Chapter 1

Experimental Summary

Chapter summary: This chapter summarises the key experimental observations on the double perovskites, emphasising the effects of antisite disorder. We highlight the spatially correlated nature of antisite disorder as inferred from electron microscopy and x-ray absorption fine structure (XAFS) studies. We move on to describe the impact of antiferromagnetic superexchange, present across the antiphase boundary, on the bulk magnetisation. We then discuss the temperature dependence of resistivity, including the effect of antisite disorder and grain boundaries, and magnetoresistance in single crystals and polycrystals. Finally, we comment on the impact of antisite disorder on half-metallicity, and the status of the search for non-ferromagnetic metallic phases.

1.1 Introduction

Perovskites are materials of the form ABO$_3$, where A is an alkaline earth or rare earth cation (Ca, Sr, La etc.), and B is an electronically active transition metal cation (Mn, Fe, Co, Ni, V, Cu etc.). The B ion sits in an octahedral environment (BO$_6$) while the A cations occupy the vacant space between the corner shared BO$_6$ octahedra. Perovskite oxides have been intensely studied over the last few decades since they show a rich variety of magnetic, electrical and optical properties. The manganites [1], cuprates [2], vanadates [3], etc., are a few prominent examples. Since our study is mostly concerned with the magnetism in double perovskites, let us start with a quick description of an important ‘simple’ perovskite, the manganites, to set the stage.
Activity on the manganites started with studies of the impact of doping on the properties of LaMnO$_3$ [4]. LaMnO$_3$ is an antiferromagnetic insulator. With Sr doping it goes to a ferromagnetic phase, with transition temperature $T_c \approx 250$K for La$_{0.825}$Sr$_{0.175}$MnO$_3$ [5]. On a wider range of doping and cation combination the magnetic order in manganites vary from ferromagnetic to antiferromagnetic to spin-glass, while the transport character changes from metallic to insulating.

The doping induced ferromagnetic phase shows a spectacularly large decrease in resistivity on application of a magnetic field [6]; this property is also known as colossal magnetoresistance (CMR). The strong coupling of electronic, magnetic, and structural degrees of freedom gives rise to a wide spectrum of properties involving charge, orbital, and magnetic ordering [7]. Doped manganites show CMR effect at relatively low temperature and high magnetic field, which undermine its application in mass storage memory devices. This encouraged further studies on oxide materials with magnetic ordering temperatures substantially higher than the manganites.

## 1.2 Double perovskites

The double perovskite, Sr$_2$FeMoO$_6$ [8] (SFMO), was found to have several desirable properties. Ordered Sr$_2$FeMoO$_6$ exhibits pronounced negative magnetoresistance [9] at lower magnetic fields and higher temperatures compared to the doped manganites. It has a ferrimagnetic ground state with transition temperature $T_c \approx 420$K. It shows half-metallic character, i.e., only one spin channel conducts, which makes it applicable in spintronic devices. Although it does not (yet) have the rich doping induced phase diagram of the manganites, SFMO does show several unusual magnetic and transport properties [8].

This in turn inspired the study of more complex and potentially richer double perovskites: materials of the form ABO$_3$.AB’O$_3 \equiv A_2BB’O_6$ (Figure 1.1). They have two kinds of octahedra, BO$_6$ and B’O$_6$, repeating in all three directions, instead of only the BO$_6$ octahedra as in perovskite. B and B’ are electronically active transition metal cations.
1.3 Magnetic order

The large number of possible B, B’ combinations in double perovskites lead to a variety of magnetic phases. As an illustrative list:

- Ferromagnets - listed in Table: 1.1
- Antiferromagnets - listed in Table: 1.2
- Spin glass - Sr$_2$FeCoO$_6$ [10], Ba$_2$YMoO$_6$ [11]

Apart from the magnetic phases, double perovskites can be superconducting. Partially melted ceramic material Sr$_2$YRu$_{0.85}$Cu$_{0.15}$O$_6$, shows superconductivity with an onset temperature of T$_c$ ≈ 45K [12,13] at ambient pressure.

Let us start our discussion with a brief overview of the ferromagnets. We will consider insulators, since the metallic phase will be discussed in detail later.

1.3.1 Ferromagnetic insulating phase

In double perovskites A$_2$BB’O$_6$, each B and B’ sits in an octahedral environment (BO$_6$ and B’O$_6$), due to which there is a crystal-field splitting of d-states of B and
Table 1.1: Ferromagnetic double perovskites

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure</th>
<th>Magnetic order T&lt;sub&gt;c&lt;/sub&gt;</th>
<th>Transport property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr&lt;sub&gt;2&lt;/sub&gt;FeMoO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Tetragonal</td>
<td>420K</td>
<td>Half-metallic [14]</td>
</tr>
<tr>
<td>Ba&lt;sub&gt;2&lt;/sub&gt;FeMoO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Cubic</td>
<td>345K</td>
<td>Half-metallic [15]</td>
</tr>
<tr>
<td>Sr&lt;sub&gt;2&lt;/sub&gt;FeReO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Cubic</td>
<td>400K</td>
<td>Half-metallic [16,17]</td>
</tr>
<tr>
<td>Sr&lt;sub&gt;2&lt;/sub&gt;CrReO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Cubic</td>
<td>635K</td>
<td>Half-metallic [18]</td>
</tr>
<tr>
<td>Ca&lt;sub&gt;2&lt;/sub&gt;CrReO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Monoclinic</td>
<td>360K</td>
<td>Insulating [18]</td>
</tr>
<tr>
<td>Ca&lt;sub&gt;2&lt;/sub&gt;FeReO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Monoclinic</td>
<td>520K</td>
<td>Insulating [17,19]</td>
</tr>
<tr>
<td>La&lt;sub&gt;2&lt;/sub&gt;NiMnO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>Monoclinic</td>
<td>280K</td>
<td>Insulating [20]</td>
</tr>
</tbody>
</table>

B’ into t<sub>2g</sub> and e<sub>g</sub> manifolds [21]. In Ca<sub>2</sub>FeReO<sub>6</sub> the small size of Ca induces monoclinic distortion in the structure, which further lifts the degeneracy of t<sub>2g</sub> levels on the Re sites (with two t<sub>2g</sub> electrons per Re). Due to this monoclinic distortion there is deviation of bond angle (Fe-O-Re) from 180° to ∼156°. This reduces the Re-Re overlap, by misaligning the t<sub>2g</sub> orbitals. This bond-angle distortion reduces the effective d-electron hopping energy via the reduced hybridization between transition-metal d and oxygen p states, leading to the insulating character in Ca<sub>2</sub>FeReO<sub>6</sub> [17,22].

La<sub>2</sub>NiMnO<sub>6</sub> is an important member of this family, as it is a promising candidate for technological application. It has a ferromagnetic transition temperature T<sub>c</sub> ∼ 280K [20]. Here Mn-O-Ni superexchange interaction gives rise to ferromagnetism [23]. It shows magnetoresistance and magnetocapacitance effects [24], indicating a coupling between the magnetic, electronic, and dielectric properties, which can be controlled by the application of magnetic fields. The observation of such effects close to the room temperature makes it a strong candidate for practical spintronic applications.

1.3.2 Antiferromagnetic insulating phase

Double perovskites show antiferromagnetic insulating character for some combination of B and B’. Sr<sub>2</sub>FeWO<sub>6</sub> is one typical member of this family. It has antiferromagnetic transition temperature T<sub>N</sub> ∼ 40K, with Fe<sup>2+</sup> ion in the high-
Table 1.2: Antiferromagnetic insulating double perovskites

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure</th>
<th>Magnetic order</th>
<th>T [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr₂FeWO₆</td>
<td>Monoclinic</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>Sr₂MnMoO₆</td>
<td>Tetragonal</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td>Sr₂NiMoO₆</td>
<td>Tetragonal</td>
<td></td>
<td>71.5</td>
</tr>
<tr>
<td>Ca₂NiWO₆</td>
<td>Monoclinic</td>
<td></td>
<td>52.5</td>
</tr>
<tr>
<td>Sr₂CoWO₆</td>
<td>Tetragonal</td>
<td></td>
<td>24</td>
</tr>
<tr>
<td>Sr₂YRuO₆</td>
<td>Monoclinic</td>
<td></td>
<td>26</td>
</tr>
</tbody>
</table>

Spin state (S = 2), and W⁶+ ion (5d⁰) in a non-magnetic state. There is a large exchange splitting of the localised electrons at the Fe-site. Strong hybridisation between the W-5d and the O-2p states drives the hybridised states above the t₂g ↓ level of Fe. The electron is transferred from the W-5d O-2p hybridised state to the Fe 3d level, leading to an insulating compound with formally W⁶+ and Fe²⁺ states. In absence of any delocalized electrons, the Fe²⁺ sites couple via superexchange to give rise to an antiferromagnetic insulator [26, 35]. The magnetic structure with a wave vector (0 1 1) can be described as a set of alternating ferromagnetic planes that are coupled antiferromagnetically [25] with each other.

1.3.3 Spin glass phase

The spin glass phase arises broadly either due to large B-site disorder (as in Sr₂FeCoO₆) or due to geometric frustration (as in Ba₂YMoO₆).

In Sr₂FeCoO₆, using neutron diffraction and subsequent bond valence sum analysis [10], it has been observed that the B site is randomly occupied by Fe and Co in the mixed valence states of Fe³⁺/Fe⁴⁺ and Co³⁺/Co⁴⁺. Comparable ionic radii of the B-site cations (Fe and Co) lead to large B-site disorder in the sample. Due to randomly distributed B-site cations, there is a competition between nearest neighbor and next nearest neighbor superexchange interactions giving rise to the local magnetic frustration in the lattice. This magnetic frustration leads to spin glass behavior in Sr₂FeCoO₆.

In contrast, Ba₂YMoO₆ crystallizes in face-centered cubic (FCC) lattice struc-
ture. In this compound Mo is in 5+ oxidation state (Mo$^{5+}$, S = $\frac{1}{2}$) with a singly occupied degenerate $t_{2g}$ orbital in a cubic crystal field, while Y$^{3+}$ ion does not carry a magnetic moment. The S = $\frac{1}{2}$ Mo$^{5+}$ moments are located on an FCC lattice and coupled antiferromagnetically. This arrangement is geometrically frustrated, which in conjunction with quantum fluctuations gives rise to spin glass behavior in Ba$_2$YMoO$_6$. No magnetic order is observed down to 2K in ac and dc magnetic susceptibility, heat capacity, and muon spin rotation [11] experiments.

1.3.4 Ferromagnetic metallic phase

One way to classify the ferromagnetic double perovskites could be in terms of the nature of B and B’. One category would be those where only one of the ions is intrinsically magnetic, the other in which both are magnetic (both 3d elements, say). In the first category would be Sr$_2$FeMoO$_6$, while in the second would be Sr$_2$FeReO$_6$, Ca$_2$FeReO$_6$, and Sr$_2$CrReO$_6$. Since our theoretical work is concerned with double perovskites in which only the B-site is magnetic, we will mainly concentrate on the properties of Sr$_2$FeMoO$_6$.

Sr$_2$FeMoO$_6$

Among the ferromagnetic double perovskites Sr$_2$FeMoO$_6$ is the most studied due to the following electronic and magnetic properties [8].

- Large saturation moment.
- High ferromagnetic T$_c$ $\sim$ 420K.
- Large low field magnetoresistance.
- Half-metallic behavior.
- Non FM metallic phases on La doping.

This compound has surprisingly high ferromagnetic transition temperature T$_c$ $\sim$ 420K, indicating a large interatomic (Fe-Fe) exchange coupling. Using site-specific x-ray absorption spectroscopy with linearly polarized light, S. Ray et al. [36] have established that the formal valence of Fe in Sr$_2$FeMoO$_6$ is 3+ (3d$^5$).
Figure 1.2: Density of states of $\text{Sr}_2\text{FeMoO}_6$ using the density functional method. It shows the total density of states with majority \textit{up} and minority \textit{down} spins as well as the local density of states for the elements [9].

Detailed investigation of x-ray magnetic circular dichroism data confirms a large moment at the Fe site ($S = \frac{5}{2}$). Mo has the oxidation state of 5+ (4d$^1$). In this compound, each of the Fe$^{3+}$ ($S = \frac{5}{2}$) and Mo$^{5+}$ ($S = \frac{1}{2}$) sublattices are arranged ferromagnetically, while the two sublattices are coupled to each other antiferromagnetically. $\text{Sr}_2\text{FeMoO}_6$ shows ferrimagnetic spin arrangement with $4\mu_B (\frac{5}{2} - \frac{1}{2})$ magnetic moment per Fe-Mo unit, in the ideal ordered double perovskite structure.

**Density of states: $\text{Sr}_2\text{FeMoO}_6$**

Kobayashi \textit{et al.} [9] have calculated the electronic structure of this ordered perovskite by the density functional method, as shown in Figure 1.2. The ground state of this compound shows half-metallic nature; the density of states for the down-spin band is present at the Fermi level, whereas the up-spin band has a
gap at the Fermi level. The occupied up-spin band is mainly composed of Fe 3d electrons hybridized with oxygen 2p states (corresponding to the 3d$^5$ up-spin configuration) and much less of the Mo 4d electrons. The nominal Mo t$_{2g}$ and e$_g$ up-spin bands are above the Fermi level. By contrast, the down-spin band is mainly occupied by oxygen 2p states and the states around the Fermi level are shared by the Mo 4d t$_{2g}$ and Fe 3d t$_{2g}$ electrons, which are strongly hybridized with oxygen 2p states. Such a half-metallic nature gives rise to 100% spin-polarized charge carriers in the ground state. In view of the fairly high T$_c$ and high spin polarization, ordered SFMO is suitable for spintronic applications.

**Magnetoresistance: Sr$_2$FeMoO$_6$**

Kobayashi et al. [9] have shown that the ordered double perovskite Sr$_2$FeMoO$_6$ exhibits pronounced negative magnetoresistance (Figure 1.3) at lower magnetic fields and higher temperatures compared to the doped manganites. The saturation magnetization at 4.2K is 3$\mu_B$ per formula unit. This small deviation from ideal value of 4$\mu_B$ is due to the mis-site-type imperfection of the B-site order, which was partly confirmed by the Rietveld analysis (giving 87% order on the B-site). The magnetization at 300K nearly saturates around 2.2$\mu_B$ per formula unit, indicating a high spin polarization (above 60%). The magnetoresistance magnitude at 7 T is as large as 42% and 10%, at 4.2K and 300K, respectively.

**Resistivity: Sr$_2$FeMoO$_6$**

Sr$_2$FeMoO$_6$ is very sensitive to oxidation and its resistivity is strongly dominated by electron scattering at the grain boundaries. At high temperature (between 300K and 900K), when the oxygen atoms placed at the grain boundaries are removed, it undergoes two metal-insulator transitions. Below 405K, it is metallic and magnetically ordered, and above 590K it again shows metallic behavior [37]. However in the intermediate temperature range, the system presents a possible Anderson localization of the carriers with semiconducting behavior.

Upon application of high pressure, intrinsic negative magnetoresistance is unaffected in single crystals and gets suppressed in polycrystalline samples, particularly at low field [38]. Large pressure effects on the tunneling magnetoresistance
Figure 1.3: Isothermal magnetoresistance (upper panels) and magnetization $M$ curves (lower panels) for polycrystalline ceramics of $\text{Sr}_2\text{FeMoO}_6$. (a) at 4.2K; (b) at 300K. The insets show a magnification of the field- hysteretic magnetoresistance (upper panels) corresponding to the magnetic hysteresis (lower panels) in a low-field region.

originates from the spin-polarized tunneling at grain boundaries in the polycrystalline sample, in sharp contrast to the behavior for a single crystal. The connectivity between grains is enhanced by pressure to give rise to a suppression of the magnitude of the tunneling magnetoresistance.

$\text{Sr}_2\text{FeReO}_6$: double moment ferrimagnet

Contrary to a single magnetic moment present in $\text{Sr}_2\text{FeMoO}_6$, both B-sites possess a magnetic moment in $\text{Sr}_2\text{FeReO}_6$. Here, significant orbital moment of Re plays a crucial role in determining the magnetic properties. $\text{Sr}_2\text{FeReO}_6$ bears a close resemblance to $\text{Sr}_2\text{FeMoO}_6$ in terms of magnetic and transport properties. $\text{Sr}_2\text{FeReO}_6$ has half-metallic ferrimagnetic magnetic ground state with a transition temperature $\sim 400\text{K}$. Polycrystalline ceramics of $\text{Sr}_2\text{FeReO}_6$ exhibits significant intergrain tunneling magnetoresistance even at room temperature (Figure 1.4). The magnitude of intergrain tunneling magnetoresistance with a magnetic field of 7 T at 4.2K and 300K is as large as 21% and 7%, respectively, reflecting high spin polarization of carriers.
Figure 1.4: Isothermal magnetoresistance $\rho(H)$ (upper panels) and magnetisation $M$ curves (lower panels) for polycrystalline ceramics of $\text{Sr}_2\text{FeReO}_6$ at 4.2K (a) and 300K (b) \cite{39}.

$\text{Ca}_2\text{FeReO}_6$ and $\text{Sr}_2\text{CrReO}_6$

In the $\text{A}_2\text{FeReO}_6$ series, $\text{Ca}_2\text{FeReO}_6$ shows insulating behavior with the maximum $T_c$ of 520K. Optical and x-ray absorption spectroscopy combined with density functional theory studies \cite{40} have established the presence of subtle interplay of spin-orbit coupling, electron correlation, and lattice distortion in this compound.

In the $\text{Sr}_2(\text{Fe}_{1-x}\text{Cr}_x)\text{ReO}_6$ series, $\text{Sr}_2\text{CrReO}_6$ is nearly half-metallic with the maximum $T_c$ of 625K, which is the highest $T_c$ in an oxide compound without Fe. Re, being a 5d transition metal with substantially large spin moment, is expected to bear substantial spin-orbit coupling. Full-potential band-structure calculations including spin-orbit coupling \cite{41} found that the magneto-optic spectra show substantially large Kerr rotations, suggesting potential application as read heads or optical data storage devices.

1.4 Impact of doping

The properties of the parent double perovskites change significantly upon hole and electron doping. We will discuss this impact using the example of $\text{Sr}_2\text{FeMoO}_6$.
1.4.1 Impact of hole doping

Upon partially substituting W for Mo in SFMO (Sr\(_2\)FeMo\(_x\)W\(_{1-x}\)O\(_6\)), which is equivalent to hole doping, it shows a metal-insulator transition \[42\]. Compounds with \(1.0 \geq x \geq 0.3\) show metallic behavior, while for \(0.2 \geq x \geq 0\) they are insulating. All compounds with \(1.0 \geq x \geq 0.2\) are ferrimagnetic, while Sr\(_2\)FeWO\(_6\) \((x = 0)\) is antiferromagnetic with a Néel temperature \(T_N \approx 37\text{K}\) \[43\]. All samples with \(x \geq 0.3\) show a significant negative magnetoresistance.

1.4.2 Impact of electron doping

The properties of the ferromagnetic and metallic double perovskites Sr\(_2\)FeMoO\(_6\) change significantly upon electron doping, i.e., substituting divalent Sr with trivalent La. Upon doping, \(T_c\) can rise up to 70K above that of SFMO \[44\]. This is accompanied by a substantial reduction of the saturation magnetization, mainly due to increase in antisite disorder \[45\]. There is also a decrease in the magnetoresistance (Figure 1.5), which affects the functionality of the material. By analysing the magnetotransport data for different electron-doped double perovskites, D. Rubi et al. \[46\] argue that a gradual loss of spin polarization of the conduction electrons is responsible for the decrease in the magnetoresistance.
1.4.3 Isoelectronic doping

If we dope Sr$_2$FeMoO$_6$ with a small amount of Ba or Ca on the Sr sites, it increases the magnitude of magnetoresistance significantly [47]. There is drastic enhancement of low-field magnetoresistance in the Ba doping region with the optimization of low-field magnetoresistance at Sr$_{0.4}$Ba$_{1.6}$FeMoO$_6$. And Ca doped sample is optimized at Sr$_{1.9}$Ca$_{0.1}$FeMoO$_6$, which also has an enhanced ferrimagnetic transition temperature.

1.5 Antisite disorder

The promise of rich functionality in the double perovskites remains unfulfilled due to inevitable B, B’ mislocation. The similar location of B and B’ ions promotes tendency towards defect formation. In order to understand this disorder properly, let us consider a 2D version of Sr$_2$FeMoO$_6$, for ease of visualization. Ordered structure will refer to alternation of B and B’ octahedra in each direction. By antisite disorder we mean replacing some B ion by B’. Thus, two similar octahedra (B-B or B’-B’) will now be nearest neighbor, as shown in Figure 1.6.

This interchange of B-B’ ions in principle can happen in a random manner. However, as we will see in the next section, this antisite disorder is spatially correlated instead of being random. There will be locally ordered regions, phase slipped with respect to one another.
1.5.1 Spatial nature of mislocation

In this section we will describe some of the experimental observation of the spatially correlated antisite disorder. Using transmission electron microscopy \[48\] of a single crystal of an ordered double perovskite \(\text{Ba}_2\text{FeMoO}_6\), Asaka et al. (Figure 1.7) have established the presence of crystallographic domains, i.e., regions having high degree of short range order. They have also investigated the relation between magnetic and crystallographic domains. Magnetic domain walls perfectly coincide with the crystallographic antiphase domain boundaries. Spins across a domain wall are antiferromagnetically aligned.

Similarly, using high-resolution electron microscopy (HREM) Navarro et al. \[49\] have studied \(\text{Sr}_2\text{FeMoO}_6\) ceramics samples (Figure 1.8: left panel) and they have found the existence of antiphase domains. Using Fourier reconstruction, they have clearly established the presence of antiphase boundary in the sample. In the schematic illustration of the atomic structure at the antiphase boundary they have shown that two similar entities (either Fe-Fe or Mo-Mo) sit next to each other at the antiphase boundary.

In a separate study, using x-ray absorption fine structure in conjunction with synchrotron radiation x-ray diffraction, Meneghini et al. \[50\] have studied the nature of disorder in the polycrystalline double perovskite \(\text{Sr}_2\text{FeMoO}_6\). Figure
Figure 1.8: Left panel: (a) HREM image: atomic structure, (b) Fourier reconstruction, clearly revealing an antiphase boundary (APB), (c) Schematic illustration of the atomic structure at the APB. Right panel: Slices of 3D models of Fe/Mo cubic lattices.

1.8 (right panel) shows a slice of 3D models of Fe/Mo cubic lattices, where light and dark grey sites represent Fe and Mo ordered positions, red (blue) sites being Fe (Mo) on the Mo (Fe) sublattice, with degree of long range order $S = 0.51$ and large antiphase regions with degree of short range order $\xi = 0.99$. Samples with varying degree of disorder reveal that a very high degree of short range order is preserved even in samples with highly reduced long range chemical order.

Overall, the experiments clearly establish the presence of antisite disorder and indicate that it is spatially correlated rather than being random. Hence, even though antisite disorder suppresses long range structural order, there is still a high degree of short range order that survives.

### 1.5.2 Impact on magnetisation

In double perovskites, we get correlated domains of locally ordered patches. At the antiphase boundary, we have two similar atoms (B-B or B′-B′) sitting next to each other and inside a domain we have dissimilar neighboring atoms in all three directions. At antiphase boundary two spins have antiferromagnetic superexchange coupling which makes two neighboring domains antiparallel [49] (Figure. 1.9). Magnetic domain walls seems to perfectly coincide with the crystallographic
Figure 1.9: Schematic of magnetic coupling in disordered Sr$_2$FeMoO$_6$\textsuperscript{[49]}. F/AF stands for ferromagnetic/antiferromagnetic interactions.

In antisite disordered samples, bulk saturation magnetization reduces from 4 $\mu_B$ per formula unit, expected in the ordered case. Suppression in the saturation moment is large for the sample with large antisite disorder. The magnetic effects of antisite disorder are similar in both single crystals\textsuperscript{[14]} and polycrystals\textsuperscript{[9,51]}, shown in Figure 1.10.

### 1.5.3 Impact on spin-polarisation

Ordered Sr$_2$FeMoO$_6$ has a ferrimagnetic spin arrangement with large Hund’s coupling on the magnetic (Fe) sites. Thus, only electrons oppositely oriented to the core magnetic ions will be able to conduct leading to a half-metallic state. In the correlated antisite disordered systems (Figure 1.7), magnetic domains coincide with the crystallographic antiphase domains\textsuperscript{[48]}. Spins in the adjacent domains are oppositely oriented. Within each domain the conduction electron has only one spin polarisation at low temperature, but averaged over the system both up and down electrons have finite density of states at the Fermi level. A local probe with area smaller than typical domain size will allow only spin polarised tunneling, while a probe averaging over domains will see both spin polarisation. Thus, antisite disorder destroys the half-metallicity.
1.5.4 Impact on transport properties

Temperature dependence

Behavior of resistivity is widely different between single crystals and polycrystals as shown in Figure 1.11. Let us start by discussing the impact of antisite disorder on transport of a single crystal. Single crystals [14] show residual resistivity $\rho \sim 0.1$ m$\Omega$cm, and metallic behavior, $d\rho/dT > 0$. Unfortunately to best of our knowledge, systematic study of resistivity with varying degree of antisite disorder is not available.

On the contrary, polycrystalline samples have been studied for a wide range of antisite disorder [49, 51–55]. The transport in these materials is also affected by the grain boundary resistance. The residual resistivity in these samples [51] range from $\sim 0.5$ m$\Omega$cm for low antisite disorder ($M/M_{max} \sim 1.0$) to $\sim 10$ m$\Omega$cm at high antisite disorder ($M/M_{max} \sim 0.5$). Ordered polycrystals show $d\rho/dT > 0$, while less ordered ones show $d\rho/dT < 0$ [51, 52].

Even in a single crystal, for a given fraction of mislocated sites, there can be widely varying degree of short range order. For example, the mislocated sites
can arrange themselves in a few large domains or in many smaller domains. The degree of short range correlation would also affect the transport properties. There is no experiment yet which clarifies this issue. Grain boundary effects add to the complexity of the problem in polycrystalline samples. The effects of antisite disorder and grain boundaries on the resistance have not been deconvolved yet in polycrystalline samples.

**Magnetic field dependence**

In a single crystal measurement Y. Tomioka et al. [14] (Figure 1.7) have measured the temperature profiles of resistivity in several magnetic field for single crystals of Sr$_2$FeMoO$_6$ with 8% ASD. The magnetoresistance is weak (< 10%) at low temperature at a field of 5T. Unfortunately, magnetoresistance of single crystal with systematic variation of antisite disorder is not available.

For polycrystalline samples the grain boundary effect is also present, as we have seen above. The magnetoresistance can be large (∼ 40%, Figure 1.12) at low temperature and at a field of 5T [52], and seems to be dominated by grain
boundary effects \cite{54,55}. Some results indicate a decrease \cite{52} in magnetoresistance with increasing antisite disorder, while others show an increase \cite{49}. Here again, effects of antisite disorder and grain boundaries on magnetoresistance have not been deconvolved yet.

1.6 Non-ferromagnetic metallic phases

In addition to the well known ferromagnetism, double perovskites are also expected to exhibit non-ferromagnetic order on sufficient electron doping, driven by electron delocalisation. Even \textit{simple perovskite} transition metal oxides - the cuprates, manganites, or cobaltates, have a rich phase diagram \cite{56}, with a strong dependence on the doping level. The manganites, for instance, exhibit not just ferromagnetism, but also the CE-type magnetic order and A, C, and G type antiferromagnetic phases \cite{57}, depending on the hole doping level. Non-ferromagnetic phases have been predicted also for double perovskites using ab initio calculations with simple collinear arrangement of the core spins \cite{58,59}.

Clear experimental indication of such antiferromagnetic order is limited, possibly because of increase in the antisite disorder with doping \cite{44}. Samples have
indeed been synthesised with large La doping on Sr$_2$FeMoO$_6$ \cite{60,61}. Low field magnetisation gets suppressed with increasing doping, which is an indication of increase in the disorder with doping (Figure 1.5). Using different magnetic and spectroscopic tools Jana et al. \cite{61}, have studied in detail the electronic and magnetic structures of La$_x$Sr$_{2-x}$FeMoO$_6$ double perovskites with (1.0 \leq x \leq 1.5). This reveals that the compound settles in an unusual antiferromagnetic metallic ground state for $x \geq 1.4$. The cross-over from ferromagnetic to antiferromagnetic behavior is largely dominated by the electronic changes, which establishes the role of kinetic energy driven mechanism \cite{62}.

There is unfortunately no detailed understanding of the role of antisite disorder in these samples yet, or data on resistivity and magnetoresistance.
Bibliography


