ is due to a spin-dependent Seebeck effect arising from the thermal gradient inducing spin-tunnelling between the grains. This type of magneto-thermopower has currently only been observed in magnetic tunnelling junctions where one or more of the layers is ferromagnetically ordered and displays electronic spin polarisation. In the case of magnetic tunnel junctions with an insulating barrier between the two spin polarised metallic layers, the magnetothermopower has been modelled in the semiclassical relaxation time approximation and assuming elastic scattering where Walter et al. [95],

$$S = \frac{-e}{k_B T G} \int t(E)(E - E_F) \left(\frac{-\partial f}{\partial E} \right) dE \quad (16)$$

where e is the electron charge, k_B is Boltzmann constant, G is the tunnelling conductance, $t(E)$ is the tunnelling transmission function, E is the energy, and f is the Fermi function. The tunnelling conductance can be written as Walter et al. [95],

$$G = \frac{e^2}{h} \int t(E) \left(\frac{-\partial f}{\partial E} \right) dE \quad (17)$$

where h is Planck's constant. If $t(E)$ does not strongly depend on energy within a few $k_B T$ of E_F then S reduces to the Mott formulae,

$$S = -\frac{\pi^2 k_B^2 T}{3e} \left(\frac{1}{G(E)} \frac{\partial G(E)}{\partial E} \right)_{E_F} \quad (18)$$

where $G(E)$ is the energy-dependent tunnelling conductance. The change in the magneto-thermopower is then,

$$\Delta S = S_P - S_{AP} = -\frac{\pi^2 k_B^2 T}{3e} \left[\left\{ \frac{1}{G_P(E)} \frac{\partial G_P(E)}{\partial E} \right\}_{E_F} - \left\{ \frac{1}{G_{AP}(E)} \frac{\partial G_{AP}(E)}{\partial E} \right\}_{E_F} \right] \quad (19)$$

where S_P and G_P are the spin-tunnelling thermopower and conductance for the magnetisation parallel for both layers and S_{AP} and G_{AP} are the spin-tunnelling thermopower and conductance when the magnetisation from both layers is antiparallel. Equation 19 predicts that ΔS will be linearly dependent on T , which is observed up to ~ 50 K in $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$.

The slope of ΔS below ~ 50 K for $\text{Sr}_2\text{FeMoO}_6$ is nearly the same for $x=0$ and $x=0.2$ and it is smaller for $x=0.4$. It is possible that this is due to a change in E_F for $x=0.4$. The intergrain tunnelling model proposed for the magnetoresistance response of these materials suggests that there is a disordered region near the grain boundaries and that there is a reduction in spin polarisation in this disordered region [76]. The effect of changes in E_F or spin polarisation on ΔS can be illustrated using a simple model where $t(E)$ can be written as $t_P(E) = (N_\uparrow N_\uparrow + N_\downarrow N_\downarrow) t$ and $t_{AP}(E) = (N_\uparrow N_\downarrow + N_\downarrow N_\uparrow) t$, where $N_\uparrow$ is the majority carrier density of states (DOS), $N_\downarrow$ is the minority DOS, and t is the energy independent tunnelling transmission function [96]. It can then be shown from Equation 17 and Equation 18 that

$$S_P = -\frac{\pi^2 k_B^2 T}{3e} \frac{1}{N_\uparrow N_\uparrow + N_\downarrow N_\downarrow} \left[\left\{ 2N_\uparrow \frac{\partial N_\uparrow(E)}{\partial E} \right\}_{E_F} + \left\{ 2N_\downarrow \frac{\partial N_\downarrow(E)}{\partial E} \right\}_{E_F} \right] \quad (20)$$

and

$$S_{AP} = -\frac{\pi^2 k_B^2 T}{3e} \frac{1}{N_\uparrow N_\downarrow + N_\downarrow N_\uparrow} \left[\left\{ 2N_\uparrow \frac{\partial N_\downarrow(E)}{\partial E} \right\}_{E_F} + \left\{ 2N_\downarrow \frac{\partial N_\uparrow(E)}{\partial E} \right\}_{E_F} \right]$$

(21)

. If we take a simple DOS with $N_{\uparrow} = a_1\sqrt{E}$ and $N_{\downarrow} = a_2\sqrt{E - E_0}$ then

$$\Delta S = S_P - S_{AP} = -\frac{\pi^2 k_B^2 T}{6eE_F} \left[\frac{2}{1 - zx} - \frac{2 - x}{1 - x} \right] \quad (22)$$

where $x = \frac{E_0}{E_F}$, $x < 1$ and $z = \frac{a_2^2}{(a_1^2 + a_2^2)}$. This is negative provided that $z > \frac{1}{(2-x)}$. This simple example shows how a negative spin-tunnelling magneto-thermopower can occur purely from majority and minority DOS effects. ΔS will decrease if E_F increases or if P decreases. The smaller ΔS gradient for $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ with $x=0.4$ may suggest that E_F is larger for $x=0.4$, which would appear to be consistent with electron doping by La.

The departure from linearity above ~ 70 K for $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ can occur if $t(E)$ is energy-dependent. The envelope functions $(E - E_F) \left(\frac{-\partial f}{\partial E} \right)$ and $\left(\frac{-\partial f}{\partial E} \right)$ in Equation 16 and Equation 17 probe $t(E)$ within $\sim \pm k_B T$ of E_F . Thus, if $t(E)$ displays a large energy dependence for $|E - E_F| > \sim 6 \text{ meV}$ then ΔS will be approximately linear only for low temperatures, which is what is observed. It is possible that the departure in $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ above ~ 70 K is due to inelastic scattering that has not been included in the model above.

Figure 36: Resistivity and thermopower of SFMO at 250 K as a function of applied field.

It is interesting to look for a relationship between the magnetothermopower and magnetoresistance. It is apparent in [Figure 36](#) that $\rho(B)$ and $S(B)$ for SFMO decrease with magnetic field in a similar manner, where the data is plotted for measurements done at 250 K. Measurements of $\rho(B)$ and $S(B)$ were also done at different temperatures using the PPMS thermal transport option and the results are shown in [Figure 37](#) where ΔS is plotted against $\sqrt{MRT}$. Surprisingly it can be shown that ΔS varies linearly as $\sqrt{MRT}$.

Figure 37: ΔS as a function of $\sqrt{MRT}$ for SFMO

4.7 THERMAL CONDUCTIVITY

The thermal conductivity (κ) of a material refers to its ability to transfer thermal energy. The thermal conductivity of SFMO was measured from 2 K to 300 K in zero field as well as in an applied magnetic field of 6 T (Figure 38). The thermal conductivity values are smaller than that of a metal and it increases with temperature for the measured temperature range. There is also no noticeable difference in thermal conductivity in a magnetic field of 6 T. According to Wiedemann-Franz law, the ratio, κ/σ , of the electronic contribution to the thermal conductivity (κ) and the electrical conductivity (σ) of a metal is proportional to the temperature (T) and the proportionality constant $\kappa/\sigma T$ is called the Lorenz number [35]. We have already seen that the resistivity and the diffusion thermopower of SFMO vary in a magnetic field. Therefore from Wiedemann-Franz law, one would have expected to see a change in thermal conductivity in an applied field if there was a significant electronic contribution to the thermal

conductivity of polycrystalline SFMO. The fact that the thermal conductivity is invariant in a magnetic field would suggest that lattice contribution dominates the thermal conductivity of this sample and this lattice or phonon component does not change much in magnetic fields up to 6 T.

Figure 38: Thermal Conductivity of SFMO

4.8 HALL RESISTIVITY

The Hall resistivity measurements were done on $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x=0.0, 0.2, 0.4$) as a function of field at different temperatures from 10 K to 360 K. The Hall effect data at 77 K and 150 K are shown in [Figure 39](#).

Figure 39: The magnetic field dependence of the Hall resistivity at 77 K and 150 K for $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$.

The Hall resistivity has both normal and anomalous contributions which are illustrated in Figure 40. For all the samples, the Hall resistivity initially increases with increasing magnetic field and then decreases after magnetic moment saturation. The Hall resistivity is given by the empirical relation [13], $\rho_{xy} = R_H\mu_0H_z + R_S\mu_0M_z$ where R_H is the normal Hall coefficient, H_z is the applied magnetic field, R_S is the anomalous Hall coefficient, μ_0 is the permeability of free space and M_z is the magnetisation.

Figure 40: Normal (red dashed line) and anomalous (green dashed curve) contributions to Hall resistivity (black circles).

The negative slope of the normal Hall coefficient beyond magnetisation saturation suggests that the carriers are electron-like. Hence these samples have a positive anomalous Hall coefficient (R_S) and a negative normal Hall coefficient (R_H). This result is in agreement with earlier studies on SFMO single crystals [75] [79] and epitaxial thin films [97].

The normal Hall coefficients were obtained by performing a linear fit of the high field Hall resistivity data. The normal Hall coefficients for all the samples show weak temperature dependence with R_H (absolute value) decreasing with increasing temperature for the measured temperature range Figure 41.

Figure 41: The normal Hall coefficient versus temperature for $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ samples.

For La-doped samples, the normal Hall coefficients are found to be slightly less in magnitude than the undoped one but there is no systematic change as observed in the case of thermopower, *i.e.*, there is no further decrease in the absolute value of R_H while going from $x=0.2$ ($\text{Sr}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$) to $x=0.4$ ($\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$). Using the simple relation $R_H = -1/ne$ where n is the carrier density and e is the electronic charge, the carrier density is estimated to be of the order of 10^{22} cm^{-3} . The initial decrease in R_H could be attributed to increase in conduction electrons with electron-doping. But there seems to be no more increase in charge carrier density at higher doping which is similar to the resistivity data (Figure 27) where no further reduction in longitudinal resistivity was observed for $\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$.

The high field linear component of Hall resistivity is subtracted off to get the anomalous contribution. Figure 42 shows the plot of anomalous Hall resistivity along with magnetisation for one sample at 150 K. It is clear that the anomalous Hall resistivity follows the magnetisation.

Figure 42: The anomalous contribution to Hall resistivity (black squares) and magnetisation (red stars) measured at 150K as a function of applied magnetic field for $\text{Sr}_2\text{FeMoO}_6$.

The anomalous Hall coefficient is then obtained by dividing anomalous Hall resistivity ($R_S \mu_0 M_z$) by the magnetisation ($\mu_0 M_z$). The plot of R_S as a function of temperature is shown in [Figure 43](#). Even the anomalous Hall coefficient shows a gradual increase for temperatures up to 360 K. It is interesting to note that R_S values for $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$ are almost the same for the measured temperature range. There is an increase in anomalous Hall coefficient for $\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$.

Figure 43: Anomalous Hall coefficient versus temperature for $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ samples.

The anomalous Hall effect (AHE) is believed to have an intrinsic contribution which depends only on the band structure as well as other extrinsic components [13]. Since no major change in band structure is expected for $x=0.4$ ($\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$) [69], the change in AHE should be from skew scattering or side jump. AHE data on single crystal SFMO were found to indicate skew scattering behaviour [75]. The rise in impurity or disorder with increased La concentration resulting in more scattering could be the reason for higher R_s value in $\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$.

4.9 SUMMARY

Magnetisation, magnetoresistance, magnetothermopower, thermal conductivity and Hall effect studies were carried out on polycrystalline $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ samples. The antisite disorder of $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ increased with increasing La concentration. The temperature dependence of resistivity for all the samples were

found to approach the expected Fermi liquid T^2 behaviour at higher temperatures. The residual resistivity was not correlated with either the La concentration or ASD. The field dependent magnetoresistance data could be fitted using the intergrain model with the grain boundary magnetisation modelled using an exponential term. The magnetoresistance ratios for pure and La-doped SFMO decreased with temperature probably due to increased spin scattering. Also, the MR ratios were lower for La-doped SFMO. This could be an effect of increased ASD as well as the existence of new conduction channels in doped samples which were not affected by the applied magnetic field.

Magnetothermopower was observed in pure as well as La-doped SFMO samples. The magnetothermopower could be explained in terms of a spin-tunnelling contribution to the thermopower between grains which changes in an applied magnetic field. But the thermal conductivity did not vary in an applied magnetic field which would indicate that lattice contribution dominates the thermal conductivity of this material and this lattice or phonon component is unaffected by the applied magnetic field.

The normal Hall coefficients were lower for La-doped samples as expected for electron doping. But the R_H values were nearly the same for $\text{Sr}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$ and $\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$ which could be related to ASD. The anomalous hall coefficients were nearly the same for $\text{Sr}_2\text{FeMoO}_6$ and $\text{Sr}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$ but higher for $\text{Sr}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$. The absence of a systematic change in R_S with doping could be due to the fact that the scattering mechanisms that lead to the anomalous Hall effect were dominated by disorder effects rather than electron doping.

DOUBLE PEROVSKITE $\text{Ba}_2\text{FeMoO}_6$

5.1 INTRODUCTION

$\text{Ba}_2\text{FeMoO}_6$ (BFMO) is another strongly correlated oxide belonging to the double perovskite family theoretically predicted to have a high degree of electronic spin polarisation. BFMO has an ordered double perovskite structure similar to SFMO where the Ba atoms replace Sr. Neutron powder diffraction data indicates that the structure is cubic only at temperatures above T_C and the structure is pseudocubic or tetragonal below the Curie temperature [98]. It also exhibits a large magnetoresistance which would be of interest from a spintronics device perspective [99, 100]. The reported Curie temperature is around 310 K [101, 102, 98] which is lower than that reported for SFMO [65].

The electronic structure calculations of BFMO (Figure 44) show a structure similar to SFMO [18]. The Fermi level falls into a gap of the majority spin-up electrons while the minority spin-down electrons are metallic, resulting in 100% spin-polarised conduction electrons at E_F . The large hybridisation between the Fe d and O p states and between the Mo d and O p states is apparent in the similarity of peak positions and intensity distribution. A large exchange splitting of 4 eV is observed in Fe $3d$ states, while exchange splitting of the Mo $4d$ and O $2p$ states is negligible. The fully occupied majority spin Fe $3d$ bands and about 0.5-1 electron occupancy of the minority spin Fe t_{2g} bands result in an Fe valence of about +2 to +2.5. About one electron occupies the minority spin t_{2g} band of Mo $4d$ giving a valence state

of $\text{Mo } 5^+$. The fermi level is within a spin-down band comprising of $\text{Fe}(t_{2g}\downarrow)\text{--O}(2p)\text{--Mo}(t_{2g}\downarrow)$ sub-band orbitals.

Figure 44: The density of states of $\text{Ba}_2\text{FeMoO}_6$ [18].

Similar to SFMO, even BFMO can be electron doped by substituting Ba with trivalent cations. The changes to the electronic and magnetic properties of BFMO on electron doping could provide us with valuable insights into the underlying interaction mechanisms in this compound in particular and double perovskites in general.

5.2 EXPERIMENTAL DETAILS

A series of polycrystalline $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ ($x = 0, 0.2$ and 0.4) samples were prepared by a solid-state reaction method from stoichiometric mixes of $\text{Ba}(\text{NO}_3)_2$, Fe_2O_3 , MoO_3 , and La_2O_3 . The powder was denitrated at 700°C in air. After pressing the powder at 20 MPa, the pellets were placed in air at 1200°C for 8 h. The pellets were about 10 mm in diameter and about 2-3 mm thick. The samples were then ground, pressed into pellets, and then sintered at 1150°C in an atmosphere of 5% H_2 – 95% N_2 for 3 h. The last step in the synthesis process was repeated until all the minority phases were removed and homogeneous samples were obtained. The phase composition and purity were determined from x-ray diffraction measurements using $\text{Co K}\alpha$ radiation. XRD measurements show that all the $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ samples are single phase. The magnetisation measurements were performed using the Vibrating Sample Magnetometer (VSM) option of the physical property measurement system (PPMS 9T, Quantum Design). For high temperature magnetisation measurements above 300 K, the VSM Oven option was used. The electrical resistances were measured in four-terminal configuration using the resistivity option of PPMS and the thermoelectric power was measured using the thermal transport option.

5.3 XRD

The x-ray diffraction measurements for all the samples were done at room temperature. [Figure 45](#) shows the XRD patterns for single phase $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ samples after the final sinter. The degree of Fe-Mo anti-site disorder (ASD in %) was estimated from the ratio (R in %)

of the (101) peak intensity at 22° divided by the (200) peak intensity at 37° using the relation $R = 0.001365(\text{ASD})^2 - 0.136592(\text{ASD}) + 3.417842$ [72]. ASD values obtained were 5%, 6% and 9% respectively for $\text{Ba}_2\text{FeMoO}_6$, $\text{Ba}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$, and $\text{Ba}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$. Similar to

Figure 45: XRD patterns of $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$

SFMO, the increase in ASD on substitution of Ba ions by La ions could be due to the reduction in the charge difference between Fe and Mo cations which is required for ordering [74, 68, 73]. The increase in ASD on La substitution for BFMO is much less compared to SFMO. This could indicate that the charge difference between Fe and Mo cations could be larger in BFMO. And small amounts of electron doping does not alter the charge difference enough to affect ionic ordering.

5.4 MAGNETISATION

Magnetisation measurements obtained under applied magnetic fields of up to 6T at 10 K are plotted in Figure 46. $\text{Ba}_2\text{FeMoO}_6$, $\text{Ba}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$, and $\text{Ba}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$ samples were found to

have T_C values of around 320 K, 330 K, and 350 K respectively. The

Figure 46: Field dependent magnetisation data for $Ba_{2-x}La_xFeMoO_6$.

saturation magnetisation of pure BFMO was found to be $3.78 \mu_B/f.u.$ which is close to the theoretically predicted value of $4.0 \mu_B/f.u.$. The value of saturation magnetisation does not change much for $Ba_{1.8}La_{0.2}FeMoO_6$ and it drops to $3.24 \mu_B/f.u.$ for $Ba_{1.6}La_{0.4}FeMoO_6$. Hence there is no major reduction in saturation magnetisation for La-doped BFMO which indicates that anti-site disorder (ASD) is not a major concern for these samples. ASD estimated from the saturation magnetisation according to the equation [70], $M_s = 4.0 - 9.0 \times ASD$, are around 3% for Ba_2FeMoO_6 and $Ba_{1.8}La_{0.2}FeMoO_6$ and 8% for $Ba_{1.6}La_{0.4}FeMoO_6$.

5.5 HIGH TEMPERATURE MAGNETISATION

DC magnetisation measurements in the paramagnetic regime were done on $Ba_{2-x}La_xFeMoO_6$ samples in temperatures up to 800 K under magnetic fields up to 8 T. The measurements were done in the

paramagnetic phase rather than the ferromagnetic phase because the Curie-Weiss (CW) law can be applied in this regime. The effective magnetic moments obtained from these magnetic measurements enable us to understand the Fe and Mo valence and interaction mechanisms in these compounds. The field dependent magnetisation meas-

Figure 47: Magnetisation of BFMO as a function of magnetic field at temperatures above T_C .

urements (Figure 47) indicate that there is a ferromagnetic component even above 400 K which is well above the reported Curie temperature for BFMO. This ferromagnetic component that saturates below 1 T could be from tiny amounts of impurities as in the case of $\text{Sr}_2\text{FeMoO}_6$ [92]. In order to get rid off the ferromagnetic contribution, the temperature dependent magnetisation measurements were done at high magnetic fields of 2 T and 8 T (Figure 48) and the difference between the magnetic moments at these two fields was used in further analysis.

The magnetic susceptibility (χ) is the quantitative measure of the extent to which a material can be magnetised in an applied magnetic

Figure 48: Magnetisation of BFMO as a function of temperature at 8 T (red line) and 2 T (black line).

field. It is given by, $\chi = M/H$ where M is the magnetisation, and H is the applied magnetic field. The molar magnetic susceptibility χ_m of a ferromagnet in the paramagnetic region above the Curie temperature is given by the Curie-Weiss (CW) law,

$$\chi_m = \frac{C}{T - \theta} = \frac{\mu_0 N_A \mu_{eff}^2}{3k_B(T - \theta)} \quad (23)$$

where C is the Curie constant, T is the absolute temperature, θ is the Weiss constant (θ is higher than T_C for $T \gg T_C$), μ_0 is the permeability of free space, N_A is Avogadro's number, μ_{eff} is the effective moment, and k_B is the Boltzmann constant. The effective magnetic moment of the material arises from the total orbital and spin angular momentum of the unpaired electrons present. In the case of BFMO, the unpaired electrons belong to the Fe ion for which the orbital component is quenched. The spin only effective moment is then given by $\mu_{eff} = g\sqrt{S(S+1)}\mu_B$ where S is the total spin ($S = \frac{1}{2}$ for one unpaired electron, $S = 1$ for two unpaired electrons etc.), μ_B is the Bohr

magneton, and g is the g factor. If Fe is considered to be in a Fe^{2+} state, then the effective moment is expected to be $\mu_S = 4.9 \mu_B$ corresponding to $3d^6$ configuration whereas the $3d^5$ configuration of Fe^{3+} would yield an even higher moment of $\mu_S = 5.9 \mu_B$.

Figure 49: Plot of the inverse of the molar susceptibility after subtraction of the temperature-independent term for $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ with $x=0$, 0.2 , and 0.4 . The arrow indicates increasing x . The dashed lines are high field extrapolations.

The molar magnetic susceptibilities for $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ samples were calculated from the magnetisation measurements. At temperatures much higher than T_C , the inverse of susceptibility increases linearly with temperature (Equation 23). The plot of $1/(\chi - \chi_0)$ as a function of temperature is shown in Figure 49 where χ_0 is an offset subtracted from the measured susceptibility. The effective moments were obtained from the slope of the linear region of the plot. The extrapolation of the straight line fit to $\frac{1}{(\chi - \chi_0)} \rightarrow 0$ yielded the Weiss constants. The subtracted χ_0 values and the μ_{eff} and θ values obtained from the CW fit are tabulated in Table 2.

It can be clearly seen that the Weiss constants increase with La-doping. This is consistent with earlier studies which show an increase in T_C with electron doping [103, 104]. The μ_{eff} values are less than

	χ_0 (m ³ mol ⁻¹)	θ (K)	μ_{eff} (μ_B)
Ba ₂ FeMoO ₆	5×10^{-9}	343	3.99
Ba _{1.8} La _{0.2} FeMoO ₆	10×10^{-9}	377	3.63
Ba _{1.6} La _{0.4} FeMoO ₆	11×10^{-9}	398	3.26

Table 2: Effective moments and Weiss constants for Ba_{2-x}La_xFeMoO₆ from CW fits.

those reported for Sr₂FeMoO₆ [91, 105, 92]. This could be another indication that the oxidation state of Fe in BFMO is more closer to Fe²⁺ [106] than Fe³⁺ as predicted for Sr₂FeMoO₆ [107]. X-ray absorption spectroscopy studies claim increasing Fe valences with increase in La doping [108]. But the paramagnetic effective moments deduced here from CW fits decrease with electron doping Table 2.

The observed effective moments are all less than $4.9 \mu_B$ and hence cannot be explained in terms of the local moments of Fe ions alone. Tovar *et al* [92] attributed the reduced effective moment in Sr₂FeMoO₆ to an interaction between the spin polarised itinerant conduction electrons and the localised moments. A similar approach was used earlier to model the magnetic behaviour of Heusler alloys [109]. According to these studies, the total magnetisation of the system has contributions from localised (M_S) and mobile (M_e) electrons,

$$M_e = \chi_e^0(T) (H + \lambda M_S), \quad (24)$$

$$M_S = \chi_S^0(T) (H + \lambda M_e + \alpha M_S), \quad (25)$$

where $\chi_e^0(T)$ and $\chi_S^0(T)$ are the susceptibilities in the absence of interactions, λ is the coupling constant for the interaction between

localised moments and itinerant electrons, and α denotes the coupling between second neighbour Fe moments. The bare susceptibility χ_e^0 of one the coupled systems is temperature independent because this system is delocalised. Therefore the total susceptibility from the above equations is given by,

$$\chi = \chi_S(T) + \chi_e(T) = \chi_e^0 + \frac{C'}{T - \theta} \quad (26)$$

The Curie constant from the CW-like part of the equation is, $C' = C_S(1 + \lambda\chi_e^0)^2$ with $C_S = \chi_S^0 T = \frac{\mu_0 \mu_S^2 N_A}{3k_B}$. The effective moment of the coupled system is given by

$$\mu_{eff} = \mu_S(1 + \lambda\chi_e^0), \quad (27)$$

and the Curie-Weiss temperature,

$$\theta = C_S(\lambda^2\chi_e^0 + \alpha). \quad (28)$$

The interaction between second neighbour Fe ions in double perovskites is expected to be weak and therefore α is small. From [Equation 27](#) and [Equation 28](#), we get the coupling constant (λ) for the interaction between itinerant electrons and Fe cores,

$$\lambda = \frac{\frac{\theta}{C_S}}{\frac{\mu_{eff}}{\mu_S} - 1} \quad (29)$$

λ values were calculated assuming $\mu_S = 4.9\mu_B$ and were then be used in [Equation 27](#) to calculate electronic susceptibilities, χ_e^0 . The values obtained are tabulated in [Table 3](#).

From [Table 3](#), we can see that the calculated χ_e^0 values are in the range of χ_0 values experimentally determined ([Table 2](#)). This indicates that the mechanism described here is a reasonable explanation

	λ (mol m ⁻³)	χ_e^0 (m ³ mol ⁻¹)
Ba ₂ FeMoO ₆	-4.9×10^7	3.8×10^{-9}
Ba _{1.8} La _{0.2} FeMoO ₆	-3.9×10^7	6.7×10^{-9}
Ba _{1.6} La _{0.4} FeMoO ₆	-3.2×10^7	11×10^{-9}

Table 3: Calculated λ and χ_e^0 assuming $\mu_S = 4.9 \mu_B$.

for the lower than expected effective moment for BFMO. The negative value of λ points towards an antiferromagnetic interaction between the localised moments and itinerant electrons. The absolute values of the coupling constants decrease with La-doping. The bare electronic susceptibility (χ_e^0) is related to the density of states at the fermi level [110]. The plot of the Curie-Weiss temperature against the bare itinerant electron susceptibility for Ba_{2-x}La_xFeMoO₆ with x=0, 0.2 and 0.4 and assuming that $\mu_S = 4.9 \mu_B$ is shown in Figure 50. It is clear from Figure 50 that θ is correlated with χ_e^0 and since χ_e^0 depends on the DOS at E_F then θ is correlated with the DOS at E_F. This is consistent with earlier reports on BFMO where electron doping with La resulted in a higher T_C [103].

Figure 50: Plot of the Curie-Weiss temperature against the bare itinerant electron susceptibility for Ba_{2-x}La_xFeMoO₆ with x=0, 0.2 and 0.4.

5.6 MAGNETORESISTANCE

The magnetoresistance values of BFMO at fields of up to 8 T is shown in Figure 51. The sample shows a negative magnetoresistance of about -9% at room temperature which increases to -37% at low temperatures.

Figure 51: Magnetoresistance of BFMO as a function of field.

The magnetoresistance response is similar to SFMO with a large drop in resistivity values at low fields and a gradual decrease at higher fields, although the low-field decrease in resistivity at low temperatures is sharper in BFMO as reported earlier by Hemery *et al* [84]. Also, MR values are higher in BFMO probably due to less ASD resulting in a more ordered region near the grain boundaries. Even the BFMO magnetoresistance data can be fitted using the inter-grain tunnelling magnetoresistance model. The fits to the magnetoresistance data at 10 K, 77 K and 300 K using $MR = \frac{-P^2 m_{gb}(H)^2}{1+P^2 m_{gb}(H)^2}$ and $MR = \frac{-P^2 m_{gb}(H)^2}{1+P^2 m_{gb}(H)^2} - \alpha H$ with the exponential model for the magnet-

isation in the vicinity of the grain boundary region are shown in [Figure 52](#).

Figure 52: Field dependent magnetoresistance fits for BFMO at different temperatures using [Equation 13](#) (blue dashed line) and [Equation 14](#) (red solid line).

It is clear that there is a linear component to the magnetoresistance of BFMO at higher fields and hence the MR equation with a linear term gives a good fit. From this model, we get a spin polarisation of about 71% at 10 K. The values for the degree of spin polarisation (P) and the coefficient α corresponding to the linear contribution obtained from the fits are tabulated in [Table 4](#). The degree of spin polarisation increases with decreasing temperature whereas α remains almost temperature independent.

Temperature (K)	P from fit to Equation 14	α
300	0.26	0.007
150	0.40	0.008
77	0.54	0.008
10	0.71	0.009

Table 4: Degree of spin polarisation (P) for BFMO from magnetoresistance fits.

The magnetoresistance shows similar behaviour in La-doped samples, but the MR values decrease with increasing La concentration as reported earlier [111]. The high field magnetoresistance at 10 K for $\text{Ba}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$ is -31% and -26% for $\text{Ba}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$.

5.7 THERMOELECTRIC POWER

Temperature dependent thermopower measurements were done on pure as well as La-doped samples from low temperatures up to about 260 K and are plotted in [Figure 53](#).

Figure 53: Thermoelectric power versus temperature for $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ samples. (Inset) Comparison of BFMO (black) and SFMO (blue) thermopower.

The thermopower for pure as well as La-doped BFMO is negative for the entire temperature range indicating that electrons are majority charge carriers. But there is no systematic increase in thermoelectric power with increasing La concentration as reported in the case of SFMO [67]. The absolute values of thermopower show a gradual increase with temperature. However for pure BFMO, the absolute value of thermopower starts decreasing from around 200 K. This feature is absent in SFMO (Inset of Figure 53) and is consistent with the thermopower values reported for double perovskites by Fisher *et al.* [112], although the low temperature thermopower values of BFMO and SFMO are not the same in our case. $\text{Ba}_{1.8}\text{La}_{0.2}\text{FeMoO}_6$ and $\text{Ba}_{1.6}\text{La}_{0.4}\text{FeMoO}_6$ follow more or less the same temperature dependence as pure sample, but without the reversal in thermopower around 200 K.

To understand the unusual thermoelectric power of BFMO, measurements were done from low temperatures up to 360 K (Figure 54).

Figure 54: Thermoelectric power versus temperature for $\text{Ba}_2\text{FeMoO}_6$ samples in zero field (black circles) and in a magnetic field of 8 T (red circles).

It is apparent that the increase in the thermopower above $\sim 200\text{K}$ seen in Figure 53, saturates at $\sim 320\text{K}$ where there is a peak in the thermopower and it then falls with increasing temperature. This peak in the thermopower is close to the reported Curie temperature of BFMO [98]. It resembles the reduction in the thermopower observed below the metal-insulator transition in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ and below the charge ordering temperature in $\text{Sr}_8\text{Fe}_8\text{O}_{23}$ [113, 114]. Neutron diffraction measurements on BFMO show a structural transition from cubic above T_C to tetragonal below T_C [98]. Thus, this transition is likely to cause a change in the electronic structure that leads to an initial drop in the thermopower below T_C . This is not clearly seen in the SFMO data because the Curie temperature is higher than the measured temperature range.

Figure 55: Magnetothermopower of BFMO as a function of temperature from the data in Figure 54. The solid red line is a guide to the eye.

The difference in the thermopower in a magnetic field was observed for the entire measured temperature range. A larger magnetothermopower was observed as the temperature approached T_C . The magnetothermopower ($\Delta S = S(0T) - S(8T)$) values are shown in Figure 55. The magnetothermopower mechanism is likely to be similar to that observed in SFMO and discussed in chapter 4, where there is a spin-tunnelling thermopower. Since the thermopower values go to zero as we approach absolute zero temperature, magnetothermopower is small at low temperatures. Unlike SFMO, the magnetothermopower is linear up to ~ 270 K as predicted from Equation 22. The higher magnetothermopower in BFMO compared to SFMO and the linearity to high temperature could be attributed to the higher degree of spin polarisation (Table 4). This provides even stronger support of the model whereby ΔS is due to a spin-tunnelling thermopower at the grain boundaries. The departure from linearity above ~ 270 K is not surprising because the temperature is starting to approach T_C .

Figure 56: Thermoelectric power versus applied magnetic field for $\text{Ba}_2\text{FeMoO}_6$ at 220 K and 320 K.

The field dependent TEP measurements at 320 K and 220 K are shown in Figure 56. At 220 K and in the region where ΔS is linear in temperature, it can be seen that the field dependence of magnetothermopower is similar to that found for SFMO. In particular, it has similarities to the magnetoresistance where the MR increases at a faster rate at lower fields and starts to saturate for high magnetic fields. At 320 K ΔS and MR are both nearly linear in field.

5.8 SUMMARY

Magnetisation, magnetoresistance and magnetothermopower studies were carried out on polycrystalline $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ samples. The ASD is low and there is no significant change in the ASD with partial substitution of La for Ba. The results from high temperature magnetisation studies on $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ reveal that a localised electron model with antiferromagnetic coupling to itinerant electrons can account for the carrier concentration dependent effective moments. The

correlation between the bare itinerant electron susceptibility and the Curie-Weiss temperature supports the kinetic energy driven model that has been used to account for the electronic spin polarisation and high Curie temperatures. The magnetoresistance is even higher than that found in SFMO. The field dependent magnetoresistance data could be fitted using the same intergrain tunnelling model as in the case of SFMO. The temperature dependent thermopower values of BFMO shows a peak around the reported Curie temperature which could be related to a structural transition from cubic above T_C to tetragonal below T_C . A magnetothermopower was observed that was linear even up to ~ 270 K, which is consistent with the spin tunnelling magnetothermopower model. The magnetic field dependence of the magnetothermopower of BFMO has features comparable to the magnetoresistance.

Co₂MnSi HEUSLER ALLOY

6.1 INTRODUCTION

The intermetallic Heusler alloys are proving to be a promising class of materials for spin transport electronics applications [26]. The full Heusler alloys are particularly interesting because some of them (for e.g., Co₂MnSi, NiMnSb, PtMnSb) are theoretically predicted to display 100% electronic spin polarisation [26, 115], have very high Curie temperatures (985 K for Co₂MnSi) [116], and are nearly lattice matched to commonly available substrates like GaAs. However, the half-metallicity can be significantly degraded by antisite disorder [117]. The full Heusler alloys have the form X₂YZ, where X is a transition or noble metal such as Co, Ni, Cu, Y is normally Mn and Z is usually a group-IIIB or -IVB element such as Al, In, Si, or Ge. They possess the L₂₁ crystal structure which consists of four interpenetrating face-centred-cubic (fcc) sublattices: two occupied by atoms of element X, one occupied by Mn atoms, and one occupied by Z atoms [19].

Figure 57: Schematic representation of the L₂₁ structure of Co₂MnSi full Heusler alloy [19].

One of the full Heusler alloys predicted to have a half-metallic band structure is Co₂MnSi [115] and moreover it has the highest Curie temperature of 985 K among the known Heusler alloys [116]. The spin-resolved density of states for Co₂MnSi is shown in Figure 58. Neutron diffraction and some theoretical studies indicate that they possess a finite very small spin-down DOS around the Fermi level [118, 19]. Hence they are not perfect half-metals but still display a high degree of spin polarisation. It is interesting to compare Co₂MnSi thin films with low and high amounts of anti-site disorder and understand the effects of disorder on magnetisation, resistivity, magnetoresistance and Hall effect.

Figure 58: Spin-projected DOS for the Co_2MnSi compound [19].

6.2 EXPERIMENTAL DETAILS

Magnetotransport measurements were done on single phase Co_2MnSi epitaxial films on GaAs substrates produced by pulsed laser deposition (PLD) [119, and references therein]. The PLD set up consisted of a KrF excimer laser Lambda Physik LPX 220 I ($\lambda = 248 \text{ nm}$, $\tau = 20 \text{ ns}$) which was operated at 7 Hz for 20,000 to 50,000 pulses [120]. The substrates were kept at a temperature of around 473 K. Magnetisation measurements were carried out using the Magnetic Property Measurement System (MPMS 7T, Quantum Design). Resistivity and Hall effect measurements were performed using the resistivity option of the Physical Property Measurement System (PPMS 9T, Quantum Design). The thickness estimate was done using Rutherford backscattering spectrometry by Peter Murmu at GNS Science. Optical reflectance of bulk and film samples were carried out by Nick Strickland at Industrial Research Limited. These measurements were done at 300 K and over a wavelength range extending from the ultraviolet to the far infrared using a high accuracy spectrophotometer and a Fourier transform IR spectrometer (0.05 eV to 5 eV).

6.3 MAGNETISATION

DC magnetisation measurements were done on Co_2MnSi films at 10 K and 300 K. The diamagnetic contribution from the substrates were subtracted and the net magnetisation values are plotted in Figure 59. One of the films (Figure 59 a) have a saturation magnetic moment (M_s) of about $3.8 \mu_B/f.u.$ at 10 K which reduces slightly as the temperature is increased to 300 K due to increasing excitation of spin waves [35]. The saturation magnetisation of the PLD target is $3.8 \mu_B/f.u.$. Though this saturation magnetisation is below the $5 \mu_B/f.u.$ reported in polycrystalline and single crystal samples [118, 116], it has a low coercive field and saturation field which are characteristics of a magnetically ordered film. One of the reasons for the lower than expected saturation magnetic moment for the good quality film could be the error in the estimated film thickness. The other film (Figure 59 b) has a saturation magnetic moment of about $2.1 \mu_B/f.u.$ at 10 K which reduces to $0.9 \mu_B/f.u.$ at room temperature. This film also exhibits a higher coercive field. Reduced M_s in other Heusler thin films is attributed to antisite disorder [121]. Hence the film with higher magnetic moment is expected to have a low degree of antisite disorder whereas the one with lower M_s could be highly disordered. First principle studies indicate that Co-Mn substitution disorder rather than Mn-Si disorder is what contributes to the reduced magnetic moment [122].

Figure 59: Magnetisation as a function of magnetic field at 300 K and 10 K for the (a) ordered and (b) disordered Co_2MnSi films.

6.4 OPTICAL MEASUREMENTS

Figure 60: Optical conductivity of the ordered (red line) Co_2MnSi thin film compared to the bulk target (black line).

The optical conductivities of the ordered Co_2MnSi thin film along with that of the bulk target from 0.05 eV to 5 eV are shown in [Figure 60](#). The target and the ordered Heusler film show similar optical behaviour. At high energies, we observe a broad feature which peaks at zero. This Drude peak is typical of a metal where the free carriers move coherently in response to the optical electric field. In addition to the Drude peak, the ordered film shows an inter-band transition around 1.6 eV. The bulk target also shows broadened transitions from 1.0 eV to 1.4 eV. Theoretical predictions indicate transitions between 2 and 3 eV[123]. The earlier studies on Co_2MnSi thin films reported peaks and structures close to the theoretically predicted values. But the samples used in that study had a high degree of antisite disorder and they exhibited only a small drude peak [119]. The measurements shown in [Figure 60](#) were done on an ordered Co_2MnSi film and there

is a pronounced Drude peak as expected of a good metal. But the band structure calculations do not predict a transition around 1.6 eV [123]. This would suggest parameters used for band structure calculations might need some readjustment.

6.5 RESISTIVITY AND MAGNETORESISTANCE

Figure 61: Temperature dependent resistivity for the ordered and disordered Co_2MnSi films.

The temperature dependent resistivities of the ordered and disordered Co_2MnSi films are displayed in Figure 61. The resistivity of both the films are of the same order of magnitude and the room temperature resistivity of the ordered film is almost the same as that obtained from optical conductivity measurements. But the temperature dependencies of the ordered and disordered films are quite different.

Figure 62: Temperature dependent resistivity for the magnetically ordered Co_2MnSi film. The red solid line is the best fit to the linear region.

The resistivity of the ordered film increases weakly with temperature (see Figure 62), and shows a residual resistivity of about 0.38 mΩ·cm associated with disorder-induced scattering [124]. The weak and linear temperature dependence is a characteristic of Co-based Heusler compounds [125, 124, 126]. The linear temperature dependence indicates that phonon scattering dominates at higher temperatures.

The resistivity increases with decreasing temperature for the disordered film resulting in a higher residual resistivity of 0.78 mΩ·cm Figure 63. This is similar to the Co_2MnSi films grown by sputter deposition where a negative temperature coefficient of resistivity is observed for the as prepared and ones annealed at lower temperatures, but at higher annealing temperatures a more conventional metallic behaviour is seen [127]. This is another indication of strong disorder in one of the films [40]. Both Mn-Si and Co-Mn disorders are expected to produce an increased resistivity in Heusler films [122].

It is interesting to consider the origin of the negative temperature coefficient of resistivity (TCR) in the disordered film. One possibility

Figure 63: Temperature dependent resistivity for the disordered Co_2MnSi film and the fit (red solid line) from 100 K to 300 K to the resistivity model in [20].

is that the disordered film is inhomogeneous consisting of metallic clusters with resistance $R_m(T) = R_0 + R_1T$, embedded in a semi-conducting matrix with resistance $R_s(T) = R_2 \exp(\frac{\Delta E}{2k_B T})$. It is interesting to fit the observed resistivity to $R_s(T) + R_m(T)$ [20]. The fit to this model is shown in Figure 63 (red solid line) and it is obvious that this model is not a good fit. Another possible reason for the increase in resistivity at low temperatures is weak localisation (WL) which would be expected in metallic systems with resistivity in the range of the present samples[128, 129, 130]. A shallow minimum in the resistivity at low temperatures is expected for weak localisation [127, 40]. Here in the case of disordered film, the resistivity increases from around 250 K to low temperatures. The increase in resistivity from close to room temperature to low temperatures is also seen in strongly disordered conventional metals which is attributed to incipient localisation [127]. Incipient localisation is an intermediate effect between weak and strong localisation [131]. The following equation was used to fit the temperature dependent resistivity in other materi-

Figure 64: Temperature dependent resistivity for the disordered Co₂MnSi film and the fit (red solid line) to the resistivity model in [Equation 30](#).

als where quantum corrections to the conductivity (QCC) like WL and renormalisation of the effective electron-electron interactions (REEI) were applied in 3D[[41](#), [42](#)].

$$\rho(T) = \frac{1}{\sigma_0 + a_1 T^{\frac{p}{2}} + a_2 T^{\frac{1}{2}}} + bT^n \quad (30)$$

where $\sigma_0 = \frac{1}{\rho_0}$ is the residual conductivity and ρ_0 is the residual resistivity, $a_1 T^{\frac{p}{2}}$ is the WL term with $p = 2$ or $p = 3$ for electron-electron or electron-phonon interactions, $a_2 T^{\frac{1}{2}}$ is the REEI correction term and bT^n is the high temperature scattering term. We get a good fit ([Figure 64](#)) for the resistivity of the disordered film using [Equation 30](#) with $\sigma_0 = 1.30425$, $a_1 = 0.00028$, $a_2 = 0.00964$, $b = 0.00116$, $p = 3$ and $n = 1$. This would indicate that QCC are important in the highly disordered regime and electron-phonon interactions are dominant. Whereas for the ordered film, $a_1 \approx a_2 \approx 0$ resulting in

a temperature dependence of resistivity given by $\rho(T) = \rho_0 + bT$ as seen in [Figure 62](#).

The resistivities of these films were also measured in a magnetic field with the field parallel to current and they exhibit a decrease in resistivity in an applied magnetic field.

Figure 65: Magnetoresistance at 10 K for the ordered Co_2MnSi film.

The magnetoresistance ratios for the ordered film at 10 K in magnetic fields up to 8 T is shown in [Figure 65](#). The film shows a negative magnetoresistance of 0.16% at 8 T.

Figure 66: Magnetoresistance at 10 K for the ordered Co_2MnSi film.

The disordered film shows similar features but a higher MR ratio compared to the ordered film (Figure 66). One of the possible origins of the negative magnetoresistance in spin polarised systems is intergrain tunnelling as observed in the case of polycrystalline double perovskites. Since there is a slight increase in magnetoresistance with disorder, it is interesting to apply the intergrain magnetoresistance model to the magnetoresistance of Co_2MnSi films as in the case of polycrystalline double perovskites.

Figure 67: Intergrain magnetoresistance model fits to MR ratios of (a) ordered and (b) disordered Co_2MnSi films.

The fits to the MR data using the intergrain magnetoresistance model (Equation 13) are shown in Figure 67. This model does not give a good fit, failing to capture either the high or low field behaviour, and hence the intergrain MR model with a disordered region near the grain boundary cannot be used to describe the observed magnetoresistance in these Heusler alloy films. Obaida *et al.* claims that spin disorder scattering is not possible in the case of Co_2MnSi films because the negative MR disappears at higher temperatures where there should not be any change in spin disorder. This is consistent with the conclusion reached above when considering the temperature dependent resistivity. Instead they have attributed the high field MR at low temperature in Heusler alloy films to weak localisation effects [127]. The magnetic field destroys weak localisation phase coherence leading to a reduction in resistance.

Figure 68: Low field MR and magnetisation for the ordered Co_2MnSi film at 10 K.

The expanded view of the low field magnetoresistance and magnetisation are shown in Figure 68 and Figure 69. There is a sharper drop in resistance at lower fields and then a more gradual decrease with field for our Heusler films. The change in the slope of the magnetores-

istance seems to correspond with the saturation magnetic field. This behaviour could be due to domain wall scattering, although weak localisation effects could also be important. The present results show the sensitivity of the Heusler alloys to disorder, and highlight the need for further in-depth study of the MR in these systems.

Figure 69: Low field MR and magnetisation for the disordered Co₂MnSi film at 10 K.

6.6 HALL EFFECT

The Hall resistivity (ρ_{xy}) in ferromagnetic materials is empirically given by [13],

$$\rho_{xy} = R_H \mu_0 H_z + R_S \mu_0 M_z, \quad (31)$$

where R_H is the normal Hall coefficient, H_z is the perpendicular magnetic field, R_S is the anomalous Hall coefficient, μ_0 is the permeability of free space and M_z is the magnetisation. The first term in Equation 31 corresponds to the normal Hall contribution and the second term is the anomalous part. R_H depends mainly on the carrier concentration. R_S could depend on a number of material specific parameters including longitudinal resistivity (ρ_{xx}). $R_S \sim \rho_{xx}^n$ with $n = 1$ for skew

scattering from impurities and $n = 2$ if the dominant mechanism is side jump deflection from impurities. Using these, Equation 31 may be rewritten as,

$$\rho_{xy} = R_H \mu_0 H_z + \alpha \rho_{xx}^n \mu_0 M_z, \quad (32)$$

where α is the proportionality constant.

Figure 70: Hall resistivities as a function of applied field for the (a) ordered and (b) disordered Co_2MnSi films at different temperatures.

The Hall resistivity measurements were done on Co_2MnSi films as a function of field at different temperatures from 10 K to 300 K. The Hall effect data at 10 K, 200 K and 300 K are shown in Figure 70. The Hall resistivities for the Heusler films have a dominant anomalous contribution wherein the Hall resistivity initially increases sharply with increasing magnetic field before tending to saturate at high field. Similar Hall effect behaviour with a large anomalous component was reported in Co_2MnSi and other Heusler films [132, 127, 126, 124, 133, 134]. The anomalous Hall resistivity increases with increasing temperature

for the ordered sample whereas it decreases with increasing temperature for the one with high antisite disorder. The temperature dependence of anomalous hall resistivity follows the temperature dependence of longitudinal resistivity (Figure 61) here as well, as expected from Equation 32. The magnetisation data in Figure 59 was done with the applied magnetic field parallel to the surface of the film. But the Hall effect measurements were done with the magnetic field perpendicular to the plane of the film. Therefore it is not possible to directly compare the magnetisation and Hall resistivity to see if the anomalous Hall resistivity follows magnetisation as in Equation 31. If χ_{true} is the actual magnetic susceptibility, the measured susceptibility when the film is perpendicular to field ($\chi_{apparent}$) is given by, $\chi_{apparent} = \frac{\chi_{true}}{1+N\chi_{true}}$, where N is the demagnetisation factor. The value of N will be close to 1 (but not more than 1) when the magnetisation is normal to the surface for a thin film. The value of saturation magnetisation (M_s) will be same for both the cases, but the saturation magnetic fields will be different. Taking this into account, $N = \frac{1}{\mu_0 M_s} (\mu_0 H_{apparent}^{sat} - \mu_0 H_{true}^{sat})$ where $H_{apparent}^{sat}$ is the magnetic saturation field strength for the perpendicular orientation and H_{true}^{sat} is the actual magnetic saturation field strength. In our case we get M_s and H_{true}^{sat} from Figure 59. Also, $H_{apparent}^{sat}$ could be estimated from Figure 61. For the ordered Co₂MnSi film at 10 K, these values are $M_s = 781788 \text{ Am}^{-1}$, $\mu_0 H_{true}^{sat} = 0.003 \text{ T}$ and $\mu_0 H_{apparent}^{sat} = 1.15 \text{ T}$. Using these we get $N = 1.17$ which is not physically possible. This is probably due to the low value of M_s obtained because of the error in thickness estimation of the film. If we use the expected saturation magnetisation of about $1.01 \times 10^6 \text{ Am}^{-1}$, the demagnetisation factor will be 0.9 which is reasonable. This is another reason to believe that the saturation magnetic moment of the high quality Co₂MnSi film is indeed close to the theoretically predicted value of $5 \mu_B / f.u.$.

Figure 71: Hall resistivities as a function of applied field for the (a) ordered and (b) disordered Co_2MnSi films at high magnetic fields.

It is interesting to study the temperature dependence of R_H and R_S as in the case of $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$. But a reliable estimation of the normal Hall coefficient is difficult in the case of Heusler films [127]. This is because anomalous Hall component overshadows the normal Hall contribution. So if the magnetisation does not saturate at high fields, there will be an anomalous contribution that increases with magnetic field. An expanded view of the high field Hall resistivities of ordered and disordered Co_2MnSi films are shown in Figure 71. The high quality film has a negative high field slope whereas the disordered film exhibits a positive slope. A comparison of the magnetisation and the Hall resistivity (Figure 72) reveals that the magnetisation of the disordered film does not saturate even at high fields which results in increasing Hall resistivity. Therefore it is extremely difficult to extract R_H for the disordered film. Even for the ordered film, the high field

Figure 72: High field Hall resistivity and magnetisation for the disordered Co_2MnSi film at 10 K.

Hall resistivity data at 10 K is too noisy to get a reliable estimate of R_H .

Figure 73: Normal Hall coefficients for the ordered Co_2MnSi film extracted from the high-field Hall effect data.

The normal Hall coefficients for the ordered film at temperatures above 100 K were obtained by taking the slope at high fields where the AHE has saturated, and the values are plotted in Figure 73. The R_H values are more or less temperature independent in this range. The

Figure 74: Carrier concentration and mobility for ordered Co_2MnSi film.

carrier concentrations (n) and mobilities (μ_e) are shown in Figure 74. The carrier concentration is large and independent of temperature, as expected for a metal, while the mobility is very small with little temperature dependence showing the dominant role of disorder. Another Hall effect study on Co_2MnSi reports a value of $0.4 \text{ cm}^2/(\text{V}\cdot\text{s})$ for electron mobility [134]. The mobility values obtained here are of the same order and a nominal charge carrier density of about 3 electrons per unit cell is estimated.

The temperature dependence of saturation anomalous Hall resistivities are plotted in Figure 75. The anomalous Hall resistivity values are bigger for the disordered film compared to the ordered one. This could be due to increased scattering from impurities expected in a highly disordered material. Again, the anomalous Hall coefficient (R_S)

Figure 75: Saturation anomalous Hall resistivity versus temperature for Co_2MnSi films.

could be estimated only for the ordered film and the values are shown in [Figure 76](#).

Figure 76: Anomalous Hall coefficients versus temperature for ordered Co_2MnSi film.

R_S for the ordered sample shows only a weak temperature dependence. The plots of anomalous Hall coefficient versus longitudinal resistivity (ρ_{xx}) for the ordered Heusler films is shown in Figure 77. It can be seen that R_S scales almost linearly with ρ_{xx} for the ordered film. This would indicate that skew scattering from impurities is the major contributing factor to anomalous Hall effect at least in the case of the high quality Heusler film [13, 135]. But no simple scaling relation is found between the anomalous Hall resistivity and longitudinal resistivity for the disordered film.

Figure 77: Anomalous Hall coefficient versus longitudinal resistivity (black circles) for the ordered Heusler film and a linear fit (red line).

6.7 SUMMARY

Experimental studies were done on ordered and disordered Co_2MnSi epitaxial thin films. The disorder is induced by Co and Mn ASD and is seen by a reduction in the saturation magnetic moment. The sat-

uration magnetic moment for the ordered film is lower than the expected value of $5\mu_B/f.u.$ possibly because the film thickness is overestimated. The optical conductivity of the ordered film is similar to that found in the target and the results suggest that the band structure should be recalculated. The resistivity of the ordered Co₂MnSi thin film is linear in temperature. However, the resistivity of the disordered film increases at low temperature due to weak localisation and electron-phonon interactions. A magnetoresistance is observed in the ordered and disordered films. For low applied magnetic fields it is possible that there is a contribution from spin scattering at domain walls. For high magnetic fields the reduction in the resistivity may be due to a magnetic field induced reduction in the weak localisation resistivity. The ordinary Hall coefficient for the ordered film is temperature independent. There is a large anomalous component to the Hall resistivity observed in the ordered and disordered Co₂MnSi thin films. The anomalous Hall coefficient for the ordered film scales linearly with resistivity which indicates that this contribution arises from skew scattering.

SUMMARY AND CONCLUSIONS

This thesis reports the results from the magnetic, magnetotransport, and magnetothermopower measurements on polycrystalline double perovskites and thin film Heusler alloys. All the materials studied have a high degree of electronic spin polarisation and are predicted to be half-metallic with a high Curie temperature. The double perovskites were $\text{Sr}_{2-x}\text{La}_x\text{FeMoO}_6$ and $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ and La partial substitution for Sr or Ba was used to change the carrier concentration. The Heusler alloy epitaxial thin films were Co_2MnSi and ordered and disordered films were studied.

In chapter 4 it was shown that the ASD systematically increased with increasing La concentration. However, there was no correlation between the residual resistivity and the ASD. A magnetoresistance was observed due to spin tunnelling in disordered regions at the grain boundaries. At high magnetic fields where the magnetoresistance is suppressed, the resistivity is close to that expected in a Fermi liquid. A magnetothermopower was observed in pure and La-doped SFMO. This magnetothermopower can be explained in terms of a spin-tunnelling contribution to the thermopower between grains that changes when a magnetic field is applied. The appearance of a magnetothermopower should also lead to a change in the electronic contribution to the thermal conductivity. However, this was not observed, which was probably due to the thermal conductivity being dominated by phonons. Hall effect measurements showed that the carrier concentration is lower for the La partially substituted samples. There was no

trend with increasing La concentration, which was probably because of ASD. An anomalous Hall effect was also observed. It is larger in the 0.4 La sample, which may be because the anomalous Hall effect is dominated by disorder induced by ASD.

Chapter 5 presents the results from measurements on pure and La-doped BFM0. The ASD is low and there is no significant change in the ASD with La partial substitution for Ba. The magnetoresistance is even higher than that found in SFMO. A magnetothermopower was observed that was linear even up to ~ 270 K, which is consistent with the spin tunnelling magnetothermopower model. The magnetic field dependence of magnetothermopower has features comparable to the magnetoresistance. The results from high temperature magnetisation studies on $\text{Ba}_{2-x}\text{La}_x\text{FeMoO}_6$ reveal that a localised electron model with antiferromagnetic coupling to itinerant electrons can account for the carrier concentration dependent effective moments. The correlation between the bare itinerant electron susceptibility and the Curie-Weiss temperature supports the kinetic energy driven model that has been used to account for the electronic spin polarisation and high Curie temperatures.

In chapter 6, the results from measurements on ordered and disordered epitaxial Co_2MnSi thin films are reported. The disorder is induced by Co and Mn ASD and is seen by a reduction in the saturation magnetic moment. The optical conductivity of the ordered film is similar to that found in the target and the results suggest that the band structure should be recalculated. The resistivity of the ordered Co_2MnSi thin film is linear in temperature. However, the resistivity of the disordered film increases at low temperature due to weak localisation and electron-phonon interactions. A magnetoresistance is observed in the ordered and disordered films. For low applied magnetic fields it is possible that there is a contribution to magnetoresistance

from spin scattering at domain walls. For high magnetic fields the reduction in the resistivity may be due to a magnetic field induced reduction in the weak localisation resistivity. There is a large anomalous component to the Hall resistivity observed in the ordered and disordered Co_2MnSi thin films. The anomalous Hall coefficient for the ordered film scales linearly with resistivity which indicates that this contribution arises from skew scattering.

For future work, it is interesting to study the effect of antisite disorder on the magnetothermopower of SFMO. For BFMO, a comparative study of the magnetoresistance and magnetothermopower would provide a better understand of the correlation between them. It would also be interesting to see if the magnetothermopower in BFMO changes with electron doping. In order to understand the magnetoresistance behaviour of Co_2MnSi Heusler alloy, the magnetoresistance measurements could be repeated at a range of temperatures.

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