Chapter 3

Impact of Antisite Disorder on the Ferromagnetic Phase

Chapter summary: This chapter presents our results on the impact of antisite disorder on the ferromagnetic phase. For antisite disorder with a high degree of short-range correlation, the antiphase boundaries also act as magnetic domain walls. Increasing antisite disorder reduces the low-field magnetisation, destroys half-metallicity, and finally makes the ground state insulating. While these are disadvantages, we also notice that the ferromagnetic $T_c$ is only weakly affected by moderate antisite disorder and the low-field magnetoresistance is dramatically enhanced by disorder. Our real space approach allows an interpretation of these results in terms of the antisite domains and the intra and inter domain magnetic correlations and are consistent with the spatial imagery from recent experiments. The intra-grain effects highlighted here would be directly relevant to the single crystals. They also define the starting point for incorporating grain boundary effects in a theory of polycrystalline materials.

3.1 Introduction

Several double perovskite materials \[1\] of the form $A_2BB'O_6$ exhibit high ferromagnetic $T_c$ and significant low-field magnetoresistance. They are also a candidate source of spin-polarized electrons. The potential usefulness of these materials is, however, frustrated by inevitable mislocation of the B and B’ ions, which do not organise themselves in the ideal alternating structure. This results in a
strong dependence of physical properties on the preparative conditions, reducing the magnetisation and destroying the half-metallicity. In this chapter we provide results on the impact of spatially correlated antisite disorder (ASD), as observed experimentally \cite{2-4}, on the ferromagnetic double perovskites. The antisite domains not only suppress magnetism and half-metallicity, as already known from studies of uncorrelated disorder, but also lead to an enhancement of the low-field magnetoresistance (MR). The properties depend not only on the gross degree of disorder (fraction of mislocated sites), but also on the degree of short range correlation.

### 3.2 Magnetic domain formation

In order to study the impact of correlated antisite disorder on the ferromagnetic phase, we have chosen four sets of disordered configurations, with increasing degree of mislocation, generated using a simple lattice-gas model \cite{5}, discussed in detail in the last chapter. On this correlated background, we have used a real space spin-fermion Monte Carlo method to solve the magnetic problem and study \cite{6} the magnetic order, half-metallicity, transport, etc.

To get the ground state spin configuration, we anneal the electron-spin system down to very low temperature on a given structural motif, top row in Figure 3.1. Bottom row of Figure 3.1 shows the ground state magnetic snapshot. We have plotted the spin overlap factor $g_i = S_0 \cdot S_i$, where $S_0$ is a reference spin (left-lower-corner) in the lattice. For all disorder families, we find that structural and magnetic domains coincide with each other. This is consistent with the experimental observation by Asaka, et al. (Figure 1.7). Using transmission electron microscopy \cite{7} of a single crystal of Ba$_2$FeMoO$_6$ they have established that magnetic domain walls coincide with the crystallographic antiphase boundaries and the spins across the domain wall are antiferromagnetically aligned.

### 3.3 Temperature dependence of magnetisation

Let us examine the effect of the antisite disorder on the magnetic properties. Since rotation invariance, in the absence of an applied field, can lead to precession of the
Figure 3.1: Structural and magnetic domains: Top row shows ASD configurations, one from each disorder family with $S = 0.98, 0.76, 0.50, 0.08$. Bottom row shows the corresponding ground state spin overlap factor $g_i$, in a Monte Carlo snapshot. $g_i = S_0 \cdot S_i$, where $S_0$ is the left lower corner spin in the lattice. Lattice size $40 \times 40$.

direction of the total magnetisation, $\vec{M}$, we prefer to calculate $\langle M^2 \rangle$, where $\vec{M} = (1/N_s) \sum_i S_i$. $\langle \rangle$ represents thermal average over equilibrium spin configurations and $N_s$ is the number of B sites. This is related to the structure factor $D(Q)$: the Fourier transform of the correlation function of the spins at the B sites.

$$D(Q) = \frac{1}{N_s^2} \sum_{i,j} \langle S_i \cdot S_j \rangle e^{iQ \cdot (R_i - R_j)}$$

At $Q = (0, 0)$, $D(Q)$ breaks up into two decoupled sums and is simply $\langle M^2 \rangle$.

Suppose the fraction of mislocated B, B' sites is $x$, and the structure is organised into domains such that the ratio of “perimeter” to “bulk” sites of the domains is small, i.e., there is a high degree of short range correlation present in the system. The antiferromagnetic coupling between adjoining domains would polarise them antiparallel, and the net moment at $T = 0$, $h = 0$ would be proportional to the volume difference of up and down domains. We should have $M(T = 0, h = 0) \sim (1 - x) - x = 1 - 2x = S$, so $M^2 = S^2$. Given our structural order parameter, $S^2 = 0.96, 0.58, 0.25, 0.01$ in almost perfect correspondence with the $T \to 0$ values in Figure 3.2. The elaborate calculation arrives at an obvious answer.
Figure 3.2: Left panel- The ferromagnetic peak in the structure factor, $M^2$, for different degrees of antisite disorder. Results are on a $40 \times 40$ lattice, averaged thermally and over 10 copies of disorder. Right panel- Comparison of our saturation magnetisation (at $T = 0$) with experimental measurement by Navarro et al. [8].

This behavior of $M(T)$ can also be described by an effective Heisenberg model

$$H_{eff} = \sum_{\{ij\}} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$

where $\{\}$ represents the set of nearest neighbor and next nearest neighbor sites. $J_{ij}$ is the effective coupling (FM/AFM) between the local moments at $\mathbf{r}_i$ and $\mathbf{r}_j$ sites. In our two dimensional ASD configurations $J_F/t = -0.04$ operates between two local moments when they are at the next nearest neighbor position and $J_{AF}/t = 0.065$ is active when the moments are at the nearest neighbor position (a B-O-B arrangement). The Heisenberg result for the ferromagnetic structure factor $S(0,0)$ as a function of temperature matches very well, shown in Figure 6.2, with the electronic Hamiltonian result for all antisite disordered configurations. This is discussed in Chapter-6 in detail.

The onset temperature for magnetic order seems to be insensitive to the ASD, i.e., the intra-domain order sets in at $T \sim$ the bulk $T_c$. Note that for an $O(3)$ model in 2D, the $T_c$ vanishes in the infinite volume limit. We should ideally speak of a size dependent ‘correlation temperature’ but will not make this distinction.
Figure 3.3: The \( d.c. \) resistivity, \( \rho(T) \), for varying antisite disorder. Results are on a \( 40 \times 40 \) lattice, averaged thermally and over 10 copies of disorder.

Experimental measurement also shows a small variation in \( T_c \) with increasing antisite disorder upto \( S = 0.3 \) \[8\]. While our answer for the suppression of magnetisation is \( M \sim (1 - 2x) \), a 3D calculation, with uncorrelated disorder, had found \[9\] \( M \sim (1 - 1.9x) \).

### 3.4 Temperature dependence of resistivity

We have studied the transport behavior on this correlated ASD background as shown in the Figure 3.3. The temperature dependence of resistivity \( \rho(T) \) remains similar from weak to intermediate disorder, with a sharp drop near \( T_c \). The only effect of increasing disorder is an increase in the residual resistivity. It is as if there is a temperature independent structural scattering that gets added to the temperature dependent magnetic scattering. However, at large antisite disorder this correspondence breaks down: the low temperature resistivity is very large (and grows with growing system size) and \( d\rho/dT < 0 \). There seems to be a metal-insulator transition (between \( S = 0.50 \) and \( S = 0.08 \)), in this two dimensional model, driven by antisite disorder.

To create an understanding of this let us focus on \( T = 0 \), where the magnetic
configuration is simple (collinear). The down spin electrons inhabit the up core spin domains and vice versa. The conductance arises from the inter-penetrating parallel channels for up and down spin electrons. One could call it *complementary percolation*. Let us identify up spin electrons with the *majority* phase and down spin with the *minority* phase. The net conductivity is \( \sigma_{\text{tot}}(S) = \sigma_{\text{maj}}(S) + \sigma_{\text{min}}(S) \), which reduces monotonically with reducing S, as shown in Figure 3.3. At fixed S one could increase \( \sigma_{\text{tot}} \) systematically by increasing \( p_{\text{corr}} \), i.e., reducing the fragmentation of the conduction paths. Thus, this insulating state at low temperature is different from the usual disorder induced insulating state like Anderson localization *etc.*, rather it arises due to the fragmentation of conduction path with increase in antisite disorder. Weak localisation effects, *etc.*, in two dimensions could show up at much longer lengthscales.

Since the antisite disorder configuration is temperature independent, the primary sources of temperature dependence in transport are:

1. weakening of the antiferro locking across the domain boundaries, and
2. fluctuations about the ferromagnetic state within a domain.

The first effect enhances the conductivity, while the second serves as a source of scattering. Their relative importance depends on zero temperature conductivity. For weak disorder (large S) the fragmentation is weak and the increase in resistivity due to intra-domain magnetic scattering is larger than the decrease from inter-domain tunneling. However, by the time S=0.50, there is already a weak upturn in \( \rho \) as \( T \to 0 \), the intra-domain effect is visible, and this becomes the dominant effect as \( S \to 0 \). An analysis of the spin-spin correlations illustrates the antiferro locking of domains at low temperature and how this weakens with increasing temperature.

The first column in Figure 3.4 reproduces one set of antisite disorder configurations from Figure 2.7 (first column). The next three columns show the magnetic overlap \( g_i = S_0 \cdot S_i \), where \( S_0 \) is the lower left corner spin in each configuration, for a Monte Carlo snapshot at \( T/t=0.03, 0.05, 0.07 \). These pictures would correspond to magnetic domains, if the patterns survive even after thermal averaging. The antiphase boundary (APB) and the magnetic domain wall (MDW) pattern coincide at \( T/t = 0.03 \). However at \( T/t=0.05 \) (close to the
Figure 3.4: Temperature dependence of short range magnetic correlations. The left column shows ASD configurations, one from each disorder family. $S=0.98, 0.76, 0.50$ and $0.08$, top to bottom. The 2nd, 3rd and 4th panel along each row is a map of a spin overlap factor, $g_i$, in a Monte Carlo snapshot. $g_i = S_0 \cdot S_i$, where $S_0$ is the left lower corner spin in the lattice. The temperatures are $T/t = 0.03, 0.05, 0.07$.

bulk $T_c$), there is no correlation between the APB and the $g_i$ pattern. There is significant core spin overlap across the boundary, and large fluctuation, overall, in spin orientation. This bears out the transport mechanism we suggested in the preceding section.

Our results above are relevant to the effect of ASD on single crystals. Single crystalline Sr$_2$FeMoO$_6$ \[10\] shows a residual resistivity $\rho \sim 0.1 \text{ m}\Omega\text{cm}$, and metallic behavior $d\rho/dT > 0$ but we have not been able to locate single crystal data for varying degree of ASD. Polycrystalline samples \[11\] (Figure \[1.11\]) show a trend similar to ours but transport in these materials is also affected by the grain boundary resistance apart from antisite disorder. The residual resistivity in
these samples ranges from \( \sim 0.5 \, \text{m\Omega cm} \) for low antisite disorder \((M/M_{\text{max}} \sim 1.0)\) to \( \sim 10 \, \text{m\Omega cm} \) at high antisite disorder \((M/M_{\text{max}} \sim 0.5)\). Ordered polycrystals show \( d\rho/dT > 0 \), while less ordered ones show \( d\rho/dT < 0 \).\textsuperscript{11,12}

### 3.5 Field dependence of resistivity

The field dependence of magnetisation and resistivity is shown in Figure 3.5, at relatively low temperature \((T/t=0.03)\) in (a)-(b) and at high temperature \((T/t=0.07)\) in (c)-(d). Three energies play out when \( h \neq 0 \):

1. the bulk Zeeman cost of the *minority* domains \( \sim hV_{\text{min}} \), where \( V_{\text{min}} \) is the volume of the minority phase,

2. the interfacial antiferromagnetic energy \( \sim J_{\text{AF}}V(1-p_{\text{corr}}) \), where \((1-p_{\text{corr}})\) is the fraction of antiferro bonds on the lattice,

3. the *gain in electronic kinetic energy* on removal (or rotation) of MDW’s.

Here, the first and third prefer domain alignment while the second prefers to retain domain walls. In a ‘spin only’ model the third would be absent. This delocalisation energy gain serves to reduce the field at which domain rotation can occur. At low temperature, Figure 3.5 (a)-(b), the ordered samples have a high degree of magnetic order, so the field induced increase in \( M \) and the decrease \( \Delta \rho/\rho(0) \), is quite small, where \( \rho(0)=\rho(h)|_{h=0} \) and \( \Delta \rho = \rho(0) - \rho(h) \). However, the low temperature low field response is dramatic for low \( S \) samples. These samples have \( M(h=0) \sim 0 \) and a large \( \rho(0) \) due to the fragmented (spin selective) conduction path. A field as small as \( h/t \sim 0.001 \) leads to \( M^2 \sim 0.1 \), so \( M \sim 0.3 \). The corresponding impact on spin correlations is shown in the lowest row in Figure 3.6, where the MDW pattern is strongly affected by \( h \). While the domain rotation effect is visible for both \( S = 0.50 \) and \( S = 0.08 \), the less disordered sample had a larger conductivity at \( h = 0 \), so the fractional change is much larger for \( S = 0.08 \). At high temperature, Figure 3.5 (c)-(d), the domains cease to exist and conductance gain from domain rotation is irrelevant. In the large \( S \) samples there are few antiferro links so the applied field just suppresses the magnetic fluctuations leading to large \( \Delta \rho/\rho(0) \). In the most disordered samples
there are \((1 - p_{\text{corr}})/2 \sim 7\%\) of antiferro bonds. Although there are no domains, these act as a source of scattering. The gain in conductivity is slower in the disordered samples compared to the more ordered ones.

This dramatic enhancement of the low-field magnetoresistance for low \(S\) samples is different from the large magnetoresistance observed in polycrystalline samples, where the magnetoresistance is derived from the magnetic polarization of grain-boundary regions acting like spin valves, and dominant mechanism is inter-grain tunneling across physical grain boundaries \[13\].

In a single crystal measurement Tomioka \textit{et al.} \[10\] (Figure 1.11) have measured the temperature profiles of resistivity in several magnetic fields for an antitise disordered Sr\(_2\)FeMoO\(_6\) crystal with \(S = 0.84\). The MR is weak (< 10\%) at low temperature at a field of 5T. Unfortunately, the MR of single crystals with systematic variation of ASD is not available. For polycrystalline samples
Figure 3.6: Field dependence of magnetic spatial correlations. We show the usual $g_i = S_0.S_i$, defined earlier. The left column shows the ASD domains, the central column shows $g_i$ at $h/t = 0$, and the right column is for $h/t=0.001$. The temperature is $T/t=0.03$.

the grain boundary effect is also present, as we have seen above. The MR can be large, $\sim 40\%$ (Figure 1.12), at low temperature and at a field of $5T$ [12], and seems to be dominated by grain boundary effects [13, 14]. Some results indicate a decrease [12] in MR with increasing antisite disorder, while others show an increment [15]. Similar to the temperature dependence of resistivity, the effects of antisite disorder and grain boundaries on MR have not been deconvolved yet.

### 3.6 Half-metallicity

Ordered $\text{Sr}_2\text{FeMoO}_6$ has ferrimagnetic spin arrangement with large positive Hund’s coupling on the magnetic (Fe) sites. Thus, only those electrons which are oppositely oriented to the core magnetic ions are able to conduct. Since it allows
only one spin channel to conduct, it is half-metallic. Antisite disorder destroys the half-metallicity. We have studied the impact of antisite disorder on the spin resolved density of states and its thermal evolution.

### 3.6.1 Impact of disorder at low temperature

Figure 3.7 shows the spin resolved density of states at low temperature with increasing antisite disorder. Left column of the top row is for the ordered double perovskite. Here up-spin electrons are localized and only down-spin electrons conduct. Hence, at low temperature it shows half-metallic behavior. But this potentially useful property gets destroyed by the antisite disorder. As we can see in the right column of the top row that antisite disorder $\sim 12\%$ has already created density of states for the minority electrons.

### 3.6.2 Temperature dependence

Figure 3.8 shows the thermal evolution of spin resolved density of states at weak and moderate antisite disorder ($S = 0.98$ and $0.50$) at temperatures ranging be-
between 0.01 and 0.07. Upon increasing the temperature, the up-spin density of states gets broader due to the thermal fluctuation of spins around the ferromagnetic state. At high temperature (T/t = 0.07) up and down-spin density of states become similar. Here we observe a dip in the density of states around $\omega = 0$ due to the band narrowing (hopping suppression) effect of spin disorder. This dip is weaker in the moderately disordered case due to the competing band broadening effect of structural disorder.

### 3.6.3 Polarisation and itinerant moment

These systems are unusual because at $T = 0$ within each domain the conduction electron has only one spin polarisation, but averaged over the system both up and down electrons have density of states present at $\epsilon_F$. A local probe, with probe area $\ll \xi^2$, where $\xi$ is the typical domain size, will allow only spin polarised tunneling, while a probe averaging over domains will see both $D_\uparrow(\epsilon_F)$ and $D_\downarrow(\epsilon_F)$. Figure 3.9 shows polarisation $P = (D_\uparrow(\epsilon_F) - D_\downarrow(\epsilon_F)) / (D_\uparrow(\epsilon_F) + D_\downarrow(\epsilon_F))$ and itinerant moment $\mu = (n_\uparrow - n_\downarrow) / (n_\uparrow + n_\downarrow)$, as a measure of half-metallicity. These are unity only in the absence of ASD at $T = 0$, and in general have a behavior that broadly mimics the behavior of the core spin magnetisation, (Figure 3.2), in its disorder and temperature dependence.
Figure 3.9: Half-metallicity, estimated as \( \frac{D_\uparrow(\epsilon_F) - D_\downarrow(\epsilon_F)}{D_\uparrow(\epsilon_F) + D_\downarrow(\epsilon_F)} \) and \( \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow} \), for varying temperature and different degrees of antisite disorder.

3.7 Discussion

Unlike the simple perovskite oxides, the double perovskite oxides possess inevitable B-site antisite disorder, due to similar sizes of B-site cations. The disorder has a high degree of short ranged correlation. In order to completely characterise the sample one has to specify the gross degree of disorder (i.e., fraction of mislocated sites \( x \)) and the degree of short-ranged correlation \( p \) in it. The magnetisation, and the half-metallicity are not strongly affected by this correlated disorder. The domain structure of antisites makes the most difference in the transport: there is rise in the resistivity at low temperature due to transmission blocking at antiferro domain boundaries, and large low field magnetoresistance due to domain rotation. There are three issues we want to touch upon, to relate our work to the real double perovskites.

3.7.1 Role of dimensionality

We have concentrated on two dimensions since we wanted to study large system sizes. This helps in capturing the impact of antisite disorder correctly and also aids visualisation. It is well known that localisation effects are stronger in 2D compared to 3D, so we performed the entire calculation on a 16³ system to check out the trends in transport. We solved the same model as discussed earlier in 3D.
Figure 3.10: Left panel - The ferromagnetic peak in the structure factor $M^2$, where $M$ is the magnetisation, for different degrees of antisite disorder. Right panel - The dc resistivity, $\rho(T)$ for varying antisite disorder. Results are on a $16^3$ lattice, averaged thermally and over 10 copies of disorder.

Antisite disordered backgrounds on lattice sizes upto $16^3$ [16]. In that case both the kinetic energy and magnetic ordering have a 3D character. The results on magnetisation and resistivity are shown in Figure 3.10. The trends in both $M^2$ and $\rho(T)$ are similar to what we have obtained in 2D case as shown in the Figure 3.2 and 3.3 respectively. There is a sharp increase in the $T = 0$ resistivity (although possibly no insulating phase) with increasing antisite disorder. The low-temperature upturn in $\rho(T)$ is also present, but weaker, in 3D. The trends in magnetoresistance are also similar between 2D and 3D.

### 3.7.2 Hubbard interactions

The primary mechanism behind magnetism in the double perovskites is a variant of double exchange, driven by the large Hund’s coupling on the B site. This is adequate in a one band context. When band degeneracy is considered, as is true of the real material, the inter-orbital Hubbard effect on the B (magnetic) site, and weaker correlation effects on the B’ (nonmagnetic) site would be needed for a quantitative theory of the itinerant moment. However, comparison of our data [16] with existing results [17] shows that the qualitative trends in disorder
dependence remain the same. Although we are mainly interested in the disorder
dependence, the correlations effects also need to be included to understand results
like photoemission in Sr$_2$FeMoO$_6$.

3.7.3 Effect of grain boundaries

In the absence of a chemical characterisation of the grain boundary material,
and an electronic model for the grain boundary, it is hard to construct a com-
prehensive theory. However, since grain size, $l_G \gg \xi$ (where $\xi$ is the structural
correlation length), it should be possible to study the role of antiphase boundaries
and magnetic domain walls via probes that focus on a single grain.

The *intra-grain* effects highlighted here would be directly relevant to single
crystals, and define the starting point for a transport theory of the polycrystalline
double perovskites.

3.8 Conclusion

We have studied a double perovskite model on antisite disordered backgrounds
with a high degree of short-range correlation. In this situation, the antiphase
boundaries coincide with the T=0 magnetic domain walls. Growing ASD reduces
the low-field magnetisation, destroys the half-metallicity, and leads to a low-
temperature metal-insulator transition. While these are disadvantages, we also
note that the ferromagnetic $T_c$ is only weakly affected by moderate ASD and
the low-field magnetoresistance is dramatically enhanced by disorder. Our real
space results allow an interpretation of these in terms of the domain pattern,
the effective exchange, and the short-range magnetic correlations. They are also
consistent with explicit spatial imagery from recent experiments. The "intra-
grain" effects highlighted here would be directly relevant to single crystals, and
define the starting point for a transport theory of the polycrystalline double
perovskites.
Bibliography


